REDUCING NITROUS OXIDE EMISSIONS WHILE SUPPORTING SUBTROPICAL CEREAL PRODUCTION IN OXISOLS

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KEYWORDS

Nitrous oxide, Oxisols, subtropical, cereal cropping systems, sustainable intensification, fertilisation, legumes, nitrification inhibitor, DMPP, urea, maize, sorghum, wheat, alfalfa, sulla, nitrogen management practices, nitrogen uptake, nitrogen recovery efficiency, ^{15}N tracer technique, automated greenhouse gas measuring system, climate change, DAYCENT.

ABSTRACT

Mitigating climate change and achieving food security are two of the key challenges of the twenty-first century. By 2050 the world’s population is forecast to be over a third larger than at present and cereal demand is predicted to increase by 60%. Pronounced intensification of cereal production is expected to take place in Oxisol-dominated tropical and subtropical regions (Smith *et al.*, 2007), identifying the need for more nitrogen (N) to be supplied to these agroecosystems. It is established however that boosting food production though an increased use of synthetic N fertilisers will result in sharp increases in greenhouse gas emissions, especially N_2O. It is therefore critical to identify alternative N management strategies aimed at supporting future intensification of tropical and subtropical agricultural systems without provoking an increase of N_2O emissions from these agroecosystems.

A unique dataset of high-frequency observations and N recovery data referring to multiple cropping seasons, crop rotations and N fertiliser strategies was gathered in this study using a fully automated greenhouse gas measuring system, ^{15}N-tracer techniques and a process-based biogeochemical model. The aim was to define profitable, agronomically viable and environmentally sustainable N management strategies to support future intensification of cereal production on subtropical Oxisols. This study also aimed to improve the current understanding of environmental factors influencing N_2O emissions in fertilised Oxisols and to assess the magnitude and main pathways of fertiliser N losses that limit crop yields in these agroecosystems. These aims were achieved by way of the following three research objectives:

- Evaluating the use of urea coated with the DMPP nitrification inhibitor to limit N_2O emissions and increase grain yields compared to conventional urea.
- Evaluating whether the introduction of a legume phase in a cereal-based crop rotation can reduce the reliance of cereal crops on synthetic N fertilisers and minimise N_2O emissions during the cereal cropping phase.

- Use model simulations to test the hypotheses underlining the first two objectives and assess the sustainability of the N management practices investigated under a broader spectrum of environmental conditions.

The results of this study indicate that in subtropical Oxisol-based cereal cropping systems there is significant scope for limiting N_2O losses and improving the fertiliser N use efficiency, especially during the summer cropping season. The warm and humid soil conditions of subtropical summers, associated with the higher N fertiliser rates applied to summer crops, were conducive for greater nitrification and denitrification rates compared to winter. Among the N management strategies tested, the application of DMPP urea was the most effective in minimising N_2O losses during a summer crop.

The slower nitrification rates of DMPP urea enabled a better match between the NO_3^- released by the fertiliser and plant N uptake, resulting in almost no accumulation of NO_3^- in the topsoil and therefore effectively limiting denitrification. As a result, the use of DMPP urea on average abated N_2O emissions by 65% compared to the same N rate with conventional urea. However, the enhanced synchrony of DMPP urea was limited to the top soil and DMPP did not increase crop productivity compared to conventional urea. The high clay content of the soil prevented fertiliser N losses via deep leaching, while the low soil C and the short-lived periods of soil saturation limited N_2 emissions. Consequently, a good synchrony between fertiliser N supply and plant uptake was achieved with conventional urea and DMPP had limited scope to increase the N use efficiency of the urea-based fertiliser.

The introduction of a legume phase in a cereal-based crop rotation showed multiple environmental and agronomic advantages. Planting the cereal crop shortly after incorporating legume residues ensured the synchrony between the crop N uptake and the mineral N progressively released by the decomposition of the residues. This practice avoided the accumulation of relevant amounts of N in the soil that would have been available to nitrifying and denitrifying microorganisms, and N_2O emissions were primarily a function of the N fertiliser rate applied. As a result, decreasing the synthetic N rates applied to the cereal in the legume crop rotation led on average to a 35% reduction of N_2O losses. Concurrently, the incorporation of legume residues provided enough readily available N to support crop development and grain yields were not affected by the reduction of synthetic N.

Overall, the results of this study reveal that the use of DMPP urea in subtropical Oxisols cannot be regarded as an economically viable standard farming practice to reduce N_2O emissions unless governmental incentive policies are established. Conversely, introducing a legume phase in cereal-based crop rotations is the most effective N management practice under the environmental and agronomical perspective. If properly implemented, this strategy enables to significantly reduce N_2O emissions, achieve high yields, reduce the costs associated with N fertilisation and provides greater flexibility to the farmer in terms of timing and rate of fertiliser application. The results of this study will contribute to define N management practices for the sustainable intensification of subtropical cereal production.

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LIST OF ABBREVIATIONS

AE_{fN}	Agronomic Efficiency of Fertiliser N
AgMIP	Agricultural Model Intercomparison and Improvement Project
C	Carbon
C:N	Carbon-to-Nitrogen ratio
CO_2	Carbon dioxide
DMPP	3, 4-dimethylpyrazole phosphate
EEF	Enhanced Efficiency Fertilisers
EF	Emission Factor
FAO	Food and Agriculture Organization (UN)
RE_{fN}	Recovery Efficiency of Fertiliser N
GHG	Greenhouse Gas
GWP	Global Warming Potential
IPCC	Intergovernmental Panel on Climate Change (UN)
N	Nitrogen
N_2	Dinitrogen
N_2O	Nitrous oxide
NH_2OH	Hydroxylamine
NH_3	Ammonia
NH_4^+	Ammonium
NO	Nitric oxide
NO_2^-	Nitrite
NO_3^-	Nitrate
NI	Nitrification Inhibitor
O_2	Oxygen
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
WFPS	Water Filled Pore Space

PUBLICATIONS INCORPORATED INTO THE THESIS

De Antoni Migliorati M, Scheer C, Grace PR, Rowlings DW, Bell M, McGree J (2014). Influence of different nitrogen rates and DMPP nitrification inhibitor on annual N_2O emissions from a subtropical wheat–maize cropping system. Published in Agriculture, Ecosystems & Environment, 186, 33-43.

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STATEMENT OF ORIGINAL AUTHORSHIP

The work contained in this thesis has not been previously submitted to meet requirements for an award at this or any other higher education institution. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made.

Signature: QUT Verified Signature

Date: 9th March 2015

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Chapter 1: Introduction

1.1 Background and significance

Agriculture in the twenty-first century faces unprecedented challenges. The coming decades will demand agricultural systems to provide adequate food supply to a growing world population without increasing the already elevated anthropic pressure on natural resources. Increasing food production without provoking unacceptable levels of environmental damage is not however just an extremely complex problem, is also a matter of urgency. By 2050, less than forty years from now, global agricultural production will have to double to meet the increasing demand of a world population forecast to be over a third larger than at present (Godfray *et al.*, 2010; Tilman *et al.*, 2011).

A major contribution to the increased global calorie demand will come from cereals, which contribute 50% of daily energy intake worldwide and up to 70% in some developing countries (Kearney, 2010). As a result, global cereal demand is predicted to increase by 60% (FAO, 2009). Specifically, virtually all the increase in cereal consumption will come from the tropical and subtropical regions of Africa, South America and Asia (Alexandratos and Bruinsma, 2012), where the vast majority of future global demographic growth is projected to take place (UNFPA, 2011).

It is recognised that future increases in cereal production should be achieved through augmenting current crop yields (intensification) rather than converting more land to cultivation (extensification) (Godfray *et al.*, 2010; Foley *et al.*, 2011; Phalan *et al.*, 2011). This will result in increasing pressure on cereal cropping systems in the tropics and subtropics, where productivity will need to be maximised to meet the needs of those countries. The increase in tropical and subtropical cereal production will be supported largely by farming systems conducted in Oxisols (USDA Soil Taxonomy), the most common soil type in these regions (Fageria and Baligar, 2008).

Oxisols occupy 46% and 23% of soil area in the tropics and subtropics, respectively (von Uexküll and Mutert, 1995; Buol and Eswaran, 1999; Thomas and Ayarza, 1999) and, together with Ultisols, are the soil type where half of the world's population currently lives (Yang *et al.*, 2004). The fact that Oxisols have low natural fertility and moderately high susceptibility to degradation can limit crop yields in these agricultural systems. However, many of these constraints can be amended with modern technologies and, when managed with correct agronomic practices, Oxisols are capable of high productivity levels. This, in conjunction with the favourable climatic conditions of tropics and subtropics, makes Oxisols capable of supporting multiple cropping cycles each year.

Due to their extent and potential productivity, Oxisols are today regarded as the most extensive agricultural frontier in the world (Borlaug and Dowswell, 1997), which means that if appropriate agronomic techniques are implemented, the quantity of cereal produced in these soils will significantly contribute to meeting future grain demand.

1.2 The problem statement

Nitrogen (N) deficiency is one of the major factors limiting crop production in Oxisols. For example, Sánchez and Salinas (1981) have estimated that in tropical and subtropical regions of the American continent soil N deficiency is a major agricultural constraint in over 90% of Oxisols. N deficiency results in an inability of Oxisols to sustain continuous crop production (Fageria and Baligar, 1995) and as such the addition of sufficient quantities of fertiliser N becomes a key factor to enable the intensification of cereal production in these agroecosystems.

It is widely recognised that both the manufacture and use of synthetic N fertilisers in crop production generate substantial environmental threats (Tilman *et al.*, 2002; Crews and Peoples, 2004; Jensen *et al.*, 2012). The synthesis and transport of N fertilisers are associated with high fossil fuel requirements and every year are responsible for the emission of over 300 Tg of carbon dioxide (CO_2), the primary greenhouse gas emitted through human activities (Barker *et al.*, 2007). Once applied in the field, fertiliser N can be lost via soil erosion, runoff, nitrate (NO_3^-) leaching or gaseous emissions into the atmosphere in the form of ammonia (NH_3), mono-nitrogen oxides (NO_x), dinitrogen (N_2) and nitrous oxide (N_2O). The majority of these compounds are identified as pollutants and their emissions in the environment can cause severe damage both on a local and global scale (Crews and Peoples, 2004; Goulding, 2004).

Amongst these environmental threats, the emission of significant amounts of N_2O is arguably one of the most important. The environmental relevance of N_2O emissions resides both in terms of its elevated global warming potential (298 times that of CO_2 over a 100 year time horizon (Myhre *et al.*, 2013)) and its contribution to the depletion of the ozone layer in the stratosphere (Ravishankara *et al.*, 2009). Agricultural soils are the main anthropogenic source of N_2O emissions, contributing approximately 50% of the global human-derived N_2O emissions (Ehhalt *et al.*, 2001; Syakila and Kroeze, 2011; Smith *et al.*, 2012). Numerous studies on agricultural soils have proven a clear correlation between N_2O emissions and N fertilisation, with increasing N_2O fluxes corresponding to increasing N fertilisation rates (Matthews, 1994; Kroeze *et al.*, 1999; Bouwman *et al.*, 2002a; Del Grosso, 2006; Butterbach-Bahl *et al.*, 2013; Shcherbak *et al.*, 2014).

Reducing the contribution of agriculture to global warming is paramount since numerous studies indicate that increased temperatures and climate change will likely have a negative impact on tropical and subtropical agriculture and therefore food production in these regions (Alexandratos and Bruinsma, 2012; Hoffmann and UNCTAD secretariat, 2013). In fact, if specific mitigation strategies are not implemented, climate change is expected to cause a decrease in average yields ranging between 15% and 30% in the next 70 years (Hoffmann and UNCTAD secretariat, 2013). This decline will be particularly acute in the tropical and subtropical regions of Sub-Saharan Africa, South Asia and Central America, the territories that are most exposed to climate change (Ericksen *et al.*, 2011). It is critical therefore to identify alternative N management strategies to support future intensification of tropical and subtropical agricultural systems without exacerbating N_2O emissions from these agroecosystems. Critically, these strategies will have to be profitable for the farmer and transferable to both low- and high-income cropping systems in order to guarantee their widespread adoption.

One proposed method to sustain high crop productivity while limiting N_2O emissions is the application of fertilisers coated with nitrification inhibitors. Coating urea-based fertilisers with nitrification inhibitors has been shown in some cases to improve yields through reducing the amount of N lost via leaching, nitrification or denitrification (Linzmeier *et al.*, 2001a; Pasda *et al.*, 2001; Hatch *et al.*, 2005). On the other hand, nitrification inhibitors are expensive and on average increase fertilisation costs by 10% (Weiske, 2006; Eagle *et al.*, 2012). Moreover, their agronomic efficiency is affected by soil properties and climatic conditions, and several authors have reported no significant yield increase when using fertilisers coated with nitrification inhibitors (Díez López and Hernaiz, 2008; Liu *et al.*, 2013).

Alternatively, the reintroduction of legumes in cereal-based cropping systems has been suggested as one possible strategy to reduce the synthetic N inputs required and consequently to decrease N_2O emissions due to synthetic N fertilisers (Jensen and Hauggaard-Nielsen, 2003; Emerich and Krishnan, 2009). However, the efficacy of this strategy depends on site-specific environmental conditions and in some cases elevated N_2O emissions have been reported after the incorporation of legume residues (Jensen *et al.*, 2012).

To date, research has focused primarily on the agronomic and environmental efficacy of these N management strategies in temperate agroecosystems. Even though the technical feasibility of increasing cereal production in Oxisols has attracted considerable research interest over the last decade (Fageria and Baligar, 2001; Calegari *et al.*, 2008; Fageria and Baligar, 2008), efforts have focused on the correction of the key constraints of these soils (soil acidity, available phosphorus and soil organic matter). This means that data on N_2O emissions from tropical and subtropical cereal systems in Oxisols are still sparse and the efficacy of the abovementioned N management strategies in these environments remains unclear. Quantifying N_2O emissions in these agroecosystems is made even more critical by the fact that the warm and humid conditions typical of tropical and subtropical summers can potentially exacerbate N_2O losses from fertilised soils (Bouwman *et al.*, 2002b; Stehfest and Bouwman, 2006). Together, these issues confirm that research on alternative means of intensification is crucial to avoid the increase of future tropical and subtropical cereal production through an overuse of synthetic N, which will increase N_2O emissions from these agroecosystems.

1.3 Research aim and objectives

The primary aim of this study was to define profitable, agronomically viable and environmentally sustainable N management strategies to support future intensification of cereal production in Oxisols. Established with a focus on subtropical conditions, this study also aimed to extend the current understanding of environmental factors influencing N_2O emissions in fertilised Oxisols and to determine the magnitude and main pathways of fertiliser N losses that limit crop yields in these agroecosystems. These aims were achieved by way of the following three research objectives.

Objective 1 – *Evaluate the use of urea coated with a nitrification inhibitor to limit N_2O emissions and increase grain yields compared to conventional urea.*

The hypothesis underlying this objective was that nitrification inhibitors decrease N_2O emissions both directly, via slowing the nitrification rates, and indirectly, by reducing the amount of NO_3^- available to denitrifying microorganisms. By reducing N movements beyond the rooting zone, nitrification inhibitors can increase the synchrony between fertiliser-derived NO_3^- and plant uptake, and therefore increase yields compared to conventional urea.

Objective 2 – *Evaluate whether the introduction of a legume phase in a cereal-based crop rotation can reduce the reliance of cereal crops on synthetic N fertilisers and minimise N_2O emissions during the cereal cropping phase.*

In this case, the hypotheses were: i) the N mineralised from legume residues can substantially reduce the synthetic N input required by the following cereal crop and therefore limit the “direct” N_2O emissions due to mineral fertilisation, and ii) N_2O losses due to the mineralisation of legume residues can be minimised via synchronising the release of N derived from the residues with the N demand of the subsequent cereal crop.

Objective 3 – *Assess the sustainability of the N management practices investigated in Objectives 1 and 2 under a broader spectrum of fertiliser N rates and environmental conditions.*

This objective was identified by the fact that the data collected in this study were influenced by the specific seasonal weather conditions encountered during the monitored cropping seasons. Moreover, some of the abovementioned hypotheses could not be completely verified using only field measurements. The hypothesis underlying this objective were that a simulation approach can be used to i) assess the validity and robustness of the hypotheses underlying the previous two objectives, and ii) improve the understanding of the environmental factors driving N_2O emissions and crop productivity in subtropical cereal cropping systems.

This study was conducted at a research station managed by the Australian Department of Agriculture, Fisheries and Forestry in South-East Queensland, Australia, in consideration of three main factors. In the first instance, the experimental site needed to be located in a region dominated by Oxisol-type soils. Secondly, the necessity of replicating the farming practices adopted in cereal-based agroecosystems required the experiments to be performed in close collaboration with an organisation able to perform field operations. Lastly, the constant maintenance needed by the instruments used in this study required the field study to be located in close proximity to the Queensland University of Technology.

The study, funded by the Australian Grains Research and Development Corporation, involved two years of field experiments carried out in close collaboration with local research structures and agronomists. While conducted in a subtropical region (Cfa, according to Köppen climate taxonomy (Peel *et al.*, 2007)), the insight into N fertiliser dynamics and N_2O losses provided by this study is also valid for tropical cereal production systems in Oxisols. This is because the mild, dry winters and the warm, humid summers typical of Cfa-type climate are very similar to the tropical Aw-type, the climate where the vast majority of tropical cereal production is carried out globally (Chapter 2.2). Significantly, the two summer seasons monitored in this study were characterised by exceptionally elevated rainfall events (Chapters 3.4.1 and 4.4.1), providing even greater similarity to tropical summer cropping conditions and increasing the possibility of elevated N losses.

This is the first study on subtropical Oxisols to establish a comprehensive dataset on N_2O emissions and fertiliser N dynamics referring to multiple cropping seasons, crop rotations and N fertilisation strategies. This research constitutes a unique framework aimed at establishing agronomically viable and environmentally sustainable N management strategies to support future intensification of subtropical cereal production. The results of this study are largely transferable to similar cropping systems in tropical regions and as such can contribute to define sustainable N management practices valid for these environments.

1.4 Thesis outline

The investigation on N_2O emissions and fertiliser N dynamics presented in this thesis consists of seven chapters. Chapter 2 follows the introduction and sets the context of this study, analysing the topics related to N_2O emissions and sustainable intensification of cereal production in the subtropics. The thesis is based on publications, and following is a description of the four papers that together address the overall objectives of the study.

The first paper (Chapter 3) addresses the first objective of the study and compares the influence of conventional urea and urea coated with a nitrification inhibitor on seasonal N_2O emissions and grain yields. The efficacy of these fertilisation strategies was tested under different environmental conditions by applying the two fertilisers to a winter and a summer cereal crops. The outcomes of the study were threefold, namely to:

1. Generate baseline information on environmental factors influencing N_2O emissions, to be used as a reference case to define operational details for the design of the experiments addressing objective 2.
2. Quantify the magnitude of seasonal N_2O emissions in these agroecosystems using different synthetic N fertilisers.

3. Determine which cropping season presents the greatest scope for limiting N_2O emissions in these agroecosystems.

The results of this first study were published in:

De Antoni Migliorati M, Scheer C, Grace PR, Rowlings DW, Bell M, McGree J (2014). Influence of different nitrogen rates and DMPP nitrification inhibitor on annual N_2O emissions from a subtropical wheat–maize cropping system. Agriculture, Ecosystems & Environment, 186, 33-43.

The second paper (Chapter 4) addresses the second objective of the study and evaluates the reintroduction of legumes in cereal cropping systems as a strategy to reduce synthetic N inputs and diminish the N_2O intensity of the cereal phase. The results described in the first paper (Chapter 3) highlighted that N_2O emissions during the winter season were minimal. The second paper therefore focused exclusively on evaluating alternative N management practices in a summer cereal crop. The cereal crop was planted after a legume pasture, and N_2O emissions and yields were compared to those of the same cereal in rotation with a non-leguminous pasture. The outcomes of this experiment were to:

1. Confirm the average magnitude of seasonal N_2O intensities in these agroecosystems when legumes are not included in the crop rotation.
2. Assess the environmental and agronomic advantages and limitations of using legumes in the crop rotation to reduce the synthetic N requirements of the cereal.

The results of this second study were published in:

De Antoni Migliorati M, Bell M, Grace PR, Scheer C, Rowlings DW, Liu S (2015). Legume pastures can reduce N_2O emissions intensity in subtropical cereal cropping systems. Agriculture, Ecosystems & Environment, 204, 27-39.

The third paper (Chapter 5) complements the previous two papers by assessing the N recoveries of the N managements strategies investigated. This paper analyses the results of a multi-season ^{15}N tracer recovery experiment conducted on the same cereal crops monitored in the investigations described in the first and second papers (Chapter 4 and 5, respectively). The outcomes of the field study described in this paper were to:

1. Compare the fertiliser N recoveries of the different fertilisation strategies tested in this study.
2. Determine the main pathways of fertiliser N losses that limit N recovery in subtropical Oxisols.
3. Identify the most effective strategies to reduce fertiliser N losses and increase fertiliser N recovery in these agroecosystems.

The results of the third paper were published in:

De Antoni Migliorati M, Bell M, Grace PR, Rowlings DW, Scheer C, Strazzabosco A (2014). Assessing the agronomic and environmental implications of different N fertilisation strategies in subtropical grain cropping systems in Oxisols. Nutrient Cycling in Agroecosystems*, 100, 369-382.*

The fourth paper (Chapter 6) addresses the third objective of the study. In this paper, the entire dataset collected during this multi-season study was used to validate the DAYCENT biogeochemical model and evaluate how variations in seasonal weather conditions and fertiliser N rates can affect the agronomic and environmental performances of these N management practices. The aim of the investigation was to provide agronomists, researchers and policy-makers with an exhaustive evaluation of the N management strategies assessed in this study.

The results of this study have been submitted to:

De Antoni Migliorati M, Parton WJ, Del Grosso SJ, Grace PR, Bell M, Rowlings DW, Scheer C. Legumes or nitrification inhibitors to reduce N_2O emissions in subtropical cereal cropping systems? Agriculture, Ecosystems & Environment on 24 February 2015.

The thesis closes with Chapter 7, which synthesises the outcomes from all four papers and discusses the overall study findings. The practical implications and limitations of the study are analysed, discussing also the future research needs and the main findings of this study.

Chapter 2: Background and Literature Review

The release of vast amounts of N_2O in the atmosphere has significant repercussions on the environment. The relevance of this molecule in terms of climate change is analysed in section 2.1, with special focus on its impacts on global warming (section 2.1.2) and the factors regulating its emissions in the atmosphere (section 2.1.3). Specifically, N fertilisation plays a fundamental role in the increase of N_2O in the atmosphere, making agricultural soils the main contributor to anthropogenic N_2O emissions. Worldwide, the vast majority of fertiliser N is used to grow cereals, which demand is predicted to escalate in tropical and subtropical regions in response to future demographic growth. The challenges of enabling the intensification of agricultural systems in the tropics and subtropics without exacerbating N_2O emissions from these agroecosystems are identified in section section 2.2.

N_2O emissions represent a loss of fertiliser N and indicate inefficiency in the fertilisation process. Consequently, N management strategies aimed at minimising N_2O losses collimate with those aimed at maximising the recovery efficiency of fertiliser N in the crop (RE_{fN}). Achieving elevated RE_{fN} is therefore paramount for the sustainability and profitability of these strategies, a claim examined in section 2.3.

The use of nitrification inhibitors (section 2.3.1) and introduction of legumes in the crop rotation (section 2.3.2) are among the most promising N management strategies to maximise RE_{fN}. However, these strategies are highly dependent on local climate and soil conditions, and little data are available for tropical and subtropical regions. The accurate quantification of N_2O losses and RE_{fN} in tropical and subtropical cereal cropping systems is therefore crucial to assess the sustainability and profitability of N management strategies. The different approaches for measuring N_2O emissions and RE_{fN} values at field scale are analysed in section 2.4, where the potential of process-based models in testing the N management strategies at greater temporal and spatial scales is also examined.

The key points of the review are summarised in section 2.5, focusing on the implications of future intensification of cereal production in the subtropics and the urgent need for research to develop sustainable and profitable N management practices for these agroecosystems.

2.1 N_2O and global warming

2.1.1 Global warming: trends and predicted impacts on agriculture

Tropospheric air temperatures over land and oceans have increased dramatically over the last 100 years (Figure 2-1) and analyses of the Planet's radiative budget indicate a net positive energy imbalance resulting in an increased global heat content of the Earth system. In its latest report (Hartmann *et al.*, 2013), the International Panel for Climate Change (IPCC) corrected the previous analysis, stating that the total increase between the average temperature of the 1850–1900 period and the 2003–2012 period was 0.78 [0.72 to 0.85] °C. This was a further increment of +0.04°C and +0.18°C compared to the estimates presented in the previous IPCC reports for the period 1906-2005 (Forster *et al.*, 2007) and 1901-2000 (Ehhalt *et al.*, 2001), respectively. Critically, these results highlight that the average tropospheric temperature of the last three decades has been successively higher than that of any preceding decade since 1850.

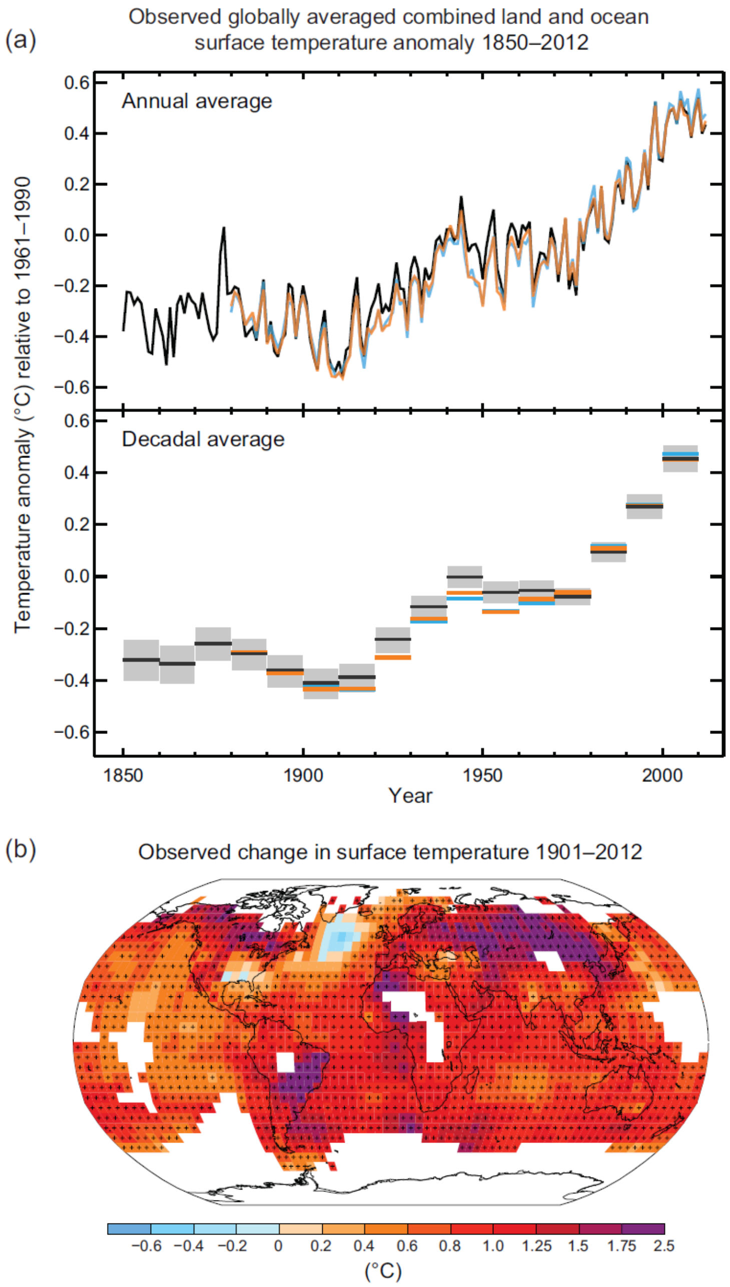

Figure 2-1 - (a) Observed global mean temperature anomalies (relative to the mean of 1961−1990) calculated from 1850 to 2012 using three independents datasets. Top panel reports annual mean values, while in the bottom panel are depicted the 10-year average values including the estimates of uncertainty. (b) Map representing the observed surface temperature changes from 1901 to 2012. (Hartmann *et al.*, 2013).

Importantly, IPCC projections indicate with a high confidence that the average temperature of the troposphere will continue to increase in the 21st century. Predictions of changes in the climate system are made using different climate models that simulate changes based on a set of scenarios called Representative Concentration Pathways (RCPs). For example, the tropospheric temperature increase for the period 2016–2035 is expected to be in the range of 0.3°C to 0.7°C relative to 1986–2005. Compared to the same reference period, the surface temperature increase for the interval 2081–2100 is projected to vary between 0.3°C and 4.8°C, depending on the RCP employed for the simulation (Figure 2-2). Overall, almost all RCP scenarios predict the global surface temperature of the end of the 21st century to exceed at least 1.5°C relative to the period 1850 to 1900. Importantly, all RCP scenarios except one predict that global surface warming will continue beyond 2100.

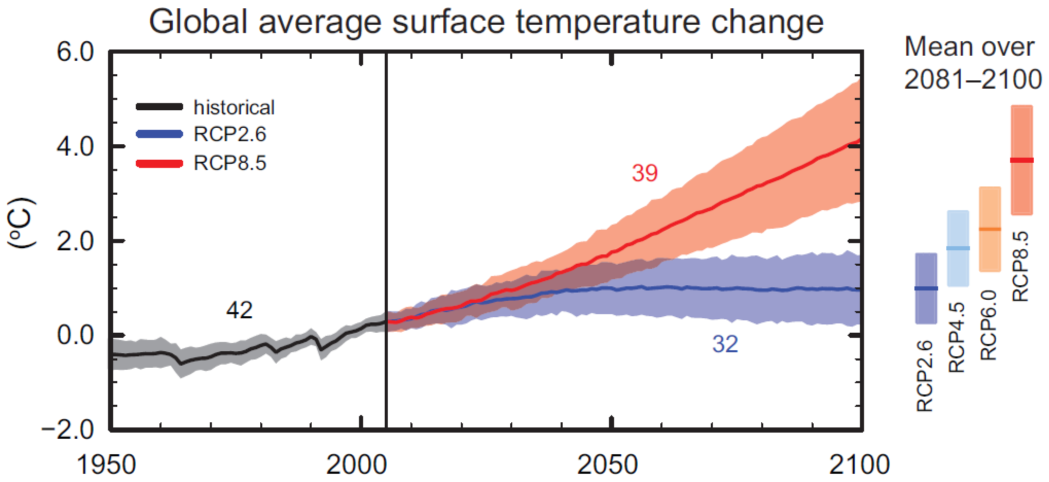

Figure 2-2 - Predicted variations in global surface temperature for the rest of the 21st century relative to the period 1986–2005. (IPCC, 2013).

The variations in atmospheric average temperatures have caused a series of modifications in various aspects of climate, a global phenomenon defined as Climate Change. These alterations include changes in the hydrogeological cycle, the occurrence of more frequent extreme meteorological events, or variations in atmospheric circulation patterns. For example, there is substantial evidence that on the global scale the number of cold days and nights has decreased and the number of warm days and nights has increased since the 1950s. Over the same period, the incidence of heat waves and extended periods of drought have increased in large parts of the European, Asian and Australian continents, while the extension of land areas subject to heavy precipitation events has considerably expanded. Importantly, many of these changes are projected to intensify in the next decades (Cubasch *et al.*, 2013).

In tropical and subtropical regions, significant variations are expected to occur in the Monsoon, El Niño-Southern Oscillation and Tropical Cyclone systems. Global monsoon precipitation is likely to strengthen in the 21st century, with sharp increases in terms of area and intensity. Meteorological extremes, such as precipitation intensity and consecutive dry days, are expected to augment while the overall duration of the monsoon season will expand. Additionally, rainfall variability due to El Niño-Southern Oscillation will intensify and the frequency of intense storms is projected to substantially increase (Christensen *et al.*, 2013).

Collectively, these changes will have a significant impact on agricultural systems. Increases of surface temperature exceeding 2°C compared to those of the late 20th century are predicted to have negative effects on yields for the three major world crops (wheat, rice and maize) in both tropical and temperate regions (IPCC, 2014). These effects will vary among regions and will include increased occurrence of pest diseases, reduced water supplies and higher ozone concentration in the troposphere (Hoffmann and UNCTAD secretariat, 2013). If mitigation strategies are not implemented, significant negative impacts on average yields are considered likely to occur from the 2030s. Median yield impacts up to -2% per decade will continue for the rest of the century and after 2050 the risk of more severe impacts will intensify, especially in the tropics and subtropics (Porter *et al.*, 2014).

2.1.2 Causes of global warming and relevance of N_2O

The Earth’s climate is determined by the energy radiated by the Sun and the properties that influence the absorption, reflection and emission of this energy within the Earth’s surface and atmosphere. Although changes in incoming solar energy, due for example to variations of the Solar activity, can substantially affect the Earth’s energy budget, the magnitude of these changes in the last two centuries has not been sufficient to determine the tropospheric temperature increase described in section 2.1.1 (Cubasch *et al.*, 2013). Changes in the properties of the Earth's atmosphere and surface have instead been dramatic in the last 200 years (Barker *et al.*, 2007; Cubasch *et al.*, 2013). Variations in the composition of the atmosphere or alterations of land, ocean, biosphere and cryosphere conditions can alter the Earth's radiation budget, producing a radiative forcing that affects climate. Radiative forcing is a measure of the influence of a given factor in altering the balance of incoming and outgoing energy in the Earth-atmosphere system. Positive forcing means a warming effect, while negative a cooling effect.

Radiative forcing has increased more rapidly since the 1970s and the value measured in 2011 was 2.29 W m^{-2} higher than in 1750, the year used to indicate the beginning of the industrial revolution. It is now established with high confidence that this increase has been caused primarily by the emission in the atmosphere of four principal greenhouse gases (GHG): carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and hydrochlorofluorocarbons (HCFCs) (Solomon *et al.*, 2007; Cubasch *et al.*, 2013). HCFCs emissions have however declined in the last two decades due to their phase-out under the Montreal Protocol (1989), and their role in the global warming will not be further examined in this study.

CO_2, CH_4 and N_2O are defined as long-lived GHGs since their chemical stability allows them to persist in the atmosphere over time scales of a decade to centuries. These gases adsorb thermal radiation emitted from the Earth surface and re-radiate it in multiple directions. The fraction of this re-radiation scattered downward conveys heat to the lower layers of the atmosphere and to the Earth's surface via the mechanism called the greenhouse effect. The result is an elevation of the average surface temperature above what it would be in the absence of the gases. The concentration of CO_2 CH_4 and N_2O has markedly increased in the terrestrial atmosphere since the beginning of the industrial era (Figure 2-3), reaching levels that substantially exceed the highest concentrations recorded in ice cores during the past 800,000 years (Trenberth *et al.*, 2007).

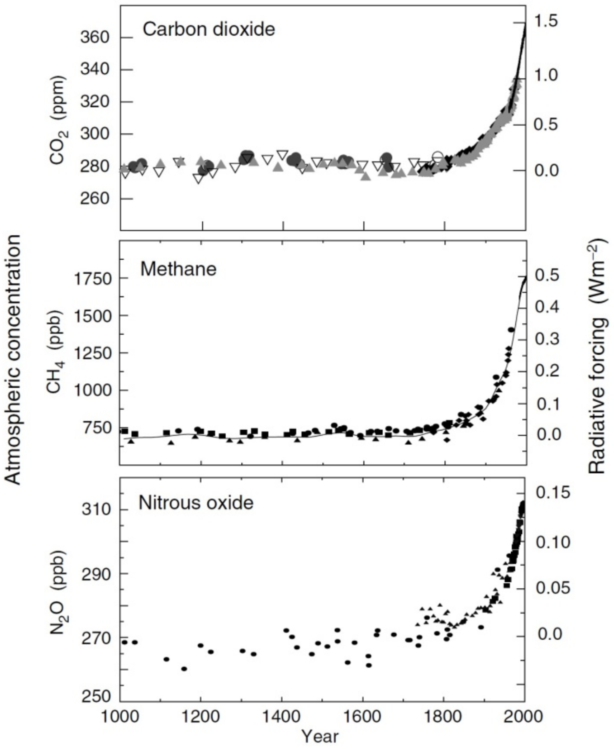

Figure 2-3 - Atmospheric concentrations of the three main long-lived greenhouse gases over the last 2000 years. Increases since about 1750 are attributed to human activities in the industrial era. (Cubasch *et al.*, 2001).

The concept of Global Warming Potential (GWP) was first introduced in 1990 by IPCC to compare the contribution of different gases to global warming. GWP is calculated over a specific period, typically 20, 100 and 500 years, and relates the radiative forcing of a mass of a specific gas to that of the same mass of CO_2. The relevance of N_2O in terms of global warming resides both in its elevated GWP and its increasing emission rates.

N_2O has the highest GWP among long-lived GHGs, i.e. 298 times that of CO_2 and almost 14 times that of CH_4 over a 100-year time horizon (Myhre *et al.*, 2013). The high GWP potential of N_2O is due to the elevated chemical stability of this molecule, which results in a lifetime of 114 years in the atmosphere (Montzka and Fraser, 2003), and to the high radiative forcing of N_2O (Forster *et al.*, 2007). As a result, N_2O presently contributes approximately 8.1% to the global warming effect caused by GHGs (Myhre *et al.*, 2013). Studies (Crutzen, 1981; Ravishankara *et al.*, 2009) have shown that N_2O is also involved in the depletion of the stratospheric ozone layer, which plays an essential role in protecting the terrestrial biosphere from the mutagenic and carcinogenic effects of solar ultraviolet radiation.

N_2O atmospheric concentration has exponentially increased in the last two centuries (Figure 2-3): globally averaged atmospheric N_2O concentration was 324.2 ppb in 2011 (Hartmann *et al.*, 2013), a 20% increase over the value of 270 ± 7 ppb estimated for pre-industrial levels (Prather *et al.*, 2012). Importantly, projections indicate that N_2O concentrations will continue to rise linearly in the next decades, unless mitigation strategies are implemented (Figure 2-4).

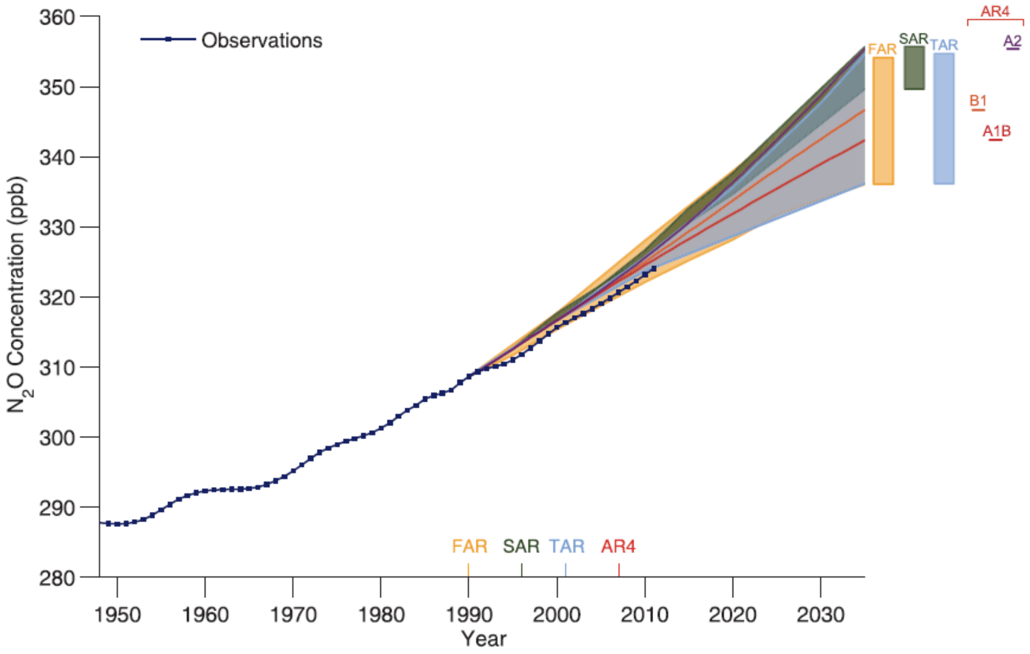

Figure 2-4 - Observed and predicted globally averaged N_2O concentrations from 1950 to 2035. The shading shows the largest model projected range of global annual N_2O concentrations from the first IPCC assessment report (FAR, 1990), second IPCC assessment report (SAR, 1996), third IPCC assessment report (TAR, 2001), and from three different emission scenarios presented in the fourth IPCC assessment report (AR4, 2007). (Cubasch *et al.*, 2013).

2.1.3 Factors controlling N_2O production

N_2O is produced both by anthropogenic and natural sources, the latter being estimated to contribute between 60% and 64 % to the total N_2O emissions worldwide (Forster et al., 2007; US-EPA, 2010). Soils are the largest direct source of N_2O emissions, emitting approximately 60% of N_2O produced by natural sources (US-EPA, 2010).

In soils, N_2O is produced as an obligate intermediate or a by-product of two microbial-mediated mechanisms: nitrification and denitrification (Figure 2-5). Nitrification occurs in aerobic conditions and consists of the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-), while denitrification - the reduction of NO_3^- to nitrogen gas (N_2) - takes place in anaerobic environments. During nitrification, chemoautotrophic bacteria oxidise N through a two-step aerobic process. In the first step bacteria of the genera Nitrosomonas and Nitrospira oxidise NH_4^+ to nitrogen dioxide (NO_2^-) by using the enzyme ammonia-monooxygenase, then in the second step NO_2^- is converted into NO_3^- by bacteria of the genus Nitrobacter (Conrad, 2001). Although studies have shown that under certain conditions heterotrophic bacteria can be a source of N_2O, in most soils chemoautotrophic microorganisms are largely, if not entirely, responsible for N_2O losses due to nitrification (Hutchinson and Davidson, 1993; Bremner, 1997).

During denitrification, heterotrophic bacteria (such as Paracoccus denitrificans and various species of Pseudomonas) use NO_3^- as a substitute of oxygen for terminal electron acceptor, reducing NO_3^- to N_2 (Bollmann and Conrad, 1998). N_2O losses due to denitrification can be significantly larger than those due to nitrification. During nitrification, small amounts of N_2O can be lost as a by-product of the first step of the process, when the organisms use NO_2^- as an alternative electron acceptor. During denitrification N_2O is instead produced as an obligate intermediate, meaning that if conditions are not favourable for the completion of the process, large amounts of nitrified N can be lost as N_2O and not as N_2.

The nitrification and denitrification processes, and therefore the magnitude of N_2O emitted by soil, is affected by three levels of regulation (Firestone, 1989; Bouwman, 1998a). The first level comprises the factors influencing the size of the microbial pool, which are primarily soil N and carbon (C) availability, and soil temperature. The second level includes the factors controlling the partitioning of soil N into NO, N_2O or N_2, i.e. soil moisture and pH. The final level consists of those soil properties that effect the diffusion of the gases produced in the previous steps.

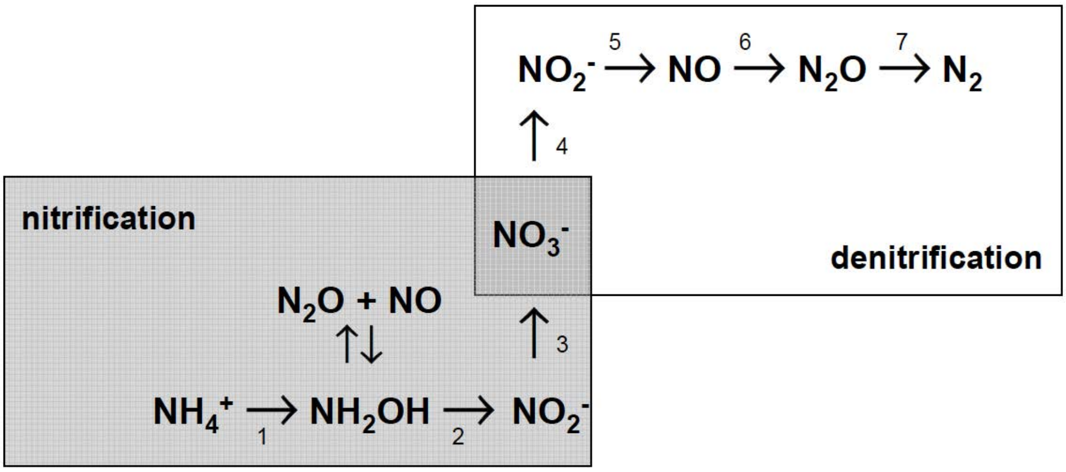

Figure 2-5 - The processes of nitrification and denitrification. The numbers indicate enzyme reactions, i.e., 1: ammonium monooxygenase; 2: hydroxylamine oxidoreductase; 3: nitrite oxidoreductase; 4: nitrate reductase; 5: nitrite reductase; 6: NO reductase; 7: N_2O reductase. (Conrad, 2001).

Among first-level controllers, soil N is usually the main factor limiting N_2O production. In these environments nitrification rates are in fact limited by the slow mineralisation of N produced by the decomposition of plant and animal residues (Dalal *et al.*, 2003). This process is however substantially accelerated in agricultural soils, where the addition of rapidly nitrifiable forms of N (especially NH_4^+-based fertilisers such as urea) and the soil aeration caused by tillage increase the amounts of N available to nitrifiers (Robertson and Groffman, 2007). N_2O emissions due to denitrification are instead mainly controlled by the size of the soil NO_3^- pool. Low concentrations of NO_3^- prolong the reduction of N_2O to N_2 performed by denitrifying microorganisms, decreasing therefore N_2O:N_2 ratio. Conversely, elevated concentrations of NO_3^- almost completely inhibit this process, resulting in larger amounts of N lost as N_2O instead of N_2. Denitrification rates are also affected by soil organic carbon, since denitrifying bacteria are heterotrophic and use C as a source of energy. In anaerobic conditions therefore, the presence of high contents of soluble C or readily decomposable organic matter can significantly increase denitrification rates (Dalal *et al.*, 2003; Li *et al.*, 2005a). The effects of organic materials on denitrification varies with their resistance to decomposition and easily decomposable substrates such as glucose increase denitrification rates more than materials that decompose with difficulty such as lignin (Bremner, 1997). As with other biological processes, nitrification and denitrification are positively influenced by temperature. Moreover the chemical processes conducted by nitrifying bacteria are slightly modified at higher temperatures and enhanced N_2O emissions have been observed at temperatures exceeding 25°C (Dalal *et al.*, 2003).

Amongst second-level controllers, the amount of water in the soil is the predominant factor regulating the activity of nitrifying and denitrifying bacteria. Nitrification is typically the main source of N_2O emissions when water-filled pore space (WFPS) is below 40% (Figure 2-6), while denitrification rates rapidly intensify with increasing water content, becoming the predominant process over 70% WFPS (Bouwman, 1998a; Kiese and Butterbach-Bahl, 2002; Werner *et al.*, 2006). Above 65%-75% WFPS anaerobic conditions start to occur in the soil, promoting denitrification and therefore the production of both N_2O and N_2 (Panek *et al.*, 2000). When soil water content exceeds 80%-90% WFPS, denitrifying bacteria can complete the reduction of NO_3^-, emitting predominantly N_2 as the end product of the reaction. Consequently, the N_2O:N_2 ratio starts to decrease as the soil water content exceeds 75% WFPS (Dalal *et al.*, 2003).

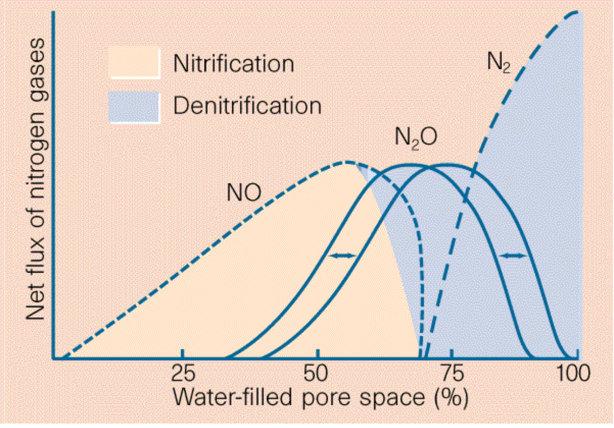

Figure 2-6 - Relationship between water-filled pore space (WFPS) of soils and the relative fluxes of nitrogen gases from nitrification and denitrification. (Bouwman, 1998b).

The metabolic activity of both nitrification and denitrification bacteria is negatively affected by acid soil conditions and generally highest N_2O production rates are observed at pH values between 7 and 8.5. The inhibitory effect of low pH on the bacterial metabolic activity have been associated with the decreased availability of organic C and mineral N under acid conditions (ŠImek and Cooper, 2002). Although the net N_2O production tend to diminish at low soil pH values, several studies (Dalal *et al.*, 2003; Liu *et al.*, 2010a) have reported increased $N_2O:N_2$ production ratios when soil pH was below 7. Acid soil conditions inhibit the reduction of N_2O to N_2 more than the reduction of NO_3^- to N_2O, favouring in this way the emission of N_2O over N_2. Consequently, as pH increases, denitrification products tend more or completely towards N_2 production (Chapuis-Lardy *et al.*, 2007).

Among third-level controllers are those factors that determine the volume of soil pores, such as texture, bulk density, aggregate stability and organic matter content. These parameters are pivotal in regulating the soil water content and therefore soil aeration, gas production and diffusion. For example, the higher amount of air present in coarser soils (e.g. sandy soils) tends to favour nitrification, while the greater quantity of water that can be stored in fine-textured soils (e.g. clay soils) promotes denitrification (Bollmann and Conrad, 1998). The smaller pore size of fine-textured soils also reduce the soils hydraulic conductivity, creating more persistent waterlogging conditions (Granli, 1995). Moreover, smaller pores rapidly fill with water, creating anaerobic microsites that enable denitrification to occur at lower soil water contents than coarse-textured soils (Parton *et al.*, 2001).

2.2 N_2O emissions from tropical and subtropical cereal cropping systems

Agricultural soils play a fundamental role in the increase of N_2O in the atmosphere, contributing approximately 50% of global anthropogenic N_2O emissions (Smith *et al.*, 2007). The reason for the importance of agricultural soils as a source of N_2O resides in the addition of N to support crop production. As described in section 2.1.3, the factor most commonly limiting nitrification and denitrification rates is soil N availability. In agricultural fields, this limitation is substantially overcome when N is supplied in the form of synthetic fertiliser, animal manure or N fixed by leguminous crops, promoting therefore elevated N_2O emission rates.

Many studies have shown a direct correlation between N_2O emissions and synthetic N fertilisation, measuring increasing N_2O fluxes when agricultural soils are fertilised with higher N rates (Bouwman *et al.*, 2002a; Del Grosso, 2006; Shcherbak *et al.*, 2014). Synthetic fertiliser N can be lost from the soil-crop system also via soil erosion, runoff and NO_3^- leaching, causing the hypertrophication of water bodies and promoting indirect N_2O emissions from these sources (Tilman *et al.*, 2002; Crews and Peoples, 2004; Jensen *et al.*, 2012). Consequently, it is now established that the augmented global N fertiliser use observed in the last decades played a central role in the increase of N_2O concentration the atmosphere (Penman *et al.*, 2000; Smith *et al.*, 2007; Smith *et al.*, 2014).

2.2.1 Intensification of tropical and subtropical cereal production

Worldwide consumption of synthetic N fertilisers has increased by 332% in the last 40 years, expanding from 32 Mt yr^{-1} in 1970 to 106 Mt yr^{-1} in 2010 (FAOSTAT website, accessed October 2014). Critically, almost 60% of worldwide N fertiliser is used to crop cereals (Ladha *et al.*, 2005), which are by far the world's most important sources of food, via both direct human consumption and input for livestock production (FAO, 2012). Specifically, cereals contribute on average 50% of daily energy intake, reaching levels close to 70% in some developing countries (Kearney, 2010).

Global cereal demand is predicted to increase by 60% in the next 40 years (FAO, 2009). Nearly all of the increase in cereal consumption will come from the tropical and subtropical regions of Africa, South America and Asia (Alexandratos and Bruinsma, 2012), where the vast majority of future global demographic growth is projected to take place (UNFPA, 2011). This increased demand translates into a need to increase current tropical and subtropical cereal production by at least 60% (Alexandratos and Bruinsma, 2012).

There is consensus that this target should be pursued though augmenting current cereal yields to minimise the need for expanding cropland, a strategy that would cause habitat loss and reduce biodiversity (Godfray *et al.*, 2010; Foley *et al.*, 2011; Phalan *et al.*, 2011). Average cereal yields are presently low in most tropical and subtropical countries (Figure 2-7). This means that if future food security targets are to be achieved, in the next decades the productivity of these cereals will need to increase between 1.2% and 2.4% every year (Alexandratos and Bruinsma, 2012; Ray *et al.*, 2013).

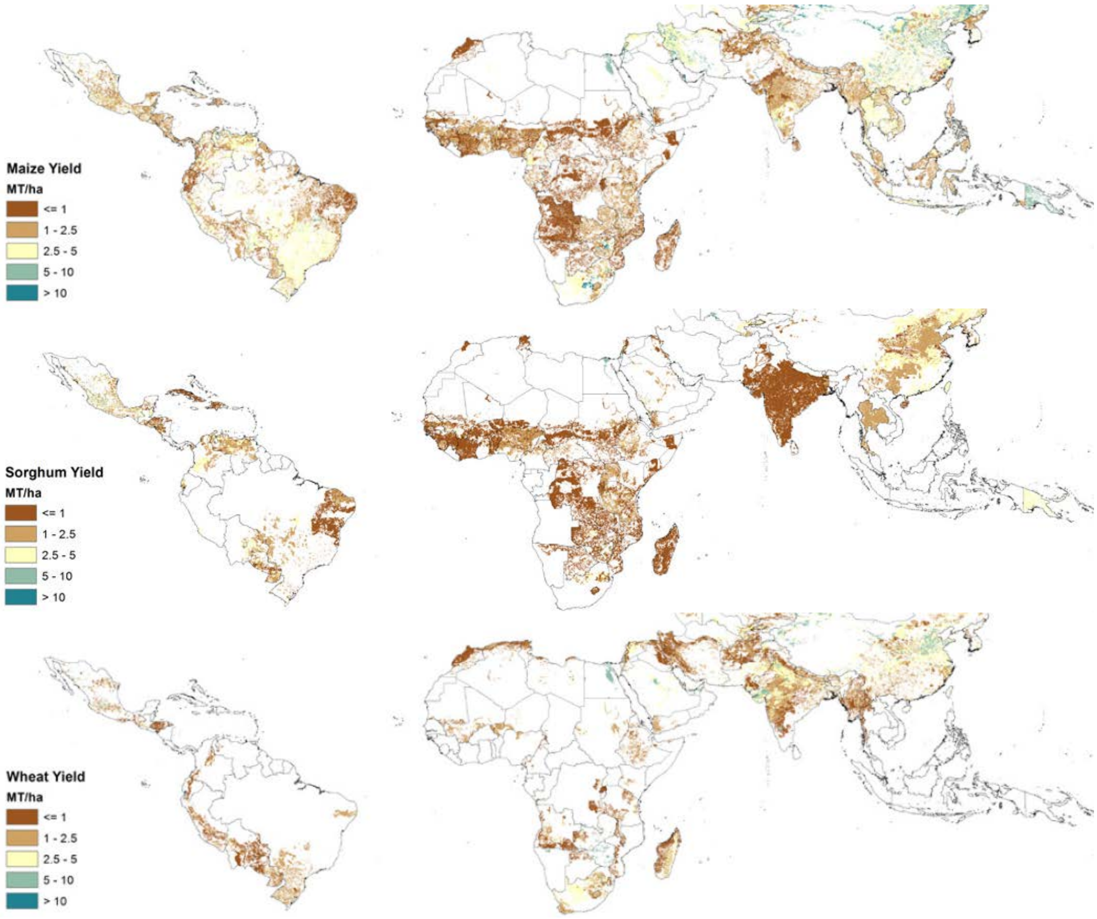

Figure 2-7 - Current maize (above), sorghum (centre) and wheat (below) yields in tropical and subtropical countries of Central and Latin America, Africa and Asia. Yields are expressed in Mt ha^{-1}. (Ericksen *et al.*, 2011).

Currently, tropical and subtropical cereal production occurs largely in Oxisols, the most common soil type in these regions (Figure 2-8). Grain yields in Oxisol regions are often limited by the constraints of these soils, namely low native N content, reduced natural fertility, soil acidity and low levels of soil organic matter. However, many of the chemical constraints of Oxisols can be amended with modern agronomic technologies and since Oxisols are characterised by a favourable topography for agriculture, suitable temperatures and sufficient moisture availability for crop growth throughout the year, the potential productivity of these agroecosystems is among the highest in the world (Figure 2-9).

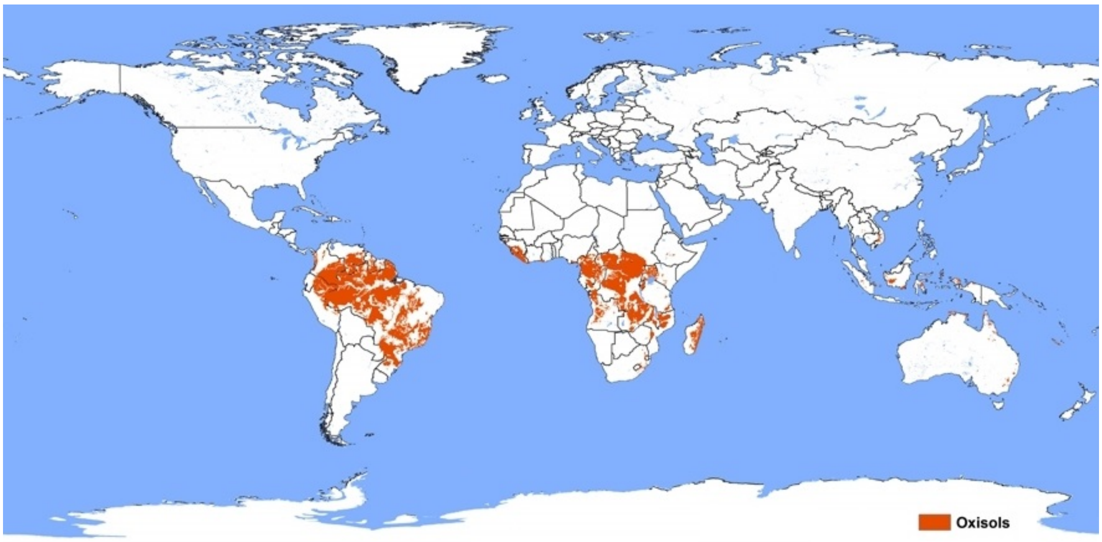

Figure 2-8 - Global distribution of Oxisols. (USDA-NRCS).

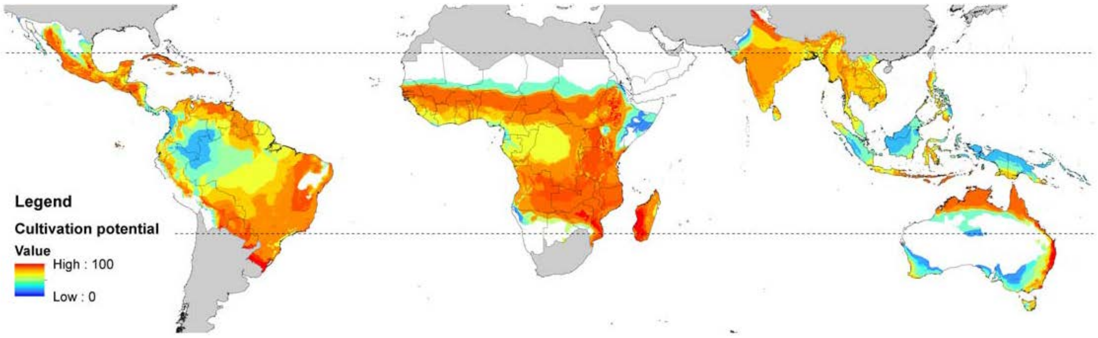

Figure 2-9 - Cultivation potential for drier-climate cereal crops (e.g. maize, sorghum and wheat) in the tropics. Cultivation potential is calculated as the ‘‘agro-climatically attainable yield’’ for each rainfed crop as a percentage of the global maximum for that crop. (Phalan *et al.*, 2013).

N fertilisation is a key factor to enable the intensification of cereal production in Oxisols. Several studies have highlighted that N deficiency is usually the major agricultural constraint limiting crop production in these agroecosystems (Sánchez and Salinas, 1981), resulting in the inability of Oxisols to sustain continuous cereal production without the provision of adequate amounts of N (Fageria and Baligar, 1995).

Current N management strategies in Oxisols vary largely depending on the scale of farming operations. For example, fertiliser N inputs are usually elevated in the large commercial farms of central Brazil (Fageria and Baligar, 2001; Gitti *et al.*, 2012), North-Eastern Australia (Angus, 2001; Chen *et al.*, 2008b) or, in some cases, Central Africa (Cheru and Modi, 2013). On the contrary, N inputs are extremely limited and usually insufficient in African and South American smallholder farms due to the socioeconomic constraints that prevent smallholders to access synthetic N fertiliser (Sánchez and Salinas, 1981; Crawford *et al.*, 2003). Regardless of farm scale however, in the absence of alternative N management strategies there will be pressure to apply more synthetic N fertiliser in the attempt to boost cereal production and meet a pressing grain demand (Denning *et al.*, 2009; Alexandratos and Bruinsma, 2012; Branca *et al.*, 2013). This intensification of synthetic N fertiliser use will result in increased N_2O emissions from these agroecosystems, undermining global efforts to limit global warming.

It is therefore critical to identify alternative N management strategies aimed at supporting future intensification of tropical and subtropical cereal production without causing an increase of N_2O emissions from these agroecosystems. Although largely valid also for tropical conditions, the N management strategies described in the following sections have been selected among the most promising to support the sustainable intensification of subtropical cereal cropping systems in Oxisols.

2.3 Alternative N management strategies to reduce N_2O emissions and sustain subtropical cereal production

N_2O emissions represent a loss of fertiliser N and indicate inefficiency in the fertilisation process. Consequently, N management strategies aimed at minimising N_2O losses collimate with those aimed at maximising the efficiency of fertiliser N recovery in the crop (RE_{fN}). The RE_{fN} is defined as the percentage of fertiliser N that is taken by the crop (Ladha *et al.*, 2005) and is intimately connected to the concept of synchrony. Synchrony is a condition that occurs when the N released by the fertiliser coincides with crop demand in terms of timing and amount (Figure 2-10a).

Asynchrony between fertiliser N supply and crop demand can result in temporary N deficiency or in mineral N excess in the soil, resulting in conditions that can limit crop growth or enhance N losses (Figure 2-10b). Nitrification, denitrification, ammonia volatilisation and NO_3^- leaching are the major contributors to N losses (Mosier *et al.*, 2004a).

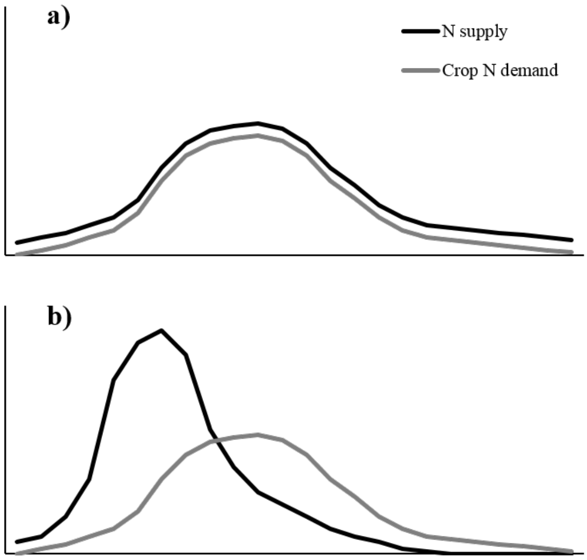

Figure 2-10 - Example of synchrony (a) and asynchrony (b) between crop N demand (grey line) and N supply (black line). Adapted from Crews and Peoples (2005).

Synchronising fertiliser N supply with crop uptake is therefore a key factor in defining sustainable N management strategies to achieve the potential productivity of subtropical cereal cropping systems. To enable their widespread adoption, these strategies will have to be profitable for the farmer and transferable also to low-income cropping systems, where investments and research have often been neglected (Alexandratos, 2009; Branca *et al.*, 2011). Urea is by far the dominant formulation used in agriculture, due to its low costs of production, distribution, storage and handling per unit of N (Figure 2-11). It is for this reason that this study focused on assessing the environmental and agronomic performances of N management systems based on the use of urea.

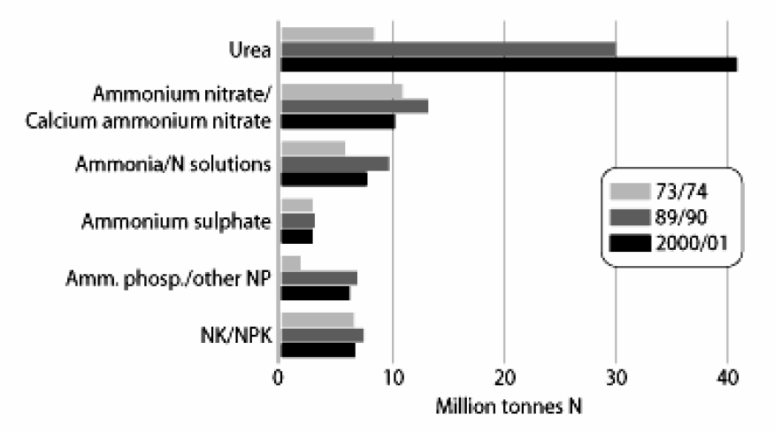

Figure 2-11 - Global N fertiliser consumption by product. (IAEA, 2008).

2.3.1 Nitrification inhibitors

One method to synchronise fertiliser N release with the estimated plant N uptake is the addition of nitrification inhibitors to NH_4^+-based fertilisers. Nitrification inhibitors are antibiotics that slow the activity of the Nitrosomonas bacter, the genus responsible for the oxidation of NH_4^+ to NO_2^-. Maintaining fertiliser N in the NH_4^+ form reduces the chances of N to be lost via leaching or denitrification when soil moisture conditions are elevated. Nitrification inhibitors have been reported by several studies to substantially decrease N_2O emissions and increase crop yields in humid, high rainfall environments (Prasad and Power, 1995; Linzmeier *et al.*, 2001a; Pasda *et al.*, 2001; Hatch *et al.*, 2005). Importantly, these are the environmental conditions that are prevalent during subtropical summers.

Among nitrification inhibitors, 3,4-dimethylpyrazole phosphate (DMPP) has been reported as one of the most efficient in slowing nitrification and reducing N_2O losses (Weiske *et al.*, 2001a; Weiske *et al.*, 2001b; Liu *et al.*, 2013). DMPP is the result of a joint research project lead by BASF in the early 1990s to develop a new inhibitor capable of effectively limit nitrification even when applied at low concentrations (Zerulla *et al.*, 2001). DMPP is usually applied at a rate of 6 g of DMPP per kg of urea and, depending on environmental conditions, is effective in inhibiting nitrification for a period of 4 to 10 weeks (Barth *et al.*, 2001; Pasda *et al.*, 2001).

Nitrification inhibitors though are expensive and, on average, increase fertilisation costs by 10% (Weiske, 2006; Eagle *et al.*, 2012). Moreover, their agronomic efficiency is affected by soil properties and climatic conditions, and the effects on yields have been contrasting. Positive yield responses to application of nitrification inhibitors have been reported under conditions that favour high drainage rates (e.g. cropping systems with intense rainfall patterns during the fertilisation period) or that limit the synchronisation between fertiliser release and plant N uptake (e.g. when high N fertiliser inputs are applied) (Majumdar *et al.*, 2002; Di and Cameron, 2005; Ma *et al.*, 2013). Conversely, no significant yield increase with fertilisers coated with nitrification inhibitors have been reported for fine-texture soils or low-rainfall cropping systems even when high N fertiliser inputs were applied (Arregui and Quemada, 2006; Díez López and Hernaiz, 2008; Liu *et al.*, 2013).

In addition to the conflicting results on the agronomic efficiency of nitrification inhibitors in cereal cropping systems, the vast majority of data on their effect on N_2O emissions refer to temperate regions (Linzmeier *et al.*, 2001b; Weiske *et al.*, 2001a) or laboratory conditions (Khalil *et al.*, 2009; Suter *et al.*, 2010). As a result, the efficacy of this fertilisation strategy in increasing cereal production and reducing N_2O emissions in subtropical environments is unclear.

2.3.2 Introducing legumes in cereal-based cropping systems

The reintroduction of legumes in cereal-based cropping systems has been proposed as one possible strategy to reduce the environmental threats associated with synthetic N fertiliser use and sustain cereal production (Crews and Peoples, 2004; Jensen *et al.*, 2012). Legume rotations have progressively become less common in the last decades, as farmers in many regions of the world have increased their reliance upon synthetic N fertilisers. Synthetic N fertilisers are crucial in supporting high yields and reducing the uncertainties related to plant development by empowering farmers with a high level of flexibility in terms of timing and amount of N application. They also reduce the planning required by the farmer to manage the N supplied to a given crop by enabling the elimination of the fertility-generating stage of a rotation sequence.

Legumes however offer multiple agronomic and environmental advantages due to their unique ability to fix atmospheric N_2 in symbiosis with rhizobia bacteria. The incorporation of legume residues releases the nutrients accumulated during the cropping phase and can therefore reduce the fertiliser N demand of the following cereal crop, consequently decreasing N_2O emissions associated with synthetic N fertilisation. Overall, legumes are economically accessible and their use is technically adoptable in both low- and high-income subtropical cropping systems.

An extensive review on the use of legumes to mitigate climate change (Jensen *et al.*, 2012) concluded that N_2O emissions during the legume growing season did not differ substantially from unplanted or non-fertilised soils. However, elevated N_2O losses were sometimes reported after the termination of legume-based ley pastures, when crop residues were returned to the soil (Gomes *et al.*, 2009; Pappa *et al.*, 2011). The low C:N ratio of legume tissues can lead to rapid mineralisation rates once residues are incorporated into the soil. As a result, accumulation of mineral N can occur in the soil and the readily mineralisable C from the legume residues becomes available to support elevated denitrification rates (Jensen *et al.*, 2012).

These N_2O emissions were often measured when the field site had been left fallow for long periods (Wagner-Riddle *et al.*, 1997; Wagner-Riddle and Thurtell, 1998; Pappa *et al.*, 2011). The risk for low levels of synchronicity between N supply and crop demand is highest when an extended fallow period follows a legume, as either no plants are present to utilize the NO_3^- generated by the legumes or the demand for N by newly sown crops is small. As a result, high amounts of mineral N can accumulate in the soil, increasing the possibility of elevated denitrification losses.

The most viable strategy for reducing N_2O emissions after the termination of legume-based ley pastures is therefore to minimise the time that fields are left uncropped. Typically, the highest N mineralisation rates from most legume residues are reported to occur six weeks from incorporating the residues into the soil (Fox *et al.*, 1990; Becker and Ladha, 1997; Robertson, 1997; Park *et al.*, 2010), a timeframe that well matches the crop requirements of most subtropical cereal crops.

It must be highlighted however that the N mineralisation rates of legume residues and the associated N_2O losses are highly dependent on local climate and soil conditions (Rochette *et al.*, 2004), and while numerous studies have investigated N_2O emissions after the termination of legume ley pastures prior to a return to cropping, the vast majority were conducted in temperate regions. Consequently, scant data are available on the application of this N management strategy in Oxisols-based cereal cropping systems (Wagner-Riddle and Thurtell, 1998; Baggs *et al.*, 2000; Robertson *et al.*, 2000; Rochette *et al.*, 2004; Schwenke *et al.*, 2010).

2.4 Quantifying N_2O emissions and RE_{fN} in subtropical cereal agroecosystems

N_2O fluxes and RE_{fN} are highly variable in croplands. N_2O fluxes are a result of soil microbial activity, which is influenced by site-specific soil properties, climatic conditions and agricultural management, such as fertilisation, tillage and irrigation practices. Significant emissions of N_2O typically occur between 0 and 30 days after applying N fertiliser and are often triggered by rain or irrigation events (Eagle *et al.*, 2012). Liu *et al.* (2010b) for example observed that almost 30% of annual N_2O emissions in cotton occurred in the one-month period following N fertilisation, while in maize Parkin and Kaspar (2006) measured almost 50% of the cumulative annual N_2O flux during two emission pulses that followed rainfall. At a plot scale, the spatial and temporal occurrence of N_2O emissions is further complicated by the method of fertiliser application (e.g. broadcasting vs. banding) and the type of fertiliser used (e.g. ammonium- vs. nitrate-based, conventional vs. enhanced efficiency fertilisers) (Eagle *et al.*, 2012). The combination of different factors can therefore have a considerably greater influence on N_2O fluxes than the fertiliser N rate itself, and predicting emissions merely on the basis of N input can lead to significant errors.

As for N_2O fluxes, the RE_{fN} of a given N management practice is influenced by many factors. RE_{fN} can vary substantially among cereal cropping systems depending on climate, crop, soil conditions as well as the rate, source, placement and timing of fertiliser application (Ladha *et al.*, 2005; Bruulsema *et al.*, 2011). Obtaining accurate measurements of N_2O losses and RE_{fN} in subtropical cereal cropping systems in Oxisols is therefore crucial to define profitable, agronomically viable and environmentally sustainable N management strategies to support future intensification of these agroecosystems.

2.4.1 Measuring N_2O emissions

N_2O fluxes at a field scale can be measured using micrometeorological and chamber-based techniques (FAO, 2001). Micrometeorological techniques allow for great spatial integration, with fluxes typically measured for areas as large as 1-10 km^2 (Dalal *et al.*, 2003). On the other hand, these systems require large areas of a uniformly treated crop, a feature that prevents their use for measuring emissions form small-scale plots under different treatments. Moreover, micrometeorological techniques are less sensitive that chamber-based techniques in measuring low fluxes and their detection limit is affected by weather conditions.

Chamber-based techniques can be applied to fragmental landscapes and field experiments with multiple small plots. Importantly, they are relatively inexpensive, versatile and can measure fluxes under unstable meteorological conditions. For this reason chambers have been the most commonly used method for measuring N_2O fluxes from agricultural soils (Denmead, 1979; Rochette *et al.*, 1997; Breuer *et al.*, 2000; Kiese and Butterbach-Bahl, 2002). Chamber-based techniques can employ either flow through or non-flow through designs, the latter being however the most widespread (Bouwman *et al.*, 2002a).

Non-flow through chambers, often referred to as “static chambers”, rely on the accumulation of N_2O within an open-bottomed chamber placed on the soil surface. Gas samples are taken periodically and analysed using gas chromatographic techniques to determine the variation of N_2O concentration in time. Gas sample collection can be conducted either manually, with samples analysed in the laboratory (manual chamber systems), or automatically, with samples analysed directly in the field (automated chamber systems).

Manual chamber systems have the disadvantage of being highly labour intense and can cover relatively short measuring periods with low time resolution (at most few daily measures per week). Automated chamber systems are capable of measuring fluxes for an entire cropping season with sub-daily resolution. These systems are also adaptable to a wide range of conditions and can analyse emission rates ranging from the order of 1 $\mu g\ m^{-2}\ h^{-1}$ to more than 10 $mg\ m^{-2}\ h^{-1}$ (Hensen *et al.*, 2013).

Briefly, automated chamber systems consist of multiple mechanically-operated chambers linked to a sampling unit that collects and conveys the gas samples from the chambers to an in-situ gas chromatograph (Figure 2-12). The functioning of the automated chamber system employed in this study is detailed in Chapter 3.3.3.

Figure 2-12 - Automated closed static chamber during the sampling campaign in wheat (see Chapter 3). The automated sampling unit and the analytical equipment are both housed in the white trailer seen in the background. Photo credit: Massimiliano De Antoni Migliorati.

Automated chamber systems have the ability to capture diurnal variations in emissions. Diurnal fluctuations in N_2O emissions are affected by soil temperature variations (Christensen, 1983; Maljanen *et al.*, 2002) and lags of several hours between maximum flux and maximum temperature have been reported in studies using automated chambers. For example, Scheer *et al.* (2012) observed that the diurnal variations of N_2O fluxes from subtropical irrigated wheat was greater than 10-fold for some chambers. The high temporal variability of N_2O emissions means that the sampling frequency throughout a cropping season can have a profound effect on the calculation of cumulative emissions. Consequently, automated chamber systems greatly improve the ability to measure the effects of different N management practices.

2.4.2 Measuring RE_{fN}

The RE_{fN} of a given fertilisation strategy can be assessed using two procedures: estimating the agronomic efficiency of fertiliser N use (AE_{fN}) or using the ^{15}N-tracer technique. The AE_{fN} procedure, also referred to as the difference method, is defined as the extra grain yield obtained per kg of fertiliser N applied (Ladha *et al.*, 2005). The major limitaton of this method is the assumption that the N uptake patterns are similar in fertilised and non-fertilised plants (IAEA, 2008), disregarding the influence of N availability on root development (Olson and Swallow, 1984; Belford *et al.*, 1986). This technique also does not allow the discrimination between fractions of the plant N originating from applied fertiliser, soil supply or irrigation water (Smith *et al.*, 1989).

Precise RE_{fN} measurements can be obtained using the ^{15}N-tracer technique, also known as ^{15}N dilution method. This technique demands extreme accuracy during sampling and computations, the collection of large numbers of samples, and the availability of expensive laboratory equipment. Importantly, this method does not need control plots and enables to distinguish between fertiliser- and soil-N taken by the crop. In this approach, a fertiliser labelled with the ^{15}N isotope (tracer) is added to the soil and the percentage of fertiliser N recovered in the plant tissues or in the soil is determined with mass spectrometry methods (IAEA, 2001). Fertiliser N losses are calculated by subtracting the N recovered in the soil-plant system from the amount of ^{15}N-labelled fertiliser originally applied. The amount of N that cannot be accounted for in the monitored soil-plant system is assumed to be lost in the atmosphere (as N_2, N_2O, NH_3 or NO_x) or via runoff and deep leaching (NO_3^-). It must be acknowledged however that part of the unaccounted N can be due to errors associated with each of the measured N sinks, resulting therefore in slight under- or overestimations of the N losses.

When using the ^{15}N-tracer technique, losses via NH_3 volatilisation or runoff can be minimised with the adoption of specific experimental set-ups. In this way the amount of N lost via deep leaching can be estimated by interpolating soil water content data with the fertiliser N amounts recovered in the lower layers of the soil profile. Using these techniques, the bulk of unaccounted fertiliser N can be therefore limited to N_2O, N_2 and NO_x emissions, the latter being negligible from a N balance perspective.

The adoption of the ^{15}N-tracer technique in this study, together with the use of an automated chamber system to determine N_2O emissions, constituted a powerful technique to calculate the overall fertiliser N budget and compare the RE_{fN} of different N management strategies. Details on the methodology and calculations used in this study are provided in 5.2.6.

2.4.3 Modelling N_2O emissions and cereal production

Field experiments are crucial to deepen the understanding of factors regulating N_2O emissions and limiting crop production. Experiments are however conducted at particular points in time and space and the results obtained can be generalised only to a certain extent. Moreover, field experiments are time-consuming and expensive, and can investigate only a limited number of treatments (Jones *et al.*, 2003). Simulation models have been developed to overcome these limitations so to predict nutrient flows in the soil-plant-atmosphere system at temporal and spatial scales where it would not be possible to implement the required measurement intensity.

Numerous approaches have been adopted for the development of models able to predict nutrient dynamics in agroecosystems, and processed-based models are among the most accurate. These models use a mechanistic approach to represent the complex biophysical processes that influence greenhouse gas emissions and plant growth, such as soil organic matter, soil water content, fertiliser N management and plant N availability (Del Grosso *et al.*, 2009). Processed-based models enable to simulate N losses and assess the RE_{fN} of different fertilisation strategies, as well as to quantify the gap between potential and actual yields (Boote *et al.*, 1996; Ladha *et al.*, 2005). In this respect, models have become indispensable tools to investigate how variations in N management practices and different environmental circumstances can affect crop production and N_2O emissions.

Few processed-based models can simulate crop yields and N_2O emissions at the field-scale (Chen *et al.*, 2008a). Among these, only a limited number have been tested under different environmental conditions around the globe and have potential relevance to Australian agroecosystems. For example, models such as WNMM (Li *et al.*, 2007; Li *et al.*, 2008; Li *et al.*, 2013) have been tested under Australian and Chinese conditions but, to present, have not been extensively used in other environments. This section examines the structure, strengths and limitations of the three most extensively tested soil and plant simulation models currently used in the Agricultural Model Intercomparison and Improvement Project (AgMIP website): DNDC, APSIM and DAYCENT.

DNDC

The DeNitrification-DeComposition (DNDC) model was first developed by Li *et al.* (1992) to model N_2O emissions from agricultural soils in the United States (US-EPA, 1995) and consists of two main components (Figure 2-13). The first comprises soil climate, crop growth and decomposition submodels, and calculates soil temperature, water content, pH fluctuations, redox potential (Eh), and nutrient dynamics based on environmental drivers such as climate, soil properties, vegetation and anthropogenic activity. The second component consists of the nitrification, denitrification and fermentation submodels and simulates NO, N_2O, and NH_3 fluxes based on soil variables (Chen *et al.*, 2008a).

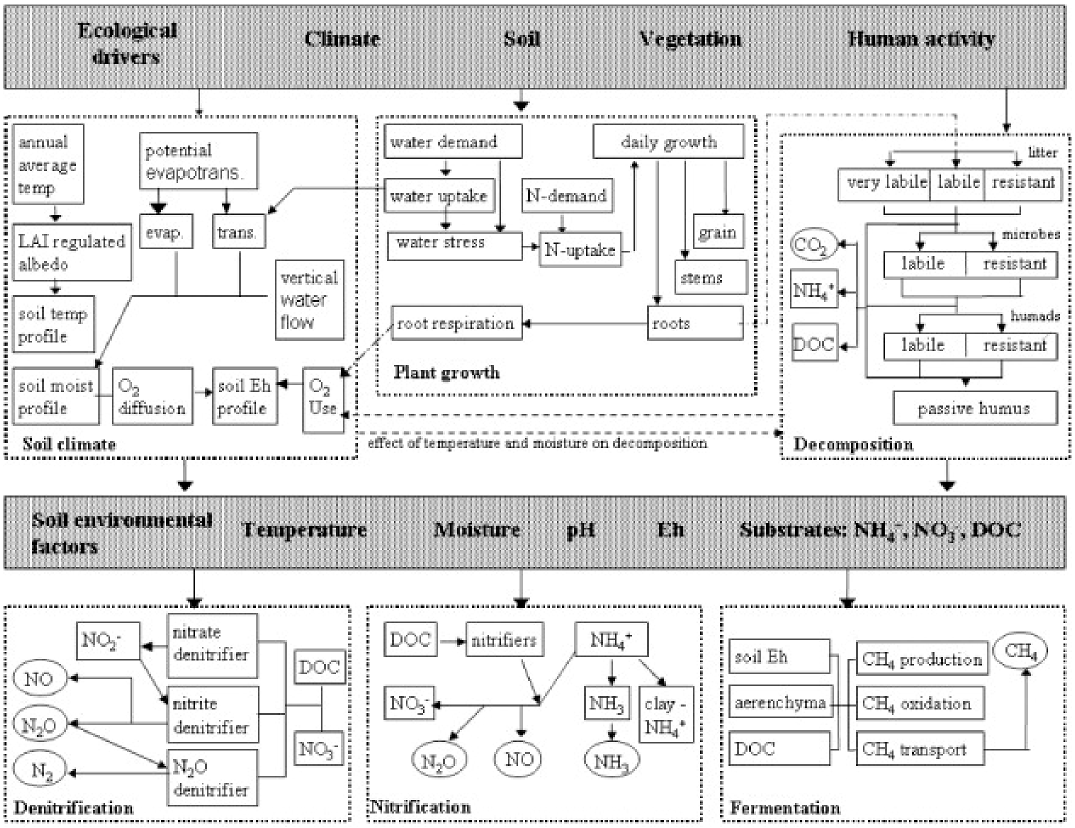

Figure 2-13 - Schematic diagram of DNDC model structure. (Giltrap *et al.*, 2010).

The nitrification submodel controls the ratio of NH_4^+ nitrified to NO_3^- and predicts N losses via NO and N_2O, or via plant uptake, leaching, transformation to NH_3 (and subsequent volatilisation) or adsorption onto soil clay minerals. The hourly-time-step denitrification submodel of DNDC is activated by rain/irrigation events and increments in soil temperatures, and simulates NO and N_2O emissions based on soil Eh, pH, dissolved organic carbon and soil NO_3^- (Chen *et al.*, 2008a). Crop development is modelled using crop-specific daily crop growth curves and is subject to the modelled availability of water and N in the rooting zone (Li *et al.*, 1994).

The default soil parameters in DNDC have been optimised for North-American agroecosystems, and re-parameterisation of soil properties or even modification of the model equations is frequently necessary when modelling cropping systems in other regions of the world (Giltrap *et al.*, 2010). These limitations forced many research groups to create DNDC variants optimised for specific regions (i.e. NZ-DNDC, UK-DNDC, China-DNDC, DNDC- Europe, BE-DNDC), cropping systems (i.e. Crop-DNDC, Rice-DNDC, Forest-DNDC) or fertiliser sources (Manure-DNDC), resulting in 18 different versions of the same model (Global Research Alliance Modeling Platform).

To date the DNDC model has been tested on several cropping systems in more than 15 countries and the agreement between simulated and measured data has been reported to vary significantly depending on climate, soil, and crop conditions (Giltrap *et al.*, 2010). For example, Frolking *et al.* (1998) observed that DNDC substantially over- or under-predicted N_2O emissions when the standard model parameterisation was used in arid and temperate cropping systems, respectively. Overall, the main shortcoming of the DNDC model is its high geographical specificity and the results obtained with this model often cannot be transferred to similar cropping systems in different climatic regions.

APSIM

The Agricultural Production Systems Simulator (APSIM) is a modelling framework first started in 1991 with the aim of developing a farming systems simulator able to accurately estimate crop yields and predict the long-term consequences of farming practice on soil properties (Keating *et al.*, 2003).

APSIM contains an array of modules for simulating crop development and yield dynamics as well as their interactions with the soil. The APSIM-SoilN and SurfaceOM modules simulate the N and C dynamics at daily time-steps. N mineralisation, N immobilisation, nitrification, denitrification, and NO_3^- and NH_4^+ adsorption and movement are explicitly simulated in each soil layer. These N processes are controlled by the soil water content and water movements through the soil profile, which are simulated by the APSIM-SoilWat (Probert *et al.*, 1998) or APSWIM (Verburg *et al.*, 1996) submodels (Figure 2-14).

Nitrification rates are calculated as a proportion of nitrified N by the APSIM-SoilN submodel and follow the Michaelis–Menten response to available soil ammonium (Parton *et al.*, 2001). Denitrification is modelled with the algorithm used in the DAYCENT model (Del Grosso *et al.*, 2000), which calculates N_2O emissions based on an N_2 to N_2O ratio (Thorburn *et al.*, 2010).

The plant submodel simulates key physiological processes and operates on a daily time step in response to daily weather data, soil characteristics and crop management events. The physiological principles are the same among all plant species and only differ in regard to the thresholds and shapes of their response functions to varying environmental conditions (Wang *et al.*, 2002).

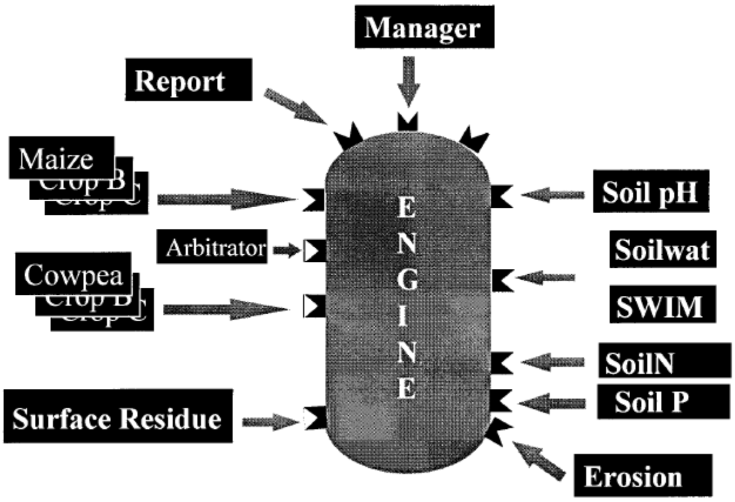

Figure 2-14 - Visual representation of the APSIM simulation framework with individual crop and soil modules, module interfaces and the simulation engine. (Keating *et al.*, 2003).

The comparison of APSIM simulations with observed crop production and soil nutrient dynamics has been performed by many model users under a wide range of conditions (Asseng *et al.*, 1998; Hammer *et al.*, 2010; Mohanty *et al.*, 2012; Luo *et al.*, 2014). To date however, APSIM validation has focused mainly on the effects on different farming practices on crop development and soil properties (Holzworth *et al.*, 2014). Little research has instead been conducted to test the nitrification and denitrification components of the APSIM-SoilN model using field measurements (Huth *et al.*, 2010; Thorburn *et al.*, 2010).

DAYCENT

DAYCENT was first developed in 1998 as the daily time-step version of the CENTURY biogeochemical model to explicitly represent the nitrification and denitrification processes that lead to N_2O, NO_x, and N_2 emissions (Parton *et al.*, 1998; Kelly *et al.*, 2000; Del Grosso *et al.*, 2001).

DAYCENT simulates exchanges of C, N and other nutrients among the atmosphere, soil, and plants as well as farming management practices such as cultivation, stubble management and fertiliser addition. DAYCENT includes submodels for plant productivity, decomposition of dead plant material and soil organic matter, soil water and temperature dynamics, and N gas fluxes (Figure 2-15).

The N gas submodel of DAYCENT simulates soil N_2O and NO_x gas emissions from nitrification and denitrification as well as N_2 emissions from denitrification. N gas flux from nitrification is assumed to be a function of soil NH_4^+ concentration, water content, temperature, and pH (Parton *et al.*, 1996; Parton *et al.*, 2001). Nitrification increases exponentially with temperature and stabilises when soil temperature exceeds the site-specific average high temperature for the warmest month of the year. Nitrification rates increase linearly with soil NH_4^+ concentration and a maximum of 10% of soil NH_4^+ can be nitrified in a day.

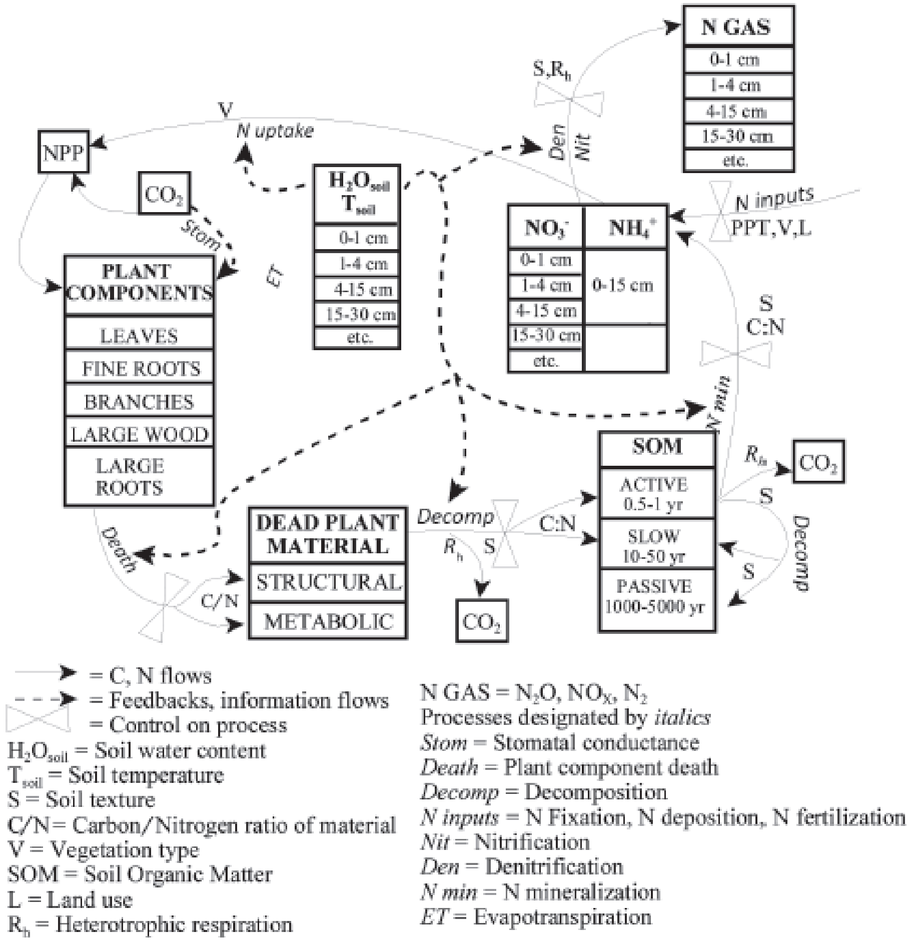

Figure 2-15 - Conceptual diagram of the DAYCENT ecosystem model. (Del Grosso *et al.*, 2011).

Denitrification is a function of soil NO_3^- concentration, labile C availability, WFPS, and soil physical properties related to texture that influence gas diffusivity (Parton *et al.*, 1996; Del Grosso *et al.*, 2000). No denitrification is assumed to occur until WFPS values exceed 50% to 60%, then denitrification increases exponentially until WFPS reaches 70% to 80%, and stabilises as soil water content approaches saturation. N_2 and N_2O emissions from denitrification are regulated by the parameter (NO_3^-, labile C, WFPS) that is most limiting. Maximum daily denitrification rates range from approximately 15% to almost 100% of soil NO_3^- depending on soil NO_3^- concentration. N_2O emissions are calculated from total N losses due to denitrification using a N_2:N_2O ratio function.

Crop growth and development are functions of nutrient availability, soil water and temperature, shading, vegetation type, and plant phenology (Metherell *et al.*, 1993).

Net primary productivity is a function of soil water content and nutrient availability and is divided among leafy, woody, and root compartments on the basis of plant type and phenology.

DAYCENT was chosen for the purposes of this study because it is currently the model that has been most extensively tested to simulate both crop production and N_2O emissions in cereal cropping systems (Del Grosso *et al.*, 2002; Del Grosso *et al.*, 2005; Del Grosso *et al.*, 2006; Del Grosso *et al.*, 2008; Halvorson *et al.*, 2008; Scheer *et al.*, 2013a) and it is currently used to estimate N_2O emissions for the U.S. National GHG Inventory (US-EPA, 2014) under the United Nations Framework Convention on Climate Change (Del Grosso *et al.*, 2006).

2.5 Summary and implications

Warming of the climate system is unequivocal and many of the changes observed since the 1950s are unprecedented over decades to millennia (IPCC, 2013). Paradoxically, agriculture is simultaneously a key driver and a major victim of global warming. The increased average temperature of the atmosphere has already modified various aspects of climate, such as precipitation patterns and frequency of extreme weather events (Christensen *et al.*, 2013). This trend is predicted to continue and have particularly dramatic effects on tropical and subtropical agricultural systems (Alexandratos and Bruinsma, 2012; Hoffmann and UNCTAD secretariat, 2013).

Global warming is caused by the increased concentration in the atmosphere of the four principal greenhouse gases: CO_2, CH_4, N_2O and CFCs. Among them, N_2O has the highest global warming potential and its emissions in the atmosphere are constantly increasing. The application of N fertilisers is the main factor stimulating nitrification and denitrification rates in agroecosystems (Robertson and Groffman, 2007), making agricultural soils the main anthropogenic source of N_2O (Smith *et al.*, 2007). Worldwide consumption of synthetic N fertilisers has increased by 332% in the last 40 years (Ladha *et al.*, 2005) and is predicted to increase in the future, further exacerbating N_2O emissions and therefore global warming.

By 2050, global cereal demand is estimated to increase by 50% to meet the food demand of a world population 30% larger that at present (Ray *et al.*, 2013). Virtually all the increment in cereal consumption will come from tropical and subtropical countries (Alexandratos and Bruinsma, 2012), creating an urgent need to increase productivity levels in these regions. This increase will be extensively sustained by agricultural systems in Oxisols, which are the most common soil type in these regions (von Uexküll and Mutert, 1995; Buol and Eswaran, 1999).

There is consensus that pursuing food security through a further increase in synthetic N use would result in unacceptable levels of environmental damage (FAO, 2010; Foley *et al.*, 2011; Tilman *et al.*, 2011). It is therefore critical to identify alternative N management strategies aimed at supporting future intensification of tropical and subtropical agricultural systems without provoking an increase of N_2O emissions from these agroecosystems.

To be successful both environmentally and agronomically, these strategies will have to maximise the recovery efficiency of fertiliser N in the crop (RE_{fN}) and, ultimately, yield production. One proposed method to maximise RE_{fN} and minimise N_2O emissions from agricultural soils is the application of fertilisers coated with nitrification inhibitors. Nitrification inhibitors reduce N losses both directly, via slowing the nitrification rates and, indirectly, by reducing the amount of NO_3^- available for denitrification. Among them, DMPP (3,4-dimethylpyrazole phosphate) has often been reported to be one of the most efficient in slowing nitrification and reducing N_2O fluxes (Weiske *et al.*, 2001a; Liu *et al.*, 2013). Nitrification inhibitors are however expensive and, on average, increase fertilisation costs by 10% (Weiske, 2006), while their agronomic efficiency is affected by environmental conditions and N management practices. In fact, several authors have reported no significant yield increase with fertilisers coated with nitrification inhibitors (Díez López and Hernaiz, 2008; Liu *et al.*, 2013).

Alternatively, the reintroduction of legumes in cereal-based cropping systems has been suggested as one possible strategy to reduce the amount of synthetic N required and consequently decrease N use inefficiencies associated with elevated fertiliser N rates (Jensen and Hauggaard-Nielsen, 2003; Emerich and Krishnan, 2009). However, the efficacy of this strategy also depends on site-specific conditions and in some cases elevated N_2O emissions have been reported after the incorporation of legume residues (Jensen *et al.*, 2012).

Research to date has primarily focused on assessing these N management strategies in different soils under temperate climatic conditions. Data on RE_{fN} and N_2O emissions in tropical and subtropical cereal systems in Oxisols are therefore still sparse and there is a urgent need for research to develop N management practices that are environmentally sound and economically viable for the intensification of cereal production in these agroecosystems (Fageria and Baligar, 2008).

The availability of precise N_2O and N recovery field measurements, in combination with the use of process-based biogeochemical models, is instrumental to rigorously assess different N management strategies under varying seasonal conditions. This study, through the use of state of the art technology, adopts a holistic approach to investigate the environmental and agronomic implications of using fertilisers coated with nitrification inhibitors and reintroducing legumes in crop rotations to enable a sustainable intensification of cereal production in the subtropics.

Statement of Contribution of Co-Authors for Thesis by Published Paper

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;

2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;

3. there are no other authors of the publication according to these criteria;

4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and

5. they agree to the use of the publication in the student's thesis and its publication on the Australasian Research Online database consistent with any limitations set by publisher requirements.

In the case of this chapter:

Influence of different nitrogen rates and DMPP nitrification inhibitor on annual N_2O emissions from a subtropical wheat-maize cropping system.

Contributor	Statement of contribution*
Massimiliano De Antoni Migliorati	Performed experimental design, conducted fieldwork and laboratory analyses, data analysis, and wrote the manuscript.
Signature	
9th March 2015	
Clemens Scheer	Aided experimental design and data analysis, and reviewed the manuscript.
Peter R. Grace	Aided experimental design and data analysis, and reviewed the manuscript.
David W. Rowlings	Aided experimental design and data analysis, and reviewed the manuscript.
Mike J. Bell	Aided experimental design and data analysis, and reviewed the manuscript.
James McGree	Aided data analysis

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

Peter R. Grace		9th March 2015
Name	Signature	Date

Chapter 3: Influence of different nitrogen rates and DMPP nitrification inhibitor on annual N_2O emissions from a subtropical wheat-maize cropping system (*Paper 1*)

3.1 Abstract

Global cereal production will need to increase by 50 to 70% to feed a world population of about 9 billion by 2050. This intensification is forecast to occur mostly in tropical and subtropical regions, where warm and humid conditions can promote high N_2O losses from cropped soils. New nitrogen (N) fertiliser management strategies are necessary to secure high crop production without exacerbating N_2O emissions in these regions. This one-year study evaluated the efficacy of a nitrification inhibitor (3,4-dimethylpyrazole phosphate - DMPP) and different N fertiliser rates to reduce N_2O emissions in a wheat-maize rotation in subtropical Australia. N_2O emissions were monitored for the entire duration of the experiment using a fully automated greenhouse gas measuring system. Four treatments were fertilised with different rates of urea, including a control (40 kg-N ha^{-1} year^{-1}), a conventional N fertiliser rate adjusted on estimated residual soil mineral N (120 kg-N ha^{-1} year^{-1}), a conventional N fertiliser rate (240 kg-N ha^{-1} year^{-1}) and a conventional N fertiliser rate (240 kg-N ha^{-1} year^{-1}) with nitrification inhibitor (DMPP) applied to both crops at top dressing. The maize season was by far the main contributor to annual N_2O emissions due to the high soil moisture and temperature conditions, as well as the elevated N rates applied. Annual N_2O emissions in the four treatments amounted to 0.49, 0.84, 2.02 and 0.74 kg N_2O-N ha^{-1} year^{-1} respectively, and corresponded to emission factors of 0.29, 0.39, 0.69 and 0.16% of total N applied.

Halving the annual conventional N fertiliser rate in the adjusted N treatment led to N_2O emissions comparable to the DMPP treatment but extensively penalised maize yield. The application of DMPP produced a significant reduction in N_2O emissions only in the maize season. The use of DMPP with urea at the conventional N rate reduced annual N_2O emissions by more than 60% but did not affect crop yields. The results of this study indicate that: i) future strategies aimed at securing cereal production while limiting N_2O emissions in the subtropics should focus on the fertilisation of the summer crop; ii) adjusting conventional N fertiliser rates on estimated residual soil N is an effective practice to reduce N_2O emissions but can lead to substantial yield losses if the residual soil N is not assessed correctly; iii) the application of DMPP is a feasible strategy to reduce annual N_2O emissions from subtropical wheat-maize rotations. However, at the N rates tested in this study DMPP urea did not increase crop yields, making it impossible to recoup the additional costs associated with this fertiliser. The findings of this study will support farmers and policy makers to define effective fertilisation strategies to reduce N_2O emissions from subtropical cereal cropping systems while maintaining high crop productivity. More research is needed to assess the use of DMPP urea in terms of reducing conventional N fertiliser rates and subsequently enable a decrease of fertilisation costs and a further abatement of fertiliser-induced N_2O emissions.

3.2 Introduction

Agricultural soils play a fundamental role in the increase of nitrous oxide (N_2O) in the atmosphere, contributing approximately 50% of the global anthropogenic N_2O emissions (Ehhalt *et al.*, 2001). The environmental relevance of increasing concentrations of N_2O in the atmosphere resides both in the elevated global warming potential of N_2O (298 CO_2-eq over a 100 year time horizon) and its contribution to the depletion of the ozone layer in the stratosphere (Ravishankara *et al.*, 2009).

The increase of N_2O emissions from agricultural soils is directly connected to the increment in worldwide nitrogen (N) fertiliser use (Bouwman, 1990; Kroeze *et al.*, 1999). About 60% of worldwide N fertiliser is presently used to crop cereals (Ladha *et al.*, 2005). However, more fertiliser N is expected to be used in cereal cropping systems to meet the cereal demand of 9 billion people in 2050 (Ladha *et al.*, 2005; UNFPA, 2011). This intensification of cereal production is forecast to occur mostly in tropical and subtropical regions (Smith *et al.*, 2007), where warm and humid climatic conditions can promote high N_2O losses from fertilised soils (Bouwman *et al.*, 2002b). New fertiliser management strategies are necessary to secure future cereal production in the tropics without increasing N fertiliser use and therefore N_2O emissions.

Conventional N fertiliser rates used in subtropical cereal systems are often defined without taking into account the N left in the soil profile by the previous crop (called residual soil N). Many studies have observed that the proportion of N_2O losses as a function of N fertiliser rates rise in nonlinear patterns when soil N amounts exceed plant need (Van Groenigen *et al.*, 2010; Grace *et al.*, 2011). The application of excessive amounts of fertiliser N rates can be avoided by taking into account site-specific conditions affecting residual soil N, such as crop management and crop rotations (Dobermann and Cassman, 2002; Pampolino *et al.*, 2007). The fertiliser N rates necessary to reach maximum yield potential can be therefore calibrated taking into account the amount of N left by the previous crop.

As a result, our first hypothesis in this study was that by reducing conventional N rates after accounting for residual soil N, N_2O emissions can be abated without significantly penalising yields. The second hypothesis of this research was that N_2O emissions generated by the application of conventional fertiliser rates can be effectively reduced by nitrification inhibitors. The application of nitrification inhibitors to urea-based fertilisers has been shown to decrease N_2O emissions both directly, via slowing the nitrification rates and, indirectly, by reducing the amount of NO_3^- available to denitrifying microorganisms (Linzmeier *et al.*, 2001a; Hatch *et al.*, 2005; Suter *et al.*, 2010). Among nitrification inhibitors, 3,4-dimethylpyrazole phosphate (DMPP) has been reported by many authors as the most efficient in slowing nitrification and reducing N_2O losses (Weiske *et al.*, 2001a; Weiske *et al.*, 2001b; Liu *et al.*, 2013).

However, the vast majority of data on N_2O emissions from fertilised cereal systems refer to temperate regions or laboratory conditions and the efficacy of these fertilisation strategies in reducing N_2O emissions in the subtropics still remains unknown. The efficiency of DMPP in reducing N_2O emissions from urea can be strongly influenced by site-specific conditions such as soil temperature and soil water content (Chen *et al.*, 2010; Menéndez *et al.*, 2012).

The overall aims of this study were therefore to: i) determine whether a reduction in conventional N fertiliser rates according to local crop history can reduce N_2O emissions without affecting crop yields; ii) evaluate the effects of DMPP urea applied at conventional rates on N_2O emissions and crop yields; iii) improve the understanding of environmental factors influencing N_2O emissions from subtropical cereal cropping systems.

In this study N_2O emissions from a wheat-maize crop rotation in subtropical Queensland (Australia) were monitored for one year using a fully automated greenhouse gas measuring system. Both crops were fertilised with different rates of urea, including a control, a conventional N fertiliser rate adjusted according to estimated residual soil N, a conventional N fertiliser rate and the conventional rate with DMPP urea.

This is the first study to report annual N_2O emissions from a cereal cropping system under subtropical conditions, the results of which will help to define fertilisation strategies aimed at reducing N_2O emissions from subtropical cereal cropping systems while maintaining high crop productivity.

3.3 Materials and Methods

3.3.1 Study site

Annual N_2O fluxes were measured from wheat (July to November 2011) in rotation with maize (December 2011 to June 2012) at the J. Bjelke Petersen Research Station of the Department of Agriculture, Fisheries and Forestry (DAFF). The research site is located in Taabinga (26°34’54,3’’ Latitude South, 151°49’43.3’’ Longitude East, altitude 441 m a.s.l), near Kingaroy, in the southern inland Burnett region of southeast Queensland, Australia. The climate is classified as subtropical (Figure 3-1), with warm, humid summers and mild winters. Monthly mean maximum and minimum temperatures are 18.9°C and 4.0°C in winter and 29.6°C and 16.5°C in summer, respectively (Figure 3-2). Mean annual precipitation is 776.2 mm and varies from a minimum of 28.6 mm in August to a maximum of 114.1 mm in January (Figure 3-3) (Australian Bureau of Meteorology website).

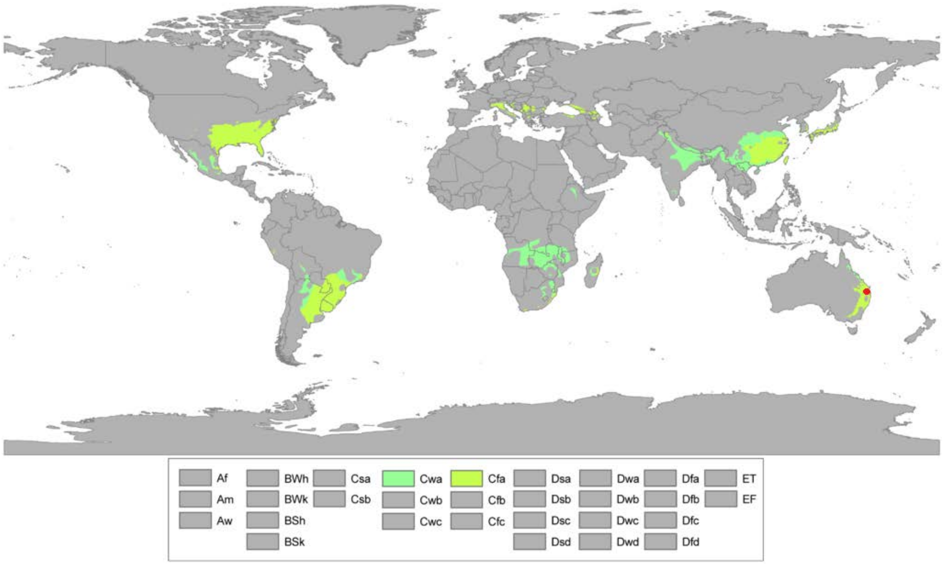

Figure 3-1 - Global distribution of humid subtropical climate zones. The red mark indicates the location on the experiment. (Peel *et al.*, 2007).

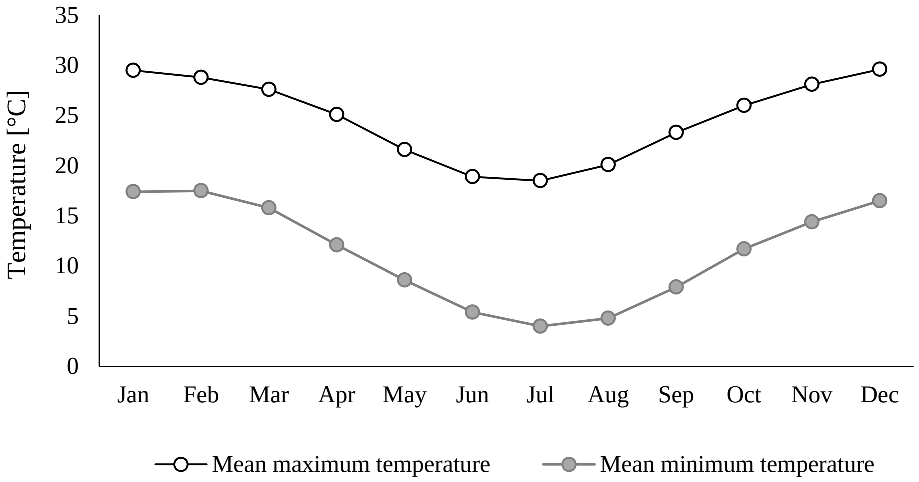

Figure 3-2 - Monthly mean maximum and minimum temperatures at Kingaroy research station. Values are calculated using observations from 1905 to present. (Australian Bureau of Meteorology website).

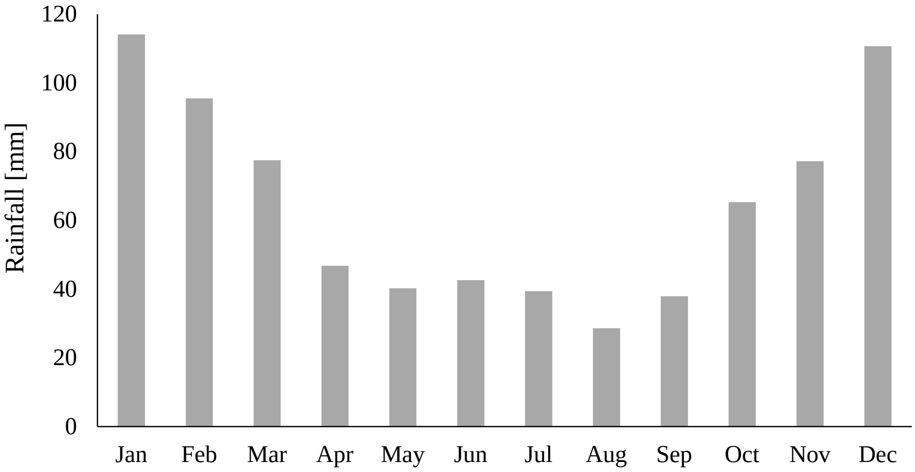

Figure 3-3 - Mean monthly rainfall (mm) at Kingaroy research station. Values are calculated using observations from 1905 to present. (Australian Bureau of Meteorology website).

The soil is classified as Tropeptic Eutrustox Oxisol (USDA Soil Taxonomy, USDA (1998)) or as a Brown Ferrosol (Australian Soil Classification, Isbell (2002)), is moderately permeable, with a high clay content (50-65% clay) in 1.2 m of effective rooting zone and a water holding capacity of 100 mm. Physical and chemical soil properties are listed in Table 3-1.

Table 3-1 - Main soil physical and chemical properties of the experimental site at Kingaroy research station, Queensland, Australia.

Soil Property	**0-10 cm**	**10-20 cm**	**20-30 cm**
Carbon (g kg^{-1})	14.67 ± 1.36	14.07 ± 0.55	10.82 ± 2.41
Total N (g kg^{-1})	0.92 ± 0.09	0.86 ±0.06	0.57 ± 0.04
pH (H_2O)	5.50 ± 0.08	5.57 ± 0.03	5.66 ± 0.05
Texture (USDA)	Clay	Clay	Clay
CEC (meq+/100g)	14.14 ± 0.10	14.71 ± 0.45	15.54 ± 2.29
Bulk density (g cm^{-3})	1.23	1.40	1.36
Clay (%)	50	55	60
Silt (%)	17	14	10
Sand (%)	33	31	30

3.3.2 Experimental design

The field study was a randomised complete block design with three replicates per treatment. Each plot measured 13 m in length x 6 m in width, with crop rows oriented NNW-SSE. To avoid edge effects, each plot was separated by a buffer of 6 m and 0.8 m along the width and length, respectively.

The field was cropped to wheat (*Triticum aestivum* L., cultivar Hartog) from 6 July to 29 November 2011 and to maize (*Zea mays* L., cultivar 32P55) from 21 December 2011 to 20 June 2012. Local farmer practice was followed and during the early stages of crop development the entire field study was sprinkler irrigated with surface stored dam water. All treatments received the same amount of water simultaneously at each event. Irrigation was applied at a rate of 10 mm h^{-1} when water filled pore space (WFPS) values approached 40%. This method avoided water stress limiting the potential yields and prevented fertiliser N to be leached beyond the rooting zone.

As reported in Table 3-2, throughout the duration of the experiment four fertilisation treatments were tested:

- Control test (CNT): no N fertiliser applied to wheat, N fertiliser applied at rate of 40 kg N ha^{-1} to maize to guarantee a minimum crop establishment.
- Conventional N fertiliser rate adjusted according to estimated residual soil N (CONV-ADJ): N applied at rates of 20 and 100 kg N ha^{-1} to wheat and maize, respectively. Seasonal rates were defined to avoid the build-up of high levels of soil N following fertilisation events and to obtain average crop yields. The annual fertiliser rate was reduced to half of the conventional treatment.
- Conventional fertiliser rate (CONV): N applied at rates of 80 and 160 kg N ha^{-1} to wheat and maize, respectively. Rates were similar to local farmer practice and designed to achieve maximum yield potential.
- Conventional fertiliser rate using urea coated with DMPP nitrification inhibitor (CONV-DMPP): N applied at rates of 80 and 160 kg N ha^{-1} to wheat and maize, respectively. In each season DMPP urea was only applied at top dressing (60 kg N ha^{-1} to wheat and 120 kg N ha^{-1} to maize), when higher amounts of seasonal N

were applied to the crop. DMPP urea, commercially available as Entec® (Incitec Pivot fertiliser, Australia) was applied as prills.

The decision of applying DMPP urea only at top dressing was due to the high cost of this product. Since DMPP urea was 30% more expensive than conventional urea, a double application was not considered economically viable as standard farming practice. For this reason, DMPP urea was only used at top dressing, when the bulk of fertiliser N was applied to the crop.

Table 3-2 - N fertilisation rates and amount of irrigation water applied on a wheat-maize rotation at Kingaroy research station in 2011 -2012.

Date	**Crop**	**Fertilisation [kg-N ha^{-1}]**				**Irrigation**
		CNT	**CONV-ADJ**	**CONV**	**CONV-DMPP**	**[mm]**
06/07/2011	Wheat		20 (DAP)	20 (DAP)	20 (DAP)	
11/08/2011						40
15/09/2011				60 (urea)	60 (DMPP urea)	21
27/09/2011						30
05/10/2011						45
21/12/2011	Maize	40 (MAP)	40 (MAP)	40 (MAP)	40 (MAP)	
05/01/2012						26
19/01/2012			60 (urea)	120 (urea)	120 (DMPP urea)	
23/01/2012						40

Wheat season

The cropping history for the five years before the commencement of this experiment is listed below (seasons and yields are reported within brackets): Peanuts (*Arachis hypogaea* L., summer 2005/2006, 1.5 Mg ha^{-1}), peanuts (summer 2006/2007, 1.4 Mg ha^{-1}), maize (*Zea mays* L., 2007/2008, 3.1 Mg ha^{-1}), peanuts (summer 2008/2009, 1.5 Mg ha^{-1}), barley (*Hordeum vulgare* L., winter 2009, crop not harvested, all 1.3 Mg ha^{-1} of biomass ploughed in), maize (summer 2009/2010, 3.0 Mg ha^{-1}) and mungbean (*Vigna radiata* L., summer 2010/2011, 0.66 Mg ha^{-1}). Before sowing wheat, mungbean residues were incorporated and the seedbed was prepared with three cultivations: chisel plough (20 cm), offset discs (20 cm) and rotary hoe (15 cm).

Wheat was planted 6 July (inter-row 15 cm, intra-row plant space 9 cm, seed planting density of 140 seeds m^{-2}) and harvested 29 November 2011. Emergence was observed 20 July 2011 with an average plant density of 125 plants m^{-2} while anthesis started 6 October 2011. Average soil mineral N content prior to planting (0-30 cm) was approximately 60 kg N ha^{-1} across the field study (Figure 3-4a and Figure 3-4b). Taking into account an average N content of 1.5% in the stover (Bushby and Lawn, 1992; Thomas *et al.*, 2004), it was estimated that the incorporation of 1.32 Mg ha^{-1} of mungbean residues would have provided a further 20 kg N ha^{-1} to the soil. Although it was estimated that a total of 80 kg N ha^{-1} would have been available to the crop throughout the wheat season, a conservative approach was taken and the N fertiliser rate in the CONV-ADJ treatment was reduced by 60 kg N ha^{-1} (75%) compared to CONV. Over the season the plots were irrigated on four occasions: 40 mm on 11 August, 21 mm on 15 September, 30 mm on 27 September and 45 mm on 5 October.

At planting, treatments CONV-ADJ, CONV and CONV-DMPP received 20 kg N ha^{-1} by banding 110 kg of diammonium phosphate (DAP, 18-20-0). The CNT treatment was instead base dressed with 100 kg ha^{-1} of Triple Super Phosphate (TSP, 0-46-0) to supply a source of phosphorus without adding N. At booting stage the CONV and CONV-DMPP treatments were manually top dressed with 60 kg N ha^{-1} to meet maximum yield potential. The two treatments were broadcasted with conventional urea and DMPP urea, respectively. Since chambers were moved every two weeks to a different frame (see section 3.3.3), at top dressing the exact proportion of urea was weighed separately and then manually distributed within all frames of the CONV and CONV-DMPP treatments. Fertilisation and irrigation amounts and timing are shown in Table 3-2.

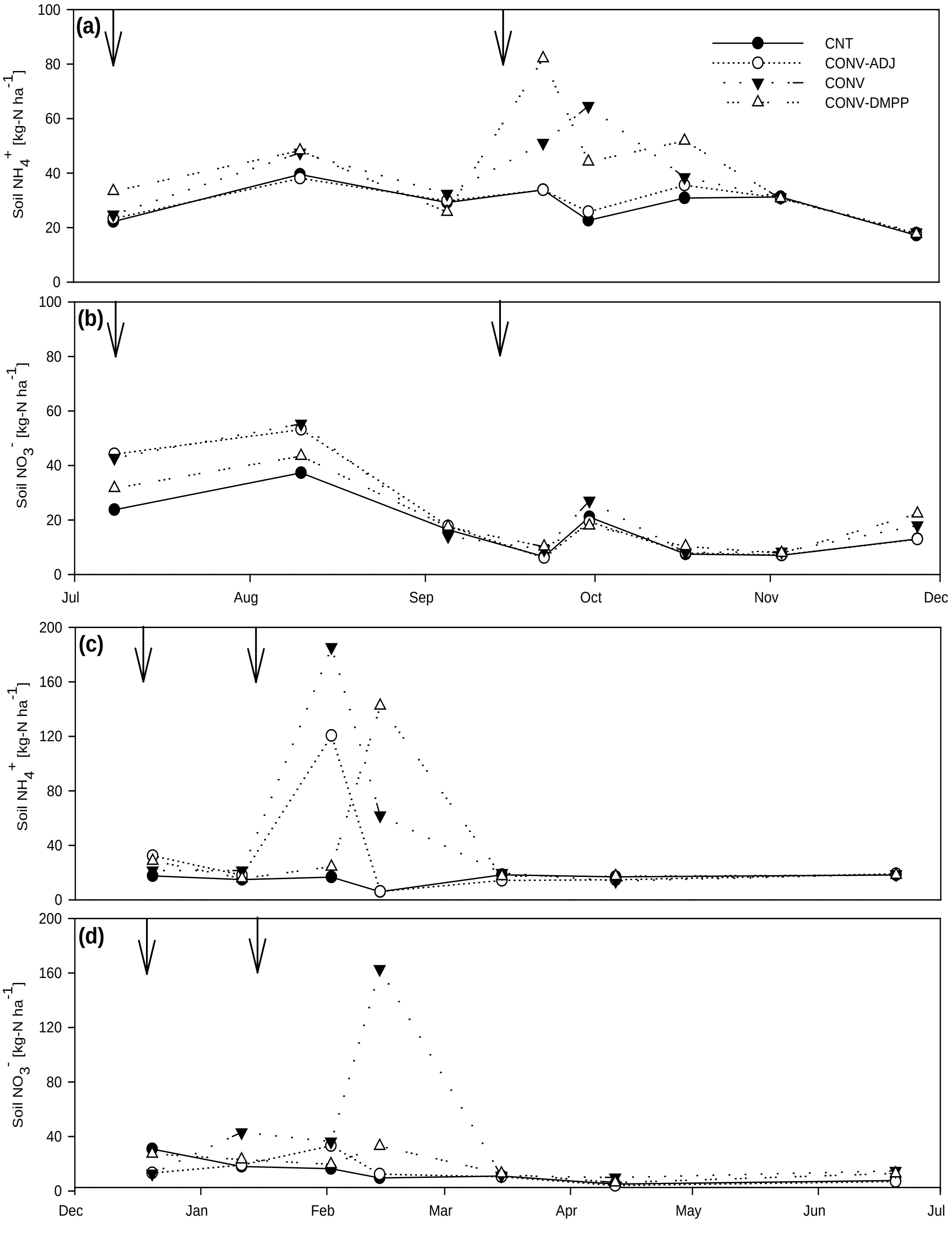

Figure 3-4 - Soil ammonium and nitrate contents (0-30 cm) for four fertilisation treatments during the wheat (a, b) and maize (c, d) seasons in Kingaroy (Queensland, Australia) in 2011/12. Arrows indicate the timing of N fertiliser applications.

Maize season

After the wheat harvest all residue was slashed and mulched. The entire trial field was broadcasted with lime (2500 kg ha^{-1}) before being cultivated with chisel plough (to 20 cm), offset discs (20 cm) and rotary hoe (15 cm). The seedbed was finally prepared with offset discs (20 cm) and tyned harrows after being spread with muriate of potash (120 kg ha^{-1}). Maize was planted 21 December 2011 with an inter-row of 93 cm (intra-row plant space 23 cm, seed density: 6 seeds m^{-2}) and irrigated on two occasions: 26 mm on 5 January and 40 mm on 23 January (Table 3-2). Emergence was first observed 28 December 2011 at a density of 5 plants m^{-2} while tasseling started 13 February 2012.

Due to the high initial N requirement of maize, supplying no N to this crop during the early stages of crop development could potentially have caused an uneven or poor crop establishment. For this reason, a zero N treatment was not considered possible and all treatments (including control) were base dressed by banding 40 kg N ha^{-1} with monoammonium phosphate (MAP, 11-52-0, Incitec Pivot fertiliser). At the end of the wheat season the average soil mineral N content (0-30 cm) in the CONV-ADJ plots was approximately 35 kg N ha^{-1} (Figure 3-4a and Figure 3-4b) and the wheat straw contained an average N content of 0.48%. It was estimated that the mineralisation of the 5.3 Mg ha^{-1} of wheat residues incorporated in the soil before planting maize would have provided an extra 25 kg N ha^{-1} throughout the maize season. A total of 60 kg N ha^{-1} was therefore expected to become available to the maize plants during the cropping season. During the maize season the N fertiliser rate in the CONV-ADJ treatment was cut by 60 kg N ha^{-1} (40%) compared to CONV to better evaluate the feasibility of reducing the fertiliser N rate in accordance with estimated residual soil N.

At V10 physiological stage (beginning of tenth leaf) treatments CONV-ADJ, CONV and CONV-DMPP were side dressed and inter-row cultivated to supply N during the period of maximum crop demand (Miller *et al.*, 1975; Binder *et al.*, 2000): CONV-ADJ received 60 kg N ha^{-1} using conventional urea while 120 kg N ha^{-1} was applied to the CONV and CONV-DMPP treatments using conventional urea and urea coated with DMPP, respectively. The crop was harvested 20 June 2012.

3.3.3 Continuous N_2O measurements

During each cropping season N_2O measurements were automatically taken using one acrylic sampling chamber per plot. During the wheat season the chambers were located randomly inside each plot since the crop inter-row (15 cm) was smaller than the chamber side (50 cm). This approach was not possible with maize, where the crop inter-row was 90 cm, so to provide a good representation of the soil spatial variability the chamber placement was based on the methodology established by Kusa *et al.* (2006) and Parkin and Kaspar (2006). For each treatment two of the three replicate chambers were positioned over the crop row and the third one in the inter row. Chambers were positioned over the crop row to guarantee the banded fertiliser (4 cm from the plant row) was included in the chamber area.

Each chamber measured 50 cm x 50 cm x 15 cm and was clipped via a rubber seal to stainless steel frames inserted 10 cm into the ground. The chambers were equipped with lids operated by pneumatic pistons and connected to a fully automated system composed of a sampling unit and a gas chromatograph. During a normal measurement cycle (60 min) one set of four chambers closed at one time and four gas samples were taken from each chamber at 15 min intervals. The chambers were reopened at the end of the cycle and the next replicate set of four chambers closed to be sampled. A full measuring cycle of twelve chambers took 180 min to complete, allowing up to 8 single fluxes to be determined per chamber per day. The air samples taken from each chamber were automatically pumped through a 3 ml sample loop and injected into a gas chromatograph (Model 8610C, SRI Instruments, USA) equipped with a ^{63}Ni electron capture detector (ECD) for N_2O analysis. A column filter containing sodium hydroxide-coated silica (Ascarite, Sigma-Aldrich, St. Louis, MO, USA) was installed upstream of the ECD to adsorb CO_2 and water vapour that could interfere with N_2O measurements. The system was automatically calibrated twelve times every measurement cycle by a single point calibration using certified gas standard of 500 ppb N_2O (BOC –Munich, Germany- and Air Liquide –Dallas, TX, USA). A multi-point calibration was performed using certified gas standards of 500, 980, 5030 ppb N_2O (BOC –Munich, Germany) and the GC response over this range was determined to be linear.

The detection limit of the system with and without chamber extensions, based on the methodology described by Parkin *et al.* (2012), was approximately 2 and 0.5 g

N_2O-N ha^{-1} day $^{-1}$ for N_2O. The design and operation details of the automated gas measuring system can be found in Scheer *et al.* (2013b) and Rowlings *et al.* (2012). The whole system was constantly checked for leaks throughout each season, making the sample dilution due to leakage negligible.

Chambers were programmed to open if a rain event exceeded 5 mm or the internal air temperature within the chamber exceeded a threshold value of 55 °C. During irrigation events the system was stopped and all chamber lids were opened to allow water to reach the soil surface covered by the chambers. The measuring system was deployed immediately after planting at the beginning of each cropping season and temporarily withdrawn to permit farming operations.

During the wheat season, the chamber height was increased to 75 cm using clear acrylic extensions to accommodate the crop growth. This strategy was not applicable during the maize season, when plant size exceeded the extension height. The plant inside each chamber situated in the inter row was therefore cut over the brace roots at V1 stage, as practiced in other studies (Drury *et al.*, 2008; Halvorson *et al.*, 2008; Hu *et al.*, 2013).

Chambers were relocated to another position within the plot every two weeks, a practice recommended by several authors (Barton *et al.*, 2011; Scheer *et al.*, 2012; Liu *et al.*, 2013) to minimise the impact of the chamber on plant growth and soil processes. To meet this requirement, two different strategies were adopted for the two seasons. During the wheat season two frames were located in each plot and chambers were shifted between the two frames every two weeks. During the maize season cutting the plant inside the chamber over the crop row was considered to have marginal impacts on soil C and N dynamics. The practice was limited to the plant inside the chamber while plants adjacent the chambers were left undisturbed. Nevertheless, to further reduce the possible side effects of this practice during the entire maize season, chambers and frames were moved to a completely new position every two weeks.

3.3.4 Ancillary measurements

Chamber air temperatures and soil temperatures (buried at 10 cm, 20 cm, 30 cm in the proximities of three chambers) were measured every 5 minutes using resistance temperature detectors (RTD, Temperature Controls Pty Ltd, Australia). The soil water content of the top 10 cm of soil was measured every 30 minutes with four time domain reflectometers (TDR, MP406 probes, ICT International, Australia) buried inside the measuring chambers. Four frequency domain reflectometers (FDR, EnviroScan probes, Sentek Sensor Technologies, Australia) were installed at the field site to assess the water dynamics throughout the soil profiles. After calibration, the FDR were inserted in the ground to measure the volumetric soil water content at three depths (0-10 cm, 10-20 cm, 20-30 cm) at 30 minute intervals. Water-filled pore space (WFPS) was determined for each depth using a particle density of 2.79 g cm^{-3} and the bulk density was calculated by the arithmetic mean of four samples collected at the beginning of each season.

At the beginning and end of each cropping season soil cores were collected from every plot with a manual open-faced bucket auger (10 cm diameter) at three depths (0-10, 10-20, 20-30 cm) and analysed for texture (hydrometer method as described by Carter and Gregorich (2007)), total carbon (C%) and total nitrogen (N%) (TruMac Series Macro Determinator, LECO Corporation, St Joseph, MI, USA), pH, Cation Exchange Capacity (ICP, Varian Vista-MPX), NH_4-N and NO_3-N. NH_4^+ and NO_3^- were extracted from the soil samples by adding 100 mL of 1M KCl to 20g of soil and shaking the solution for 1 hour. The solution was then filtered and stored in a freezer until analysed colorimetrically for NH_4-N and NO_3-N using an AQ2+ discrete analyser (SEAL Analytical WI, USA). Routine soil sampling was conducted every two weeks during each season. Soil samples were taken at three depths (0-10, 10-20, 20-30 cm) and analysed for NH_4-N and NO_3-N. At harvest, grain yield was measured in each plot by harvesting two strips 1.65 m wide for the plot length using a plot combine. Total N content of grain, wheat straw and maize stover samples was measured using a 20-22 isotope ratio mass spectrometer (Sercon Limited, UK).

3.3.5 Calculations and statistical analysis

N_2O fluxes were calculated to determine the slope of the linear increase or decrease in gas concentration during the 60 minutes of chamber closure period using the method described by Barton *et al.* (2008) . The obtained data were corrected for internal air temperature, atmospheric pressure and ratio of chamber volume and soil area. Measurements were quality-checked using the Pearson correlation and fluxes above the detection limit discarded if the regression coefficient (r^2) was < 0.80. For each treatment, mean daily N_2O fluxes [g N_2O-N ha^{-1} d^{-1}] were calculated performing a weighted average of the two chambers over the crop row and the chamber placed in the inter row. Cumulative N_2O fluxes [kg N_2O-N ha^{-1}] were determined by summing the mean daily N_2O fluxes for each season, and for the entire study period.

Daily N_2O fluxes missing due to occasional failures of the measuring system, and between wheat harvest and maize planting, were simulated using the Amelia II multiple imputation model (Honaker and King, 2010) using daily values of WFPS (0-10 cm, 10-20 cm and 20-30 cm) and mineral N content (0-30 cm). Statistical analyses were performed within the R 2.15 environment (R Development CoreTeam, 2008). The temporal patterns of daily N_2O emissions were analysed with the autoregressive integrated moving average (ARIMA) model to assess differences between treatments (Box and Pierce, 1970). The Tukey *post hoc* test was used to compare cumulative N_2O emissions and N_2O emissions occurred after top dressing, while yields were compared with the Bonferroni test. Correlations between N_2O emissions and soil parameters were examined with the Pearson correlation analysis.

Emission factors, expressed as a percentage of N fertiliser lost as N_2O, were corrected for background emissions by subtracting the total amount of N_2O-N lost in the non-fertilised treatment from the total N_2O-N emitted by each fertilised treatment (Kroeze *et al.*, 1997). For the maize season, where an non-fertilised treatment was not present, seasonal background emissions were estimated using the methodology described by Liu *et al.* (2010b). The cumulative emissions from a hypothetical non-fertilised soil were estimated using the seasonal N_2O fluxes of the CNT treatment minus those emissions exceeding 1 g N_2O-N ha^{-1} d^{-1} that were measured during the 16 days after 21 January 2012. Emissions during this time gap were simulated using the Amelia II multiple imputation model fed with a dataset including soil temperatures and WFPS values (0-10 cm, 10-20 cm and 20-30 cm) for the whole season, plus N_2O fluxes and mineral N contents (average 0-30 cm) measured prior to, and 16 days after 21 January 2012. The model was calibrated for site-specific conditions using measured annual N_2O fluxes, Mineral N contents, soil temperatures and WFPS values from all treatments. To validate the precision of the calibrated model in predicting missing N_2O emissions, 16 day gaps were simulated in the other treatments. Simulated emissions in all treatments fell within the confidence interval calculated with the ARIMA model. The overall seasonal emissions from the non-fertilised maize field, estimated to be 0.12 kg-N ha^{-1}, are confirmed by similar studies (Cai *et al.*, 2002b; Pelster *et al.*, 2011).

3.4 Results

3.4.1 Environmental and soil conditions

The weather conditions recorded during this study, characterised by cool dry winters (June-August) and hot humid summers (December-February), were in line with the historic subtropical climate. Soil conditions were substantially warmer and moister during the summer season, especially at the beginning of the maize season (Figure 3-5).

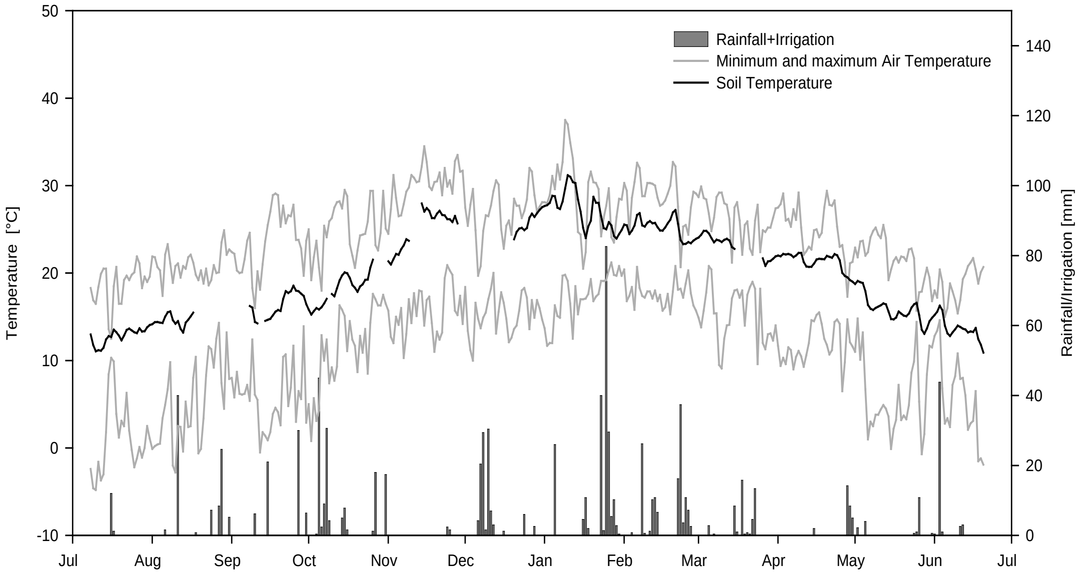

Figure 3-5 - Minimum and maximum daily air temperatures, soil temperatures (0-30 cm), rainfall and irrigation events at Kingaroy (Queensland, Australia) in 2011/12.

Throughout the wheat season soil NH_4^+ levels in the CNT and CONV-ADJ treatments varied little (Figure 3-4a). Soil NH_4^+ levels in the CONV and CONV-DMPP treatments were similar to those of the CNT and CONV-ADJ treatments until top dressing, after which they increased to 64.6 and 82.1 kg N ha^{-1}, respectively. Soil NO_3^- contents in all treatments were relatively high at planting (average 35.6 kg N ha^{-1}) and did not vary substantially over the course of the wheat season (Figure 3-4b). Soil NH_4^+ levels were similar across all treatments at the beginning of the maize season. NH_4^+ levels in CONV-ADJ and CONV peaked within 10 days from side dressing, while in CONV-DMPP culminated 20 days later (Figure 3-4c). Soil NO_3^- levels varied little across treatments during the entire season, with the exception of the CONV treatment, where NO_3^- concentrations reached the seasonal maximum 20 days after side dressing (Figure 3-4d).

3.4.2 N_2O emissions

Throughout this one-year experiment an average of 5600 valid N_2O fluxes for each treatment were obtained. Patterns and magnitudes of N_2O emissions varied significantly over time in response to seasonal weather and soil conditions, N fertilisation rates and fertiliser type.

During the wheat season N_2O emissions varied little across treatments. Two “emissions pulses” occurred in all treatments before top dressing in response to a rainfall event (July 16, 12 mm) and an irrigation event (August 11, 40 mm). A third, more sizeable emission pulse was measured in CONV and CONV-DMPP after September 15, when the entire trial was irrigated with 21 mm and the two treatments were top dressed with 60 kg N ha^{-1} (Figure 3-6a).

N_2O emissions over the maize season showed a more pronounced increase corresponding to increased N fertiliser rates (Figure 3-6b). Daily fluxes following base dressing, when all treatments were fertilised with 40 kg N ha^{-1}, remained relatively low (<10 g N ha^{-1} day^{-1}) and did not vary significantly between treatments. In the ten days following side dressing a total of 172 mm of rain fell over the trial, causing soil WFPS in the first 30 cm to stay over 80% for 5 consecutive days. N_2O emission dynamics differed significantly across treatments after this event. In the CNT treatment a relatively minor peak (<17 g N ha^{-1}) lasted for 16 days. The highest N_2O fluxes in CONV-DMPP were similar to those measured in CONV-ADJ. In the

CONV-DMPP treatment high fluxes lasted for 9 days, whereas in CONV-ADJ persisted for 21 days. In the CONV treatment N_2O emissions continued to increase until mid-February, to a maximum of 73.2g N ha^{-1} day^{-1}. Emissions in the CONV treatment returned to background levels by mid-March 2012. After that event, daily N_2O emissions in all treatments never exceeded 0.6 g N ha^{-1} day^{-1} despite several rain events in April, May and June 2012. In the wheat season cumulative emissions from the CONV treatment only were significantly higher than those measured in the other treatments (Table 3-3).

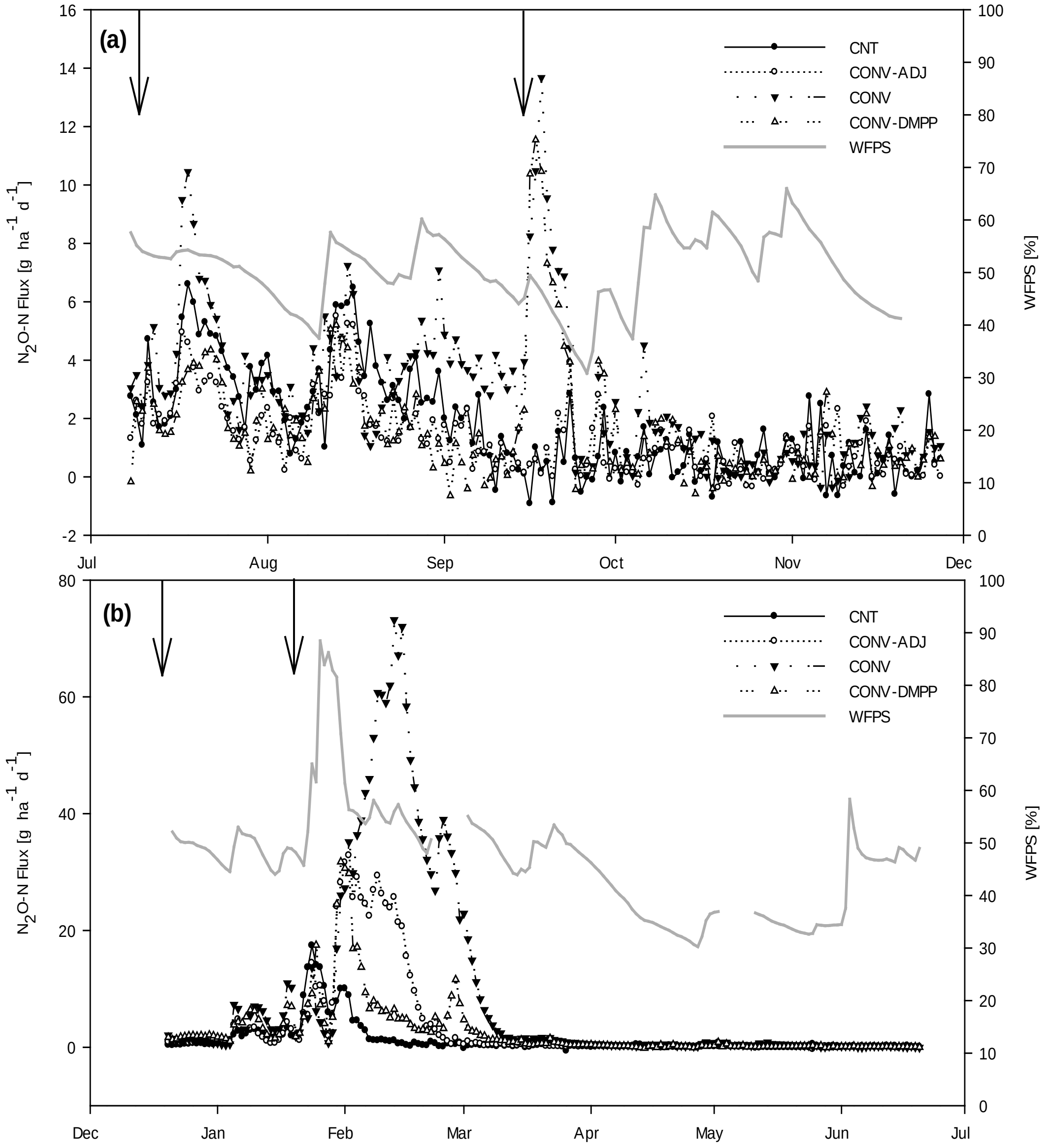

Figure 3-6 - Daily soil N_2O fluxes and water-filled pore space (WFPS, 0-30 cm) for Control (CNT), Adjusted N fertiliser rate (CONV-ADJ), Conventional (CONV) and Conventional with DMPP (CONV-DMPP) treatments during the wheat (a) and maize (b) seasons in Kingaroy (Queensland, Australia). Arrows indicate the timing of N fertiliser applications. N_2O emissions in panel (a) and (b) are reported using different scales.

Table 3-3 - Seasonal and estimated annual N_2O average fluxes, N_2O cumulative fluxes, emission factors, plant N uptake, grain yield and N_2O intensities (mean ± SE, n=3) as a function of the four fertilisation treatments. Means denoted by a different letter indicate significant differences between treatments ($p<0.05$).

Measurement	**Season**	**Fertilisation Treatment**			
		CNT	**CONV-ADJ**	**CONV**	**CONV-DMPP**
Average Flux [g N_2O-N ha^{-1} d^{-1}]	Wheat	1.74 ± 0.59 ^{a}	1.34 ±0.41 ^{a}	2.83 ±0.84 ^{b}	1.71 ± 0.68 ^{a}
Cumulative Flux [kg N_2O-N ha^{-1} $season^{-1}$]		0.25 ± 0.04 ^{a}	0.19 ± 0.02 ^{a}	0.40 ± 0.02 ^{b}	0.25 ± 0.01 ^{a}
Emissions after top dressing [kg N_2O-N ha^{-1}]*		-	-	0.13 ± 0.01 ^{a}	0.12 ± 0.01 ^{a}
Emission Factor [%]		-	-0.29	0.19	-0.005
Grain Yield (12.5% moisture) [Mg ha^{-1}]		4.4 ± 0.32 ^{a}	5.1 ± 0.10 ^{a}	5.8 ± 0.11 ^{a}	5.5 ± 0.09 ^{a}
Total plant N uptake [kg N ha^{-1}]		134.2 ± 9.6	154.9 ± 3.1	173.8 ±3.3	165.6 ± 2.7
N_2O Intensity [kg N_2O-N t-$yield^{-1}$]		0.06	0.04	0.07	0.04
Average Flux [g N_2O-N ha^{-1} d^{-1}]	Maize	1.22 ± 0.91 ^{a}	3.51 ± 2.56 ^{ac}	8.77 ± 5.57 ^{b}	2.71 ± 1.69 ^{c}
Cumulative Flux [kg N_2O-N ha^{-1} $season^{-1}$]		0.22 ± 0.03 ^{a}	0.65 ± 0.15 ^{ac}	1.61 ± 0.49 ^{b}	0.50 ± 0.12 ^{c}
Emissions after top dressing [kg N_2O-N ha^{-1}]*		-	0.52 ^{a}	1.42± 0.37 ^{b}	0.33± 0.10 ^{a}
Emission Factor [%]		0.26	0.53	0.93	0.24
Grain Yield (14% moisture) [Mg ha^{-1}]		2.6 ± 0.11 ^{a}	6.1 ± 0.26 ^{b}	8.5 ± 0.12 ^{c}	8.4 ± 0.18 ^{c}
Total plant N uptake [kg N ha^{-1}]		39.2 ± 1.7	92.3 ± 3.9	130.2 ± 1.8	128.1 ± 2.7
N_2O Intensity [kg-N_2O-N t-$yield^{-1}$]		0.09	0.11	0.19	0.06
Average Flux [g N_2O-N ha^{-1} d^{-1}]	Annual	1.40 ± 0.77 ^{a}	2.45 ± 1.91 ^{ac}	5.87 ± 4.21 ^{b}	2.22 ± 1.31 ^{c}
Cumulative Flux [kg N_2O-N ha^{-1} $season^{-1}$]		0.49 ± 0.04 ^{a}	0.84 ± 0.14 ^{a}	2.02 ± 0.48 ^{b}	0.74 ± 0.13 ^{a}
Emission Factor [%]		0.29	0.39	0.69	0.16
Grain Yield [Mg ha^{-1}]		7.01 ± 0.40 ^{a}	11.18 ± 0.24^{a}	14.29 ± 0.52 ^{b}	13.89 ± 0.55 ^{b}
N_2O Intensity [kg-N_2O-N t-$yield^{-1}$]		0.07	0.07	0.14	0.05

*- sum of N_2O emissions measured within 10 days after top dressing (wheat) and 40 days after side dressing (maize)

The time series analysis showed that N_2O emissions in the CONV and CONV-DMPP treatments were significantly higher than those in CNT and CONV-ADJ only during the 10 days following top dressing. No significant difference was detected when comparing the CONV and CONV-DMPP treatments. The N_2O losses from the CONV treatment in maize were significantly higher than in the other treatments, while N_2O fluxes observed in the CONV-DMPP treatment did not differ significantly from those in CONV-ADJ (Table 3-3). The temporal pattern of N_2O emissions in the CONV treatment differed significantly from the others only during the 40 day emission pulse following side dressing. Compared to the CNT treatment, a significant difference in N_2O emissions from CONV-ADJ and CONV-DMPP was limited to the first 20 days of emission pulse. Annual N_2O emissions (inclusive of the 22 days between wheat harvest and maize planting) and emissions factors are also reported in Table 3-3.

3.4.3 Plant yields and plant N contents

There was no distinct treatment effect on yields during the wheat season (Table 3-3). In contrast, the Bonferroni test revealed a significant ($p < 0.01$) linear response of maize grain yield to increasing N fertiliser application. In both crops the addition of DMPP to urea did not affect grain yields compared to the same rate with conventional urea (Table 3-3). Annual grain yields in the CONV treatment were similar to those in CONV-DMPP and both were significantly higher ($p < 0.05$) than those in CNT and CONV-ADJ. N content in grain and plant tissues did not differ significantly across treatments. Total plant N uptake values measured for the four treatments during the two seasons are reported in Table 3-3.

3.5 Discussion

3.5.1 Factors influencing N_2O emissions in wheat and maize

In this study N_2O fluxes occurred during the maize season were the main contributor to annual emissions in all treatments except CNT (Figure 3-7a), accounting for 46, 77, 80 and 67% of total N_2O losses in CNT, CONV-ADJ, CONV and CONV-DMPP, respectively (Table 3-3). The higher N_2O emission measured in maize can be explained considering the different soil physical conditions and N fertiliser rates compared to the wheat season. That is, during the wheat season when CONV and CONV-DMPP were top dressed with 60 kg N ha^{-1}, soil temperature was 14.8 °C and WFPS was 40.3%, while in the maize season, when CONV and CONV-DMPP were side dressed with 120 kg N ha^{-1}, soil temperature was 25.8 °C and WFPS was 64.9 % (Figure 3-7b).

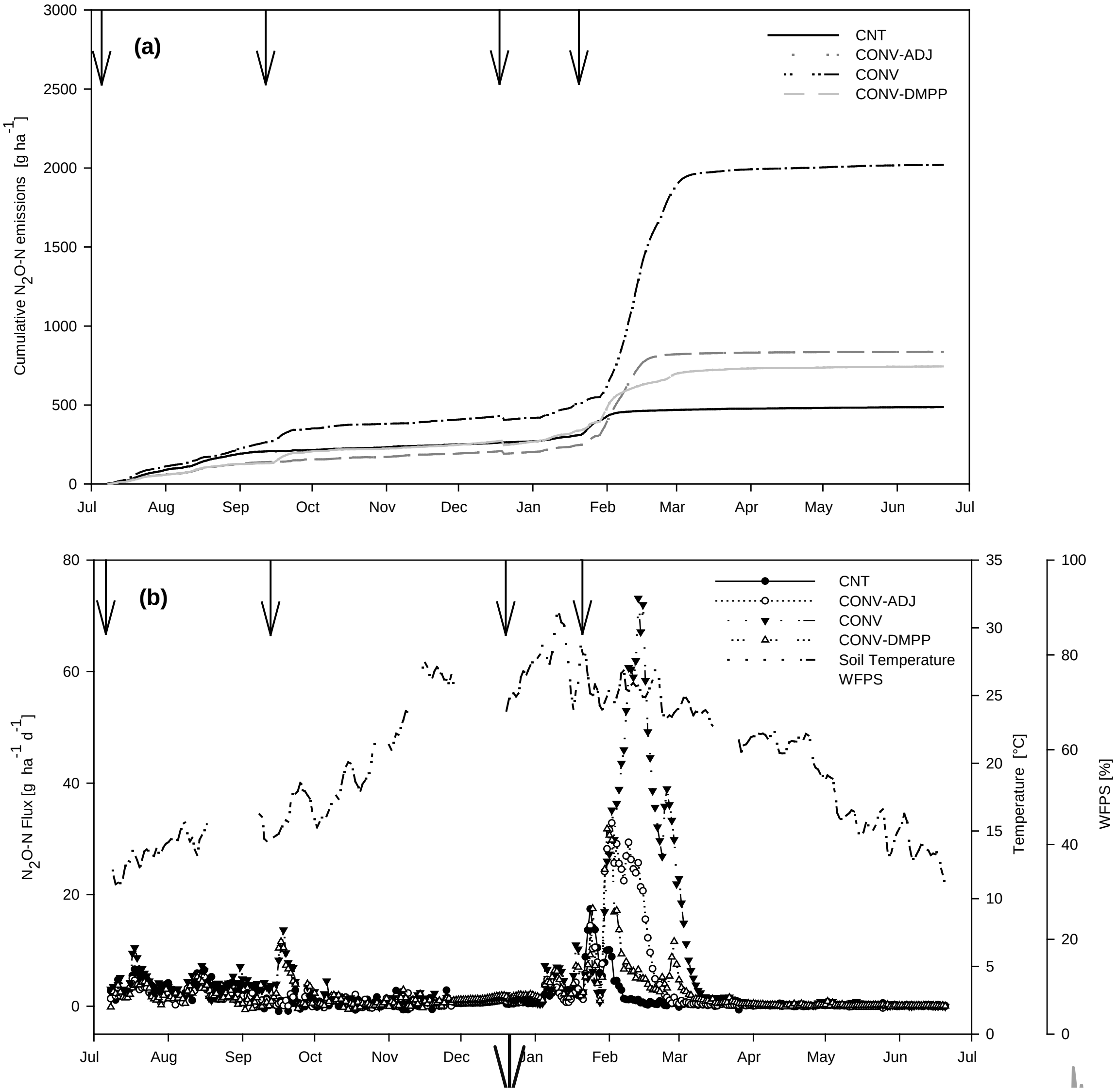

Figure 3-7 - Cumulative N_2O fluxes (a) and daily soil N_2O fluxes, water-filled pore space (WFPS, 0-30 cm), soil temperatures (0-30 cm) (b) for the four fertilisation treatments in a wheat-maize rotation at Kingaroy (Queensland, Australia) in 2011/12. Arrows indicate the of N fertiliser applications.

Daily N_2O emissions correlated mainly to soil NO_3^- and NH_4^+ contents and, to a lesser extent, soil temperature, WFPS and rainfall/irrigation events (Table 3-4). Therefore, the warmer and moister soil conditions after the side dressing of maize, together with the higher NO_3^- and NH_4^+ levels, would have significantly stimulated the activity of nitrifying and denitrifying microorganisms. That is, after top dressing wheat with 60 kg N ha^{-1} (CONV) the N_2O losses occurring during the subsequent emission pulse amounted to 134 g N_2O-N ha^{-1}. Instead in summer, after side dressing CONV-ADJ with the same amount of N total N_2O losses amounted to 524 g N_2O-N ha^{-1}. These results highlight the importance of the summer season in determining annual N_2O emissions in subtropical cereal systems and suggest that fertilisation strategies designed to secure subtropical cereal production without increasing N_2O emissions should focus on the fertilisation of the summer crop.

Table 3-4 - Correlation between daily N_2O emissions and measured soil/environmental parameters for the wheat and maize season. Soil parameters refer to the first 30 cm of soil profile.

Season	**Variable**	***n***	**N_2O flux [g N_2O-N ha^{-1} d^{-1}]**
Wheat	Soil NO_3^- [kg-N ha^{-1}]	32	.40**
	Soil NH_4^+ [kg-N ha^{-1}]	32	.26**
	Soil temperature [°C]	143	-.43**
	WFPS [%]	143	.08
	Rainfall/irrigation [mm]	143	-.05
Maize	Soil NO_3^- [kg-N ha^{-1}]	28	.84**
	Soil NH_4^+ [kg-N ha^{-1}]	28	.52**
	WFPS [%]	184	.37**
	Soil temperature [°C]	184	.30**
	Rainfall/irrigation [mm]	184	.12**

** Correlation is significant at the 0.01 level (2-tailed).

Average N_2O emissions measured during this study were at the lower end of reported emissions from wheat (Pathak *et al.*, 2002; Bhatia *et al.*, 2010; Scheer *et al.*, 2012; Hu *et al.*, 2013; Liu *et al.*, 2013) and maize (Van Groenigen *et al.*, 2004; Ding *et al.*, 2007; Liu *et al.*, 2011; Liu *et al.*, 2013). Only Pathak *et al.* (2002); Bhatia *et al.* (2010); Scheer *et al.* (2012) and Ding *et al.* (2007) however measured N_2O emissions under subtropical conditions. The low emissions can be attributed mainly to the smaller N rates applied in this study and to the limited availability of soil organic carbon at the experimental site. Nitrification and especially denitrification rates are tightly connected to soil labile carbon content and numerous studies have identified this parameter as a key factor regulating N_2O production (Bouwman *et al.*, 2002b; De Wever *et al.*, 2002; Khalil *et al.*, 2002). Soil organic carbon levels are low in the study region as a consequence of intensive conventional farming practices (Bell *et al.*, 1995) and elevated temperatures associated with high soil moisture levels during the summer months, factors that can significantly accelerate SOC mineralisation (Mann, 1986; West and Post, 2002; Lal, 2004). Accordingly, the soil N_2O emissions measured in maize during this experiment where in close agreement with those reported for cotton by Sheer (2012) in an experiment conducted in Australia on a soil with similar carbon contents.

3.5.2 Effects of reduced N fertiliser rates on N_2O emissions and yields

Compared to the CONV treatment, the reduced N fertiliser application in the CONV-ADJ treatment decreased N_2O emissions by almost 60% both in wheat and maize. On the other hand, the two crops reacted differently to the reduction of N fertiliser. Despite a 75% reduction of applied N compared to the CONV treatment, wheat grain yields in CONV-ADJ were comparable to those in CONV. In maize instead, a reduction of 40% in N fertiliser corresponded to approximately a 30% decrease in grain yield (Table 3-3).

At the experimental site mungbean residues were incorporated in the soil a few weeks before the sowing of the wheat trial. Predictably, this increased the soil organic N that would have been slowly mineralised, compensating for the N deficiency observed in the CNT and CONV-ADJ treatments. This hypothesis would also explain the high NO_3^- contents that were measured across all treatments in the first two months of the wheat season (Figure 3-4b). The high crop productions measured in CONV-ADJ during wheat can therefore be attributed mostly to the mineralisation of plant residue of the previous legume crop.

Even though the percentage reduction of fertiliser N in the maize CONV-ADJ treatment was smaller than in wheat, it ultimately proved excessive and the maize yield was severely restricted. This was due to an overestimation of the availability of the soil residual N during the first stages of the maize season. The high C:N ratio of the wheat straw potentially caused a substantial microbial immobilisation of both soil mineral N and applied N (Van Den Bossche *et al.*, 2009), leaving the maize plants without an adequate N supply during the early stages of crop growth. This is supported by the lack of increase in soil NO_3^- and NH_4^+ contents observed in all treatments during the period following base dressing (Figure 3-4c and Figure 3-4d).

The reduction of N fertiliser tested in wheat was therefore well calibrated, but excessive in maize. These results indicate that there can be substantial scope for reducing conventional N fertiliser rates in cereals following a legume crop. However, the possible immobilisation of substantial amounts of soil N has to be taken into account when planting a cereal after a crop with high C:N residues. Further research would be useful to investigate whether conventional N fertiliser rates in maize could be reduced to a lesser extent to abate N_2O losses without affecting yields.

3.5.3 Effects of DMPP application on soil mineral N and N_2O emissions

The application of DMPP urea influenced the dynamics of mineral N in the soil profile (0-30 cm). In both seasons the use of DMPP urea in the CONV-DMPP treatment compared to CONV inhibited the oxidation of NH_4^+ to NO_3^- and consequently extended the longevity of N fertiliser in the NH_4^+ form (Figure 3-4a and Figure 3-4c). However, soil NO_3^- contents in CONV-DMPP differed substantially from those in the CONV treatment only in the maize season. The low soil temperature and moisture conditions during the wheat season might have retarded nitrification, leading to a gradual release of NO_3^- in the CONV treatment as well. Taking into account also the small quantity of N applied, in both CONV and CONV-DMPP treatments plants might have been able to efficiently uptake most of the NO_3^- and thus prevent its accumulation in the soil profile. This hypothesis is supported by the N_2O emissions measured in CONV and CONV-DMPP after top dressing, which remained relatively low and did not differ significantly either in terms of temporal pattern or magnitude (Figure 3-6a).

Table 3-3 highlights that the greater seasonal N_2O emissions measured in the CONV treatment compared to CONV-DMPP were not due to the emissions measured after top dressing, but to higher N_2O losses that occurred prior to the top dressing event. Therefore, the higher emission factor of the CONV treatment for the wheat season is not directly related to a treatment effect, but to spatial variability in NH_4^+ and NO_3^- contents prior to top dressing (Figure 3-4a and Figure 3-4b) or to different soil physical conditions in the proximities of the chambers.

On the other hand, the warm and moist soil conditions measured after side dressing maize are likely to have promoted a rapid nitrification of the high amount of applied NH_4^+. At this physiological stage (V10) the maize plants were only able to use a fraction of the NO_3^- present in the soil. Asynchrony between N supply and plant N uptake resulted therefore in high soil NO_3^- levels and in the high N_2O emissions observed in the CONV treatment during this period (Figure 3-6b). Conversely, the slower nitrification rate observed in the CONV-DMPP treatment avoided the accumulation of high amounts of NO_3^- in the soil, resulting in significantly lower N_2O losses. As a result, the largest N_2O fluxes after side dressing the CONV treatment were double the magnitude and longer in duration compared to those in CONV-DMPP (Figure 3-6b). The amount of N lost as N_2O from CONV-DMPP was reduced by 77% compared to CONV (Table 3-3) and is in close agreement with several incubation studies (Chen *et al.*, 2010; Suter *et al.*, 2010) that reported average abatement rates of DMPP ranging approximately from 60% to 90% under warm and humid conditions (>25°, WFPS 60%). In line with the results of this study, Liu *et al.* (2013) reported significantly higher N_2O abatement rates of DMPP urea in maize compared to wheat.

These findings indicate that under subtropical conditions applying DMPP urea has substantial scope to abate N_2O emissions mainly in the summer season, when the warm and humid soil conditions can promote high nitrification and denitrification rates.

3.5.4 N_2O emission factors and N_2O intensities

The emission factors reported in this study refer to a one year dataset and are influenced by site-specific conditions. Even if the unpredictability of N_2O emissions is taken into account, general evaluations regarding emission factors for subtropical cereal-based systems can be established.

Over the winter season (wheat) emission factors were remarkably low (Table 3-3), suggesting relatively high background emissions. Indeed, N_2O emissions measured in the non-fertilised treatment (CNT) did not differ significantly from those in CONV-ADJ and CONV-DMPP. The elevated background emissions were most likely due to the mineralisation of the mungbean residues incorporated before sowing wheat and are in line with the results reported for cereals following a legume crop by Baggs *et al.* (2003); Barton *et al.* (2008) and Gomes *et al.* (2009). The high background emissions measured in wheat resulted in negative emission factors determined for the CONV-ADJ and CONV-DMPP treatments. These values cannot be explained biologically but are due to the methodology used for the calculation of emission factors. That is, the cumulative N_2O emissions from CONV-ADJ and CONV-DMPP did not differ significantly from the CNT treatment and therefore emission factors for CONV-ADJ and CONV-DMPP should be considered as zero. These results highlight the importance of taking into account local crop management practices when calculating emission factors and confirm that relatively small quantities of N are lost as N_2O in subtropical cereal systems over winter.

During the maize season the highest emission factor (0.93%) was measured in the CONV treatment, while the lowest (0.24%) was measured in CONV-DMPP (Table 3-3), suggesting that DMPP can effectively reduce N_2O emissions when the soil conditions are highly conducive for denitrification.

The annual emission factor measured in the CONV treatment (0.69%) was lower than reported emission factors from Ding *et al.* (2007) (0.77%) and Cai *et al.* (2013) (0.82%) for wheat-maize cropping systems fertilised with similar N rates. The efficacy of DMPP in abating N_2O emissions was confirmed by the annual emission factor of 0.16% measured in the CONV-DMPP treatment. This represents one of the lowest annual emission factors reported from fertilised subtropical cereal systems.

Overall, annual emission factors in all treatments were lower than the default values of 1% and 2.1% of applied N suggested by De Klein *et al.* (2006) and by the Australian National Greenhouse Accounts (2010) for irrigated crops, respectively. However, this comparison has to be treated with caution since the emission factors reported in this study refer to only one year of data and are influenced by crop management and site-specific conditions.

The efficacy of management strategies in maximising crop yield and reducing N_2O losses is assessed through “N_2O intensities”, defined as the ratio of N_2O emitted and grain produced. Even though N_2O intensities did not differ significantly across treatments, compared to conventional urea DMPP urea significantly reduced annual N_2O emissions without negatively impacting cumulative yields (Table 3-3). This was due primarily to the results observed in CONV-DMPP during the summer season, when yields were comparable to CONV and total N_2O emissions were lower than the CONV-ADJ treatment. These findings indicate that the application of DMPP urea is a feasible strategy to reduce absolute N_2O emissions without compromising crop production. The inhibitory effect of DMPP has been reported to last only for several weeks (Pasda *et al.*, 2001). Therefore, to achieve results similar to those reported in this study, DMPP urea would have to be applied annually at least to the summer crop.

Fertilising with DMPP urea added an extra cost of approximately USD 50 ha^{-1} but did not provide an increase in yield compared to the same N rate with conventional urea. This result was also observed by Díez López and Hernaiz (2008) and Weiske *et al.* (2001a), while Liu *et al.* (2013) reported that the yield increase in the DMPP treatment compared to the urea treatment was limited to 9.1%. However, it must be considered that in the CONV-DMPP treatment and in the abovementioned studies the crops were fertilised with high amounts of N. Most likely in these treatments N was not a limiting factor for plant development and therefore there was no significant scope for DMPP urea to better match plant N demand and thus increase crop yield.

3.6 Conclusions

Data gathered in this study indicate that in subtropical cereal systems the summer crop is the main contributor to annual N_2O emissions. The hot and humid conditions, associated with the high N fertiliser rates usually applied in this season can indeed promote emission rates up to fivefold those measured in winter. Future strategies aimed at securing subtropical cereal production without increasing N_2O emissions should therefore focus on the fertilisation of the summer crop.

Adjusting conventional N fertiliser rates according to the estimation of residual soil N can be an effective practice to reduce N_2O emissions. On the other hand, this strategy entails the substantial risk of yield loss if residual soil N availability is not estimated correctly. This limitation can be overcome by taking into account possible immobilisation of soil N following the incorporation of crop residues and therefore allowing for a margin of uncertainty when defining the adjusted N rate.

The application of DMPP urea proved to be effective in abating N_2O emissions only in the summer season, when conditions are favourable for high nitrification and denitrification rates. Critically, the additional cost of using this fertiliser was not compensated by an increase in yields, meaning that for farmers the use of DMPP urea cannot be regarded as a feasible fertilisation strategy unless governmental incentive policies are established.

Further research is proposed to investigate whether the lower N_2O losses observed with DMPP urea are an indicator of an improved synchrony between crop N demand and fertiliser supply compared to conventional urea. The enhanced synchrony obtained with DMPP urea would enable to decrease the N rates tested in this study, reducing therefore the costs associated with fertilisation and further abating N_2O emissions due to the lower soil N content.

Statement of Contribution of Co-Authors for Thesis by Published Paper

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;

2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;

3. there are no other authors of the publication according to these criteria;

4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and

5. they agree to the use of the publication in the student's thesis and its publication on the Australasian Research Online database consistent with any limitations set by publisher requirements.

In the case of this chapter:

Legume pastures can reduce N_2O emissions intensity in subtropical cereal cropping systems.

Contributor	Statement of contribution*
Massimiliano De Antoni Migliorati	Performed experimental design, conducted fieldwork and laboratory analyses, data analysis, and wrote the manuscript.
Signature	
9th March 2015	
Mike J. Bell	Aided experimental design and data analysis, and reviewed the manuscript.
Peter R. Grace	Aided experimental design and data analysis, and reviewed the manuscript.
Clemens Scheer	Aided experimental design and data analysis, and reviewed the manuscript.
David W. Rowlings	Aided experimental design and data analysis, and reviewed the manuscript.
Shen Liu	Aided data analysis

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

Peter R. Grace		9th March 2015
Name	Signature	Date

Chapter 4: Legume pastures can reduce N_2O emissions intensity in subtropical cereal cropping systems (*Paper 2*)

4.1 Abstract

Alternative sources of N are required to bolster tropical and subtropical cereal production without increasing N_2O emissions from these agroecosystems. The reintroduction of legumes in cereal cropping systems is a possible strategy to reduce synthetic N inputs but elevated N_2O losses have sometimes been observed after the incorporation of legume residues. However, the magnitude of these losses is highly dependent on local conditions and very scarce data are available for subtropical regions. The aim of this study was to assess whether, under subtropical conditions, the N mineralised from legume residues can substantially decrease the synthetic N input required by the subsequent cereal crop and reduce overall N_2O emissions during the cereal cropping phase. Using a fully automated measuring system, N_2O emissions were monitored in a cereal crop (sorghum) following a legume pasture and compared to the same crop in rotation with a grass pasture. Each crop rotation included a nil and a fertilised treatment to assess the N availability of the residues. The incorporation of legumes provided enough readily available N to effectively support crop development but the low labile C left by these residues is likely to have limited denitrification and therefore N_2O emissions. As a result, N_2O emissions intensities (kg N_2O-N yield^{-1} ha^{-1}) were considerably lower in the legume histories than in the grass. Overall, these findings indicate that the C supplied by the crop residue can be more important than the soil NO_3^- content in stimulating denitrification and that introducing a legume pasture in a subtropical cereal cropping system is a sustainable practice from both environmental and agronomic perspectives.

4.2 Introduction

Mitigating climate change and achieving food security are two of the key challenges of the twenty-first century. Cereals are by far the world's most important food source, contributing on average 50% of daily energy intake and up to 70% in some developing countries (Kearney, 2010). By 2050 the world’s population is forecast to be over a third larger than at present (UNFPA, 2011) and cereal demand is predicted to increase by 60% (FAO, 2009). Pronounced intensification of cereal production is expected to take place in tropical and subtropical regions (Smith *et al.*, 2007), identifying the need for more nitrogen (N) to be supplied to these agroecosystems.

There is consensus (e.g. Tilman *et al.* (2002); Crews and Peoples (2004); Jensen *et al.* (2012)) that both the manufacture and use of synthetic N fertilisers in crop production generate substantial environmental threats, with the emission of significant amounts of nitrous oxide (N_2O) arguably one of the most important. N_2O is a potent greenhouse gas (298 CO_2-eq over a 100 year time horizon (Myhre *et al.*, 2013)) associated also with the depletion of the ozone layer in the stratosphere (Ravishankara *et al.*, 2009). Together, these issues confirm that alternative means of intensification must be implemented to avoid the increase of tropical and subtropical cereal production through an overuse of synthetic N. If not, the result would be a net increase in N_2O emission rates from these agroecosystems.

The introduction, or in many cases, reintroduction, of legumes in crop rotations is one possible strategy to reduce synthetic N inputs whilst sustaining grain yields (Crews and Peoples, 2004; Jensen *et al.*, 2012). Owing to their ability to fix atmospheric N_2 in symbiosis with rhizobia bacteria, legumes can reduce N demand of the subsequent crop, and consequently decrease N_2O emissions associated with synthetic N fertilisers. In an extensive review on the use of legumes to mitigate climate change, Jensen *et al.* (2012) concluded that N_2O emissions during the legume growing season did not differ substantially from unplanted or non-fertilised soils. However, elevated N_2O losses were sometimes reported after the termination of legume-based ley pastures, when crop residues were returned to the soil (Gomes *et al.*, 2009; Pappa *et al.*, 2011). The low C:N ratio of legume residues can indeed lead to rapid tissue mineralisation once incorporated into the soil. As a result, accumulation of mineral N can occur in the soil, increasing the potential for substantial amounts of N to be lost as N_2O via nitrification and denitrification (Jensen *et al.*, 2012).

The magnitude of N_2O losses in response to legume residue incorporation is, however, highly dependent on local climate and soil conditions (Rochette *et al.*, 2004). Subtropical cropping systems are characterised by intense and frequent rainfall events during the summer months. The warm and moist soil conditions during these periods can accelerate legume tissue mineralisation compared to temperate environments, leading to ideal conditions for nitrifying and denitrifying bacteria and therefore magnifying the risk of high N_2O emissions (Granli and Bøckman, 1995; Skiba *et al.*, 1997).

However, little data are available for tropical and subtropical regions (Mosier *et al.*, 2004b), where warm, humid summer conditions could promote high N_2O losses from cropped soils (Bouwman *et al.*, 2002b). Although numerous studies have investigated N_2O emissions after the termination of legume ley pastures prior to a return to cropping, the vast majority were conducted in temperate regions (Wagner-Riddle and Thurtell, 1998; Baggs *et al.*, 2000; Robertson *et al.*, 2000; Rochette *et al.*, 2004; Schwenke *et al.*, 2010).

The overall aims of this study were therefore to assess whether, under subtropical conditions: i) the N mineralised from legume residues can substantially reduce the synthetic N input required by the subsequent cereal crop; ii) N_2O losses occurring after the incorporation of legume residues can be minimised via synchronising the release of N derived from the residues with the N demand of the subsequent crop; iii) reducing the synthetic N input applied to a cereal in rotation with a legume crop can significantly decrease overall seasonal N_2O during the cereal phase.

In this study seasonal N_2O emissions and yields were monitored in a cereal crop (sorghum) following a legume (legume-ley pasture) and compared to the same cereal crop in rotation with a non-leguminous crop (grass ley pasture). Each rotation included both a nil and a fertilised treatment. The N fertiliser applied to sorghum in the legume-cereal rotation was reduced compared to the grass-cereal to assess the availability of the N fixed by the legume ley pasture.

This study is the first to use a fully automated greenhouse gas measuring system to precisely quantify N_2O emissions in a subtropical cereal crop after the termination of a legume ley pasture. The results of this study will contribute to define mitigation strategies for the sustainable intensification of these agroecosystems.

4.3 Materials and Methods

4.3.1 Local climate and soil characteristics

This experiment was conducted in the subtropical region of Australia at the J. Bjelke Petersen Research Station of the Department of Agriculture, Fisheries and Forestry (DAFF). The research site is located in Kingaroy (26°34’54,3’’ S, 151°49’43.3’’ E, altitude 441 m a.s.l), in the southern Burnett region of southeast Queensland, Australia. The subtropical climate (classified as Cfa, according to the Köppen climate classification) has warm, humid summers and mild, dry winters. Daily mean maximum and minimum temperatures range from 20.1°C to 4.0°C in winter and from 29.6°C to 16.5°C in summer, respectively. Local mean annual precipitation is 776.2 mm and varies from a minimum of 28.6 mm in August to a maximum of 114.1 mm in January (Australian Bureau of Meteorology website). The soil is a Tropeptic Eutrustox Oxisol (USDA Soil Taxonomy, USDA (1998)) - Orthic Ferralsol (FAO, 1998), characterised by relatively slow permeability and high clay content (50-65% clay). The effective rooting depth is 1.2 m and the plant available water holding capacity is 100 mm. The main physical and chemical soil properties of the field site are highlighted in Table 4-1.

4.3.2 Experimental set-up

The experiment was established in a slit plot design with two main plots (legume and grass ley pastures) and two sub plots (N fertiliser rates) with three replicates. Each main plot was 30 m x 10.8 m, with main plots split into two subplots (15 m x and 10.8 m) during the sorghum cropping season. Allowing for buffer rows, the effective subplot area was 12 m x 7.2 m, or 8 crop rows spaced 0.9 m apart.

Table 4-1 - Main soil physical and chemical properties of surface 30 cm of soil profile for the two cropping histories (mean ± SE, n=3) at the beginning of the sorghum season at Kingaroy research station, Queensland, Australia.

Soil Property (0-30 cm)	**Legume**	**Grass**
pH (H_2O)	5.12 ± 0.03	5.30 ± 0.02
DOC (kg C ha^{-1})*	43.04 ± 11.98	56.05 ± 2.97
PMN (kg N ha^{-1})**	12.78 ± 1.33	9.25 ± 1.08
Bulk density 0-30 cm (g cm^{-3})	1.18 ± 0.08	
Texture (USDA)	Clay	
Clay (%)	55	
Silt (%)	14	
Sand (%)	31	

*Dissolved organic carbon. **Potentially mineralisable nitrogen.

4.3.3 Cropping histories

N_2O emissions and yields were measured in plots planted with sorghum (*Sorghum bicolor* L.) following two distinct cropping histories. One crop rotation (hereafter called legume cropping history) included two seasons of alfalfa pasture (*Medicago sativa*, L., summers 2009/2010 and 2010/2011), one season of maize (*Zea mays*, L., summer 2011/2012) and one season of sulla ley pasture (*Hedysarum coronarium* L., winter 2012) prior to sowing sorghum. The other crop rotation (hereafter called grass cropping history) included two seasons of a mixed Rhodes grass (*Chloris gayana,* K.*)* and alfalfa pasture (summers 2009/2010 and 2010/2011), one season of maize (summer 2011/2012) and one season of wheat (*Triticum aestivum* L., winter 2012). Although the mixed alfalfa pasture was sown in consociation with Rhodes grass, the Rhodes grass became rapidly predominant and by the end of the first season the pasture was composed almost completely by Rhodes grass. All crops in both rotations were not fertilised. Sulla and wheat were direct drilled in August 2012 and managed as forage crops. Both crops were terminated 28 November 2012 with all residues returned to the soil as mulch before being incorporated with four shallow cultivations (20 cm). The incorporation of sulla residues (2.3 Mg dry matter ha^{-1}, 1.57% N) was estimated to supply the soil approximately 36 kg N ha^{-1}, while wheat residues (1.24 Mg dry matter ha^{-1}, 0.75% N) about 9 kg N ha^{-1}. The entire field study was irrigated with 20 mm on 10 December 2012, two days before plots were planted with sorghum (12 December 2012). Further details on the management of the two crop rotations can be found in Bell *et al.* (2012).

4.3.4 Sorghum establishment and management

Sorghum (cultivar Pioneer G22) was planted with a plant density of 7 plants m^{-2} and an inter-row space of 90 cm. Two N fertilisation rates were tested on each cropping history, resulting in a total of four treatments:

- L0: Sorghum grown in the legume cropping history, no N applied;
- L70: Sorghum grown in the legume cropping history, 70 kg N ha^{-1} applied;
- G0: Sorghum grown in the grass cropping history, no N applied;
- G100: Sorghum grown in the grass cropping history, 100 kg N ha^{-1} applied.

Treatments L70 and G100 were base dressed at planting, banding 20 kg N ha^{-1} as urea. On 15 January 2013 (eight leaf stage) both treatments were inter-row cultivated and side dressed with banded urea, receiving 50 kg N ha^{-1} (L70) or 80 kg N ha^{-1} (G100). The N application rate for G100 was designed to achieve maximum yield potential and was representative of farming practices of the region. The synthetic N rate used in L70 was reduced compared to G100 to assess whether the estimated 30 kg N ha^{-1} resulting from the mineralisation of the sulla residues would have been available to sorghum.

During the early stages of crop development irrigation was applied at a rate of 10 mm h^{-1} when water filled pore space (WFPS) values approached 40%. This method avoided water stress limiting the potential yields and prevented fertiliser N to be leached below the rooting zone. The trial was irrigated on four and two occasions over the wheat and maize seasons, respectively. The trial was irrigated three times over the season (25 mm on 18 December 2012, 40 mm on 4 January 2013 and 40 mm on 18 January January) using surface stored dam water and overhead sprinklers. Sorghum was harvested on 18 June 2013. The trial area was left fallow until being cultivated on 6 August 2013 (offset disc and chisel plough to a depth of 20 cm) and on 19 September 2013 (offset disc to a depth of 20 cm) to prepare the seedbed for the next crop. Irrigations were conducted on 27 and 29 August 2013 (30 and 40 mm, respectively) to assess whether significant amounts of N were still available for nitrification or denitrification after harvest. Details about crop rotations and farming operations are displayed in Table 4-2.

Table 4-2 - Details of crop rotations and farming operations for the four treatments at Kingaroy research station.

Date	**L0**	**L70**	**G0**	**G100**
Summer 2009/2010	Alfalfa pasture	Alfalfa pasture	Rhodes grass + alfalfa pasture	Rhodes grass + alfalfa pasture
Summer 2010/2011	Alfalfa pasture	Alfalfa pasture	Rhodes grass + alfalfa pasture	Rhodes grass + alfalfa pasture
Summer 2011/2012	Maize	Maize	Maize	Maize
Winter 2012	Sulla pasture	Sulla pasture	Wheat	Wheat
28-30/11/2012	Pastures terminated and entire field trail cultivated four times with offset disc to 20 cm			
10/12/2012	Entire field trail irrigated with 20 mm			
12/12/2012	Sorghum planted	Sorghum planted Applied 20 kg N ha^{-1}	Sorghum planted	Sorghum planted Applied 20 kg N ha^{-1}
18/12/2012	Entire field trail irrigated with 25 mm			
04/01/2013	Entire field trail irrigated with 40 mm			
14/01/2013		Applied 50 kg N ha^{-1}		Applied 80 kg N ha^{-1}
18/01/2013	Entire field trail irrigated with 40 mm			
18/06/2013	Entire field trail harvested			
06/08/2013	Entire field trail cultivated twice with offset disc down to 20 cm			
27/08/2013	Entire field trail irrigated with 30 mm			
29/08/2013	Entire field trail irrigated with 40 mm			
19/09/2013	Entire field trail cultivated with offset disc down to 20 cm			

4.3.5 Measurement of N_2O and CO_2 emissions

The use of a fully automated greenhouse gas measuring system enabled a long-term high temporal resolution dataset to be established. N_2O fluxes were monitored for nine months, from sorghum planting (12 December 2012) to the final preparation of the seedbed for the subsequent crop (19 September 2013) to assess overall N_2O losses over the cropping season as well as the post-harvest period.

N_2O emissions were captured using twelve automated sampling chambers (one per plot). Chambers were made of transparent acrylic panels, measured 50 cm x 50 cm x 15 cm and were attached via a rubber seal to stainless steel frames inserted 10 cm into the ground. The chambers were closed airtight with lids operated by pneumatic actuators and connected to a fully automated sampling and analysis system as described in Chapter 3 and in Scheer *et al.* (2013b).

During a measurement cycle a set of four chambers closed for 60 min with each chamber sampled 4 times for 3 min. A certified gas standard of 500 ppb N_2O (BOC – Munich, Germany- and Air Liquide –Dallas, TX, USA) was pumped into the gas chromatograph every 15 min. At the end of the cycle the chambers reopened and the next set of four chambers closed for sampling. One complete cycle of twelve chambers lasted 3 hours, during which each chamber was sampled for 1 hour and remained opened for 2 hours to restore ambient conditions. This method enabled the determination of up to 8 single fluxes per chamber per day.

The air samples taken from each chamber headspace were automatically pumped to the sampling unit at a flow rate of 200 ml min^{-1}. During the 3 min sampling period the air sample was continuously analysed for CO_2 concentration using a single path infra-red gas analyser (Licor, LI 820, St Joseph, MI, USA). N_2O concentration was analysed injecting 3 ml of gas sample into the carrier gas (N_2) of a gas chromatograph (Model 8610C, SRI Instruments, USA) equipped with a ^{63}Ni electron capture detector (ECD). A column filter containing sodium hydroxide-coated silica (Ascarite, Sigma-Aldrich, St. Louis, MO, USA) was installed upstream of the ECD to minimise the CO_2 and water vapour interference on N_2O measurements. The column filter was replaced every two weeks.

During the three hours of a complete measuring cycle the system was automatically calibrated twelve times by a single point calibration using the certified gas standard of 500 ppb N_2O. Greater accuracy was achieved with a multi-point calibration during the measuring season using certified gas standards of 500, 980, 5030 ppb N_2O (BOC –Munich, Germany). The GC response over this range was determined to be linear so no correction was necessary to precisely determine high fluxes. The detection limit of the system was calculated using the methodology established by Parkin *et al.* (2012) and was approximately 0.5 g N_2O-N ha^{-1} day^{-1} for N_2O and 1 kg CO_2-C ha^{-1} day^{-1} for CO_2, respectively. Throughout the season all system components were constantly checked for leaks, making the sample dilution due to leakage negligible. The system was programmed to open the chambers if rain events exceeded 5 mm or the internal air temperature of the chamber exceeded 55°C. During irrigation events the system was stopped and all chamber lids were opened to allow water to enter inside the chambers.

The chamber placement strategy was based on the methodology established by Kusa *et al.* (2006) and Parkin and Kaspar (2006) in order to measure N_2O emissions from both a diffused source (crop residues) and a localised source (banded fertiliser). Two of the three replicate chambers of each treatment were positioned over the crop row and the third in the inter-row. Chambers positioned over the crop row included the banded fertiliser (10 cm from the plant row) in the chamber area. Sorghum plants inside the chamber positioned over the crop row were cut when exceeding the chamber headspace, a practice established by Drury *et al.* (2008); Halvorson *et al.* (2008) and Hu *et al.* (2013). As recommended by Kusa *et al.* (2006) and Parkin and Kaspar (2006), the impact of this practice on belowground C and N dynamics, and therefore N_2O emissions, was minimised by relocating all chambers placed over the crop row to a new section of the crop row every fortnight. This strategy proved to be effective as only marginal differences in daily N_2O emissions were observed in the control treatments between chambers placed in the inter-row and over the crop row (Table 4-3, Figure 4-5).

The measuring system was deployed immediately after planting and temporarily withdrawn to permit farming operations (side dressing, harvest, post-harvest cultivations). During the nine months of this study an average of 2700 valid N_2O and CO_2 fluxes were obtained for each treatment.

4.3.6 Calculation of N_2O and CO_2 emissions

Hourly N_2O fluxes were calculated with the method described by Barton *et al.* (2008), determining the slope of the linear increase or decrease of the four gas concentrations measured during the 60 minutes of chamber closure period. In contrast, hourly CO_2 fluxes were computed using the linear increase of six concentrations measured in the first two sampling intervals, a method used to avoid possible saturation of CO_2 partial pressure in the chamber. N_2O and CO_2 fluxes were corrected for the three factors of air temperature inside the chamber, atmospheric pressure and the ratio between chamber volume and soil area using:

$$F = \frac{b \cdot V_{CH} \cdot MW \cdot 60 \cdot 10^{6}}{A_{CH} \cdot MV_{corr} \cdot 10^{9}}$$

Equation 1

where F is the emission rate (µg m^{-2} $hour^{-1}$), b is the variation of gas concentration inside the chamber (ppb min^{-1}), V_{CH} is the volume of the chamber (m^3), MW is the gas molar weight (28 for N_2O-N and 12 for CO_2-C), *60* is the conversion from minutes to hours, 10^6 converts g to µg, A_{CH} is the surface area of the chamber (m^2), MV_{corr} is the mole volume (m^3 mol^{-1}) corrected for pressure and temperature as presented in Equation 2, 10^9 converts ppb to µL m^{-3}.

$$MV_{corr} = 0.02241 \cdot \left(\frac{273.15 + T}{273.15} \times \frac{p0}{p1} \right)$$

Equation 2

where 0*.02241* m3 is 22.41 L molar volume, T is the temperature of the chamber at the time of the measurement (Kelvin), *p0* is the air pressure at sea level and *p1* is the air pressure at the study site. To provide greater accuracy, air pressure at the site was determined using a barometric equation based on the local altitude.

The Pearson correlation was then used to quality-check flux measurements. Fluxes above the detection limit were discarded if the regression coefficient (r^2) was < 0.80 for N_2O and < 0.90 for CO_2, respectively. Mean daily fluxes for each treatment were calculated using weighted averages of hourly data from the three replicates. That is, for each treatment, hourly fluxes from the two chambers over the crop row (covering 50 cm around the crop row) were averaged. The obtained mean flux was then averaged with the mean of hourly fluxes measured by the chamber in the inter-row (covering 50 cm in the inter-row). This method made it possible to accurately calculate the average N_2O emissions of each treatment, accounting for the spatial variability occurring between two crop rows (98 cm). Cumulative N_2O fluxes [kg N_2O-N ha^{-1}] were determined by summing daily N_2O fluxes measured during the study period.

Emission factors were corrected for background emissions (Kroeze *et al.*, 1997) using the following:

$$EF\ \% = \frac{N_2O\ (Fert) - N_2O\ (Unfert)}{N\ fertiliser\ input} \cdot 100$$

Equation 3

where *EF %* is the emission factor reported as a percentage of *N fertiliser input* (kg N ha^{-1} season^{-1}) lost as N_2O-N, N_2O *(Fert)* and N_2O *(Unfert)* (kg N ha^{-1} season^{-1}) are the cumulative N_2O-N emissions measured in the fertilised and non-fertilised treatments with the same cropping history, respectively.

Soil CO_2 fluxes, considered a proxy data for estimating soil respiration rates (inclusive of microbial and roots respiration), were calculated using only the chambers placed in the inter-row. Missing daily N_2O and CO_2 fluxes (due to rare occasional failures of the measuring system) were estimated with the Amelia II multiple imputation model (Honaker and King, 2010) using daily values of soil Water-Filled Pore Space (WFPS) (0-10 cm, 10-20 cm and 20-30 cm) and mineral N content (0-30 cm).

4.3.7 Auxiliary measurements

Chamber air temperature and soil temperature were measured every 5 minutes using RTD probes (Temperature Controls Pty Ltd, Australia) buried at 10 cm depth near to a chamber. Four Frequency Domain Reflectometers (FDR, EnviroScan probes, Sentek Technologies, Australia) measured water dynamics of the soil profile throughout the field study. Before the beginning of the experiment all FDR probes were calibrated for the local soil type following producer recommendations (Sentek Technologies, 2011). The FDR probes were deployed at planting and programmed to measure the volumetric soil water content at three depths (0-10 cm, 10-20 cm, 20-30 cm) at 30 minute intervals. Water filled pore space (WFPS) was calculated using a particle density of 2.79 g cm^{-3}.

Soil chemical properties at the site were determined at sorghum planting, with soil samples collected from every plot with a manual open-faced bucket auger (10 cm diameter). Each plot was sampled at three depths (0-10, 10-20, 20-30 cm) and then analysed for texture (hydrometer method as described by Carter and Gregorich (2007)), pH, NH_4-N, NO_3-N, dissolved organic C and potentially mineralisable N. Routine soil sampling was then conducted at regular intervals during the growing season and soil samples (0-10, 10-20, 20-30 cm) were analysed for NH_4-N, NO_3-N. Each soil sample consisted of three subsamples taken at 10 cm intervals from the crop row of then mixed in order to ensure it represented the banded and non-banded areas of the plot.

Soil NH_4-N and NO_3-N were extracted by shaking 20 g soil in 100 mL 1 M KC1 solution at room temperature for 60 minutes (Carter and Gregorich, 2007). This solution was then filtered and stored in a freezer until analysed colorimetrically for NH_4-N and NO_3-N using an AQ2+ discrete analyser (SEAL Analytical WI, USA). Dissolved organic C was extracted at room temperature by shaking 20 g soil in 100 mL of deionised water for 60 minutes. The suspension was then centrifuged for 15 minutes at 10000 rotations per minute and the supernatant filtered with a 0.45 µm pore diameter cellulose membrane filter (based on Scaglia and Adani (2009)). The samples were analysed using a supercritical water oxidation technique with the Seivers InnoVox laboratory TOC analyser (General Electric, Boulder, CO, USA).

Potentially mineralisable N was determined by incubating soil samples at field capacity at 30°C for 0, 7 and 14 days (Bremner, 1965). The samples were taken on 12 December 2012 sampling each plot at three depths (0-10, 10-20, 20-30 cm). Mineral-N formed during the incubation was measured by 2M KCl extraction followed by automated colorimetric determination. For each treatment, the amount of potentially mineralisable N was calculated as the difference between the mineral N determined at day 7 and 14 in order to avoid the Birch effect (Birch, 1958).

Total biomass was determined at physiological maturity by collecting duplicate samples of 1m of crop row in each plot. Samples were oven dried at 60°C to determine dry weight before being weighed and ground for total N content, which was measured using a C-N analyser after Dumas combustion (LECO TruMac, LECO Corporation, St. Joseph, MI, USA). Grain yield was measured in each plot by harvesting duplicate 1.8 m wide strips for the plot length using a plot combine. Grain samples were also dried at 60°C before quantification of yields on a dry weight basis, while grain N was determined using a methodology similar to that in biomass samples.

Fertiliser N recovery in the crop (RE_{fN}) was determined applying ^{15}N-labelled urea in micro-plots (0.9 m x 1.5 m) located next to the measuring chambers. The L70 and G100 treatments received 5% excess ^{15}N enriched urea both at planting and at side dressing. The ^{15}N-labelled urea was dissolved in 1 L of deionised water and applied as a liquid solution in a sub-surface band, minimising in this way N losses via runoff and NH_3 volatilisation. Plants in the micro-plots were sampled at crop harvest by collecting above- and below-ground material. The ^{15}N analysis was performed using a 20-22 Isotope Ratio Mass Spectrometer (Sercon Limited, UK). More detailed information on the methodology used to determine the RE_{fN} is presented in Chapter 5.

4.3.8 Statistical analysis

Statistical analyses were performed within the MATLAB 2012a environment (MathWorks Inc., Natick, MA, US), where the temporal patterns of daily N_2O emissions displayed by the four treatments were compared using the autoregressive integrated moving average (ARIMA) model (Box and Pierce, 1970). This model was fitted to each time series using the following formula:

$$\Delta^d Y_t = \phi_0 + \phi_1 \Delta^d Y_{t-1} + \cdots + \phi_p \Delta^d Y_{t-p} + a_t + \theta_1 a_{t-1} + \cdots + \theta_q a_{t-q},$$

Equation 4

where $\Delta = (1 - B)$ and B are the backshift operators. The roots of the AR and MA polynomials satisfied the stationarity and invertibility conditions, respectively. The values of p, d and q were determined by the Bayesian information criterion (BIC), and the unknown parameters were estimated by least squares estimators. The residuals $\hat{a}_t$ were computed by $\widehat{\Phi}(B)\widehat{\Theta}^{-1}(B)Y_t$, where $\widehat{\Phi}(B)$ and $\widehat{\Theta}(B)$ denote the estimates of the autoregressive and moving average parameters, respectively. The bootstrap residual resampling method was used to evaluate the variation, while prediction intervals were constructed using the percentile method. A mixed-design analysis of variance (ANOVA) was performed to determine the influence of fertilisation rate or cropping history on N_2O emissions and grain yields. The Bonferroni *post hoc* test was used to compare average and cumulative N_2O emissions, N_2O intensities, grain yields, above ground biomass productions and harvest indexes. As with the method used for the calculation of daily N_2O fluxes, standard errors of average and cumulative N_2O emissions and N_2O intensities were calculated by assigning different weights to the chamber in the inter-row (0.5) and over the rows (0.25).

4.4 Results

4.4.1 Environmental conditions

Over the study period (12 December 2012 - 19 September 2013) a total of 827 mm of rain fell at the study site, including one heavy rainfall event of 234 mm during a thunderstorm on 27 January 2013. While this total corresponded to 148% of the growing season mean for the 108-year period between 1905 and 2013, it is noteworthy that over 70% of the total rainfall was concentrated between 25 January and 3 March (Figure 4-1). The mean air temperature was 17.9°C, with the maximum (38.0°C) and minimum (-4.4°C) hourly air temperatures recorded in January and August 2013, respectively. Average daily soil temperatures (0-10 cm) ranged from a maximum of 29.7°C (December 2012) to a minimum of 11.9°C (May 2013).

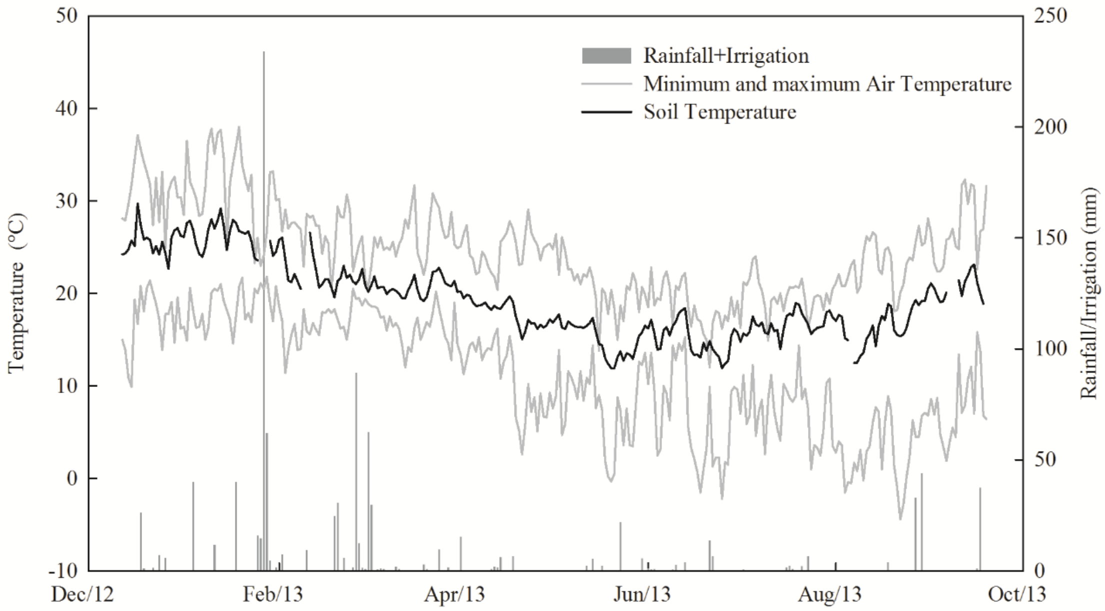

Figure 4-1 - Minimum and maximum daily air temperatures, soil temperatures (0-30 cm), rainfall and irrigation events at Kingaroy (Queensland, Australia) during the sorghum season.

4.4.2 Seasonal variability of soil conditions

The WFPS of the topsoil (0-30 cm) varied in response to rainfall, irrigation events and crop growth. At the beginning of the season WFPS values fluctuated between 36% and 47% due to the rapid crop development and irrigation events (Figure 4-2). WFPS ranged from 30% to 50% during most of the study. Values up to 66% were measured between late January and mid-March as a consequence of the intense rainfall events that occurred during this period. After March average WFPS values started gradually to decrease as a result of the declined rainfall regime.

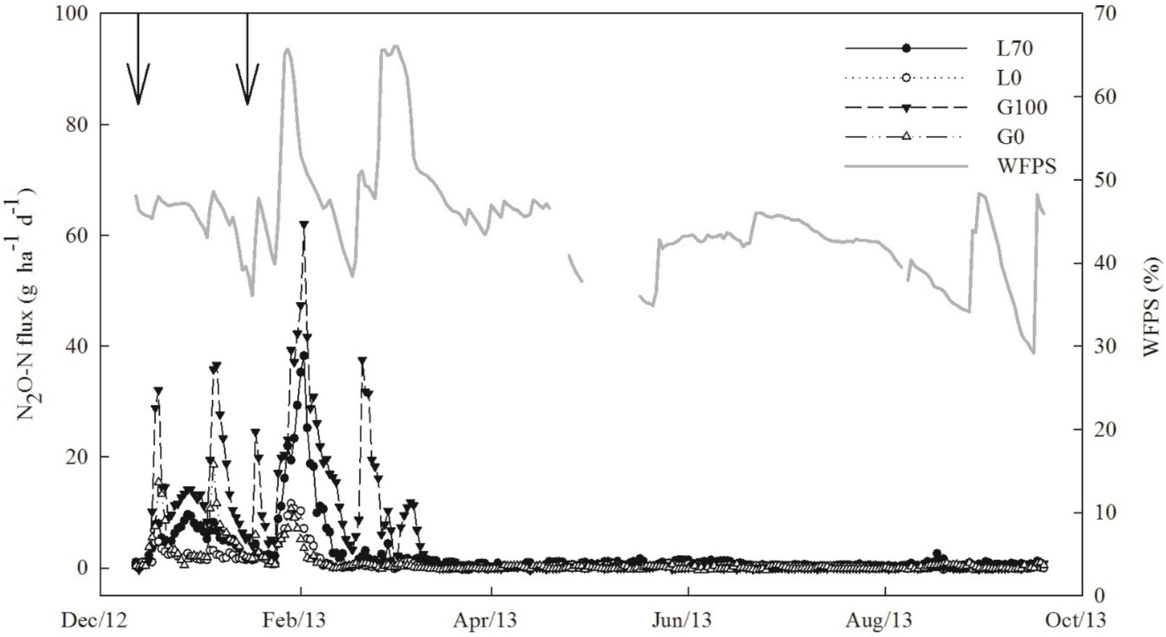

Figure 4-2 - Daily soil N_2O fluxes and water-filled pore space (WFPS, 0-30 cm) for the four treatments during the sorghum season in Kingaroy (Queensland, Australia). Arrows indicate the timing of N fertiliser applications.

In the 0-30 cm sampling zone, NH_4^+-N was the dominant form of soil mineral N. With the possible exception of the sampling event at sowing, no consistent response to history or fertiliser application was observed regarding NH_4^+-N dynamics (Figure 4-3a). At sorghum planting, NH_4^+-N contents in the top 30 cm averaged 40 kg N ha^{-1} and then stabilised between 16 and 33 kg N ha^{-1} for the remainder of the season. Limited response to history or N fertiliser application was observed also in soil NO_3^--N contents (Figure 4-3b), with the exception of the first month of the growing season. At this stage the legume histories (L0 and L70) showed higher NO_3^--N contents than the grass history equivalents, although differences were less than 20 kg N/ha.

Even though not statistically different, at the beginning of the sorghum season dissolved organic carbon contents in the grass history tended to be higher than in the legume. Slightly higher (but not statistically different) potentially mineralisable N values were observed in the legume history treatments compared to the grass (Table 4-1).

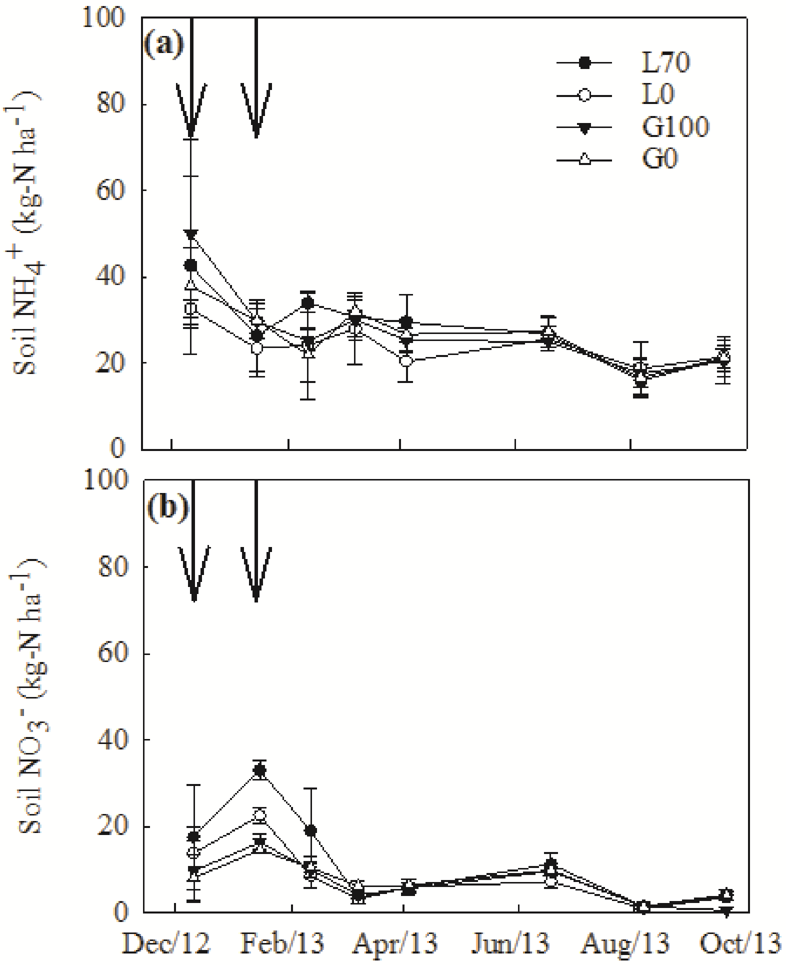

Figure 4-3 - Soil ammonium (a) and nitrate (b) contents (0-30 cm) for the four treatments during the sorghum seasons in Kingaroy (Queensland, Australia). Arrows indicate the timing of N fertiliser applications.

4.4.3 N_2O emissions

N_2O emissions varied temporally and spatially in response to N fertilisation rate and cropping history. In all treatments significant N_2O losses occurred between mid-December 2012 and mid-March 2013, when soil mineral N contents and WFPS values were higher than in the remainder of the study period (Figure 4-2, Figure 4-3). During this period N_2O emissions increased shortly after rain or irrigation events. This trend was particularly evident in the G0 and G100 treatments, where N_2O emission rates increased more abruptly than in L0 and L70 (Figure 4-2).

In all except G0 treatments, the highest emission pulse was observed after the rainfall event on 27 January, when a total of 234 mm rainfall fell over 24 hours. During this event N_2O emissions in treatments L70 and G100 were up to 4 and 6 fold those of the non-fertilised treatments, respectively. After this event, N_2O emission in all treatments progressively declined to background levels, with the only exception being G100, where a substantial N_2O emission pulse was measured after another 260 mm rainfall fell at the field site between 19 February and 3 March (Figure 4-2). After mid-March daily N_2O fluxes in all treatments never exceeded 1 g N ha^{-1} day^{-1} despite several rain events. Emissions did not increase even after the two irrigation events on 27 and 29 August 2013 or the two cultivation events on 6 August and 19 September 2013.

During the period of highest emissions (December 2012 to March 2013) the ARIMA model highlighted significant treatment effects on the temporal pattern of N_2O emissions. Before side dressing, the two N_2O emission pulses measured in G100 and G0 significantly exceeded those in L70 and L0, respectively (Figure 4-4a, b). After side dressing the emission pulse in G100 was significantly higher than that in L70, while no substantial differences were observed between G0 and L0 (Figure 4-4c, d).

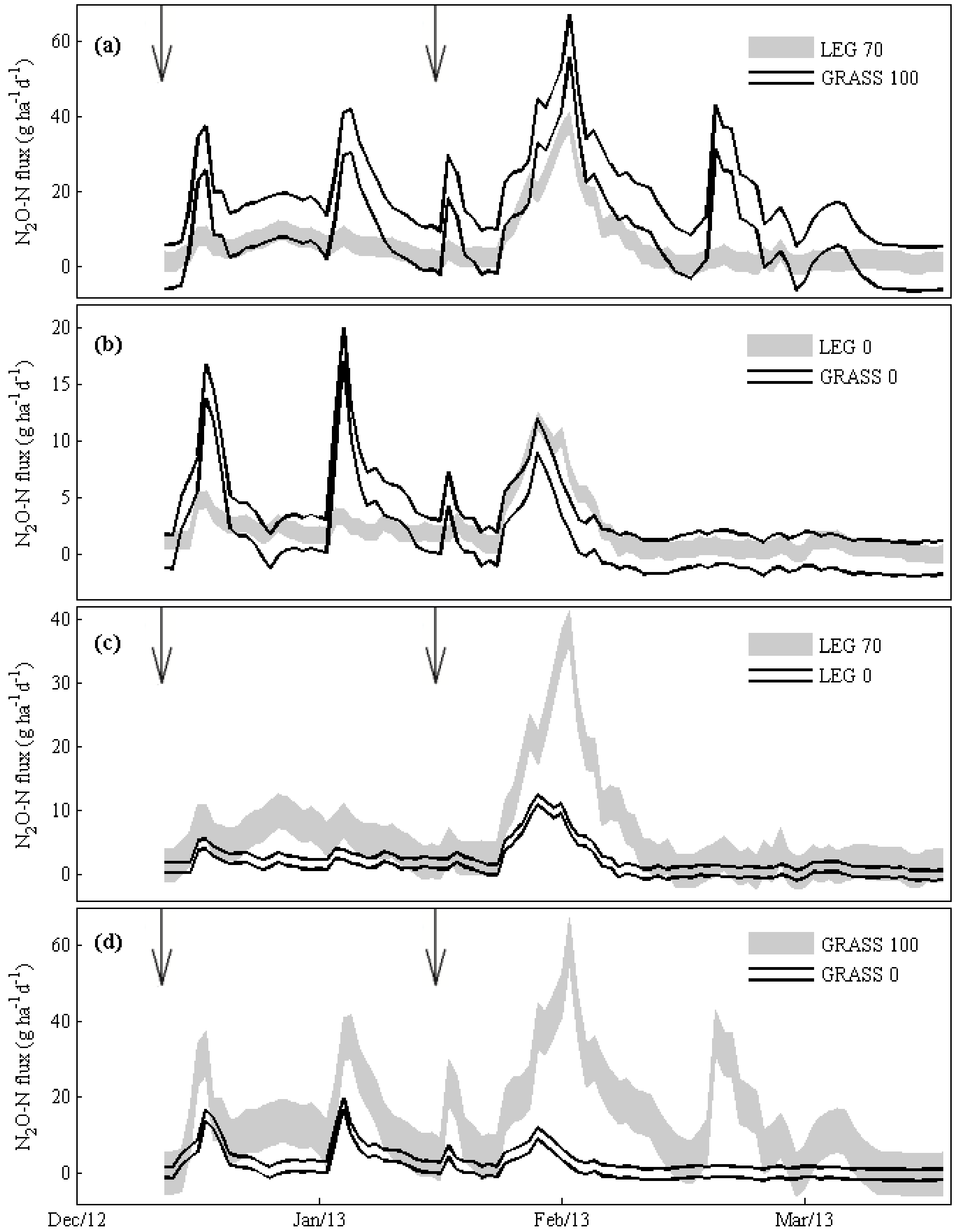

Figure 4-4 - 95% confidence intervals of N_2O fluxes in the different treatments during the period of highest emissions (December 2012-March 2013) in Kingaroy (Queensland, Australia). Confidence intervals are displayed using different scales. Arrows indicate the timing of N fertiliser applications.

The chamber placement highlighted two different patterns in the spatial variability of N_2O flux rates during the period of high emissions. In the two non-fertilised treatments and in G100, N_2O fluxes from the crop row (inclusive of the banded fertiliser) did not differ significantly from those from the inter-row (Figure 4-5b, c, d). Whereas in the L70 treatment, average N_2O emissions measured in the crop row exceeded those in the inter-row by a factor of 6 (Figure 4-5a).

Only the N_2O cumulative losses measured in G100 were significantly higher ($p<0.05$) than those of the other treatments. Cumulative losses in L70 did not display significant differences compared to the non-fertilised treatments (Table 4-3).

Table 4-3 - Seasonal N_2O average fluxes, cumulative N_2O fluxes, N_2O intensities (mean ± SE, n=3), emission factors and cumulative CO_2 fluxes as a function of the four treatments. Means denoted by a different letter indicate significant differences between treatments ($p<0.05$).

Measurement	**Treatment**			
	L0	**L70**	**G0**	**G100**
Average Flux [g N_2O-N ha^{-1} d^{-1}]	0.85 ± 0.08^{a}	2.41 ± 0.82^{a}	0.94 ± 0.18^{a}	5.07 ± 0.58^{b}
Cumulative N_2O Flux [kg N_2O-N ha^{-1} $season^{-1}$]	0.24 ± 0.02^{a}	0.68 ± 0.23^{a}	0.27 ± 0.05^{a}	1.43 ± 0.16^{b}
N_2O Intensity [kg N_2O-N t-$yield^{-1}$ ha^{-1}]	0.09 ± 0.01^{a}	0.13 ± 0.04^{a}	0.28 ± 0.05^{b}	0.28 ± 0.03^{b}
Emission Factor [%]	-	0.63	-	1.17
Cumulative CO_2 Flux [kg CO_2-C ha^{-1} $season^{-1}$]	33.4 ± 6.51^{a}	34.96 ± 5.21^{a}	29.22 ± 3.37^{a}	33.30 ± 4.92^{a}

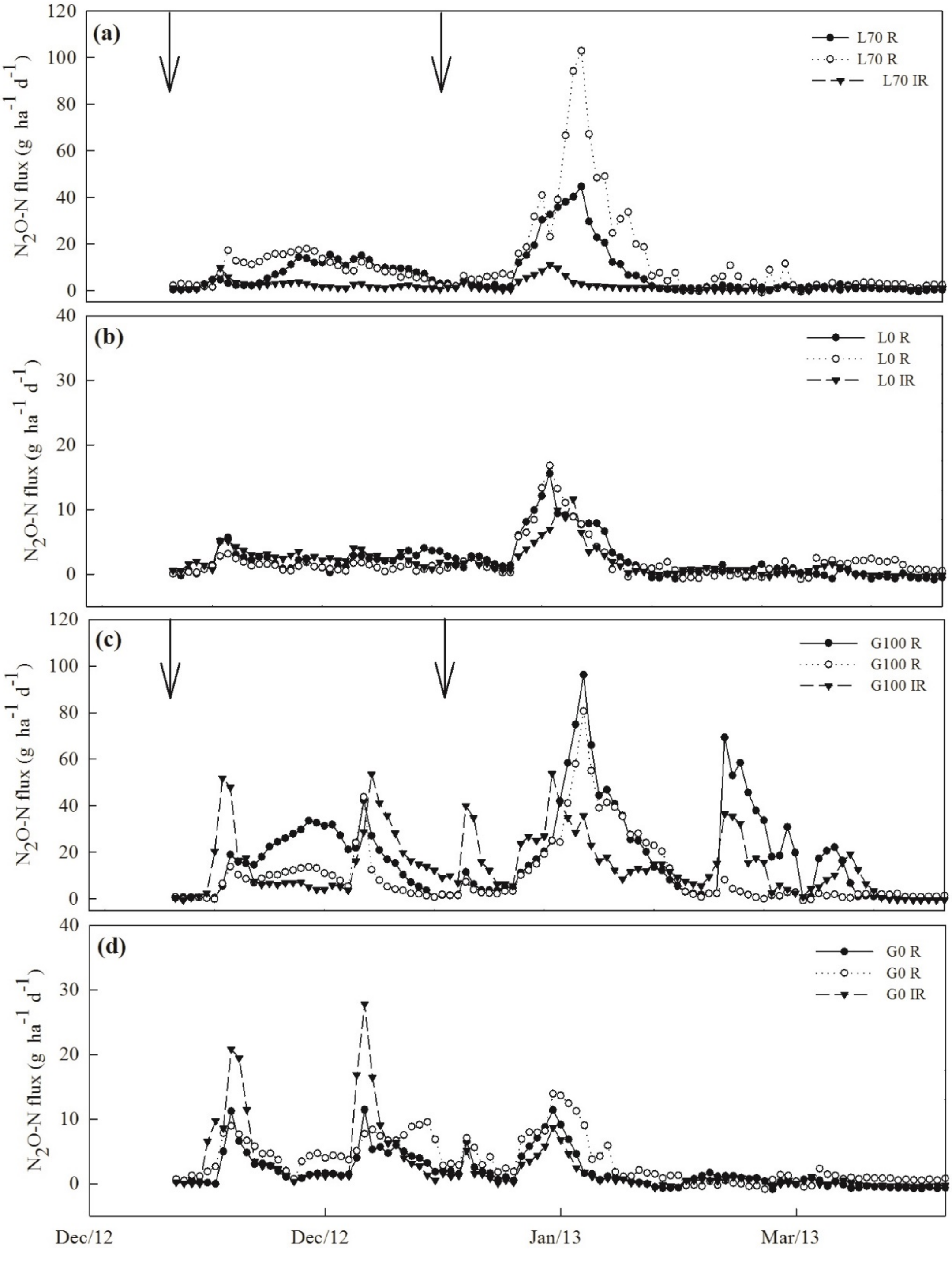

Figure 4-5 - Daily soil N_2O fluxes measured in the row (R) and inter-row (IR) chambers for the L70 (a), L0 (b), G100 (c) and G0 (d) treatments during the period of highest emissions (December 2012-March 2013) in Kingaroy (Queensland, Australia). Arrows indicate the timing of N fertiliser applications. Graphs are in different scales.

The mixed-design ANOVA analysis indicated that the main effect regulating N_2O emissions was the N fertiliser rate, while the cropping history *per se* had no significant effect on measured N_2O losses (Table 4-4).

Table 4-4 - Significance of treatment effect (applied fertiliser rate and cropping history) on N_2O emissions and grain yields during the sorghum season.

Measurement	**Factor**	***p*-Value**	***F* Statistics**
N_2O	Fertiliser rate	**	17.37
	Cropping history	NS	2.68
Grain yield	Fertiliser rate	***	255.79
	Cropping history	**	14.41

*, **, ***: probability significant at 0.05, 0.01 and 0.001 level, respectively. NS: not significant.

4.4.4 CO_2 emissions

Soil CO_2 fluxes showed little variation between treatments and exhibited a temporal pattern influenced by soil temperatures and WFPS (Figure 4-6). Average soil CO_2 emissions peaked during the warmest months (early January to late March 2013, average of 23 kg CO_2-C ha^{-1} day^{-1}) before decreasing to <10 kg CO_2-C ha^{-1} day^{-1} during the colder and drier period from April to late August 2013.During the fallow period CO_2 fluxes remained below 5 kg CO_2-C ha^{-1} day^{-1}. Emissions in all treatments did not increase after the tillage event of 6 August 2013 but rose to an average of 17 kg CO_2-C ha^{-1} day^{-1} after the two irrigation events of 27 and 29 August.

In contrast to N_2O emissions, CO_2 fluxes tended to not to rise until several days after a rainfall/irrigation event. This was particularly evident with the rainstorm on 27 January, when CO_2 emission did not start to increase until seven days after the event. Overall, cumulative CO_2 emissions measured in the inter-rows showed little variations between treatments (Table 4-3) and no significant differences in the pattern of daily CO_2 emissions was detected by the ARIMA model.

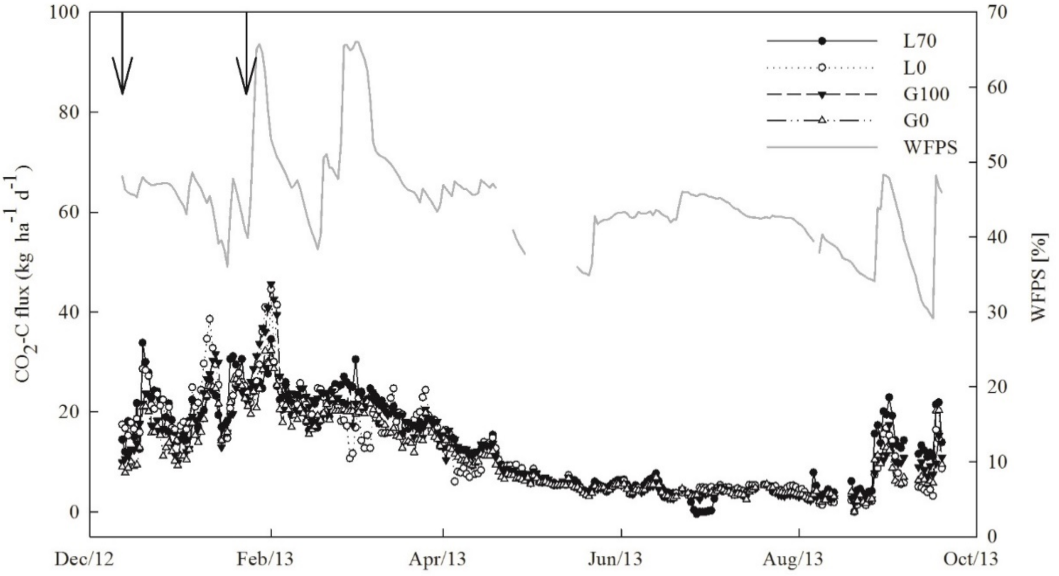

Figure 4-6 - Daily soil CO_2 fluxes and water-filled pore space (WFPS, 0-30 cm) for the four treatments during the sorghum season in Kingaroy (Queensland, Australia). Arrows indicate the timing of N fertiliser applications.

4.4.5 Crop biomass, grain production and N uptake

Sorghum biomass production and yield were substantially affected by cropping history and N fertiliser rate. Both biomass and yield in the non-fertilised sorghum following the legume ley pasture (L0) were significantly higher ($p < 0.05$) than those in the corresponding treatment following the grass ley pasture (G0). Grain and biomass production in L70 were comparable to those in G100 and both were significantly higher than those in the non-fertilised treatments (Table 4-5). The harvest index (kg grain ha^{-1} / kg total biomass ha^{-1}) of L0 was significantly higher than in G0, but comparable to that of both L70 and G100.

The mixed-design ANOVA analysis showed that both the N fertiliser rate and the cropping history had significant effects on grain yield. However, the cropping history F value was substantially lower than that of the fertiliser rate, indicating that the fertiliser rate had greater influence on yields (Table 4-4).

Soil N availability in the legume cropping history was higher than in the grass one and N uptake values measured in L0 and L70 exceeded those of G0 and G100, respectively. Though the N fertiliser rate in G100 was 30 kg N ha^{-1} higher than in

L70, the fraction of fertiliser N taken by the crop was greater in L70, exhibiting a significantly higher RE_{fN} compared to G100 (Table 4-5).

Table 4-5 - Sorghum grain yield (expressed as dry weight), above ground biomass (expressed as dry weight), harvest index, total N uptake (mean ± SE, n=3) and recovery efficiency of fertiliser N in the crop (RE_{fN}) as a function of the four treatments. Means denoted by a different letter indicate significant differences between treatments ($p<0.05$).

Measurement	**Treatment**			
	L0	**L70**	**G0**	**G100**
Grain Yield [Mg ha^{-1}]	2.52 ± 0.22 ^{b}	5.29 ± 0.22 ^{c}	0.94 ± 0.12 ^{a}	5.20 ± 0.11 ^{c}
Above ground biomass [Mg ha^{-1}]	8.38 ± 0.78 ^{b}	14.96 ± 0.73 ^{c}	4.48 ± 0.34 ^{a}	13.68 ± 0.53 ^{c}
Harvest Index	0.31 ± 0.02 ^{b}	0.36 ± 0.01 ^{bc}	0.21 ± 0.03 ^{a}	0.38 ± 0.01 ^{c}
Total N uptake [kg N ha^{-1}]	46.91 ± 4.77	118.94 ± 7.98	25.11 ± 1.53	98.52 ± 6.88
RE_{fN} [%]	-	70.9 ± 2.1		52.8 ± 6.1**

** probability significant at 0.01 level

4.5 Discussion

4.5.1 N_2O emissions from cropped soils after termination of a pasture phase

To date little research has been undertaken on N_2O emissions following the termination of ley pastures, specifically in terms of how management, climatic conditions and chemical composition of the residues influence N_2O losses during subsequent cropping seasons. This is the first study to investigate the role of these factors in two subtropical ley pasture-cereal crop rotations using a fully automated measuring system providing high temporal resolution data on N_2O emissions.

Studies conducted on various cropping systems under different environmental conditions indicate that the incorporation of legume residues *per se* is not sufficient to trigger elevated N_2O emissions. For example, extremely high N_2O emissions following the plough-down of legume pastures have often been measured in cold climates during spring, when high levels of soil moisture coincide with increasing soil temperatures (Wagner-Riddle *et al.*, 1997; Wagner-Riddle and Thurtell, 1998; Pappa *et al.*, 2011). In contrast, limited N_2O emissions following the incorporation of legume pastures have been reported under relatively dry condition in temperate, subtropical and mediterranean climates (Baggs *et al.*, 2000; Gomes *et al.*, 2009; Brozyna *et al.*, 2013; Sanz-Cobena *et al.*, 2014).

The availability of the N released by the legume residues to the soil microbial pool, and therefore the magnitude of N_2O emissions, appears therefore to be the product of several concurrent factors.

4.5.2 Factors influencing N_2O emissions and yields

In this study cumulative N_2O emissions were primarily a function of the N fertiliser rate applied, while cropping history had no significant effect. On the other hand, crop biomass and grain production showed a clear response to increased N availability in the legume history, irrespective of the N fertiliser input. While incorporation of legume residues provided an additional 20-22 kg N ha^{-1} to the sorghum crop in both L0 and L70 compared to G0 and G100, this additional N release did not significantly enhance the nitrification or denitrification processes compared to the incorporation of grass residues. Moreover, the temporal pattern of daily N_2O emissions was substantially affected by the cropping history and in the first 10 weeks after sorghum establishment N_2O emissions pulses in G0 and G100 were significantly higher than in L0 and L70, respectively.

We propose that this apparent contradiction can be explained by considering three interacting factors: the fertiliser N rate applied, the synchrony between soil N availability and crop N uptake, and the cropping history.

4.5.3 N fertilisation rates

The application of synthetic N fertiliser was the main factor responsible for enhanced N_2O emissions and the highest cumulative N_2O losses were measured in the two fertilised treatments. In L70 and G100 the highest N_2O emission rates were observed after side dressing, when the majority of the N fertiliser was applied and WFPS exceeded 60% (Figure 4-2). The abrupt emission pulses after fertilisation can be explained by considering the release dynamics of synthetic fertilisers (Crews and Peoples, 2005). Under humid soil conditions urea is rapidly hydrolysed, leading to a fast release of high amounts of mineral N in the soil. At side dressing sorghum plants were still at an early stage of physiological development and were able to take up only a fraction of the mineral N applied. Therefore, significant amounts of mineral N accumulated in the soil and became available to nitrifying and denitrifying microorganisms. Indeed, sufficient surplus N must have still been present in the highest N rate treatment (G100), where a secondary emission pulse was observed between mid-February and mid-March, one month after side dressing.

Increased N_2O emissions following the fertilisation events in this study did not correspond to elevated soil mineral N contents in the first 30 cm, due probably to the large rainfall event that fell over the trial shortly after side dressing. After this rain event a large fraction of the applied N is likely to have leached deeper into the soil profile, leaving little mineral N in the first 30 cm to be detected at the following sampling events (Figure 4-3).

Overall, N_2O emissions displayed a significant correlation with N fertilisation, rising in nonlinear patterns at increasing N fertiliser rates (0, 70 and 100 kg N ha^{-1}). As observed by several authors (McSwiney and Robertson, 2005; Hoben *et al.*, 2011; Shcherbak *et al.*, 2014), the fast release of mineral N after fertilisation can exceed the plant uptake capability when N fertiliser is applied at high rates and the resulting temporary surplus of mineral N can promote elevated nitrification and denitrification rates if the appropriate soil water conditions are met. These findings indicate that the best fertiliser management practices aimed at reducing N_2O losses coincide with those designed to achieve high levels of agronomic efficiency. N rates and fertilisation techniques should therefore be aimed at maximising the crop uptake of applied synthetic N.

4.5.4 Synchrony of N supply

Synchrony is a critical aspect in reducing N_2O losses after the termination of a legume pasture (Crews and Peoples, 2005; Jensen *et al.*, 2012), which means matching the N release resulting from the degradation of the legume residues with the N uptake of the subsequent crop. The high emissions reported after the termination of a legume pasture are often measured when the field site has been left fallow for long periods (Wagner-Riddle *et al.*, 1997; Wagner-Riddle and Thurtell, 1998; Pappa *et al.*, 2011). Conditions can be highly conducive for elevated N_2O emissions when a soil is left fallow after the incorporation of fresh legume residues since in the absence of a crop following the pasture, all the readily mineralisable C from the legume residues becomes available to support the denitrification of large amounts of NO_3^- accumulated in the soil.

In this study sorghum was planted 13 days after the termination of the pasture phase. During the fallow prior to sorghum planting only 6 mm of rainfall fell, limiting therefore the possibility of organic matter decomposition, mineral N accumulation or generation of significant N_2O emissions. Typically, the highest N mineralisation rates from legume residues are reported to occur after about six weeks from the termination of the pasture (Fox *et al.*, 1990; Becker and Ladha, 1997; Robertson, 1997; Park *et al.*, 2010). In the present study this would have coincided with the moment of maximum N uptake of sorghum, supplying in this way approximately an extra 20-22 kg N ha^{-1} to the plants in L70 and L0. The good synchrony between N release from the legume residues and N uptake of the sorghum plant is confirmed by the high RE_{fN} measured in L70 (Table 4-5).

The potential of using legumes to support the growth of the following cereal crop was highlighted by the significant enhancement of the soil N pool in the legume cropping history. While the initial mineral N contents in the top 30 cm of the profile were quantitatively similar between the legume and grass histories (Figure 4-3), there was a higher proportion of that N in the form of NO_3-N in the legume (33%) than the grass (20%) histories. These data, combined with the increases in PMN (Table 4-1), suggest greater mineralisable N reserves in the legume histories, which is also reflected in sorghum growth, grain yield and N accumulation. Moreover, while the N supply from the residue mineralisation was not substantial in G100 and G0, the heavy rain events in January are likely to have promoted substantial N_2 losses (Schwenke *et al.*, 2013), further reducing the N supply to the plants of these treatments. The high N losses via leaching would have severely limited the efficiency of the side dressing, resulting therefore in the lower RE_{fN} values measured in G100 compared to L70. Consequently, crop biomass and grain yields in L70 were comparable to those of G100 despite a 30% reduction in fertiliser rate, while yields in L0 were approximately double those in G0.

Overall, planting sorghum shortly after pasture termination proved an effective strategy to reduce N_2O losses due to the decomposition of legume residues. This practice also resulted successful in supplying an extra source of N to sorghum, increasing significantly the yields in both the fertilised (L70) and non-fertilised (L0) treatments.

4.5.5 Cropping history

Although it did not have a statistically significant effect on cumulative N_2O emissions, the cropping history substantially influenced the temporal and spatial patterns of N_2O fluxes. In the first part of the season for example, daily N_2O fluxes in G100 and G0 tended to rise immediately after rain events and on these occasions emissions were consistently higher than in L70 and L0, respectively (Figure 4-4a, b). The grass cropping history treatments constituted also a more diffused source of N_2O emissions, with G100 and G0 displaying high N_2O losses also from the inter-row, while N_2O fluxes from the inter-row in L70 and L0 never exceeded 12 g N ha^{-1} day^{-1} (Figure 4-5).

It is here hypothesised that the sharp increases of N_2O emissions following increments in WFPS, as well as the high fluxes measured across the whole field in G100 and G0, are to be attributed to higher labile C in the soil of the grass cropping history. Enhanced N_2O emissions from soils with high DOC contents have been reported by numerous studies (Elmi *et al.,* 2003; Yao *et al.,* 2009; Barton *et al.*, 2011). This positive correlation originates from the coupled biogeochemical cycles of C and N. The degradation of plant material provides soil microbes with substantial amounts of C, which under anaerobic conditions is oxidised by denitrifying microorganisms via reducing NO_3^- to N_2O (Conrad, 1996).

The DOC values observed at the beginning of the sorghum season tended to be higher in the treatments following the termination of the grass pasture, where a substantially higher amount of fine fibrous plant residues was present at sorghum planting. Whilst not quantitatively documented, the presence of undecomposed roots and crowns in the grass history would have continued to supplement the labile C pool. This would have provided a uniformly distributed C source to support microbial activity and therefore the potential for denitrification in both row and inter-row areas (Figure 4-5). While this enhanced *potential* microbial activity in G0 became increasingly N-limited by the end of December, the provision of the N side dressing in G100 allowed that activity to continue. When combined with the very wet soil conditions, this high nutrient availability resulted in the significant N_2O emissions pulses observed in G100 from late January (Figure 4-5).

Conversely, the low C:N ratio of the sulla plants residues would likely have contributed to a more rapid degradation of residues in the L0 and L70 treatments, leaving less labile C to support continued microbial activity. This may have changed during the season in the vicinity of the sorghum rows, where increasing root density would have contributed to labile C stores. The marked contrast in N_2O emissions between the rows and inter-rows in both L0 and L70 (Figure 4-5) are consistent with this hypothesis. Similar results to this study were reported by Sanz-Cobena *et al.* (2014), who observed higher N_2O emissions from maize after the incorporation of barley compared to the same crop after the incorporation of a vetch pasture.

These findings highlight the potential role of the soil labile C pool in regulating N_2O losses. Specifically, denitrifying microorganisms can be more competitive than plants in using even small amounts of NO_3^- when soil labile C content is sufficiently high to sustain elevated microbial activity in anaerobic conditions. This was evident in the non-fertilised treatments, where dry matter and grain yield in G0 were severely limited by N availability but N_2O emissions were almost identical. However, further research is advocated to corroborate the results of this study. Specifically, future studies should focus on the chemical availability of C supplied by crop residues and its role in stimulating denitrification when the soil NO_3^- content is not a limiting factor.

4.6 Implications for managing N_2O emissions from a cereal crop following a legume pasture

Introducing a legume ley pasture in a cereal-based cropping system enabled the reduction of the synthetic N fertiliser applied to the following cereal crop and significantly reduced the N_2O emission factor for this crop compared to a grass ley pasture. The emission factor of L70 (0.63%) was almost half of G100 (1.17%) and was considerably lower than the 1% recommended by the IPCC methodology for fertilised cropping systems (De Klein *et al.*, 2006). Both Tier 1 and Tier 2 approaches consider an emission factor of 1% for N derived from the mineralisation of crop residues. According to this method, in L70 the total N_2O emissions resulting from the mineralisation of approximately 30 kg N ha^{-1} contained in the legume residues and combined with the application of 70 kg N ha^{-1} would have amounted to about 1 kg N_2O-N ha^{-1}. Similarly, N_2O losses from the two non-fertilised treatments should have differed substantially, resulting in 0.3 and 0.1 kg N_2O-N ha^{-1} from L0 and G0, respectively. However, the different dynamics observed in this study suggest that the amount of N in the soil *per se* is not sufficient to correctly estimate N_2O emission factors, and that the quantity and availability of soil C should also be considered.

The importance of soil labile C is reinforced when the N_2O emissions intensity (kg N_2O-N $yield^{-1}$ ha^{-1}) of the legume and grass cropping histories are considered. This measure effectively quantifies the efficiency of agronomic practices in maximising grain yields while minimising N_2O emissions. Despite the broad range of grain yields, N_2O emissions intensities were consistent among treatments with the same cropping history, with intensities significantly lower in the legume compared to the grass history (Table 4-3).

The introduction of a legume pasture phase in a cereal-based crop rotation seems to offer multiple environmental and agronomic advantages. In the fertilised treatments it resulted in a 50% reduction of the N_2O-N emitted compared to introducing a grass pasture, proving to be an effective mitigation strategy to reduce the contribution of cereal cropping systems to greenhouse gas emissions. A pasture phase can also contribute to increasing the soil organic matter, aggregate stability, soil microbial pool and organic N content (Giller and Cadisch, 1995; Rochester *et al.*, 2001), benefiting the overall soil chemical and physical fertility. These results overall indicate that introducing a legume pasture in a subtropical cereal cropping system is a sustainable practice from both the environmental and agronomic perspective.

The implications of managing N_2O emissions from a cereal crop following a legume pasture in terms of agronomy and crop productivity are further examined in sections 6.4.2 and 7.1, while the profitability of this N management strategy is analysed in section 7.2.

Statement of Contribution of Co-Authors for Thesis by Published Paper

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;

2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;

3. there are no other authors of the publication according to these criteria;

4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and

5. they agree to the use of the publication in the student’s thesis and its publication on the Australasian Research Online database consistent with any limitations set by publisher requirements.

In the case of this chapter:

Assessing agronomic and environmental implications of different N fertilisation strategies in subtropical grain cropping systems in Oxisols.

Contributor	Statement of contribution*
Massimiliano De Antoni Migliorati	Performed experimental design, conducted fieldwork and laboratory analyses, data analysis, and wrote the manuscript.
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9th March 2015	
Mike J. Bell	Aided experimental design and data analysis, and reviewed the manuscript.
Peter R. Grace	Aided experimental design and data analysis, and reviewed the manuscript.
David W. Rowlings	Aided experimental design and data analysis, and reviewed the manuscript.
Clemens Scheer	Aided experimental design and data analysis, and reviewed the manuscript.
Alice Strazzabosco	Aided laboratory analysis and data analysis, and reviewed the manuscript.

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Chapter 5: Assessing agronomic and environmental implications of different N fertilisation strategies in subtropical grain cropping systems in Oxisols (*Paper 3*)

Abstract

A multi-season ^{15}N tracer recovery experiment was conducted on an Oxisol cropped with wheat, maize and sorghum to compare crop N recoveries of different fertilisation strategies and determine the main pathways of N losses that limit N recovery in these agroecosystems. In the wheat and maize seasons, ^{15}N-labelled fertiliser was applied as conventional urea (CONV) and urea coated with a nitrification inhibitor (DMPP). In sorghum, the fate of ^{15}N-labelled urea was monitored in this crop following a legume ley pasture (L70) or a grass ley pasture (G100). The fertiliser N applied to sorghum in the legume-cereal rotation was reduced (70 kg N ha^{-1}) compared to the grass-cereal (100 kg N ha^{-1}) to assess the availability of the N residual from the legume ley pasture. Average crop N recoveries ranged from 73% (CONV) to 77% (DMPP) in wheat and from 50% (CONV) to 51% (DMPP) in maize, while in sorghum varied between 71% (L70) and 53% (G100). Data gathered in this study indicate that the intrinsic physical and chemical conditions of these soils can be extremely effective in limiting N losses via deep leaching or denitrification. Elevated crop ^{15}N recoveries can therefore be obtained in subtropical Oxisols using conventional urea while in these agroecosystems DMPP urea has no significant scope to increase fertiliser N recovery in the crop. Overall, introducing a legume phase to limit the fertiliser N requirements of the following cereal crop proved to be the most effective strategy to reduce N losses and increase fertiliser N recovery.

5.1 Introduction

Half the world's population live in regions dominated by acid soils (Yang *et al.*, 2004), 18.4 % of which are classified as Oxisols (von Uexküll and Mutert, 1995). Oxisols are the most common soil type in the tropics and subtropics, representing approximately 46% and 23% of soil area in these regions, respectively (Buol and Eswaran, 1999), and are mainly located in South America, Africa and Asia (von Uexküll and Mutert, 1995).

More susceptible to degradation than most soils and characterised by low natural fertility, Oxisols had been relegated to marginal agricultural practices until the Green Revolution (Borlaug and Dowswell, 1997; Thomas and Ayarza, 1999). However, with modern technologies many of the constraints of Oxisols can be amended and these soils are now regarded as the most extensive agricultural frontier in the world. Today, Oxisols are capable of high productivity levels and support sufficient food production and economic returns to feed millions of peoples, particularly in tropical and subtropical regions (Fageria and Baligar, 2008). For example in Brazil, the country with the greatest extent of arable Oxisols in the world, the area of Oxisols cultivated with grain crops increased from 10 million ha in 1970 to 48 million ha in 2011 (Thomas and Ayarza, 1999; Scheid Lopes *et al.*, 2012) and alone contributes to 4.3% of the world's current cereal production (Fischer, 2009; FAOSTAT website, accessed October 2014).

However, there is growing concern about the environmental and agronomic implications of intensive cropping of Oxisols. Nearly all future demographic growth is projected to take place in tropical and subtropical countries (UNFPA, 2011), meaning a greater pressure on Oxisols to meet future cereal demand (Fageria and Baligar, 2008). There will be economic and environmental pressures for any increase in grain production to occur without intensification of synthetic N fertiliser use, as the manufacture and use of these products has major implications in terms of water quality, energy consumption and greenhouse emissions (Crews and Peoples, 2004; Jensen *et al.*, 2012; Müller and Gattinger, 2013). There is therefore an urgent need to develop N management strategies and farming systems that can reduce the need for synthetic N fertiliser in Oxisols and improve fertiliser N recovery in cereal cropping systems.

Under certain conditions, the application of nitrification inhibitors to urea-based fertilisers has been shown to improve yields through an increased crop N recovery (Linzmeier *et al.*, 2001b; Pasda *et al.*, 2001; Kawakami *et al.*, 2012). However, the efficiency of nitrification inhibitors is highly dependent on soil and climatic conditions and their use substantially increases fertilisation costs (Eagle *et al.*, 2012). Alternatively, many authors have proposed the reintroduction of legumes in cereal-based cropping systems as one possible strategy to reduce synthetic N inputs whilst sustaining crop yields (Crews and Peoples, 2004; Jensen *et al.*, 2012). The dynamics regulating the release of plant-available N from legume residues are however complex and grain yields can be limited by any asynchrony between N supplied by the legume residues and crop N uptake (Crews and Peoples, 2004).

Research to date has primarily focused on the efficacy of various N management strategies on different soils under temperate climatic conditions or, in tropical and subtropical climates, on the correction of the main constraints of Oxisols (soil acidity, available phosphorus and soil organic matter).

As a result, very scarce data on efficient N fertilisation strategies are currently available for subtropical cereal cropping systems in Oxisols. The overall aims of this study were therefore to: i) compare the N recoveries of different N fertilisation strategies on subtropical Oxisols, including the use of conventional urea or urea coated with a nitrification inhibitor and the presence or absence of legumes in the crop rotation; ii) determine the main pathways of N losses that limit N recovery in these agroecosystems and iii) evaluate the agronomic and environmental sustainability of the N supply practices examined.

Two investigations were carried out on an Oxisol supporting cereal cropping systems as part of a multi-season ^{15}N tracer recovery experiment. The first investigation focused on the N recovery efficiency of urea coated with a nitrification inhibitor and was performed on a crop rotation composed of wheat followed by maize. The second investigation assessed the fate of ^{15}N-labelled urea in sorghum following a legume ley pasture and compared it to the same crop in rotation with a grass ley pasture.

This study is the first to assess the agronomic and environmental performances of these N management practices on cereal crops in Oxisols. The results will contribute to define agronomically viable and environmentally sustainable N fertilisation strategies to support future intensification of cereal production on these soils.

5.2 Materials and Methods

5.2.1 Study site

The study was conducted at the J. Bjelke Petersen Research Station of the Department of Agriculture, Fisheries and Forestry (DAFF). The research site is located in Taabinga (26°34’54,3’’ Latitude South, 151°49’43.3’’ Longitude East, altitude 441 m a.s.l), near Kingaroy, in the southern inland Burnett region of southeast Queensland, Australia. The climate is classified as subtropical, with warm, humid summers and mild, dry winters. Daily mean maximum and minimum temperatures are 20.1°C and 4.0°C in winter and 29.6°C and 16.5°C in summer, respectively. Mean annual precipitation is 776.2 mm and varies from a minimum of 28.6 mm in August to a maximum of 114.1 mm in January (Australian Bureau of Meteorology website). The soil is classified as a Tropeptic Eutrustox Oxisol (USDA Soil Taxonomy, USDA (1998)) or as a Orthic Ferralsol (FAO Soil Taxonomy, FAO (1998)) and has a moderately slow permeability. The soil profile is relatively homogenous, characterised by a high clay content (50-65% clay), an effective rooting zone of 1.2 m and a water holding capacity of 100 mm. Physical and chemical soil properties are listed in Table 5-1.

Table 5-1 - Main soil physical and chemical properties (0-30 cm) of the experimental site at Kingaroy research station, Queensland, Australia

	First investigation	**Second investigation**	
Soil Property (0-30 cm)	-	**Legume ***	**Grass ***
pH (H_2O)	5.58 ± 0.11	5.12 ± 0.03	5.30 ± 0.02
DOC (kg C ha^{-1})	39.56 ± 2.07	43.04 ± 11.98	56.05 ± 2.97
Bulk density 0-30 cm (g cm^{-3})	1.33± 0.09	1.18 ± 0.08	1.18 ± 0.08
Texture (USDA)	Clay	Clay	Clay
Clay (%)	55	55	55
Silt (%)	14	14	14
Sand (%)	31	31	31

* Cropping history

5.2.2 First investigation (nitrification inhibitor trial)

The first investigation consisted of two cropping seasons: wheat (winter 2011) and maize (summer 2011/2012). Wheat (*Triticum aestivum* L., cultivar Hartog) was planted 6 July after the harvest of a summer mungbean (*Vigna mungo* L.) crop and subsequently harvested 29 November 2011, while maize (*Zea mays* L., cultivar 32P55) was planted 21 December 2011 and harvested 20 June 2012. Two treatments were tested:

- Conventional fertiliser (CONV): fertiliser N applied at rates of 80 and 160 kg N ha^{-1} to wheat and maize, respectively. Rates were designed to achieve maximum yield potential.
- Fertiliser coated with DMPP nitrification inhibitor (DMPP): fertiliser N applied at same rates of CONV treatment. DMPP (3,4-dimethylpyrazole phosphate) was chosen amongst other nitrification inhibitors for the high efficiency in slowing nitrification and reducing N losses (Weiske *et al.*, 2001a; Weiske *et al.*, 2001b; Liu *et al.*, 2013).

During the wheat season both treatments were base dressed with 20 kg N ha^{-1} as diammonium phosphate (DAP, banded at panting) and top dressed at booting stage broadcasting 60 kg N ha^{-1} as conventional urea (CONV) or urea coated with the DMPP nitrification inhibitor (DMPP). In maize the two treatments were base dressed at planting by banding 40 kg N ha^{-1} as monoammonium phosphate (MAP) and side dressed at V10 physiological stage (beginning of tenth leaf) with 120 kg N ha^{-1} as conventional urea (CONV) or with DMPP urea (DMPP). Given the high cost of DMPP, in each season DMPP urea was used only at top/side dressing, when 75% of seasonal N was applied to the crop. During the early stages of crop development irrigation was applied at a rate of 10 mm h^{-1} when water filled pore space (WFPS) values approached 40%. This method avoided water stress limiting the potential yields and prevented fertiliser N to be leached below the rooting zone. The trial was irrigated on four and two occasions over the wheat and maize seasons, respectively. Timings and amounts of fertiliser application are reported in Table 5-2, while further information on the study site and crop management can be found in Chapter 3.

Table 5-2 - Times of application and N rates of labelled and unlabelled fertilisers during the two investigations at Kingaroy research station, Queensland, Australia

Crop	**Time of fertiliser application**	**Fertilisation [kg-N ha^{-1}]**	
		CONV	**DMPP**
Wheat	Planting	20 (DAP)	20 (DAP)
	Top Dressing (broadcasted)	60 (urea) **	60 (DMPP urea) **
Maize	Planting	40 (MAP)	40 (MAP)
	Side Dressing (banded)	120 (urea)**	120 (DMPP urea)**
		L70	**L100**
Sorghum	Planting	20 (urea) *	20 (urea) *
	Side Dressing (banded)	50 (urea) *	80 (urea) *

** Fertiliser labelled with 10% ^{15}N urea

* Fertiliser labelled with 5% ^{15}N urea

The trial layout was a randomised complete block design with three replicates per treatment. For each treatment, three randomly placed 1 m^2 micro-plots were delimited by stainless steel frames inserted 15 cm into the ground. All micro-plots were surrounded by a buffer of 1 m along each side of the frame. The micro-plots were repositioned before planting maize to avoid ^{15}N contamination across seasons.

The ^{15}N-labelled fertiliser was only applied at top/side dressing to determine the N recovery of DMPP urea and compare it with conventional urea. Each micro-plot received 10% excess ^{15}N enriched urea, which was dissolved in 1 L of deionised water. The labelled fertiliser was applied uniformly with a dispenser over the entire micro-plot area to replicate top dressing (in wheat) or along the band to replicate banding (in maize). For the DMPP treatment the ^{15}N enriched urea was added with DMPP at a ratio of 6 g DMPP kg^{-1} urea to replicate the same ratio of commercial DMPP urea (Incitec Pivot Fertilisers, personal communication).

5.2.3 Second investigation (legume N trial)

The second investigation consisted of one cropping season (sorghum, planted 12 December 2012 and harvested 18 June 2013) and took place in a field adjacent to the one used for the first investigation. Plots were planted with sorghum (*Sorghum bicolor* L.) following two distinct cropping histories. One crop rotation (hereafter called legume cropping history) included two years of alfalfa pasture (*Medicago sativa*, L.), one season of maize (summer crop) and one season of sulla ley pasture (*Hedysarum coronarium* L., winter crop) prior to sowing sorghum. The other crop rotation (hereafter called grass cropping history) included two years of a mixed pasture predominantly composed by Rhodes grass (*Chloris gayana,* K.*),* one season of maize (summer crop) and one season of wheat (winter crop). Sulla and wheat were managed as green manure crops. The incorporation of sulla residues (2.3 Mg dry matter ha^{-1}, 1.57% N) was estimated to return approximately 36 kg N ha^{-1} to the soil, while wheat residues (1.24 Mg dry matter ha^{-1}, 0.75% N) about 9 kg N ha^{-1}. During the sorghum season two treatments were assessed:

- Sorghum grown in the grass cropping history, with 100 kg N ha^{-1} applied (G100). The fertiliser N rate was designed to achieve maximum yield potential.

- Sorghum grown in the legume cropping history, with 70 kg N ha^{-1} applied (L70);

The two treatments were base dressed with 20 kg N ha^{-1} as urea banded at planting, and side dressed at the eight leaf stage banding 50 kg N ha^{-1} (L70) or 80 kg N ha^{-1} (G100) as urea (Table 5-2). The synthetic N rate used in L70 was reduced compared to G100 to account for the expected increase in plant available N arising from the legume inputs. As in the first investigation, irrigation was applied during the early stages of crop development at a rate of 10 mm h^{-1} when WFPS values approached 40%. All plots were irrigated three times over the cropping season; see Chapter 4 and Bell *et al.* (2012) for further details on the experiment and the management of the two crop rotations.

The experiment was established in a split plot design with two main plots (legume and grass ley pastures). Lateral movement of N was considered negligible since urea was banded both at side and base dressing. During this investigation micro-plots (1.35 m^2) were therefore sited in the main plots without stainless steel frames. To account for ^{15}N uptake by adjacent plants, micro-plots (0.9 m wide) included one crop row fertilised with ^{15}N enriched urea (1.5 m) and two non-fertilised crop rows (1 m) located on either side of the row receiving the ^{15}N-enriched fertiliser. A buffer area of 0.25 m was established at either end of the fertilised crop row. The 5% excess ^{15}N enriched urea was dissolved in 1 L of deionised water and applied in single bands in each micro-plot during both application events.

5.2.4 Samples collection, preparation and analysis

At the beginning of each cropping season soil samples were collected prior to planting to establish soil ^{15}N background levels. At the end of each cropping season plant and soil samples were taken at crop harvest. In wheat and maize all above ground material in the micro-plots was cut near the soil surface using hand clippers. In both seasons the extremely dry conditions of the soil prevented the collection of representative samples of root material. Soil moisture at the end of the sorghum season was higher and plants could be dug out of the ground to collect root material. Sorghum plants from the fertilised and non-fertilised rows were collected with hand clippers and stored separately.

Soil sampling was conducted using a core sampler (10 cm diameter) and different strategies were adopted in each season in consideration of fertiliser position. In wheat, where ^{15}N-labelled fertiliser was evenly applied, six cores were randomly taken inside each micro-plot. In maize two transects of three cores each were performed across the inter-row space of each micro-plot, with one core per transect placed over the fertiliser band. In both seasons soil samples were collected at six depths (0-10, 10-20, 20-30, 30-40, 40-50, 50-60 cm). Moist soil conditions at the end of sorghum season enabled a deeper penetration of the core sampler and samples were collected at six depths to a depth of 1 m (0-10, 10-20, 20-30, 30-50, 50-70, 70-100 cm). Two transects of three cores each were performed in the inter-row space between the fertilised and non-fertilised rows of each micro-plot, with one core per transect placed over the fertiliser band. At the end of each season reference biomass and soil samples were collected outside the micro-plots as controls for background ^{15}N abundance.

Plant material was mechanically mulched and oven-dried at 60°C to constant weight. Grain, stem and roots (in sorghum) were ground in a planetary cylinder mill and analysed separately. Soil samples were oven-dried at 60°C and ground using the planetary cylinder mill. Soil and plant samples were processed in ascending order of fertiliser rate and all equipment washed with ethanol between treatments to prevent possible cross contamination. The ^{15}N analysis was performed using a 20-22 Isotope Ratio Mass Spectrometer (Sercon Limited, UK).

5.2.5 Ancillary measurements

In addition to soil sampling for ^{15}N analysis, routine soil sampling was conducted at regular intervals to assess soil N dynamics during the growing seasons. Soil samples were taken at three depths (0-10, 10-20, 20-30 cm) and analysed for NH_4-N and NO_3-N. Each soil sample consisted of three subsamples taken at 10 cm intervals from the crop row of then mixed in order to ensure it represented the banded and non-banded areas of the plot. Soil NH_4-N and NO_3-N were extracted by shaking 20 g soil in 100 mL 1 M KC1 solution at room temperature for 60 minutes (Carter and Gregorich, 2007). The solution was then filtered and stored in a freezer until analysed colorimetrically for NH_4-N and NO_3-N using an AQ2+ discrete analyser (SEAL Analytical WI, USA).

N_2O fluxes and soil mineral N content were also measured throughout the investigations as part of a comprehensive project assessing N dynamics in cereal-based cropping systems in Oxisols. N_2O emissions from each treatment were measured every three hours using a chamber-based automated greenhouse gas measuring system installed next to the micro-plots. For more information about N_2O-N losses during the two investigation see Chapters 3 and 4.

Four frequency domain reflectometers (FDR, EnviroScan probes, Sentek Sensor Technologies, Australia) were installed at the field site to continuously monitor the water content at three depths (0-10 cm, 10-20 cm, 20-30 cm). Soil temperature was measured every 5 minutes with resistance temperature detectors (RTD, Temperature Controls Pty Ltd, Australia) buried at 10 cm, 20 cm and 30 cm in the proximities of chambers. Rainfall data were obtained from a weather station located at the study site.

5.2.6 Calculations and statistical analysis

All calculations were conducted on oven-dried basis. Total recovery of applied ^{15}N-labelled fertiliser was determined by mass balance. The percentage of N derived from the labelled fertiliser (Ndff) in each plant and soil pool was determined using the following formula (IAEA, 2001):

$$Ndff = \frac{(atom\%\ ^{15}N\ _{sample} - atom\%\ ^{15}N\ _{control})}{(atom\%\ ^{15}N\ _{labelled\ fertiliser} - atom\%\ ^{15}N\ _{unlabelled\ fertiliser})} \times 100$$

Equation 1

The percentage of ^{15}N recovered in each pool was calculated as

$$^{15}N\ recovery = \frac{^{15}N\ recovered\ (kg\ N\ ha^{-1})}{^{15}N\ applied\ (kg\ N\ ha^{-1})} \times\ 100$$

Equation 2

Fertiliser N recovery in the root biomass of wheat and maize was calculated assuming a N recovery similar to the one in straw and stalks, respectively (Anderson, 1988). Root biomass was estimated using a root:shoot ratio of 0.31 for wheat

(Siddique *et al.*, 1990; Manschadi *et al.*, 2008) and 0.22 for maize (Anderson, 1988; Demotes-Mainard and Pellerin, 1992).

Statistical analyses were performed within the SPSS 22 environment (IBM Corporation, USA). Differences in ^{15}N recoveries of different pools were assessed with the ANOVA test using a confidence interval of 95%.

5.3 Results

5.3.1 First investigation

Throughout the first investigation the field study received a total of 919 mm rainfall, the majority of which occurred during the summer season (520 mm) (Figure 5-1). Soil mineral N content was relatively high at planting of wheat and gradually decreased during the two cropping seasons. Substantial increases in soil N were observed in both seasons after top/side dressing (Figure 5-2). Soil conditions were considerably warmer and wetter during the maize season, especially at the time of side dressing.

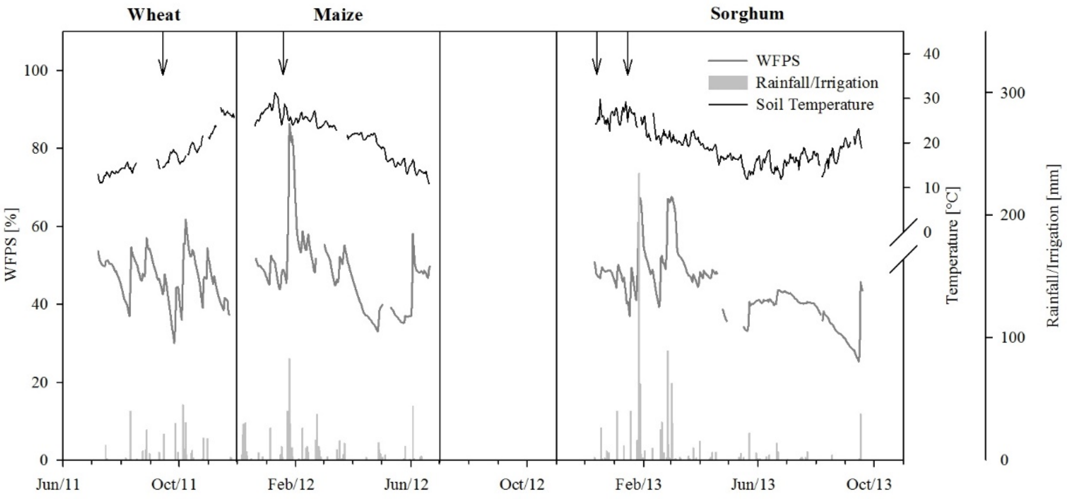

Figure 5-1 - Water filled pore space (WFPS) measured at 0-30 cm, soil temperature (0-30 cm) and rainfall and irrigation events during the wheat, maize and sorghum seasons at Kingaroy research station, Queensland, Australia. Arrows indicate the time of application of ^{15}N-labelled fertiliser.

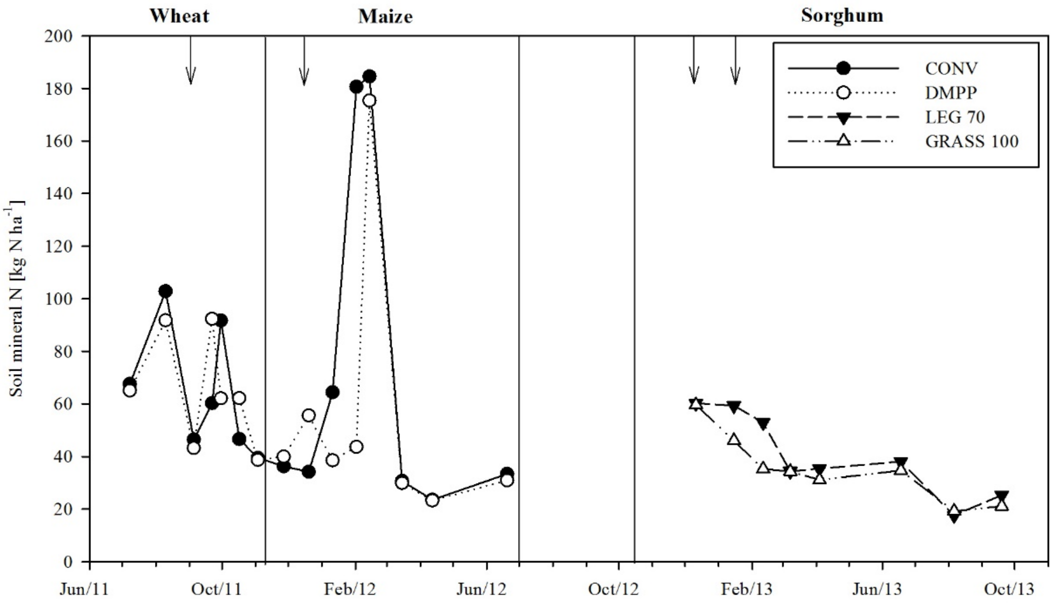

Figure 5-2 - Soil mineral N levels (NH_4^+ + NO_3^-) in the top 30 cm for the four treatments during the wheat, maize and sorghum seasons at Kingaroy research station. Arrows indicate the time of application of ^{15}N-labelled fertiliser.

In both seasons the use of DMPP urea did not significantly affect N recovery, grain yield and biomass production (Table 5-3). Plant recovery of ^{15}N-labelled fertiliser was higher in wheat (CONV: 72.9%, DMPP: 76.2%) than in maize (CONV: 49.7%, DMPP: 50.9%). The residual ^{15}N-labelled fertiliser recovered in the soil ranged from 25.8% (CONV) to 23% (DMPP) in wheat and from 35.9% (CONV) to 32.6% (DMPP) in maize. Whilst at the end of the wheat season almost all residual ^{15}N-labelled was confined to the upper 10 cm, a higher amount of N moved throughout the soil profile in maize (Figure 5-3).

In wheat about 33.8% (CONV) and 35.7% (DMPP) of plant N derived from the fertiliser N applied at top dressing, while in maize Ndff values varied between 51.9 (CONV) and 50.9 (DMPP). In both crops fertiliser N was primarily recovered in grains and secondarily in the straw/stalks and root components. The estimated proportion of ^{15}N recovered in roots was consistent with results reported by Kumar and Goh (2002) and Ichir *et al.* (2003) for wheat and by Mahmood *et al.* (2011) and Vanlauwe *et al.* (2001) for maize.

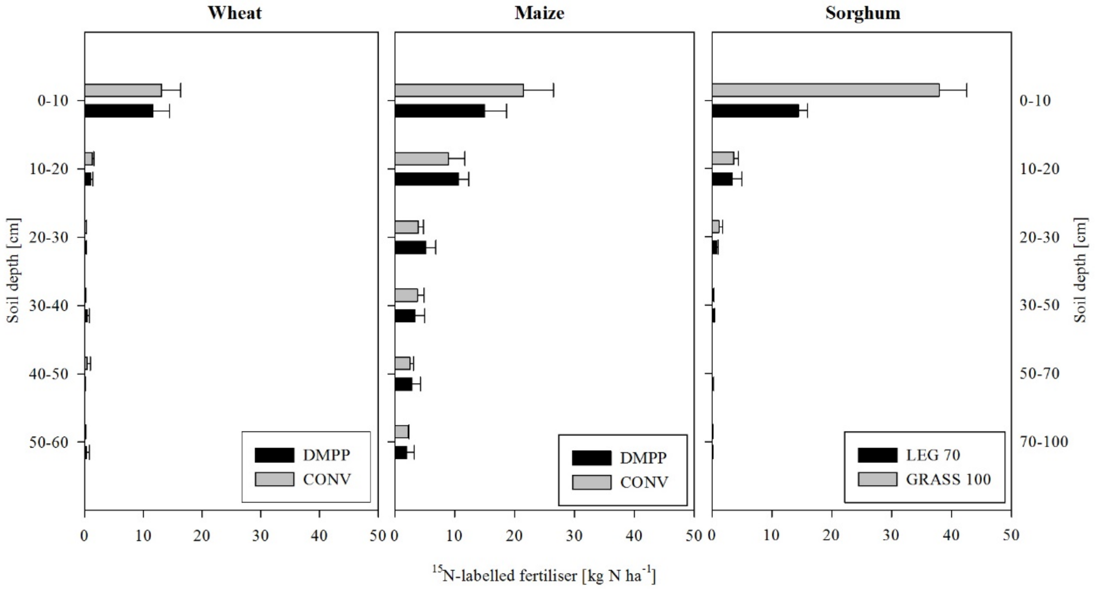

Figure 5-3 - ^{15}N-labelled fertiliser recovered in the soil by depth increment during the wheat, maize and sorghum seasons. Depth increments in maize were the same of wheat. Error bars indicate the standard errors.

N_2O-N losses measured after top dressing in wheat amounted to 0.2% of the fertiliser N applied at top dressing, while in maize they varied between 1.3% (CONV) and 0.3% (DMPP) of the N banded at side dressing (Table 5-3). Accounting for these gaseous losses, the amount of applied ^{15}N-labelled fertiliser that was not recovered in the soil-plant system during the wheat season ranged from 1.1% (CONV) to 0.1% (DMPP). During the maize season this percentage varied between 13.2% and 16.2% in the CONV and DMPP treatments, respectively (Table 5-3).

Table 5-3 - Dry matter, plant N derived from ^{15}N-labelled fertiliser (Ndff) and recovery of added ^{15}N measured at the end of the two investigations (mean ± SD, n=3). Statistically significant differences are denoted

Crop	**Pool**	**DM [Mg ha^{-1}]**		**Ndff [%]**		**^{15}N recovered [%]**	
		CONV	**DMPP**	**CONV**	**DMPP**	**CONV**	**DMPP**
Wheat	Grain	3.5 ± 0.5	3.6 ±0.8	24.8 ± 2.7	26.0 ± 2.4	53.3 ± 2.2	55.6 ± 7.5
	Straw	7.7 ± 1.3	7.8 ±1.3	6.9 ± 0.9	7.4 ± 0.7	14.9 ± .2.2	16.1 ± 3.5
	Roots [‡]	2.4 ± 0.4	2.4 ±0.4	2.1 ± 0.1	2.3 ± 0.2	4.7 ± 0.8	5.0 ± 0.8
	Plant total	13.6 ± 2.2	13.9 ±2.5	33.8 ± 2.9	35.7 ± 2.4	72.9 ± 3.3	76.7 ± 11.3
	Soil					25.8 ± 6.4	23.0 ± 5.3
	N_2O after top dressing					0.2 ± 0.02	0.2 ± 0.01
	N accounted for ^{15}N					98.9 ± 5.8	99.9 ± 8.8
	N unaccounted for ^{15}N					1.1	0.1
Maize	Grain	8.2 ± 1.3	7.7 ± 0.3	42.2 ± 3.4	42.0 ±4.8	40.3 ± 6.7	40.3 ± 0.7
	Stalks	4.7 ± 1.2	4.9 ± 0.7	8.0 ± 0.5	8.9 ±0.9	7.6 ± 1.4	8.6 ± 0.6
	Roots [‡]	1.0 ± 0.3	1.1 ± 0.2	1.8 ± 0.04	2.0 ±0.1	1.7 ± 0.4	2.0 ± 0.3
	Plant total	13.9 ± 2.7	13.7 ± 1.0	51.9 ± 3.8	52.9 ±5.4	49.7 ± 8.6	50.9 ± 0.6
	Soil					35.9 ± 5.7	32.6 ± 9.3
	N_2O after side dressing					1.3 ± 0.6	0.3 ± 0.2
	N accounted for ^{15}N					86.8 ± 12.1	83.8 ± 9.6
	N unaccounted for ^{15}N					13.2	16.2
		L70	**G100**	**L70 †**	**G100 †**	**L70 †**	**G100 †**
Sorghum	Grain	8.9 ± 1.5	7.0 ± 0.8	17.1 ± 4.5	27.7 ± 4.0 [*]	45.6 ± 4.3	32.4 ± 2.2 [**]
	Stalks	11.9 ± 1.5	9.2 ± 1.8	8.3 ± 1.4	15.4 ± 3.0 [*]	22.7 ± 5.3	18.2 ± 4.6
	Roots	2.4 ± 0.3	2.0 ± 0.3	1.0 ± 0.2	1.8 ± 0.5	2.6 ± 0.3	2.2 ± 0.7
	Plant total	23.2 ± 3.2	18.1 ± 2.7	26.3 ± 5.1	44.9 ± 5.0 [*]	70.9 ± 2.1	52.8 ± 6.1 [**]
	Soil					27.3 ± 2.8	43.3 ± 4.4 [**]
	N_2O					1.0 ± 0.3	1.4 ± 0.2
	N accounted for ^{15}N					99.1 ± 4.9	97.4 ± 2.6
	N unaccounted for ^{15}N					0.9	2.6

[‡] estimated values

† values are inclusive of N recovered by plants in non-fertilised row

[*] $p < 0.05$

[**] $p < 0.01$

5.3.2 Second investigation

Over the study period a total of 827 mm of rain fell at the study site, including one heavy rainfall event of 234 mm during a thunderstorm on 27 January 2013. Over 70% of the total rainfall was concentrated between 25 January and 3 March (Figure 5-1). A gradual decrease in soil mineral N was observed in both treatments during the growing season. No consistent response to history or fertiliser application could be measured in terms of soil mineral N (Figure 5-2). Similarly to the maize season, average soil temperatures ranged from a maximum of 29.7°C (December 2012) to a minimum of 11.9°C (May 2013).

Sorghum production was substantially affected by cropping history. Despite a 30% reduction in the amount of N fertiliser applied, the production of grain and biomass in L70 was comparable to that in G100 (Table 5-3). This was reflected in the percentage of plant N derived from fertiliser: in L70 only 26.3% of plant N originated from the fertiliser, while in G70 the percentage was 44.9%. The recovery of applied N fertiliser in L70 (70.9 ± 2.1) was significantly greater than in G100 (52.8 ± 6.1). In both treatments fertiliser N was mostly recovered in the grains, with lesser quantities in stalks and roots. The amount of ^{15}N-labelled fertiliser left in the soil in the G100 treatment (43.3 ± 4.4 %) was significantly higher than in G70 (27.3 ± 2.8) and was mainly concentrated in the top 10 cm of soil profile (Figure 5-3). After taking into consideration the N_2O-N losses, the amount of fertiliser N that could not be accounted for ranged between 0.9 (L70) and 2.6% (G100).

In both investigations unaccounted ^{15}N was assumed to be lost from the monitored crop-soil system via deep leaching or through the nitrification/denitrification processes. Losses via runoff and NH_3 volatilisation were considered negligible since in both investigations ^{15}N-labelled urea was applied as a liquid solution in a sub-surface band. On average, uncertainty due to cumulative errors associated with the analyses amounted to 9.96% and 3.83% in the first and second investigations, respectively.

5.4 Discussion

5.4.1 Fertiliser as source of crop N

As expected, the amount of plant N derived from labelled fertiliser varied widely across crops and investigations. In the first investigation, the average percentage of crop N derived from ^{15}N-labelled fertiliser was 34.7 ± 1.3 in wheat and 52.4 ± 0.7 in maize. The low reliance of wheat on N fertiliser can be attributed to the cropping history of the field study, as the site had previously been cropped with mungbean. This crop was harvested six weeks before planting wheat and mungbean residues were incorporated in the soil at a rate of approximately 1.8 Mg DM ha^{-1}. As confirmed by the high soil N levels measured at wheat planting, the mineralisation of mungbean residues supplied a substantial amount of N to the wheat plants, reducing the dependence of wheat on the synthetic N source. Similar results were reported by Dourado-Neto *et al.* (2010) for wheat in rotation with peanut cropped on an Entisol under tropical conditions.

Synthetic fertiliser represented a more important source of N in the maize season and two factors may have contributed to this. Firstly, maize was side dressed with twice the amount of N when compared to wheat and therefore maize plants had a greater pool of readily available mineral N in the soil profile (Figure 5-2, Figure 5-3). Moreover, maize was planted three weeks after wheat harvest and native soil N was lower than at the beginning of the wheat season (Figure 5-2). Continuous cereal cropping has been reported to increase the crop reliance on synthetic fertiliser N (Tilman *et al.*, 2002) and significantly lower Ndff levels (25.3-40.8%) were reported by Blesh and Drinkwater (2014) for fertilised maize (150 kg N ha^{-1}) in rotation with soybean.

A similar response to cropping history was observed during the second investigation. Despite yields and biomass production in L70 and G100 being comparable, a significantly higher reliance on fertiliser N was observed in sorghum plants in G100 (44.9% ± 5) compared to that in L70 (26.3% ± 5.1). Sorghum was planted two weeks after the incorporation of the pasture residues. Typically, the highest N mineralisation rates from legume residues occur about six weeks from the termination of the pasture (Fox *et al.*, 1990; Park *et al.*, 2010). In the present study this would have coincided with the moment of maximum N uptake of sorghum (week four - eight leaf stage), although it was not possible to determine whether the extra 25 kg N ha^{-1} available to the sorghum crop in L70 was derived from the recent small input of sulla biomass, the previous alfalfa ley phase or, more likely, a combination of both. As in the maize experiment, the greater reliance on fertiliser as a source of N in G100 was consistent with the small amount of N provided by the decomposition of grass/wheat residues and the high fertiliser N rate applied. No direct comparisons with other studies could be made for sorghum as, to the knowledge of the authors, no studies have been published on crop N derived from fertiliser for this crop under similar conditions.

Collectively, these results illustrate the implications of including legumes in cropping systems conducted in Oxisols. While Oxisols can contain large amounts of organic matter and N under native vegetation, these reserves generally decline rapidly under cultivation (Bell *et al.*, 1995). Consequently, cropped Oxisols are typically characterised by low levels of soil organic matter and native N, meaning low inherent fertility and little resilience when used for intensive cropping (Mulongoy and Kang, 1986; Vieira *et al.*, 2010). Continuous cereal cropping in these agroecosystems has the potential to rapidly erode native soil N supply and lead to a greater reliance on fertiliser N to meet crop demand (Dalal and Mayer, 1986; Tilman *et al.*, 2002). Conversely, the presence of a legume phase in a cropping system has been shown to have the potential to increase the soil organic matter and organic N content (Giller and Cadisch, 1995; Rochester *et al.*, 2001), substantially reducing therefore the reliance of subsequent crops on synthetic fertiliser N.

5.4.2 Crop N recoveries and N losses

Crop recoveries of ^{15}N fertiliser measured in the two investigations were at the higher end of values reported for cereal cropping systems conducted under tropical or subtropical climatic conditions (Ssali, 1990; Xu *et al.*, 1992; Pilbeam, 1995; Mubarak *et al.*, 2003; Dourado-Neto *et al.*, 2010). As emphasised by Dourado-Neto *et al.* (2010), N recoveries of annual crops are highly variable and are influenced by multiple factors. Amongst these, the most prominent are the synchronisation between fertiliser N release and plant N uptake, the availability of native soil N and the occurrence of environmental conditions that can stimulate N losses.

Effective synchronisation between crop N demand and fertiliser N supplied is likely to have been achieved during both investigations. Wheat and maize were top/side dressed at a stage when soil N reserves had been depleted during the early stages of crop growth (Figure 5-2), enabling a fast recovery of applied fertiliser ^{15}N. In sorghum the ^{15}N-labelled fertiliser was split between at-planting and in-season applications, with differing N rates reflecting differences in the soil N supply. The results of this study showed that crop recoveries of applied ^{15}N varied substantially across seasons and were influenced by environmental conditions and amounts of N applied. Significantly higher crop recoveries (≥70%) were observed in both treatments in wheat and in the L70 treatment in sorghum, where ^{15}N-labelled fertiliser rates were 60 and 70 kg N ha^{-1}, respectively. Conversely, ^{15}N recoveries did not exceed 53% in maize and in the G100 treatment in sorghum, where ^{15}N-labelled fertiliser rates were 120 and 100 kg N ha^{-1} (Figure 5-4).

In winter (wheat season) the environmental conditions were not conducive for excessive N losses. As indicated by the low N_2O-N losses, the nitrification and denitrification processes are likely to have been inhibited by the relatively low soil temperatures (constantly below 20°C). Moreover, the low amount of rainfall that occurred in the month following top dressing (154 mm) would not have triggered denitrification or caused important leaching events in this soil type. Accordingly, the vast majority of labelled fertiliser N not recovered in the crop was found in the top 10 cm of the soil profile (Table 5-3) and unaccounted N was limited to 1% of applied ^{15}N.

In summer, conditions at side dressing were more favourable for stimulating N losses (Figure 5-1). In both maize and sorghum seasons the high soil moisture conditions occurring concurrently with elevated soil temperatures would have stimulated the activity of nitrifying and denitrifying microorganisms. Moreover, significant rainfall events occurred a few days after side dressing, resulting in higher amounts of ^{15}N leached down the soil profile (Figure 5-3) compared to the winter season.

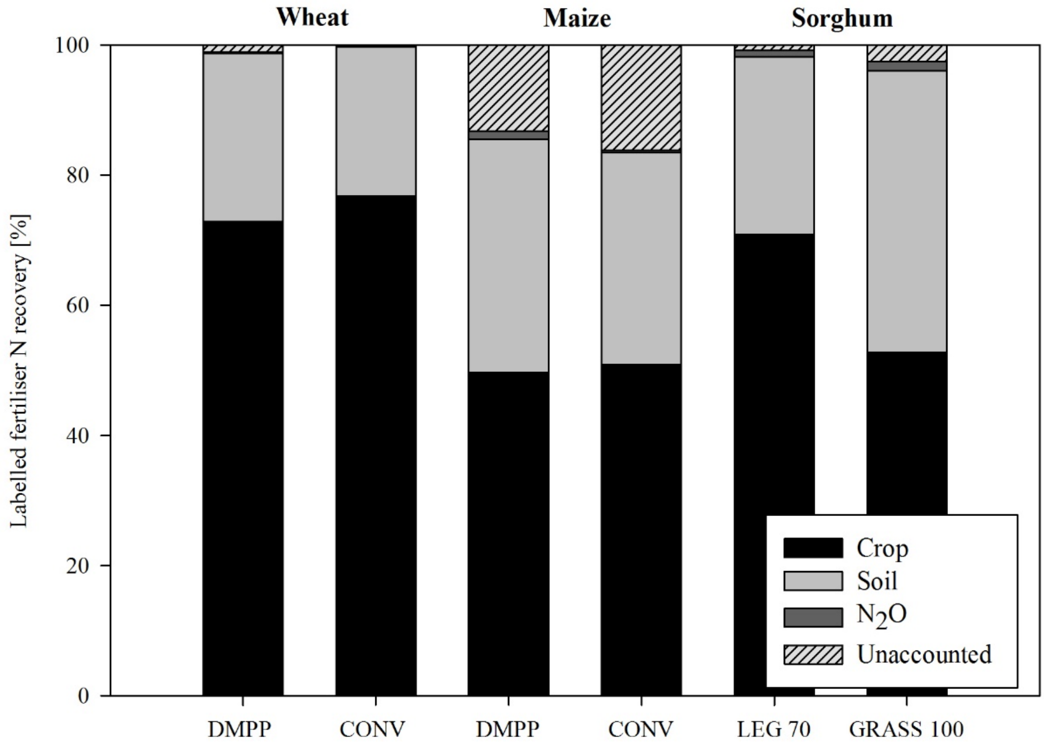

Figure 5-4 - Mean cumulative crop and soil recoveries and losses of ^{15}N-labelled fertiliser for the four treatments during the wheat, maize and sorghum seasons.

Despite soil conditions were conducive for high N losses, the amount of unaccounted ^{15}N in the maize and sorghum seasons was relatively low compared to other studies conducted on summer crops grown on soils other than Oxisols (Sanchez and Blackmer, 1988; Smil, 1999; Dourado-Neto *et al.*, 2010; Zhang *et al.*, 2010; Blesh and Drinkwater, 2014). The low N losses measured in this study can be explained considering the physical and chemical characteristics of the soil.

The permeability of the soil was sufficient to avoid prolonged periods of saturation of the soil profile even after the high summer rainfall events, while the relatively low content of soil organic C would have resulted in a limited supply of labile C to support denitrification. As indicated by the relatively low N_2O emissions measured in the two summer crops (Table 5-3), denitrification could therefore not go to completion and only moderate quantities of N_2 are likely to have been lost after significant rain events.

On the other hand, the high clay content of the soil reduced the water infiltration rates even during the intense rain events occurred during the two summer seasons (Figure 5-1). The moderate soil permeability limited NO_3^- leaching and maintained the majority of the N in the rooting zone, enabling in this way a wider window of opportunity for the plants to adsorb the N supplied with fertilisation. As a result, the unaccounted fertiliser N during the summer cropping seasons was limited to amounts varying between 0.9% (L70) and 16.2% (DMPP) of applied N fertiliser.

In this study N losses via runoff and NH_3 volatilisation were minimised by the fertiliser application method, while NO_x–N losses were considered negligible. Nitric oxide in soil is a by-product of the nitrification and denitrification processes, and several laboratory study have reported NO:N_2O emissions ratios varying from 0.01 to 1 (Skiba *et al.*, 1997). Consequently, fertiliser-induced NO emissions were estimated to range from 0.3% to 1.4% of the applied N, a value in close agreement with those suggested by Skiba *et al.* (1997) and Veldkamp and Keller (1997), and similar to that measured by Fernandes Cruvinel *et al.* (2011) in a fertilised Oxisols cropped with maize.

During the summer cropping seasons the majority of the unaccounted fertiliser N is likely to have been lost in the deeper layers of the soil profile via leeching. In maize, when the amounts of unaccounted fertiliser N were highest (13.2% and 16.2%), approximately 11% of fertiliser N was recovered in the monitored subsoil (30 - 60cm). This aspect indicates a net N movement towards the lower soil layers and suggests that a further 10% of fertiliser N could have been lost in the unmonitored strata of the soil profile, i.e. deeper than 60 cm.

DMPP was not effective in increasing crop N recovery, although values tended to be slightly higher than in the CONV treatment (Table 5-3). Several studies have reported that nitrification inhibitors have the potential to significantly increase N recoveries only when relatively large amounts of fertiliser N are lost via leaching or denitrification (Walters and Malzer, 1990; Freney *et al.*, 1993; Wolt, 2004; Chaves *et al.*, 2006; Abalos *et al.*, 2014). The intrinsic characteristics of the Oxisol monitored in this study limited the possibility of DMPP to significantly improve the fertiliser N use efficiency since relatively low N losses were observed also when conventional urea was applied.

In fact, also in the CONV treatment the majority of the fertiliser N that was not taken by the crop remained confined in the top soil. The high clay content of the Oxisols limited the vertical movement of fertiliser N in the soil and the percentage of soil ^{15}N recovered in the top 10 cm at the end of the wheat and maize seasons amounted to 84 and 50% of the total ^{15}N recovered in the soil profile, respectively (Figure 5-3). Similar results were observed in the second investigation, when after fertilising sorghum with conventional urea the ^{15}N recovered from the first 10 cm constituted 76% (L70) and 88% (G100) of the total ^{15}N recovered in the soil.

5.4.3 Implications

Overall, fertiliser N rates were the main factor limiting N recovery in the crops. Highest fertiliser N recoveries were observed in the CONV and DMPP treatments in wheat (>70%) and in the L70 treatment in sorghum (70%), which were fertilised with 60 and 70 kg ^{15}N ha^{-1}, respectively. The low N rates applied in these treatments enabled to synchronise the fertiliser N supply with plant N demand. Fertiliser N was therefore used more efficiently by the crop and less (approximately 25%) was left in the soil.

In contrast, significantly lower fertiliser N recoveries were measured in the CONV and DMPP treatments in maize (approximately 50%) and in the G100 treatment in sorghum (53%), which received 120 and 100 kg ^{15}N ha^{-1}, respectively. The amounts of ^{15}N recovered in the soil of these three treatments were remarkably similar (39.1 - 43.3 kg N ha^{-1}), while the quantities of leached or otherwise unaccounted ^{15}N were greater in the CONV and DMPP treatments in maize, where the rate of labelled N applied at side dressing (120 kg N ha^{-1}) was substantially higher than in G100 (80 kg N ha^{-1}).

The introduction of a legume phase in the cereal-based cropping system proved to be the most effective N strategy under both the agronomic and environmental perspectives. The mineralisation of the legume residues provided a substantial N supply to the following cereal crops and reduced the cereal reliance on synthetic fertiliser compared to cereals planted after a non-leguminous crop. The decreased reliance on synthetic N inputs allowed for reducing fertiliser N rates to the levels necessary to reach maximum yield potential. In particular, this strategy enabled lowering the amount of fertiliser N side dressed to the summer cereal crop, the occasion when the highest quantities of annual synthetic N are applied. Build-up of high amounts of NO_3^- in the soil following fertilisation was therefore limited and N_2O losses were caused mainly by temporary increases of NO_3^- levels due to fertiliser application. Consequently, cumulative N_2O emissions were primarily a function of the N fertiliser rate applied, while cropping history had no significant effect.

5.5 Conclusions

Collectively, the results of this study point to limiting the application rates of synthetic fertiliser N as the most effective strategy to reduce N losses and increase fertiliser N recovery in subtropical Oxisols. Future N management strategies in these agroecosystems should focus on the introduction of legumes to reduce the reliance of cereal crops on synthetic N fertilisers and minimise the agronomic inefficiencies due to fertiliser N losses. A critical aspect for the success of these N management strategies will be to achieve a good synchrony between the N released from the degradation of legume residues and the N uptake of the subsequent crop.

Assessing agronomic and environmental implications of different N fertilisation strategies in subtropical grain cropping systems in Oxisols (*Paper 3*)

Statement of Contribution of Co-Authors for Thesis by Published Paper

The authors listed below have certified* that:

1. they meet the criteria for authorship in that they have participated in the conception, execution, or interpretation, of at least that part of the publication in their field of expertise;

2. they take public responsibility for their part of the publication, except for the responsible author who accepts overall responsibility for the publication;

3. there are no other authors of the publication according to these criteria;

4. potential conflicts of interest have been disclosed to (a) granting bodies, (b) the editor or publisher of journals or other publications, and (c) the head of the responsible academic unit, and

5. they agree to the use of the publication in the student's thesis and its publication on the Australasian Research Online database consistent with any limitations set by publisher requirements.

In the case of this chapter:

Legumes or nitrification inhibitors to reduce N_2O emissions in subtropical cereal cropping systems?

Contributor	Statement of contribution*
Massimiliano De Antoni Migliorati	Performed experimental design, model calibration and validation, simulations of different N management scenarios, and wrote the manuscript.
Signature	
9th March 2015	
William J. Parton	Aided model calibration and validation, and reviewed the manuscript.
Stephen J. Del Grosso	Aided model calibration and validation, and reviewed the manuscript.
Peter R. Grace	Aided experimental design and data analysis, and reviewed the manuscript.
Mike J. Bell	Aided experimental design and data analysis, and reviewed the manuscript.
David W. Rowlings	Aided experimental design and data analysis, and reviewed the manuscript.
Clemens Scheer	Aided experimental design and data analysis, and reviewed the manuscript.

Principal Supervisor Confirmation

I have sighted email or other correspondence from all Co-authors confirming their certifying authorship.

Peter R. Grace		9th March 2015
Name	Signature	Date

Chapter 6: Legumes or nitrification inhibitors to reduce N_2O emissions in subtropical cereal cropping systems? (*Paper 4*)

Abstract

The DAYCENT biogeochemical model was used to investigate how the use of fertilisers coated with nitrification inhibitors and the introduction of legumes in the crop rotation can affect subtropical cereal production and N_2O emissions. The model was validated using comprehensive multi-seasonal, high-frequency dataset from two field investigations conducted on an Oxisol, which is the most common soil type in subtropical regions. Different N fertiliser rates were tested for each N management strategy and simulated under varying weather conditions. DAYCENT was able to reliably predict soil N dynamics, seasonal N_2O emissions and crop production, although some discrepancies were observed in the treatments with low or no added N inputs and in the simulation of daily N_2O fluxes.

Simulations were consistent with field observations and highlighted that the high clay content and the relatively low C levels of the Oxisol analysed in this study limit the chances for significant amounts of N to be lost via deep leaching or denitrification. The application of urea coated with a nitrification inhibitor (DMPP) was the most effective strategy in minimising N_2O emissions. This strategy however did not increase yields since the application of urea coated with a nitrification inhibitor did not substantially decrease overall N losses compared to conventional urea. Simulations indicated that replacing part of crop N requirements with N mineralised by legume residues is the most effective strategy to reduce N_2O emissions and support cereal productivity. The results of this study show that legumes have significant potential to enhance the sustainable and profitable intensification of subtropical cereal cropping systems on Oxisols.

6.1 Introduction

By 2050, global cereal demand is predicted to increase by 50% to meet the demands of a world population 30% larger and more affluent than at present (Ray *et al.*, 2013). Virtually all of the increase in cereal consumption will come from tropical and subtropical countries (Alexandratos and Bruinsma, 2012), implying an urgent need to increase productivity levels in these regions. This increase will be extensively sustained by agricultural systems conducted in Oxisols, which are the most common soil type in these regions (von Uexküll and Mutert, 1995; Buol and Eswaran, 1999).

Since the beginning of the Green Revolution, intensification of agricultural systems has been achieved through an increase in the use of synthetic N (Ladha *et al.*, 2005), resulting in sharp increases in greenhouse gas emissions, especially N_2O (van Beek *et al.*, 2010). N_2O is a potent greenhouse gas with a global warming potential 298 times greater than CO_2 and is also the major contributor to the depletion of the ozone layer in the stratosphere (Ravishankara *et al.*, 2009). There is consensus that pursuing food security through a further increase in synthetic N use will result in unacceptable levels of environmental damage (FAO, 2010; Foley *et al.*, 2011; Tilman *et al.*, 2011). It is therefore critical to identify alternative N management strategies aimed at supporting future intensification of tropical and subtropical agricultural systems without provoking an increase of N_2O emissions from these agroecosystems.

The use of fertilisers coated with nitrification inhibitors and the (re)introduction of legumes in cereal-based crop rotation are among the most promising strategies for this purpose. Nitrification inhibitors decrease N_2O losses both directly, via slowing the nitrification rates and, indirectly, by reducing the amount of NO_3^- available to denitrifying microorganisms (Linzmeier *et al.*, 2001b; Hatch *et al.*, 2005; Suter *et al.*, 2010). The presence of legumes in the cereal-based crop rotation instead reduces the amount of synthetic N required by the following cereal crop and consequently decrease N_2O emissions associated with synthetic N fertilisers (Jensen and Hauggaard-Nielsen, 2003; Emerich and Krishnan, 2009; De Antoni Migliorati *et al.*, 2015).

However, the efficacy of these two N management strategies has never been compared under subtropical conditions. To date, studies have extensively evaluated the effects of nitrification inhibitors and legumes on N_2O emissions and cereal yields under temperate climatic conditions, while scant data is available for subtropical Oxisols (Fageria and Baligar, 2008). Moreover, field studies are influenced by the specific seasonal weather conditions encountered during the monitoring period and several authors have reported contradicting results on the efficacy of the two N management strategies (Díez López and Hernaiz, 2008; Jensen *et al.*, 2012; Liu *et al.*, 2013; De Antoni Migliorati *et al.*, 2014).

Process-based models can overcome these limitations as they enable to assess how different N management strategies can affect crop production and greenhouse gas emissions under varying seasonal climate conditions. Several simulation studies have demonstrated that models, when calibrated and validated with appropriate input data, lead to the same results of field studies (Staggenborg and Vanderlip, 2005; Basso *et al.*, 2010; Huth *et al.*, 2010), giving researcher a useful tool for thoroughly evaluating different N management strategies

The objectives of this study were therefore to use a process-based model to: i) compare the influence of applying urea coated with nitrification inhibitors or introducing a legume phase in the cereal-based crop rotation on N_2O losses and yields in various cereal crops grown in a subtropical Oxisol; ii) determine best agronomical and environmentally sound strategies to support future intensification of cereal cropping systems in subtropical Oxisols.

The DAYCENT biogeochemical model was chosen for the purposes of this study because it is currently the model that has been most extensively tested to simulate both crop production and N_2O emissions in cereal cropping systems (Del Grosso *et al.*, 2002; Del Grosso *et al.*, 2005; Del Grosso *et al.*, 2006; Del Grosso *et al.*, 2008; Halvorson *et al.*, 2008; Scheer *et al.*, 2013a) and it is currently used to estimate N_2O emissions for the U.S. National GHG Inventory (US-EPA, 2014) under the United Nations Framework Convention on Climate Change (Del Grosso *et al.*, 2006).

The model was calibrated and validated using high temporal frequency N_2O measurements, ^{15}N recovery observations and yield data collected during two field investigations. The whole dataset included multiple cropping seasons, crop rotations, the use of fertilisers coated with a nitrification inhibitor and the introduction of a legume phase in cereal-based crop rotation. A series of scenarios embracing a range of N fertiliser rates was tested for both N management strategies. Each scenario was simulated using 15 years of local climate data.

This is the first study to employ a model validated using such an extensive dataset to assess the use of nitrification inhibitors and legumes as alternative N management strategies in subtropical cereal cropping systems on Oxisols. The results will contribute to identify agronomically viable and environmentally sustainable N fertilisation strategies to support future intensification of grain production on these agroecosystems.

6.2 Materials and Methods

6.2.1 Study site and experimental design

The two field investigations were conducted at the J. Bjelke Petersen Research Station of the Department of Agriculture, Fisheries and Forestry (DAFF). The station is located in Taabinga (26°34’54,3’’ Latitude South, 151°49’43.3’’ Longitude East, altitude 441 m a.s.l), in southeast Queensland, Australia. The climate is classified as subtropical (Cfa) according to Köppen climate taxonomy, with a mean annual precipitation of 776.2 mm. Daily mean maximum and minimum temperatures are 20.1 °C and 4.0 °C in winter and 29.6 °C and 16.5 °C in summer, respectively (Australian Bureau of Meteorology website). The soil is classified as a Tropeptic Eutrustox Oxisol (USDA, 1998) or as a Orthic Ferralsol (FAO, 1998), and is characterised by a high clay content (55%), a moderately slow permeability and an effective rooting zone of 1.2 m.

The first experiment consisted of two cropping seasons: wheat (winter 2011) and maize (summer 2011/2012). Wheat (*Triticum aestivum* L., cultivar Hartog) was planted 6 July and harvested 29 November 2011, while maize (*Zea mays* L., cultivar 32P55) was planted 21 December 2011 and harvested 20 June 2012. Four treatments were tested:

- CNT: Control test; no N fertiliser applied to wheat, urea applied at rate of 40 kg N ha^{-1} to maize to guarantee a minimum crop establishment.

- ADJ: Conventional N fertiliser rate adjusted according to estimated residual soil N; urea applied at rates of 20 and 100 kg N ha^{-1} to wheat and maize, respectively.
- CONV: Conventional N fertiliser rate; fertiliser N applied at rates of 80 and 160 kg N ha^{-1} to wheat and maize, respectively. N rates were similar to farmer practice and designed to achieve maximum yield potential.
- DMPP: Fertiliser coated with DMPP nitrification inhibitor; fertiliser N applied at same rates of CONV treatment. Given the high cost of DMPP, in both seasons DMPP urea was only used at top/side dressing, when 75% of seasonal N was applied to the crop.

The second experiment was conducted on sorghum (*Sorghum bicolor* L., planted 12 December 2012 and harvested 18 June 2013) following two distinct cropping histories. One, hereafter called legume cropping history, included two seasons of alfalfa pasture (*Medicago sativa*, L.), one season of maize and one season of sulla ley pasture (*Hedysarum coronarium* L.) prior to sowing sorghum. The other, hereafter called grass cropping history, included two seasons of a mixed pasture predominantly composed by Rhodes grass (*Chloris gayana*, K.*)*, one season of maize and one season of wheat. Both sulla and wheat were managed as green manure crops and plant residues incorporated before sowing sorghum. During the sorghum season the following treatments were assessed:

- L0: Sorghum grown in the legume cropping history, no N applied;
- L70: Sorghum grown in the legume cropping history, 70 kg N ha^{-1} applied as urea;
- G0: Sorghum grown in the grass cropping history, no N applied;
- G100: Sorghum grown in the grass cropping history, 100 kg N ha^{-1} applied as urea.

The fertiliser N applied in G100 was similar to farmer practice and was designed to achieve maximum yield potential. The synthetic N rate used in L70 was reduced compared to G100 to account for the expected increase in plant available N arising from the legume residues. During both investigations all treatment were irrigated to prevent water stress limiting the potential yields. Details of crop management and fertilisation events are highlighted in Table 6-1. See Chapters 3 and 4 for further information on the experimental set-up and crop management adopted during the two investigations.

Table 6-1 - Times of application and N rates of isotopically labelled and unlabelled fertilisers during the two investigations at Kingaroy research station, Queensland, Australia.

Crop	**Time of fertiliser application**	**Date**	**Fertilisation [kg-N ha^{-1}]**	
			CONV	**DMPP**
Wheat	Planting	06/07/2011	20 (DAP) †	20 (DAP) †
	Top Dressing (broadcasted)	15/09/2011	60 (urea)*	60 (DMPP urea)*
Maize	Planting	21/12/2011	40 (MAP) †	40 (MAP) †
	Side Dressing (banded)	19/01/2012	120 (urea)*	120 (DMPP urea)*
			L70	**L100**
Sorghum	Planting	12/12/2012	20 (urea)**	20 (urea)**
	Side Dressing (banded)	14/01/2013	50 (urea)**	80 (urea)**

* Fertiliser labelled with 10% ^{15}N urea

** Fertiliser labelled with 5% ^{15}N urea

† DAP: diammonium phosphate; MAP: monoammonium phosphate

6.2.2 Crop development and fertiliser N recovery

Crop development was monitored in all treatments by collecting plant samples at booting stage, flowering and physiological maturity. On every occasion, three samples were collected in each treatment by cutting the plants over one meter of crop row and subsequently oven-dried for 24 hours at 60°C. At harvest, average grain yield was measured in each treatment by harvesting six strips at least 1.65 m wide for the plot length using a plot combine.

Additionally, fertiliser N recoveries in the soil-plant system were assessed in the treatments where high N fertiliser rates were applied, that is CONV and DMPP in the first investigation and L70 and G100 in the second. In the CONV and DMPP treatments ^{15}N-labelled fertiliser was only applied as a side dressing to determine the N recovery of DMPP urea and compare it with conventional urea (Table 6-1). Each treatment received 10% excess ^{15}N enriched urea; in the DMPP treatment the ^{15}N enriched urea was added with DMPP at a ratio of 6 g DMPP kg^{-1} urea to replicate the same ratio of commercial DMPP urea. In the second investigation the L70 and G100 treatments received 5% excess ^{15}N enriched urea both at planting and at side dressing (Table 6-1). In both investigations ^{15}N-labelled urea was applied as a liquid solution in a sub-surface band, minimising in this way N losses via runoff and NH_3 volatilisation.

In the treatments fertilised with ^{15}N enriched urea, plant and soil samples were taken exclusively at crop harvest. In wheat and maize only above-ground material was collected, while moister soil conditions at the end of the sorghum season enabled the collection of both above- and below-ground material. Wheat root biomass was estimated using a root:shoot ratio of 0.31 (Siddique *et al.*, 1990; Manschadi *et al.*, 2008) while a root : shoot ratio of 0.22 was used for maize (Anderson, 1988; Demotes-Mainard and Pellerin, 1992). Soil sampling was performed using a core sampler; samples were collected to a depth of 60 cm in wheat and maize, and to 1m in sorghum. The ^{15}N analysis was performed using a 20-22 Isotope Ratio Mass Spectrometer (Sercon Limited, UK). For further information on experimental settings and main findings see Chapter 5.

6.2.3 N_2O emissions and ancillary measurements

The use of a fully automated, chamber-based greenhouse gas measuring system ensured N_2O emissions were monitored at a high temporal frequency throughout each cropping season. The twelve chambers were closed airtight with lids operated by pneumatic actuators and connected to a fully automated sampling and in-field analysis system as described in Chapter 3 and Scheer *et al.* (2013a). One complete sampling cycle (of twelve chambers) lasted 3 hours, with each chamber sampled for 1 hour and open for 2 hours to restore ambient conditions. This method provided eight single fluxes per chamber per day. Hourly N_2O fluxes were calculated by defining the slope of the linear increase or decrease of the four gas concentrations measured during the 60 minutes of chamber closure period (Chapter 4.3.6). Fluxes above the detection limit were discarded if the regression coefficient (r^2) was < 0.80. Daily N_2O emissions were determined by calculating the mean of the sub-daily fluxes.

Routine soil sampling was conducted at regular intervals during the growing seasons by collecting samples at three depths (0-10, 10-20, 20-30 cm). Samples were added with 100 mL of 1M KCl and analysed colorimetrically for NH_4-N and NO_3-N using an AQ2+ discrete analyser (SEAL Analytical WI, USA). Four frequency domain reflectometers (FDR, EnviroScan probes, Sentek Sensor Technologies, Australia) were installed at the field site to assess the water dynamics content at three depth intervals (0-10 cm, 10-20 cm, 20-30 cm). Rainfall data were obtained from a weather station located at the study site.

6.2.4 DAYCENT biogeochemical model

Developed as the daily time-step version of the CENTURY biogeochemical model, DAYCENT simulates C and nutrients (N, P, S) dynamics between the atmosphere, vegetation, and soil pools (Parton *et al.*, 1998; Kelly *et al.*, 2000; Del Grosso *et al.*, 2001). Main model inputs consist of data on daily maximum/minimum air temperature and precipitation, site-specific soil properties, and current and historical land management. Key submodels include crop development, soil water dynamics by layer, mineralisation of nutrients and N gaseous emissions (N_2O, N_2, NO_x).

Crop development is controlled by genetic potential, phenology, nutrient availability, water/temperature stress, and solar radiation (Metherell *et al.*, 1993). The allocation of net primary production is regulated by vegetation type, phenology and water/nutrient stress. Nutrient mineralisation is a function of the lignin content and C:N ratio of the substrate, substrate availability and water/temperature stress. No vertical movement is assumed for soil NH_4^+, which is simulated only for the top 15 cm of soil profile. NO_3^- movement is instead simulated throughout the entire soil profile and NO_3^--N can be leached below the rooting zone (Del Grosso *et al.*, 2011).

The model simulates daily soil N_2O and NO_x fluxes due to nitrification and denitrification, as well as daily N_2 fluxes from denitrification (Parton *et al.*, 1996; Del Grosso *et al.*, 2000; Parton *et al.*, 2001). Nitrification rates rise linearly with soil NH_4^+ concentration and increase exponentially with temperature until stabilising when soil temperature reaches the highest monthly value recorded for the site. The effect of soil moisture on biological activity is simulated by limiting nitrification when soil water-filled pore space (WFPS) is below 40% or above 80%. Nitrification is not limited when soil pH is above 7 but diminishes exponentially at pH levels lower than neutral. If optimal conditions are met, maximum daily nitrification rates can reach up to 10% of soil NH_4^+.

Denitrification is regulated by soil NO_3^- content, labile C availability, water content and texture (Del Grosso *et al.*, 2000). Denitrification starts to occur when water-filled pore space (WFPS) values exceed 50-60% and increases exponentially until soil water content approaches saturation (70-80% WFPS). Daily N fluxes from denitrification are calculated taking into consideration the input that is most limiting. N_2O emissions are determined as a factor of total daily denitrification using an N_2:N_2O ratio function. Depending on soil NO_3^- concentrations, maximum daily denitrification rates can vary from less than 15% to almost 100% of soil NO_3^-.

6.2.5 Model initialisation, calibration and validation

The first step of the simulation entailed the site characterization process, providing the model with information on site latitude, weather statistics and soil horizonation. Initial values of soil organic matter and nutrient pools were generated running a *spin-up* simulation reproducing historical land use (Del Grosso *et al.*, 2011). The spin-up simulation was run for almost 2000 years (ending in 1970), assuming a 15-year burn cycle and a mixed ecotype formed by subtropical grass, shrubs and eucalyptus trees. Running the spin-up simulation with the default model parameters resulted in a significant overestimation of soil C content. The decay rate of the passive soil organic matter pool was therefore increased by a factor of 2.5 to meet the total soil C content measured at the beginning of the two field investigations.

The *base* simulation was started in 1970, when the native vegetation was eliminated via controlled burning and the soil ploughed for the first time. A crop rotation including sorghum, peanuts, maize and wheat was implemented from 1970 to 2011 according to recorded local farming practices. Both spin-up and base simulations were implemented using a 15-year weather file obtained combining data from two meteorological stations located within 3 km from the study site (Australian Bureau of Meteorology website).

The model was calibrated against measurements of soil water content, soil NH_4^+ and NO_3^- levels, daily N_2O emissions, in-season biomass production, grain yield and aboveground plant N uptake in the 0N, CONV, DMPP, L0 and G0 treatments. The obtained parametrisation was validated against measurements in the ADJ, L70 and G100 treatments.

Since the current version of DAYCENT does not include a ^{15}N tracer submodel, simulated plant N uptake in the aboveground biomass was calculated detracting the plant N due to indigenous soil N pool from the total plant N. Plant N due to indigenous soil N, defined as the N present in the soil before fertilisation, was determined using the values from the CNT treatment in wheat and from L0 and G0 in sorghum. For the maize season, plant N due to indigenous soil N was calculated by simulating a treatment with no fertiliser N inputs. Fertiliser N losses measured in the field were almost entirely due to deep leaching (leaching of NO_3^- beyond the rooting zone) and gaseous emissions (N_2O and N_2) (Chapter 5). Simulated NO_3^- leaching, N_2O and N_2 emissions due to fertiliser N were corrected for background values and their sum was compared to the unaccounted N calculated with ^{15}N-tracer techniques (Chapter 5).

Data collected during the first investigation indicated that the efficiency of DMPP in inhibiting N_2O emissions was substantially higher in the maize season compared to wheat (Chapter 3). The factor regulating the reduction in nitrification rates of fertilizer N with DMPP was therefore reduced to 0.25 during the maize season and to 0.60 during wheat. In both seasons the duration of the nitrification inhibitor was set to 6 weeks (Pasda *et al.*, 2001).

6.2.6 N management scenarios

The fertiliser N rates that supported the highest yields in the two field investigations (CONV, DMPP, L70 and G100) were varied by 20% to assess and compare the robustness of each N management practice in terms of abating N_2O emissions and supporting high yields. Scenarios replicating the first investigation included three N fertiliser rates in wheat (65, 80, 95 kg N ha^{-1}) and in maize (130, 160, 190 kg N ha^{-1}) using conventional or DMPP urea. For the second investigation fertiliser N rates were 55, 70 and 85 kg N ha^{-1} in sorghum after the legume pasture and 80, 100 and 120 kg N ha^{-1} in sorghum after the grass pasture.

N application methods, crop rotations and management were left unvaried compared to those used for model calibration. Irrigation events were scheduled to occur during the initial stages of crop development when volumetric water content declined to levels lower than 20%. Sowing dates were adjusted according to weather conditions year by year. The efficiency of each N management strategy was tested under varying weather conditions running every scenario with 15 years of local climate data (1999-2013). Initial soil conditions were re-initialised at the beginning of every simulation.

6.2.7 Calculations and Statistical analysis

N_2O emission factors, expressed as the percentage of N fertiliser lost as N_2O, were corrected for background emissions using values from the CNT treatment in wheat and from L0 and G0 in sorghum. For the maize season, background emissions were calculated simulating a treatment with no fertiliser N inputs. N_2O emission intensities were calculated as the ratio of N_2O emitted (kg N_2O-N ha^{-1}) to grain produced (Mg grain ha^{-1}). Cumulative N losses were calculated for each treatment summing seasonal losses via deep NO_3^- leaching and N_2O and N_2 emissions.

Discrepancies between measured and simulated values were assessed using the root mean square error (RMSE) and the Pearson correlation (r^2). Differences in cumulative N_2O emissions and grain yields were assessed with the ANOVA test using a confidence interval of 95%. The Tukey *post hoc* test was used to compare cumulative N_2O emissions. Statistical analyses were performed within the SPSS 22 environment (IBM Corporation, USA).

6.3 Results

6.3.1 Model validation

The temporal pattern and magnitudes of modelled volumetric water content were in reasonable agreement with observed values, especially in the top 10 cm (Figure 6-1). Values of r^2 and RMSE for volumetric water content in the top 10 cm were 0.49 (*F* 292.28) and 5.06 in the first investigation and 0.43 (*F* 191.55) and 0.04 in the second investigation, respectively. The precision of simulated soil water content was inferior for the lower soil layers and r^2 and RMSE values averaged for the top 30 cm amounted to 0.28 (*F* 119.88) and 5.14 in the first investigation and 0.40 (*F* 287.64) and 0.5 in the second investigation, respectively.

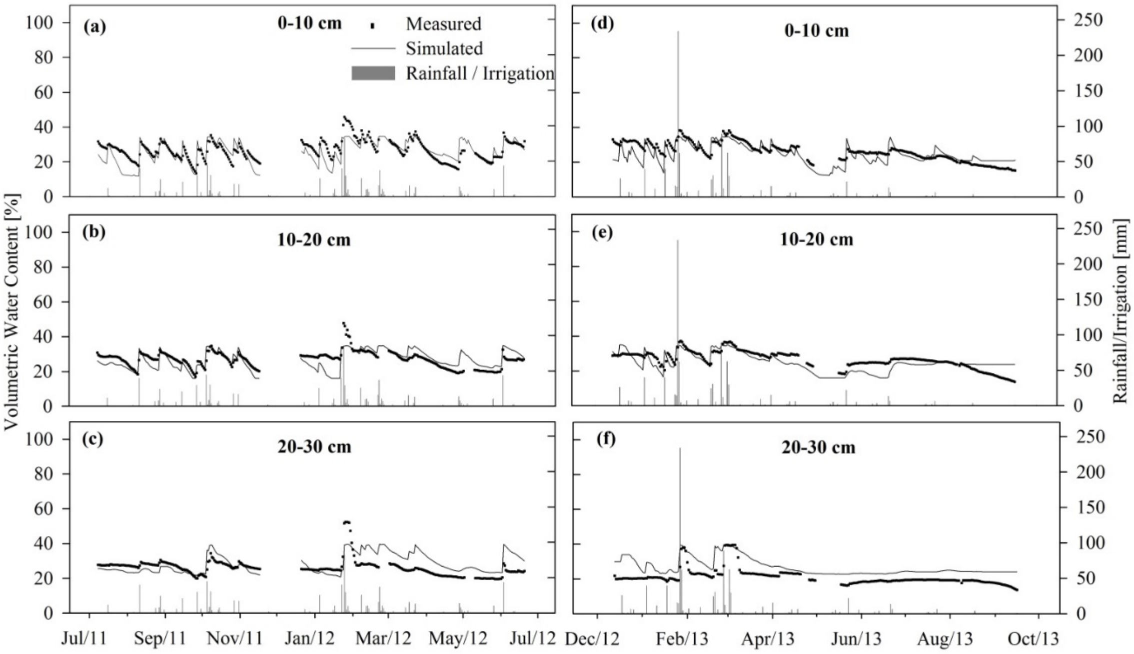

Figure 6-1 - Measured and simulated volumetric soil water content for three layers (0–10 cm, 10–20 cm, 20–30 cm) and rainfall/irrigation events during the wheat-maize (a, b, c) and sorghum (d, e, f) seasons at the Kingaroy research station, Australia.

The model was able to represent properly the magnitude of soil NH_4^+ and NO_3^- variations following fertilisation events but a slight asynchrony between simulated and observed values was often observed (Figure 6-2).

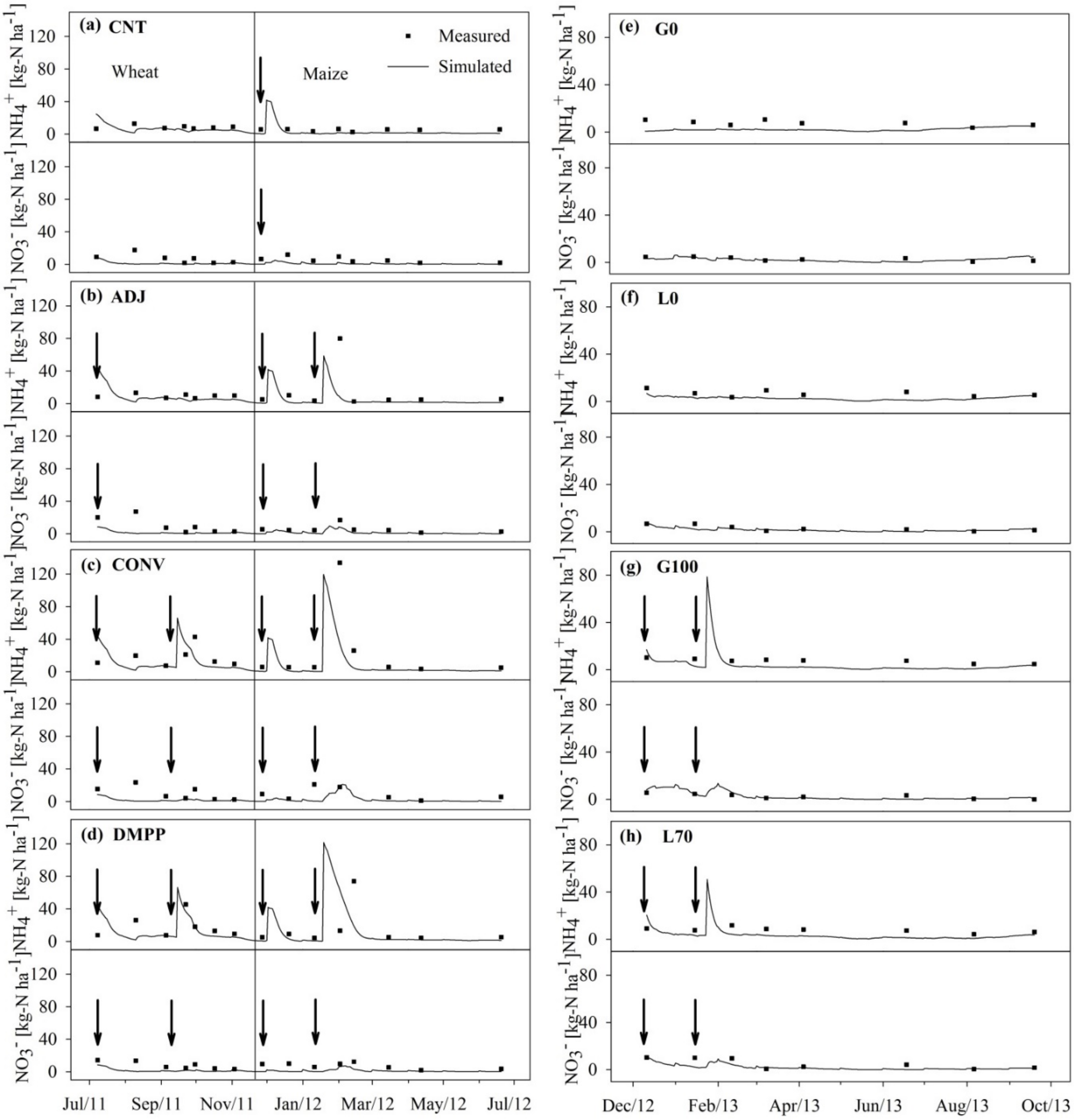

Figure 6-2 - Measured and simulated soil ammonium and nitrate contents (0-10 cm) for the eight fertilisation treatments during the wheat-maize (a, b, c, d) and sorghum (e, f, g, h) seasons in Kingaroy, Australia. Arrows indicate the timing of N fertiliser applications.

As a result, in the first investigation average r^2 and RMSE values across treatments were 0.39 (*F* 1.98) and 29.06 kg N ha^{-1} for NH_4^+ (top 30 cm) and 0.26 (*F* 4.65) and 15.04 kg N ha^{-1} for NO_3^- (top 30 cm). In the second investigation the respective values were 0.29 (*F* 2.81) and 5.31 kg N ha^{-1} for NH_4^+ (top 30 cm) and 0.51 (*F* 6.37) and 1.78 kg N ha^{-1} for NO_3^- (top 30 cm). In both investigations simulated leaching of NO_3^- below the rooting zone was minimal (< 2 kg NO_3^--N ha^{-1}), which is consistent with data reported in Chapter 5.

The model provided reliable simulations of biomass production and crop response to increasing fertiliser N rates (Table 6-2, Table 6-3 and Figure 6-3). The simulated course of crop growth was close to field observations for wheat and sorghum, while for maize tended to be slower compared to field observations. r^2 and RMSE values averaged across treatments were 0.93 (*F* 64.20) and 2.68 Mg ha^{-1} in the first investigation and 0.96 (*F* 77.42) and 1.08 Mg ha^{-1} in the second, respectively.

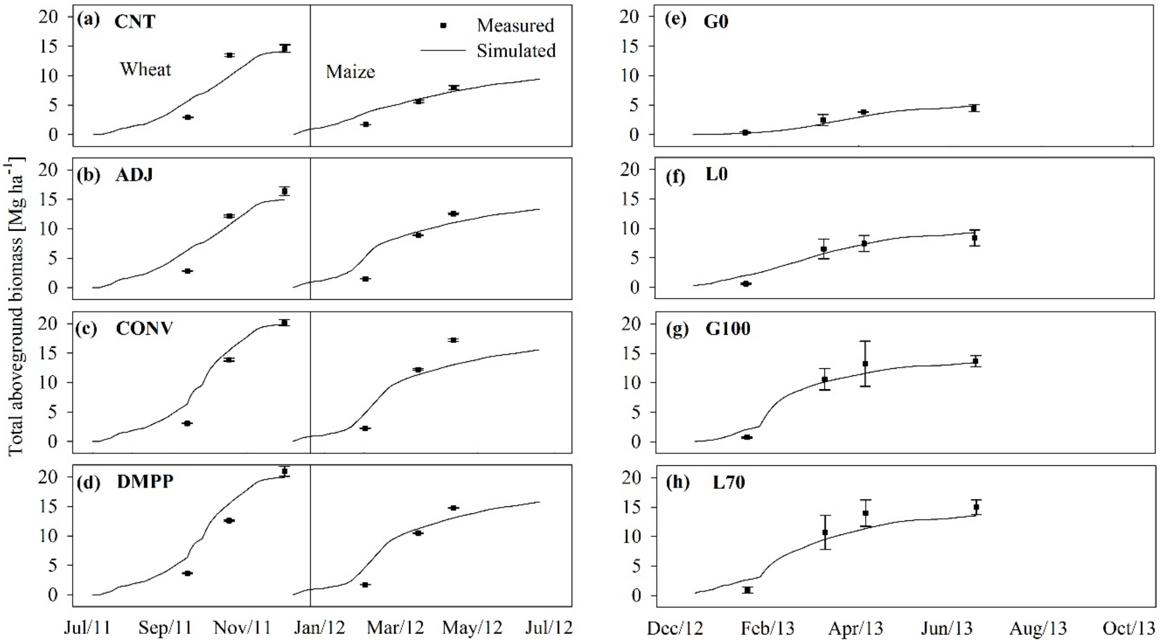

Figure 6-3 - Measured (mean ± SD) and simulated aboveground biomass (expressed as dry matter) for the eight fertilisation treatments during the wheat-maize (a, b, c, d) and sorghum (e, f, g, h) seasons in Kingaroy, Australia.

Table 6-2 - Measured (mean ± SD) and DAYCENT simulated N_2O fluxes, grain yield, aboveground (AG) plant biomass, aboveground plant N uptake, N_2O emission factors and N_2O intensities in the treatments tested during the wheat and maize cropping seasons at Kingaroy (Queensland).

Parameter	**Treatment**	**Wheat**		**Maize**	
		Measured	**Simulated**	**Measured**	**Simulated**
Cumulative N_2O Flux [kg N ha^{-1}]	CNT	0.25±0.07	0.23	0.22±0.05	0.14
Grain Yield [Mg ha^{-1}]		3.88±0.84	4.03	2.23±0.29	4.15
AG plant biomass [Mg ha^{-1}]		14.61±0.63	14.08	7.99±0.34	9.41
AG plant N uptake [kg N ha^{-1}]		140.74±38.5	148.73	50.98±13.79	65.12
N_2O Emission Factor [%]		-	-	0.26	0.04
N_2O Intensity [kg N_2O-N Mg $yield^{-1}$]		0.06	0.06	0.10	0.03
Cumulative N_2O Flux [kg N ha^{-1}]	ADJ	0.19±0.03	0.24	0.65±0.26	0.66
Grain Yield [Mg ha^{-1}]		4.48±0.27	4.26	5.20±0.67	5.87
AG plant biomass [Mg ha^{-1}]		16.40±0.77	14.89	12.55±0.11	13.32
AG plant N uptake [kg N ha^{-1}]		160.22±34.5	152.08	91.04±5.34	99.78
N_2O Emission Factor [%]		-0.29	0.06	0.53	0.54
N_2O Intensity [kg N_2O-N Mg $yield^{-1}$]		0.04	0.06	0.12	0.11
Cumulative N_2O Flux [kg N ha^{-1}]	CONV	0.40±0.03	0.31	1.61±0.85	1.49
Grain Yield [Mg ha^{-1}]		5.02±0.29	5.67	7.31±0.30	6.85
AG plant biomass [Mg ha^{-1}]		22.13±0.54	19.84	17.17±0.23	15.53
AG plant N uptake [kg N ha^{-1}]		197.65±30.9	201.91	125.73±10.9	120.26
N_2O Emission Factor [%]		0.19	0.11	0.93	0.86
N_2O Intensity [kg N_2O-N Mg $yield^{-1}$]		0.08	0.06	0.22	0.22
Cumulative N_2O Flux [kg N ha^{-1}]	DMPP	0.25±0.02	0.26	0.50±0.21	0.50
Grain Yield [Mg ha^{-1}]		4.79±0.23	5.69	7.19±0.44	6.94
AG plant biomass [Mg ha^{-1}]		20.96±0.87	19.91	14.76±0.05	15.75
AG plant N uptake [kg N ha^{-1}]		187.75±39.3	202.47	113.90±3.44	124.86
N_2O Emission Factor [%]		-0.01	0.04	0.24	0.24
N_2O Intensity [kg N_2O-N Mg $yield^{-1}$]		0.05	0.05	0.07	0.07

Table 6-3 - Measured (mean ± SD) and DAYCENT simulated N_2O fluxes, grain yield, aboveground (AG) plant biomass, aboveground plant N uptake, N_2O emission factors and N_2O intensities in the treatments tested during the sorghum cropping seasons at Kingaroy (Queensland).

Parameter	**Treatment**	**Sorghum**	
		Measured	**Simulated**
Cumulative N_2O Flux [kg N ha^{-1}]	G0	0.27±0.09	0.56
Grain Yield [Mg ha^{-1}]		0.94±0.21	1.82
AG plant biomass [Mg ha^{-1}]		4.48±0.59	4.87
AG plant N uptake [kg N ha^{-1}]		25.11±2.65	35.53
N_2O Emission Factor [%]		-	-
N_2O Intensity [kg N_2O-N Mg $yield^{-1}$]		0.28	0.31
Cumulative N_2O Flux [kg N ha^{-1}]	L0	0.24±0.03	0.45
Grain Yield [Mg ha^{-1}]		2.52±0.38	3.47
AG plant biomass [Mg ha^{-1}]		8.38±1.35	9.29
AG plant N uptake [kg N ha^{-1}]		46.91±8.26	66.49
N_2O Emission Factor [%]		-	-
N_2O Intensity [kg N_2O-N Mg $yield^{-1}$]		0.09	0.13
Cumulative N_2O Flux [kg N ha^{-1}]	G100	1.43±0.28	1.23
Grain Yield [Mg ha^{-1}]		5.20±0.19	5.01
AG plant biomass [Mg ha^{-1}]		13.68±0.92	13.42
AG plant N uptake [kg N ha^{-1}]		98.52±11.92	107.51
N_2O Emission Factor [%]		1.16	0.67
N_2O Intensity [kg N_2O-N Mg $yield^{-1}$]		0.28	0.25
Cumulative N_2O Flux [kg N ha^{-1}]	L70	0.68±0.40	0.75
Grain Yield [Mg ha^{-1}]		5.29±0.38	5.05
AG plant biomass [Mg ha^{-1}]		14.96±1.26	13.53
AG plant N uptake [kg N ha^{-1}]		118.94±13.82	106.15
N_2O Emission Factor [%]		0.63	0.43
N_2O Intensity [kg N_2O-N Mg $yield^{-1}$]		0.13	0.15

Simulated grain production was in good accordance with observed values, but in the treatments with nil of low N inputs (CNT, L0, G0) yields tended to be overestimated, especially in the two summer crops (maize and sorghum). Overall, simulated aboveground plant N uptake well matched observations obtained with the ^{15}N tracer technique, suggesting that the model generally captured the N dynamics of the soil-plant system.

The model was able to represent the magnitude and temporal variation of measured N_2O emissions (Table 6-2, Table 6-3 and Figure 6-4). However, the model tended to overestimate emissions in the non-fertilised treatments (L0, G0 and CNT in wheat) and no increase in N_2O emissions was simulated in the CNT treatment in maize after the rain event of 24 January 2012. In the two summer crops (maize and sorghum) DAYCENT anticipated the occurrence of emission pulses following side dressing (L70, G100 and ADJ and CONV in maize) but correctly simulated the attenuated N_2O emissions in the DMPP treatment. As a result, average r^2 and RMSE values across treatments were 0.37 (F 141.90) and 6.55 g N_2O-N ha^{-1} d^{-1} in the first investigation and 0.42 (F 211.76) and 4.16 g N_2O-N ha^{-1} d^{-1} in the second investigation.

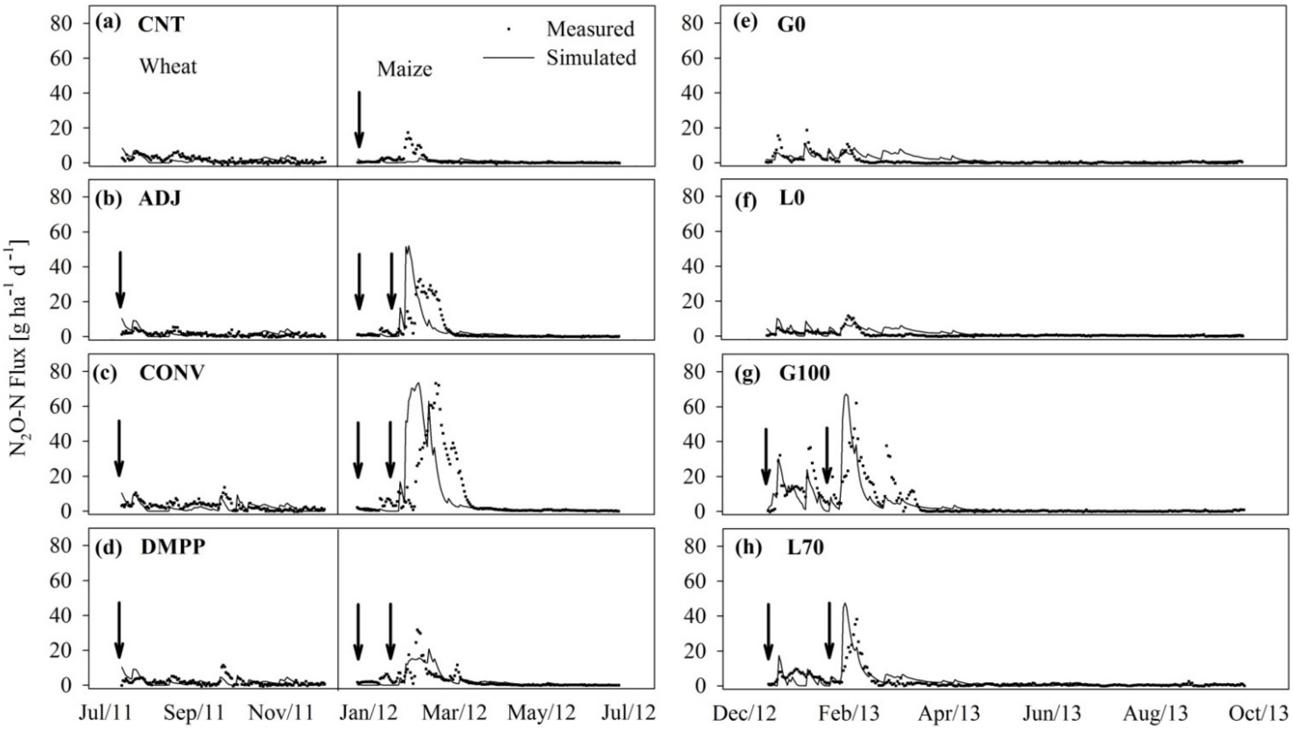

Figure 6-4 - Daily N_2O fluxes for the eight treatments during the wheat-maize (a, b, c, d) and sorghum (e, f, g, h) seasons in Kingaroy, Australia. Arrows indicate the timing of N fertiliser applications.

The discrepancies between measured and simulated N_2O emission factors varied among cropping seasons and treatments (Table 6-2 and Table 6-3). In wheat, simulated emission factors for the ADJ and DMPP treatments were higher than those calculated using field data. This was due to the high background emissions observed in the field and that led to a negative emission factor for the ADJ treatment (Chapter 3). Emission factors were accurately simulated in the maize season, with the only exception of the CNT treatment, where the high simulated yield caused an underestimation of the emission factor. Emission factors in G100 and L70 were lower than the observed values due to an overestimation of background emissions in G0 and L0, respectively. On the other hand, N_2O emission intensities were similar to those calculated with field observations (Table 6-2 and Table 6-3). The only exceptions where the non-fertilised treatments (L0, G0 and CNT in wheat), where the yield overestimation resulted in emission intensities lower than the observed.

6.3.2 N management scenarios

In the first investigation (wheat and maize) N_2O emissions increased exponentially with increasing fertiliser N rates, while in the second investigation (sorghum) the increase was linear (Table 6-4). In both investigations the correlation between fertiliser N rate and grain yield tended to be linear, even though the yield response started to plateau at the higher N rates. Significant differences in sorghum yields were only observed in the grass cropping history between the -20% and +20% treatment.

N_2O emission factors and intensities of the CONV treatments consistently exceeded those of DMPP in wheat and maize, while in sorghum they were higher in the grass compared to the legume cropping history. N_2O emission factors and intensities varied substantially with increasing fertiliser N rates only in the maize season, while in wheat and sorghum variations across N rates were minimal (Table 6-4).

The application of DMPP urea reduced cumulative N emissions compared to conventional urea, but significant difference were only observed in DMPP-20% and DMPP 160N compared to CONV+20%. Yields in the DMPP treatments were not statistically different compared to the same N rate with conventional urea (Table 6-4). Even though cumulative N losses in the legume cropping history tended to be lower than in the grass treatments, variability across seasons led to no significant differences between the two cropping histories (Table 6-4).

Table 6-4 - DAYCENT simulated grain yields, N_2O fluxes, cumulative N losses, aboveground (AG) plant N uptake, N_2O emission factors and N_2O intensities for twelve N management scenarios at Kingaroy (Queensland) using daily weather data from 1999 to 2013 (mean ± SD). Means denoted by a different letter indicate significant differences between treatments (p<0.05).

Parameter	**Crop**	**Fertiliser N rate applied**					
		CONV-20%	**CONV 80N**	**CONV+20%**	**DMPP-20%**	**DMPP 80N**	**DMPP+20%**
Grain Yield [Mg ha^{-1}]	Wheat	4.90±1.46^{a}	5.18±1.50^{a}	5.47±1.55^{a}	4.91±1.47^{a}	5.19±1.51^{a}	5.48±1.55^{a}
Cumulative N_2O Flux [kg N ha^{-1}]		0.35±0.14^{a}	0.37±0.14^{a}	0.39±0.14^{a}	0.30±0.14^{a}	0.32±0.13^{a}	0.34±0.13^{a}
Cumulative N_2 Flux [kg N_2-N ha^{-1}]		2.89±2.65^{a}	2.99±2.65^{a}	3.12±2.66^{a}	2.72±2.62^{a}	2.79±2.61^{a}	2.89±2.61^{a}
Cumulative N losses [kg N ha^{-1}] †		3.97±3.71^{a}	4.09±3.73^{a}	4.25±3.76^{a}	3.75±3.57^{a}	3.84±3.58^{a}	3.95±3.60^{a}
N_2O Emission Factor [%] *		0.15	0.15	0.15	0.08	0.08	0.09
N_2O Intensity [kg N_2O-N t yield^{-1}]		0.07	0.07	0.07	0.06	0.06	0.06
		CONV-20%	**CONV 160N**	**CONV+20%**	**DMPP-20%**	**DMPP 160N**	**DMPP+20%**
Grain Yield [Mg ha^{-1}]	Maize	6.30±1.01^{a}	7.00±0.90^{ab}	7.68±0.78^{b}	6.25±1.07^{a}	6.96±0.94^{ab}	7.62±0.82^{b}
Cumulative N_2O Flux [kg N ha^{-1}]		0.87±0.40^{a}	1.22±0.59^{ab}	1.61±0.83^{b}	0.31±0.16^{a}	0.41±0.21^{a}	0.54±0.28^{a}
Cumulative N_2 Flux [kg N_2-N ha^{-1}]		5.84±4.52^{ab}	7.83±6.05^{ab}	9.81±7.62^{b}	2.18±1.84^{a}	3.22±2.62^{a}	4.53±3.69^{ab}
Cumulative N losses [kg N ha^{-1}] †		7.65±5.59^{ab}	9.95±7.19^{ab}	12.30±8.97^{b}	3.20±2.63^{a}	4.31±3.32^{a}	5.73±4.37^{ab}
N_2O Emission Factor [%] *		0.58	0.69	0.78	0.15	0.18	0.22
N_2O Intensity [kg N_2O-N t yield^{-1}]		0.14	0.17	0.21	0.05	0.06	0.07
		G -20%	**G 100N**	**G +20%**	**L -20%**	**L70**	**L +20%**
Grain Yield [Mg ha^{-1}]	Sorghum	3.32±0.81^{a}	3.76±0.90^{ab}	4.36±1.00^{b}	3.52±0.86^{ab}	3.78±0.91^{ab}	4.12±0.99^{ab}
Cumulative N_2O Flux [kg N ha^{-1}]		0.69±0.28^{ab}	0.80±0.32^{ab}	0.89±0.35^{b}	0.45±0.17^{a}	0.52±0.20^{a}	0.58±0.22^{ab}
Cumulative N_2 Flux [kg N_2-N ha^{-1}]		9.03±4.73^{b}	9.13±4.69^{b}	9.26±4.64^{b}	3.99±2.15^{a}	4.16±2.23^{a}	4.33±2.29^{a}
Cumulative N losses [kg N ha^{-1}] †		12.23±7.40^{a}	12.40±7.43^{a}	12.61±7.41^{a}	7.36±6.47^{a}	7.55±6.55^{a}	7.78±6.58^{a}
N_2O Emission Factor [%] *		0.47	0.53	0.53	0.39	0.40	0.40
N_2O Intensity [kg N_2O-N t yield^{-1}]		0.21	0.21	0.21	0.13	0.14	0.14

*Corrected for background emissions † Sum of deep NO3- leaching and N_2O and N_2 emissions

6.4 Discussion

6.4.1 Model performance

Process-based models represent fundamental tools to assess diverse agricultural practices under varying climatic conditions to identify the most productive and sustainable N management strategies. However, models have to be accurately validated with field data to ensure that the obtained predictions are reliable and to date DAYCENT has never been used in subtropical Oxisols.

Typically, models are validated with datasets referring to laboratory conditions, single-season field experiments or reporting N_2O measurements taken, at the most, several times per week (Jarecki *et al.*, 2008; Scheer *et al.*, 2013a). Model validations based on such relatively small datasets entail significant uncertainties and often result in large errors (Kroon *et al.*, 2010). The simultaneous availability of high-frequency observations and N recovery data referring to multiple cropping seasons, crop rotations and N fertiliser strategies constitutes therefore a unique framework able to provide a rigorous validation of the DAYCENT model for a subtropical Oxisol.

The importance of testing the DAYCENT model for these environments was confirmed by the initial overestimation of the soil C content obtained using the default model parameters. The algorithms regulating C dynamics in DAYENT have been largely developed using datasets referring to temperate conditions, where mineralisation rates can be lower than in subtropical environments (Del Grosso *et al.*, 2011; Pu *et al.*, 2012). Soil C levels in the study region are low as a result of intensive conventional farming practices and the simultaneous occurrence of elevated temperatures and high soil moisture levels during the summer months (Bell *et al.*, 1995), factors that can significantly accelerate soil C mineralization (Mann, 1986; West and Post, 2002; Lal, 2004).

The necessity of increasing the decay rate of the passive soil organic matter pool has already been reported in studies testing DAYCENT under subtropical conditions. For example, Scheer *et al.* (2013a) employed a decay rate similar to that used in this study after observing that, under warm and humid conditions, the DAYCENT decomposition sub-model tends to overestimate the portion of organic C that is stabilized in finer textured soils.

Increasing the decomposition rate of the passive soil organic matter pool significantly improved model performance in predicting N dynamics in the soil-plant system. Model validation provided a strong correspondence between simulated and measured cumulative N_2O emissions across investigations, although some deviations were observed in the treatments that received low N inputs. Cumulative N_2O emissions were underestimated in the CNT treatment in maize and overestimated in L0 and G0 in sorghum. It is likely that the low N_2O fluxes simulated in CNT were due to the overestimation of total biomass, which led to an excessive plant N uptake and reduced the soil N available to nitrification and denitrification. Accordingly, no N_2O emission pulse was simulated in the CNT treatment after the rain event of 25 January 2012 (Figure 6-4a). In L0 and G0, where simulated biomass production closely matched observations, the simulated seasonal N_2O fluxes exceeded measurements (Table 6-2, Table 6-3, Figure 6-4d and Figure 6-4e). This was also observed by Del Grosso *et al.* (2008), who reported consistent overestimations of N_2O fluxes from non-fertilised treatments due to excessive background nitrification rates. On the other hand, the model correctly simulated higher N_2O fluxes in G0 compared to L0. The higher background N_2O emissions simulated in the grass cropping history were supported by a greater active soil C pool derived from the decomposition of grass residues. Conversely, the simulated levels of active soil C in the legume cropping history remained relatively low after the incorporation of the pasture residues, limiting denitrification despite the higher content of organic N (data not shown). These nutrient dynamics were consistent with field observations (Chapter 4).

DAYCENT was able to reproduce soil water and mineral N dynamics on a day-to-day basis (Figure 6-1 and Figure 6-2). The average correlation of measured vs. simulated daily N_2O emissions yielded r^2 values of 0.23 for the first investigation and 0.42 for the second, which are consistent with some of the best results (0.32-0.52) obtained with DAYCENT for various cropping systems worldwide (Li *et al.*, 2005b; Abdalla *et al.*, 2010; Scheer *et al.*, 2013a). However, in the summer crops the model tended to anticipate the N_2O emission pulses following side dressing (Figure 6-4), lowering the overall annual r^2 and RSME values.

Observed data indicated that when soil mineral N levels were elevated due to the recent fertilisations events, N_2O emission rates started to increase approximately three days after a substantial rainfall/irrigation event (> 20 mm). This time lag was probably due to a combination of reduced gas diffusivity caused by the high clay content of the soil (Smith *et al.*, 1998) and time required to the microbial pool to initiate enzyme production when nutrient and water levels reached a threshold level (Dendooven and Anderson, 1994).

These two processes are currently not simulated in DAYCENT. However, the data analysed in this study highlight that algorithms regulating microbial activity and gas diffusivity of N_2O produced at different depths should be incorporated in the model to improve DAYCENT capability of simulating the temporal patterns of daily N_2O emissions. An enhanced representation of how different soil conditions influence microbial dynamics would also allow the model to reproduce the decline in the DMPP inhibitory efficiency observed during the winter season, so to avoid the use of different inhibition factors for fertilizers applied to winter and summer crops.

The model precisely predicted the response of the three crops to the different N management strategies. Grain yields, simulated aboveground biomass productions and fertiliser N recoveries closely matched field observations (Table 6-2 and Table 6-3). DAYCENT however tended to overestimate grain production in the low-N input treatments of the two summer crops, i.e. CNT in maize and L0 and G0 in sorghum. Field observations showed that the elevated N requirements of these two crops led to a heavier reliance on fertiliser N to achieve maximum yield potential (Chapter 5). As a result, observed maize and sorghum crop productions were severely affected by below-optimal N inputs. The decline of maize and sorghum harvest indexes at decreasing fertiliser N rates was however not reproduced by the model, which simulated constant harvest indexes regardless of the N stress of the crop. These results indicate that simulated crop physiology is not optimal in DAYCENT and that improvements are needed to correctly predict plant growth dynamics under varying N stress conditions.

Overall, the model validation highlighted some shortcomings in DAYCENT ability to simulate the timing of N_2O emissions pulses and reproduce crop response to elevated N stress. However, cumulative N_2O losses, crop N uptake and yields were predicted correctly when fertiliser N rates did not cause excessive N stress to the crop. The parameterisation obtained could therefore be used to accurately evaluate different N management strategies aimed at supplying optimal N levels to subtropical cereal cropping systems.

6.4.2 Scenarios and best N management practices

Simulations highlighted that N losses during the three cropping seasons tended to be lower compared to cereal systems conducted under different environmental conditions (Van Groenigen *et al.*, 2010; Liu *et al.*, 2011; Hu *et al.*, 2013). This was essentially due to the physical and chemical properties of the Oxisol used in this study. The high clay content of the soil, constant through the entire profile, reduced the water infiltration rates also during the intense rain events occurred during the two summer seasons (Figure 6-1). The moderate soil permeability limited NO_3^- leaching and maintained the majority of the N in the rooting zone, enabling in this way a wider window of opportunity for the plants to adsorb the N supplied with fertilisation. This dynamic was observed in the field using ^{15}N tracer techniques and was correctly replicated by the model.

On the other hand, the permeability of the soil was sufficient to avoid prolonged periods of saturation of the soil profile following high rainfall events. Denitrification could therefore not go to completion and only moderate quantities of N_2 were lost after significant rain events (Table 6-4). Moreover, denitrification was limited by the relatively low amounts of soil C, a feature typical of intensively cropped Oxisols (Bell *et al.*, 1995). As a result, the 15-year mean N_2O emission factors (corrected for background emissions) ranged from a minimum of 0.08% (DMPP -20% in wheat) to a maximum of 0.78% (CONV +20% in maize, Table 6-4), and on average were substantially lower than the default values of 1% of applied N suggested by De Klein *et al.* (2006).

DMPP urea

The simulation of different N management scenarios indicated however that there is significant scope for limiting N_2O losses in these agroecosystems, especially in summer. The warm and humid soil conditions of this season, associated with the higher N fertiliser rates applied to summer crops, were conducive for substantially greater nitrification and denitrification rates compared to winter. Among the N management strategies tested, the application of DMPP urea was the most effective in minimising N_2O emission factors during a summer crop (Table 6-4).

On average, side dressing maize with high amounts of conventional urea led to short periods of asynchrony between plant N uptake and N supply in the top soil. During the investigated period soil conditions at side dressing were typically warm and moist, resulting in rapid nitrification of the NH_4^+-N applied. At this stage of crop development the crop root systems were however not sufficiently developed to effectively acquire all available NO_3^-, leading to temporary build-ups of NO_3^- levels in the top soil (i.e. where urea was banded). The increased concentrations of soil NO_3^- usually coincided with elevated soil moisture levels caused by intense rainfall events, and resulted in conditions highly conducive for denitrification and therefore for elevated N_2O emissions.

Compared to conventional urea, the slower nitrification rates of DMPP urea enabled to better match the NO_3^- released by the fertiliser with plant N uptake, resulting in almost no accumulation of NO_3^- in the top soil and therefore limiting denitrification. Consequently, the N_2O emissions factors and N_2O emission intensities of the DMPP treatments in maize were less than a third compared to those in CONV (Table 6-4).

However, the reduction of cumulative N losses simulated for DMPP urea was not sufficient to increase yields compared to conventional urea, even in the +20% treatment. Augmenting the application rate of urea by 20% (total N rate: 190 kg N ha^{-1}) was likely to result in substantial N losses that would have prevented to achieve maximum yield potential. Cumulative N losses in the CONV treatment were instead limited by soil properties and grain yields in CONV+20% were similar to DMPP+20% (Table 6-4).

In fact, the enhanced synchronicity of DMPP urea compared to conventional urea was only temporary and limited to the top soil. Deep NO_3^- leaching events after top dressing with conventional urea were prevented by the high clay content of the Oxisol, while the soil C content and the short-lived periods of soil saturation after the summer rainfall events were not sufficient for denitrification to go to completion and result in elevated N_2 losses (Table 6-4). As a result, applying N as conventional urea led to temporary accumulations of NO_3^- in the top soil (and therefore to higher N_2O emissions), but on average the majority of fertiliser N remained in the rooting zone.

These observations support the results obtained by Abalos *et al.* (2014), whose extensive meta-analysis across cropping systems evaluated the effectiveness of different nitrification inhibitors - including DMPP - in increasing crop N uptake and productivity. After examining a total of 27 studies and 160 observations on crop productivity and 21 studies with 94 observations on crop N uptake, the analysis found little or no effects on crop yields when nitrification inhibitors were applied on fine-textured soils. The reason for this inefficiency was identified in the limited susceptibility of these soils to NO_3^- leaching and N_2 losses, confirming that nitrification inhibitors have little scope to improve productivity in Oxisols.

Legume phase in a cereal-based crop rotation

The introduction of a legume pasture phase in a cereal-based crop rotation showed multiple environmental and agronomic advantages. Planting sorghum shortly after incorporating the legume pasture ensured the synchronicity between the N uptake of the cereal crop and the mineral N progressively released by the decomposition of the legume residues. This practice avoided the accumulation of relevant amounts of N in the soil that would have been available to nitrifying and denitrifying microorganisms, and simulated N_2O emissions were primarily a function of the N fertiliser rate applied. Decreasing the synthetic N rates applied to sorghum in the legume cropping history led therefore to substantial reductions of N_2O losses and emission factors were abated on average by 20% compared to the grass cropping history (Table 6-4). These results are consistent with what reported for subtropical cropping systems by Schwenke *et al.* (2015), who observed that the slow release of legume-derived N can increase the synchronicity with the demand of the following crop, leading to substantial reductions of N_2O emissions compared to synthetic N.

In particular, this strategy enabled lowering the amount of fertiliser N side dressed to the summer crop, the occasion when the highest quantities of annual synthetic N are applied. Build-up of high amounts of NO_3^- in the soil following fertilisation was therefore limited and fertiliser N was used more efficiently by the plants. These results confirm what reported in a simulation study by Huth *et al.* (2010), who reported that split application of smaller amounts of synthetic N can decrease average N_2O emissions by at least 15%.

Although not sufficient to fully meet the crop N demand, the incorporation of legume residues provided enough readily available N to support sorghum growth. The cereal crop responded positively to the N supplied by the legume residues and the higher soil N reserve in the legume cropping history decreased the reliance of the cereal crop on synthetic N fertiliser. Reducing the fertiliser N rate by 20% in the legume cropping history led to a 7% decline in sorghum yield, while the same N reduction in the a grass cropping history caused a 12% yield decrement. As a result, even when the fertiliser N rate was reduced by 20%, yields in the legume cropping history were comparable to those in the G100 and G+20% treatments (Table 6-4). Conversely, sorghum in the grass cropping history was highly reliant on synthetic N fertiliser and yields in G-20% were significantly lower than in G+20%. Similar results were obtained by Huth *et al.* (2010), who reported a 34% reduction in the amount of fertiliser N required by cereal crops when grown in rotation with legumes.

The results of this study also indicate that the presence of a legume phase in a cereal-based crop rotation reduces the risk of failing to achieve maximum yield potential due to an insufficient application of synthetic N. This strategy provides more flexibility to the farmer in terms of timing and rate of fertiliser application, especially in rainfed cropping systems. The mineralisation of legume residues can in fact supply enough N during the initial stages of crop growth, enabling the famer to modulate the synthetic N input applied at side dressing depending on seasonal weather conditions and therefore the potential yield achievable. Collectively, model simulations suggest that introducing legumes in subtropical grain-based cropping systems reduces the N_2O emission intensity of the cereal phase by 30% while sustaining the maximum yield potential of the cereal crop.

6.5 Conclusions

Even though these results are influenced by the soil and climatic conditions of the site used for the validation of the model, they provide an insight on N fertiliser dynamics and N_2O losses that could be valid for other subtropical cereal-based cropping systems on Oxisols.

Overall, simulations indicated that nitrification inhibitors can be more effective than legumes to reduce N_2O emissions during the cereal cropping phase. The use nitrification inhibitors however increases the fertilisation costs compared to conventional urea and in this study the higher costs of this practice were not compensated through increases in grain yield. The results of this study indicate therefore that in these agroecosystems the use of nitrification inhibitors to reduce N_2O emissions cannot be regarded as an economically viable standard farming practice unless governmental incentive policies are established.

On the other hand, the chances of significant N losses in these agroecosystems are limited by the moderate permeability and relatively low C content of the Oxisols. Consequently, synchronicity between fertiliser N supply and plant uptake can be achieved with conventional urea when applied at low rates. Limiting the application rates of synthetic fertiliser N is therefore the most feasible strategy to reduce N_2O losses in Oxisols.

Introducing legumes in cereal-based crop rotations reduced the reliance on fertiliser N of the cereal crop and therefore limited synthetic N rates. The mineralisation of legume residues provided sufficient N to support crop development during the early phenological stages, limiting fertiliser N requirement to the amounts necessary to attain maximum yield potential. This strategy reduced the chances of high amounts of mineral N accumulating in the top soil and therefore diminished N_2O emissions due to fertilisation. This simulation study therefore indicates that introducing legumes in cereal-based cropping systems is the most agronomically viable and environmentally sustainable N management strategy to support future intensification of subtropical cereal production in Oxisols. Further research is however advocated to confirm the efficacy of this N management strategy on different types of Oxisols under different subtropical conditions.

This study also highlighted some shortcomings in the crop and soil submodels of DAYCENT. The correction of these limitations would significantly improve the potential of the model in assessing the environmental and agronomic implications of different N management practices.

Chapter 7: Discussion and Conclusions

7.1 Overall study findings

Mitigating climate change and achieving food security are two of the key challenges of the twenty-first century. By 2050 the world's population is forecast to be over a third larger than at present (UNFPA, 2011) and cereal demand is predicted to increase by 60% (FAO, 2009). Pronounced intensification of cereal production is expected to take place in Oxisol-dominated tropical and subtropical regions (Smith *et al.*, 2007), identifying the need for more N to be supplied to these agroecosystems (Fageria and Baligar, 2008). Boosting food production though an increased use of synthetic N fertilisers will however result in sharp increases in greenhouse gas emissions, especially N_2O (FAO, 2010; Foley *et al.*, 2011; Tilman *et al.*, 2011). It is therefore critical to identify alternative N management strategies aimed at supporting future intensification of tropical and subtropical agricultural systems without promoting an increase of N_2O emissions from these agroecosystems.

A unique dataset of high temporal-frequency N_2O observations and N recovery data from multiple cropping seasons, crop rotations and N fertiliser strategies was gathered in the subtropics using a fully automated greenhouse gas measuring system, ^{15}N-tracer techniques and a process-based biogeochemical model. The aim was to define profitable, agronomically viable and environmentally sustainable N management strategies to support future intensification of cereal production on subtropical Oxisols. This study also aimed to improve the current understanding of environmental factors influencing N_2O emissions in fertilised Oxisols and to assess the magnitude and main pathways of fertiliser N losses that limit crop yields in these agroecosystems.

The major findings and conclusions from this study are presented in this section against each of the research objectives. An analysis of the environmental, agronomic and economic implications resulting from this study follows along with the recommendations for further research. The concluding statement of this research is thus presented.

Objective 1

Research objective: Evaluate the use of urea coated with a nitrification inhibitor to limit N_2O emissions and increase grain yields compared to conventional urea.

Hypotheses: i) nitrification inhibitors decrease N_2O emissions both directly, via slowing the nitrification rates, and indirectly, by reducing the amount of NO_3^- available to denitrifying microorganisms; ii) by reducing N movements beyond the rooting zone, nitrification inhibitors can improve the synchrony between fertiliser-derived NO_3^- and plant uptake, and therefore increase yields compared to conventional urea.

Applying urea coated with the DMPP nitrification inhibitor was successful in reducing N_2O emissions only in the summer crop (maize), when conditions were conducive to high N_2O emissions, while no differences with conventional urea were observed in the winter crop (wheat). In winter, the activity of nitrifying and denitrifying microorganisms was limited by the relatively low soil temperature and water content. These conditions are particularly adverse for denitrification, the process that can be the main pathway for large N_2O losses (Robertson and Groffman, 2007). As a result, N_2O emission rates in winter were naturally inhibited by the soil conditions and there was no scope for DMPP to reduce the emissions any further.

In contrast, the warm and humid soil conditions of the summer season were more conducive for nitrification and denitrification. As a result, N_2O emissions following the application of 130 kg of conventional urea (60 kg N ha^{-1}) in the summer crop were fivefold those measured after applying the same rate of conventional urea in the winter crop (Paper 1).

N_2O emissions in summer were also higher due to the asynchrony between the N released by conventional urea and the plant N uptake, particularly at the highest N rate (120 kg N ha^{-1}). When maize was side dressed with conventional urea, the summer soil conditions promoted rapid nitrification of the applied NH_4^+-N, but at this physiological stage (V10) the crop root system was not sufficiently developed to acquire all N present in the soil. As measured in the field (Paper 1) and confirmed by model simulations (Paper 4), this asynchrony resulted in a build-up of NO_3^- levels in the top soil (i.e. where urea was banded). This increase in the concentration of soil NO_3^- coincided with elevated soil moisture levels caused by intense rainfall events, and resulted in conditions highly conducive for denitrification.

The occurrence of significant summer rainfall events shortly after the side dressing of N fertiliser is typical in subtropical regions and was frequently observed during the fifteen years (1999-2013) of local climate data used for the simulation of N management scenarios (Paper 4). This pattern indicates that the conditions observed in the field experiment were representative of those usually occurring at these latitudes.

Slower nitrification rates achieved with DMPP urea enabled a better synchrony between the plant uptake and the NO_3^- derived from the fertiliser (Paper 3), and enabled a reduction of NO_3^- in the top soil during summer cropping. With less NO_3^- available for denitrification in the top soil, N_2O emissions in maize were abated (on average) by 65% compared to the same N rate with conventional urea (Paper 1 and Paper 4).

The enhanced synchrony between N availability and plant uptake afforded by DMPP urea compared to conventional urea was however confined to the top soil - where the fertiliser was banded- and did not influence the overall crop N uptake. As established in Paper 3 and Paper 4, the losses of NO_3^- via leaching were minimal in the heavy clay soil. In addition, the periods of soil saturation after the summer rainfall events were not prolonged, limiting N_2 losses from both conventional and DMPP urea. Applying N as conventional urea led therefore to a temporary accumulation of NO_3^- in the top soil, but the majority of fertiliser N remained in the rooting zone. This resulted in plants fertilised with conventional urea having an adequate window of opportunity to take-up the fertiliser N and, as reported in Paper 3, limited amounts of fertiliser N were lost from the soil-plant system. DMPP had therefore no significant scope to increase the overall ability of the plant to acquire the applied N, and no gain in yields was observed at any applied N rate (Paper 1 and Paper 4).

These observations support the results obtained by Abalos *et al.* (2014), whose extensive meta-analysis across cropping systems evaluated the effectiveness of different nitrification inhibitors - including DMPP - in increasing RE_{fN} and crop productivity. After examining a total of 27 studies and 160 observations on crop productivity and 21 studies with 94 observations on RE_{fN}, the analysis found little or no effects on crop yields when nitrification inhibitors were applied on fine-textured soils. As in the present study (Paper 1 and 4), Abalos *et al.* (2014) identified the reason for this inefficiency in the limited susceptibility of these soils to NO_3^- leaching, concluding that nitrification inhibitors have little scope to improve RE_{fN} in clay soils.

Objective 2

Research objective: Evaluate whether the introduction of a legume in a cereal-based crop rotation can reduce the reliance of cereal crops on synthetic N fertilisers and minimise N_2O emissions during the cereal cropping phase.

Hypotheses: i) the N mineralised from legume residues can substantially reduce the synthetic N input required by the following cereal crop and therefore limit the “direct” N_2O emissions due to mineral fertilisation, and ii) N_2O losses due to the mineralisation of legume residues can be minimised via synchronising the release of N derived from the residues with the N demand of the subsequent cereal crop.

Introducing a legume in a cereal-based crop rotation offered the double advantage of supplying substantial amounts of N to the following cereal crop while reducing overall N_2O emissions during the cereal season. This condition was attained because in this study the N supplied by both sources -legume residues and synthetic fertiliser- was synchronised with crop demand.

Synchronising N supply with N demand can be technically challenging when, as with the mineralisation of legume residues, N release is mediated by microbial processes. In fact, low levels of synchrony have often been reported in legume-cereal cropping systems (Wagner-Riddle *et al.*, 1997; Wagner-Riddle and Thurtell, 1998; Fillery, 2001; Pappa *et al.*, 2011), when the field was left fallow for long periods after the end of the legume phase, allowing for the accumulation of large amounts of mineral N in the soil at a time when there was no crop to use it (Jensen *et al.*, 2012). In this study the accumulation of mineral N in the top soil was avoided by minimising the period between the incorporation of the legume residues and the planting of the cereal crop (approximately three weeks). A key factor in limiting mineral N accumulation during this time was the relatively dry soil conditions, which slowed the decomposition of the legume residues. Wetter soil conditions during the fallow period would have in fact accelerated the mineralisation of the legume residues and created optimal circumstances for nitrifying and denitrifying bacteria, resulting therefore in higher N_2O losses.

In both wheat and sorghum the gradual N release from the mineralisation of legume residues (mungbean and sulla, respectively) provided a consistent flow of N that was within the uptake capability of the crop. Importantly, high levels of synchrony between the N released from legume residues and the uptake of the following crop were achieved during both the winter (wheat) and summer (sorghum) crops.

Environmental factors such soil moisture and soil temperature play pivotal roles in influencing the decomposition of the residues and different patterns of mineralisation can be expected during winter and summer. However, the environmental factors that regulate the decomposition of the residues are the same that influence the plant nutrient demand of the following crop, enabling therefore to attain high levels of synchrony under different soil moisture and temperature conditions (Myers *et al.*, 1994; Crews and Peoples, 2005).

Although not sufficient to fully meet the crop N demand (Paper 1 and Paper 2), the N released by the legume residues provided a substantial N supply to the cereal crops and reduced the crop reliance on synthetic fertiliser compared to crops planted after a non-leguminous crop (Paper 3). The diminished reliance on synthetic N inputs was confirmed by model simulations (Paper 4), which established that grain yields in legume-cereal cropping systems declined less rapidly than in cereal-cereal or grass-cereal systems when fertiliser N rates were reduced.

The decreased reliance on synthetic N inputs allowed for reducing fertiliser N rates to the levels necessary to reach maximum yield potential. In particular, this strategy enabled lowering the amount of fertiliser N side dressed to the summer crop, the occasion when the highest quantities of annual synthetic N are applied. Build-up of high amounts of NO_3^- in the soil following fertilisation was therefore limited and fertiliser N was used more efficiently by the plants. As highlighted in Paper 3, the recovery of fertiliser N in the plant was significantly higher in crops that had been fertilised with lower rates of synthetic N. Accordingly, in these treatments the amount of synthetic N left in the soil after the cereal cropping cycle was substantially lower than where crops were fertilised with elevated N rates.

Overall, the gradual mineralisation of legume residues promoted the fertiliser N recovery in the crop and N_2O losses were mainly caused by temporary increases in soil NO_3^- levels due to fertiliser application (Paper 2). Cumulative N_2O emissions increased in direct response to the rate of N fertiliser applied, with cropping history having no significant effect as confirmed by model simulations (Paper 4).

A reduction in N_2O emissions from the legume-cereal cropping systems was also due to the chemical composition of the legume residues. The low C:N ratio of the legume tissues enhanced the degradation of the residues, leaving little labile C in the soil during the cereal cropping season and reducing the potential activity of heterotrophic microorganisms, such as those responsible for denitrification (Elmi *et al.*, 2003; Yao *et al.*, 2009). As a result, although soil N concentrations after the termination of a legume phase were higher than after a non-leguminous crop, N_2O emission pulses following rainfall events were significantly lower in the legume cropping history (Paper 3). These findings support the results reported by Sanz-Cobena *et al.* (2014), who observed higher N_2O emissions from maize after the incorporation of barley, compared to the same crop after the incorporation of a vetch pasture.

Overall, the results of this study show that when legume residues are managed correctly they can play a pivotal role in improving the N synchrony and reducing N_2O emissions in high-yielding cereal-based agroecosystems.

Objective 3

Research objective: Assess the sustainability of the N management practices investigated in Objectives 1 and 2 under a broader spectrum of fertiliser N rates and environmental conditions.

Hypotheses: A simulation approach can be used to i) assess the validity and robustness of the hypotheses underlying the previous two objectives, and ii) improve the understanding of the environmental factors driving N_2O emissions and crop productivity in subtropical cereal cropping systems.

Models are useful tools for evaluating the hypotheses advanced in this study as well as to explain the N_2O emissions and crop growth patterns observed during the field experiments. Simulating the application of conventional and DMPP urea at different N rates and under diverse seasonal conditions enabled to establish that the chemo-physical characteristics of the Oxisol, and not the fertiliser type, were the main factor influencing synchronicity between N demand and fertiliser supply. Models simulation confirmed that applying DMPP urea to inhibit nitrification in these soils is effective in reducing N_2O emissions, which however represented only a fraction of the overall N losses (inclusive of N_2O and N_2 emissions, and NO_3^- leaching). Critically, DMPP urea did not substantially decrease N_2 emissions and NO_3^- leaching compared to conventional urea and therefore did not increase yields (Paper 4).

Substituting a proportion of the N requirements of the crop with N mineralised from the legume residues proved to be the most effective strategy to reduce N_2O emissions and support cereal productivity. Legume residues supplied substantial amounts of N to crops but did not lead to sharp increases in soil N levels that would have stimulated nitrification and denitrification (Paper 4). Seasonal N_2O emissions were directly related to the amount of fertiliser N applied, not of the crop rotation. Consequently, proportional reductions in N_2O emissions were obtained when fertiliser N rates could be decreased as a result of the N supplied by the legumes.

The use of model simulations also increased the overall understanding of N dynamics in subtropical Oxisols. The large dataset established in this study enabled the DAYCENT model to be calibrated for N_2O losses, plant N uptake and mineral N kinetics for the top 30 cm of these soils. Additionally, it was possible to define N losses via deep leaching by reconciling soil water content data and the recovery of fertiliser N in the lower layers of the soil profile. This technique enabled to perform a N mass balance and therefore to accurately estimate N_2 emissions from these agroecosystems.

The magnitude of N_2 losses from soils and the related N_2:N_2O ratio are largely unknown due to difficulties in measuring N_2 against a high atmospheric background (Dannenmann *et al.*, 2008; Mulvaney, 2008). N_2 losses differ greatly across agroecosystems depending on soil chemo-physical properties, fertilisation and rainfall regime (Weier *et al.*, 1993). As a result, studies on cereal cropping systems have reported N_2 emissions varying from 1% to 15% of applied N depending on environmental conditions (Weier, 1994; Bronson and Fillery, 1998; Smil, 1999; Cai *et al.*, 2002a; Janzen *et al.*, 2003). In addition to the difficulties of obtaining N_2 measurements, the uncertainty of estimating N_2 losses with DAYCENT is due to limited dataset used for developing the denitrification submodel. The denitrification equations in the DAYCENT model were defined using a series of intact core incubations (Weier *et al.*, 1993) and field measurements (Mosier *et al.*, 1996) that related C, NO_3^- and WFPS dynamics to N_2O and N_2 fluxes (Parton *et al.*, 1996). Critically, none of these experiments was conducted in Oxisols or under subtropical conditions, and no studies so far have assessed N_2 emissions from these agro-environments using DAYCENT.

The dataset gathered in this study allowed for a rigorous calibration of the DAYCENT model for subtropical cereal cropping systems in Oxisols, and therefore for the estimation of N losses due to denitrification. Even though not supported by direct N_2 measurements, model simulations enabled to estimate fertiliser-derived N_2 losses during the three cropping seasons. N_2 losses estimated in this study for conventional urea varied between averages of 1.3% of applied synthetic N for the winter season (wheat) and 4.6% for the summer seasons (maize and sorghum). In line with the results reported in Paper 3, simulation showed that N_2 losses tend to be limited in Oxisols and highlighted that average N_2:N_2O ratios of 8.5 could be adopted for estimating denitrification losses in subtropical Oxisols. These results confirmed the analysis conducted by Xu *et al.* (2013), who in an extensive review indicated that denitrification rates in acidic tropical and subtropical soils can be lower than those in their temperate counterparts. In fact, N_2 losses tend to be limited in Oxisols due to the relatively low C content of these soils, which may not be enough to support denitrification (Xu and Cai, 2007; Wang and Cai, 2008). The low soil pH of these soils is also likely to negatively affect the growth and activity of most denitrifiers, which optimal pH ranges from 6 to 8 (Aulakh *et al.*, 2001). Moreover, the permeability of Oxisols is usually sufficient to avoid prolonged periods of saturation of the soil profile following high rainfall events, resulting in low gas emission due to denitrification (Pu *et al.*, 2002; Xu *et al.*, 2013).

Overall, the use of model simulations provided a unique insight of gaseous N emissions in Oxisols, establishing that fertiliser N losses in subtropical Oxisols are limited by their intrinsic chemo-physical properties. This approach was also pivotal for determining that the introduction of legumes in these cropping systems is the best strategy to support crop production while reducing overall N_2O emissions during the cereal season. The simulation of N_2 emissions obtained in this study was however performed without the possibility of comparing modelled results with field measurements. Further research measuring N_2 losses from cropped Oxisols is therefore advocated to validate the estimates presented in this study.

7.2 Economic implications

Identifying environmentally and agronomically sound N management strategies is essential when promoting the sustainable intensification of future subtropical cereal cropping systems. Guaranteeing their widespread adoption means these strategies need to be profitable for the farmer and adoptable both in low- and high-income cropping systems. The key economic implications of the two N management strategies assessed in this study are examined here, with a clear focus on their profitability at farm-scale level.

Evaluating the specific economic implications of these N management strategies in every country with cereal cropping systems in Oxisols is extremely complex and beyond the scope of this study. The commodity prices used for this analysis refer therefore to Australian conditions, and have been calculated averaging the values obtained from the FAOSTAT database for the period 2008-2012.

DMPP urea

The application of DMPP urea in this study was the most effective strategy to abate N_2O emissions during the summer cereal crop but proved to be uneconomical at farm-scale. Urea coated with DMPP is 30% more expensive than conventional urea (Chapter 3.3.2) and the first investigation showed that top dressing the summer cereal crop (maize) with DMPP urea increases the fertilisation costs by approximately USD 50 ha^{-1}. The additional cost of using DMPP urea however was not compensated through increases in grain yield, meaning that in these agroecosystems the use of nitrification inhibitors cannot be regarded as an economically viable N management from the farmer’s perspective.

Governments or political institutions aiming to reduce N_2O emissions from cereal cropping systems could foster the use of N fertilisers coated with nitrification inhibitors by establishing subsidies covering the additional cost of these fertilisers or introducing emission trading schemes. In this study, top dressing the summer crop with DMPP urea reduced N_2O emissions by 1.1 kg N_2O-N ha^{-1} compared to conventional urea (Table 3-3), equivalent to approximately 0.33 Mg CO_2 ha^{-1}. The hypothetical carbon price necessary to refund farmers applying DMPP urea would therefore correspond to 150 USD Mg CO_2^{-1}, a value largely exceeding the 8 USD Mg CO_2^{-1} currently adopted by the European Union Emission Trading System (London Stock Exchange, accessed November 2014).

Even though in this specific study the use of DMPP urea increased fertilisation costs by 30%, a detailed study assessing various nitrification inhibitors (Weiske, 2006) suggested 10% as the average cost increase for nitrification inhibitors. Assuming a 10% cost increase however, the use of the nitrification inhibitor at top dressing would increase fertilisation costs by approximately 16 USD ha^{-1}, requiring a carbon price of 47 USD Mg CO_2^{-1}. These results indicate that the use of nitrification inhibitors to decrease N_2O emissions in subtropical Oxisols is not a profitable practice unless heavily subsidised and therefore cannot be regarded as a feasible strategy to support a sustainable intensification of these cropping systems.

Legume phase in a cereal-based crop rotation

The introduction of legume crops in a cereal-based crop rotation offered the dual advantage of reducing overall N_2O emissions while reducing fertilisation inputs, and therefore costs. The economic implications of introducing legumes in cereal cropping systems can differ substantially and depend on the characteristics of the cropping system (Bohlool *et al.*, 1992; Campbell *et al.*, 1992; Bell *et al.*, 2012; Sadeghpour *et al.*, 2013; Kirkegaard *et al.*, 2014). For example, the gross annual income of cereal cropping systems incorporating a legume phase can be increased or decreased compared to cereal monocultures depending on the legume crop (grain, forage or tree), the length of the legume phase (mono- or multi-seasonal), the original cereal-based cropping systems (mono- or double cereal cropping) and whether the legume replaces a cereal crop, a fallow phase or is intercropped with the cereal.

Generalising the profitability of introducing a legume phase in a cereal cropping system is not feasible given the large number of variables and the analysis presented in this section focuses on the N management tested in this study. This economic analysis assesses the introduction of a forage legume crop in a cereal-based crop rotation and does not consider the implications of using more profitable legumes crops, such as grain legumes. Importantly, this analysis does not cover the indirect economic benefits provided by the presence of legumes in the crop rotation, such as increased native soil fertility and disruption of pest and disease lifecycles, two factors that significantly influence the long-term productivity of a cropping system (Giller and Cadisch, 1995; Rochester *et al.*, 2001).

In this study the winter legume ley pasture was green-manured and the decomposition of the legume residues provided approximately 36 kg N ha^{-1} to the subsequent summer cereal (Chapter 4.3.3). This N supply lowered the fertiliser N requirements of the cereal crop to the levels necessary to reach maximum yield potential. Specifically, this practice enabled a reduction in the applied fertiliser rate by almost 80 kg urea ha^{-1} compared to a summer cereal not in rotation with a legume pasture.

In a crop rotation where the summer cereal is preceded by a fallow phase (cereal mono-cropping system), replacing the fallow phase with a legume pasture for green-manuring would reduce the annual N fertilisation costs by 47 USD ha^{-1} and therefore increase the annual net income. In the case where the legume pasture was harvested for hay, the legume phase would generate a gross income of approximately 400 USD ha^{-1} (assuming a legume hay price of 200 USD Mg^{-1} and an average hay yield of 2 Mg grain ha^{-1}). Additionally, the incorporation of below ground biomass would provide approximately 15 kg N ha^{-1}, resulting in a fertiliser cost reduction of 20 USD ha^{-1} during the following cereal crop. This practice would therefore increase the annual net income by 390 USD ha^{-1} compared to a cereal mono-cropping system, even while accounting for the additional costs due to the purchase of legume seeds, machinery use and labour,

On the other hand, compared to a double cropping system (winter cereal-summer cereal crop rotation), growing a legume pasture for green-manuring would preclude the possibility of growing a winter cereal. Assuming a grain price of 230 USD Mg^{-1} (FAOSTAT website, accessed October 2014) for an average winter cereal yielding 5 Mg grain ha^{-1} (Table 3-3), replacing the winter cereal with a legume crop for green manuring would lead to a net income reduction of circa 1150 USD ha^{-1} per annum. In the case the legume pasture was harvested for hay, replacing the winter cereal with a legume pasture would result in an overall income reduction of circa 730 USD ha^{-1}, indicating that under no hay management scenario replacing a cereal crop with a forage legume can be a profitable option.

Introducing a legume crops in cereal crop rotations could potentially entitle farmers to greenhouse gas emission credits since an extensive review by Jensen *et al.* (2012) highlighted that N_2O emissions during the legume growing season do not differ substantially from unplanted or non-fertilised soils and are significantly lower than during a fertilised winter cereal. The economic implications of this aspect in terms of emissions trading are however not included here since no N_2O measurements were conducted during the legume pasture phase in this study.

Overall, this analysis highlights that the use of nitrification inhibitors cannot be considered an economically feasible strategy to support cereal production while limiting N_2O emissions in subtropical Oxisols. Introducing a legume pasture phase in a cereal crop rotation instead can be a profitable N management practice, but only when adopted in a cereal mono-cropping system. This result is significant since cereal mono-cropping is a common practice in many subtropical regions, especially in rainfed cropping systems (Peter and Runge-Metzger, 1994; Herrmann *et al.*, 2014; Wratten *et al.*, 2014).

7.3 Recommendations for future research

This study showed that reducing nitrification rates in subtropical Oxisols does not improve the agronomic efficiency of applied N fertiliser. On the other hand, the introduction of a legume phase in a cereal-based crop rotation exhibited multiple environmental and agronomic advantages, highlighting the importance of achieving synchrony between soil N supply and the N demand of the following crop via the incorporation of legume residues in a cereal-based crop rotation.

Conducted on one single Oxisol subclass and having tested only one type of legume, a forage pasture, this research lays the foundation for further research to investigate how synchrony with the subsequent cereal crop can be achieved in different sub-classes of Oxisols. Importantly, such research needs to assess the agronomic, economic and environmental implication of using diverse leguminous corps (forages and grains) and cropping practices (crop rotations and intercropping) to maximise food production and limit N_2O emissions. In particular, efforts should aim to identify which constituents of the legume tissues (e.g. lignin, polyphenols, soluble C and N compounds) affect residue mineralisation, and therefore the N release and its availability to plants and the soil microbial pool (Palm *et al.*, 2001; Bolger *et al.*, 2003; Crews and Peoples, 2005). Research studies should simultaneously investigate how mineralisation patterns during the post-harvest period can be manipulated by choosing specific legume species or combining different legume crops.

However, mineralisation patterns could be affected by site-specific environmental conditions, while some crop varieties might not be fit for cultivation in certain regions. Research will therefore need to address these constraints by developing profitable grain or forage legume species optimised for different seasons, cropping regions and climates. Such results will reduce the uncertainties involved in the use of legumes as a source of N and provide subtropical farmers with a reliable N management strategy to bolster cereal production while limiting N_2O emission rates from these agroecosystems.

Additionally, the economic analysis showed that in double cereal cropping systems replacing a cereal with a non-edible legume crop (e.g. forage) can reduce the overall food production and profit. Research is necessary therefore to address this problem by investigating how grain legumes or legume management practices (crop rotations and intercropping) can maximise food production while limiting N_2O emissions in these agroecosystems.

The model simulations conducted within this study suggested that N_2 emissions in subtropical Oxisols can be up to nine times higher than those of N_2O. Future field research should therefore aim to corroborate these findings by combining automated greenhouse gas measuring systems and mass spectrometry techniques to precisely measure N_2 losses in these agroecosystems. Such results will further increase the current understanding of N dynamics in subtropical Oxisols and determine the influence of N_2 emissions on the agronomic efficiency of the tested N management strategies.

Finally, this study highlighted that simulated crop physiology is not optimal in DAYCENT and that improvements are needed to correctly predict plant growth dynamics under varying N stress conditions. Moreover, the data analysed in this study suggest that algorithms regulating microbial activity and gas diffusivity of N_2O produced at different depths should be incorporated in the model. An enhanced representation of soil microbial activity would also allow DAYCENT to reproduce the decline in the DMPP inhibitory efficiency observed under winter conditions, so to avoid the use of different inhibition factors for fertilizers applied to winter and summer crops. Overall, the correction of these limitations would significantly improve the potential of the model in assessing the environmental and agronomic implications of different N management practices.

7.4 Conclusions

This is the first study integrating high temporal frequency N_2O measurements, fertiliser N recovery observations, and model simulations to assess the environmental and agronomic implications of using urea coated with the DMPP nitrification inhibitor and reintroducing legumes in crop rotations. The results indicate that the chances of significant N losses in subtropical agroecosystems in Oxisols are limited by the moderate permeability and relatively low C content of these soils. Significantly, there is scope to improve the RE_{fN} and reduce N_2O emissions from these cropping systems, especially in summer. The high N fertiliser rates usually applied to summer crops, associated with the hot and humid conditions of this season, can indeed lead to periods of temporary asynchrony between fertiliser N supply and crop capacity to use it. As a result, nitrification and denitrification rates in summer can be up to fivefold those occurring in winter. Strategies to secure subtropical cereal production without increasing N_2O emissions should therefore focus on N fertiliser management strategies for summer crops.

DMPP was effective in delaying nitrification in the top soil, reducing N_2O losses via nitrification and denitrification. Given the chemo-physical characteristics of the soil however, DMPP had no scope for improving the fertiliser N recovery in the crop and therefore did not increase grain yields. The lack of yield increase and the higher cost of urea coated with nitrification inhibitors reduce the profitability of this fertilisation practice, highlighting that the use of nitrification inhibitors cannot be regarded as an economically viable N management strategy for the sustainable intensification of subtropical cereal cropping systems.

Soil properties and fertiliser N rates were the main factors influencing fertiliser N recovery in the soil-plant system. The lower N recoveries observed in crops when elevated amounts of synthetic N were applied indicate that limiting N rates in Oxisols is the most efficient strategy to increase the recovery efficiency of fertiliser N in the crop (RE_{fN}) and therefore reduce the amount of soil N available to nitrifying and denitrifying microorganisms.

Introducing legumes in cereal-based crop rotations decreases the reliance of the cereal crop phase on N fertiliser. When synchronisation with the cereal N demand is achieved, the mineralisation of legume residues can provide sufficient N to support crop development during the early stages of crop development, limiting fertiliser N requirement to the amounts necessary to attain maximum yield potential. This strategy reduces the chances of high amounts of mineral N to accumulate in the top soil and therefore lowers N_2O emissions due to fertiliser application. Conditions can however be highly conducive for elevated N_2O emissions when a soil is left fallow after the incorporation of fresh legume residues. The most viable strategy for reducing N_2O emissions after the termination of the legume phase and maximising the synchronicity between residue mineralisation and the cereal N demand is therefore to minimise the amount of time between incorporating the residue and planting the subsequent crop.

Reducing the fertiliser N input required by cereals in rotation with legumes provides greater flexibility for the farmers in terms of timing and rate of fertiliser application, especially in rainfed cropping systems. This strategy enables the famer to modulate the synthetic N input depending on seasonal weather conditions and reduces investment in fertiliser N at the beginning of the cropping season. This aspect is particularly significant since during the early stages of the cropping season it is not possible to predict the in-season rainfall patterns, resulting in the impossibility to determine the chances for the crop to efficiently adsorb the synthetic N applied. Critically, replacing part of the N requirements of the cereal crop with the N supplied by legume residues decreases overall fertiliser costs and can increase annual profits when adopted in a cereal mono-cropping system.

Introducing legumes in cereal-based cropping systems is the most agronomically viable and environmentally sustainable N management strategy to support future intensification of subtropical cereal production in Oxisols. Importantly, this strategy can be widely adopted in subtropical regions since it is economically accessible, requires little know-how transfer and technology investment, and can be profitable in both low- and high-input cropping systems.

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