Nitrous oxide emissions from soil in mango and banana fields:

effects of nitrogen rate, fertiliser type,

and ground cover practices

Thesis submitted by

Bronwyn Leanne Masters (B App Sci)

in June 2019

for the degree of Master of Philosophy

in the College of Science and Engineering, and

the Centre for Tropical Environmental and Sustainability Science,

James Cook University

Cairns, Queensland, Australia

This page is intentionally left blank.

Statement of Access

I, the undersigned, the author of this thesis, understand that James Cook University will make this thesis available for use within the University Library and, via the Australian Digital Theses network, for use elsewhere.

I understand that, as an unpublished work, a thesis has significant protection under the Copyright Act and I do not wish to place any further restriction to access on this work.

_____ _____

Bronwyn Masters Date

Statement on Sources

I declare that this thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from the published or unpublished work of others has been acknowledged in the text and a list of references is given.

_____ _____

Bronwyn Masters Date

Electronic Copy

I, the undersigned, author of this work, declare that the electronic copy of this thesis provided to James Cook University library is an accurate copy of the print thesis submitted, within the limits of technology available.

_____ _____

Bronwyn Masters Date

This page is intentionally left blank.

Statement on the contribution of others

Name of Assistance	Contribution	Name, Affiliations of Co-contributors
Intellectual support	Principal Supervision	Dr Paul N. Nelson (James Cook University; JCU) Dr Michael Bird (JCU) Dr John D. Armour (Dept. of Natural Resources, Mines and Energy, Queensland; DNRME)
Financial support	Research funding	Action on the Ground Round 2, Australian Department of Agriculture and Water Resources (AOTGR2-0138)
	Conference travel, accommodation and attendance - 2016 Joint Australian and New Zealand Soils Conference	Soil Science Australia student grant College of Science & Engineering (JCU) Dept. of Natural Resources, Mines and Energy, Queensland
Data Collection	Field Assistance	Nikita Tahir (DNRME) Christina Mortimore (DNRME) Anna McBeath (Dept. Agriculture and Fisheries, Queensland; DAF) Kaila Ridgway (DAF) Patrick O'Farrell (DAF)
	Laboratory Analysis (gas)	Shannon Todd (JCU) Kalu Davies (JCU)
	Laboratory Analysis (soil nutrients)	Chemistry Centre (Dept. of Environment and Science; DES)
Data Analysis	Initial assistance with statistical analysis in Genstat	Carole Wright (DAF)
	Assistance with statistical analysis in 'R'	Susannah Leahy (JCU)

This page is intentionally left blank.

Acknowledgements

I would first like to thank my supervisors: Paul Nelson, John Armour, and Michael Bird. Paul, for his guidance, advice and patience, and especially for his trust in me. John, for being such a source of wisdom, and for the many coffee meetings. Michael, for his positive approach and feedback.

I would also like to thank the organisations who funded my work, including the Australian Department of Agriculture and Water Resources (Action on the Ground Round 2) for funding the project; the Queensland Department of Natural Resources, Mines and Energy (DNRME) for in-kind support; the Graduate Research School at James Cook University for postgraduate research funding; and Soil Science Australia for a student grant.

A number of people facilitated my work and provided support at key times in my MPhil. At DNRME Nikita Tahir and Christina Mortimore were extremely dedicated and hardworking, spending countless hours in the field and back in the office collecting and processing gas and soil samples. This project simply would not have been possible without their support and positivity. I would also like to thank Anna McBeath and Kaila Ridgway for their assistance collecting samples from the South Johnstone banana trial. It was a massive effort. I also want to acknowledge the extensive effort of Shannon Todd and Kalu Davies at James Cook University, who between the two of them analysed nearly 10,000 gas samples.

I would also like to thank the farmers, Craig Buchanan and Adrian & Alfina Zugno, for participating in these farm trials. In addition, I really value the input and support from Geoff Dickinson and Patrick O'Farrell for the mango work, and Tony Pattison for the banana work.

I would also like to thank my friends and family, who gave such wonderful support and put up with all those times I said I could not come out and play.

And of course, a very special thank you to Susannah Leahy. I thought this might be some small penance for living through your PhD, but I was wrong. I, too, wouldn't have made it without you.

This page is intentionally left blank.

General Abstract

Globally, agricultural soils are the dominant source of the greenhouse gas, nitrous oxide (N_2O), and a growing body of evidence indicates that soils in tropical zones may emit disproportionately large amounts to the atmosphere. This is important as N_2O contributes approximately 6% of anthropogenically induced global warming and is also responsible for ozone depletion. These emissions primarily originate from microbial nitrification and denitrification processes in soil, which are driven by soil water content, temperature, available nitrogen (N), organic carbon (OC) and their interactions. This study investigated the effects of N fertiliser application rate and type, and ground cover, on N_2O emissions from soil in mango and banana fields in tropical northern Australia. The fertiliser types were conventional urea and two enhanced efficiency fertilisers (EEFs): urea treated with a nitrification inhibitor (3, 4-dimethylpyrazole phosphate, DMPP) and polymer sulphur-coated (PC) urea mixed with standard urea at a 40/60 ratio (in mangoes only). Ground cover treatments were bare ground versus vegetative ground cover in bananas, and bare ground versus hay mulch in mangoes. A manual chamber technique was used to measure gas emissions from three field experiments with factorial designs (randomised block, four replications of each treatment). The experiments were conducted in 1) a commercial mango orchard on a Yellow Chromosol soil at Mutchilba, 2) a commercial banana farm on a Red Ferrosol soil at East Palmerston, and 3) a banana research farm on a Brown Dermosol soil at South Johnstone.

In banana fields (Chapter 3), soil mineral N content, water content, and time since fertiliser application were the primary drivers of N_2O emissions. Low N rate treatments (12 kg N ha^{-1} mth^{-1}) had consistently lower N_2O emissions than high N rates (18 to 54 kg N ha^{-1} mth^{-1}), however overall N_2O flux was highest in all treatments when fertiliser was applied during persistently wet conditions (>68% water-filled pore space, WFPS). Urea treated with DMPP had approximately half the N_2O emissions than untreated urea on the Brown Dermosol, but did not significantly reduce emissions on the Red Ferrosol. Vegetative ground cover reduced N_2O emissions compared to bare soil during wet conditions and with higher N rates, presumably due to N uptake by the ground cover decreasing soil mineral N concentrations. In the mango orchard (Chapter 2), N_2O emissions were lower than under bananas at the other sites. The mango site soil had less mineral N, lower water holding capacity and lower OC content. N_2O emissions were not lowered by using EEFs rather than urea at application rates <25 kg N ha^{-1}. However, at a higher fertiliser application rate of 42 kg N ha^{-1}, DMPP approximately halved N_2O emissions.

Mulching also lowered N_2O emissions, however sufficient irrigation after fertiliser application to mulch is recommended to reduce potential ammonia volatilisation.

Overall, the management factors examined influenced soil mineral N, water content, temperature and possibly OC, all of which played important roles in determining total N_2O emissions in both crops. In banana fields, using lower N rates and DMPP treated urea during wet conditions will reduce N_2O losses. However, vegetative ground covers do not appear to be a reliable or consistent method of N_2O mitigation, as any reduction may be offset by the potential additional N required to compensate for plant competition and to avoid yield decline. In mangoes the most benefit would be gained from mulching, due to the reduction in N_2O and an increase in yield. However, further research is required to substantiate the N_2O reduction of hay mulch over the longer term. There appeared to be little justification for N_2O mitigation measures with EEFs in mangoes, due to generally negotiable N_2O emissions in the Yellow Chromosol, and the additional cost of EEFs. On the whole, more research is required around the mechanisms reducing the efficacy of DMPP-treated urea in Red Ferrosols and during hot conditions (35–45^{o}C). Finally, the PC urea product in this study needs to be tested in more suitable conditions that favour denitrification (higher N rate and soil water content) in order to more appropriately assess its impact on N_2O production.

Table of Contents

List of Tables

List of Figures

List of Common Acronyms

ANOVA	One-way analysis of variance
C	Carbon
CH_4	Methane
CO_2	Carbon dioxide
DCD	Dicyandiamide
DMPP	3, 4-dimethylpyrazole phosphate
DNRA	Dissimilatory nitrate reduction to ammonium, or nitrate ammonification
EC	Electrical conductivity
EEF	Enhanced efficiency fertiliser
EP	East Palmerston
GWP	Global warming potential
HN-bare	High N rate, no ground cover
HN-veg	High N rate, vegetative cover
LN-bare	Low N rate, no ground cover
LN+DMPP-bare	Low N rate with DMPP, no ground cover
LSD	Least significant difference (Fisher's 95% protected)
N	Nitrogen
NO	Nitric oxide
NOR	NO reductase
NH_3	Ammonia
NH_4^+	Ammonium
NH_4^+-N	Ammonium-nitrogen
NO_2	Nitrogen dioxide
NO_3^-	Nitrate
NO_3^--N	Nitrate-nitrogen
N_2	Di-nitrogen
N_2O	Nitrous oxide
N_2OR	N_2O reductase
OC	Organic carbon
O_2	Oxygen
PC	Polymer sulphur-coated
SJ	South Johnstone
TC	Total carbon
U	Urea
U-bare	Standard urea, no ground cover
U+DMPP-bare	Urea with DMPP, no ground cover
U-mulch	Standard urea, with ground cover
U+PC-bare	PC (40%) and urea (60%) mix, no ground cover
WFPS	Water-filled pore space

This page is intentionally left blank.

Chapter 1: General Introduction

1.1 Rationale for study

Global climate is changing due to anthropogenic increases in the atmospheric concentrations of carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4) and halocarbons (IPCC, 2013). These 'greenhouse gases' absorb infrared light and trap thermal radiation emitted from the earth's surface. Global mean surface temperatures are predicted to increase by 1.5 to 4.5°C if mitigation measures are not taken to reduce the emission rates of these gases (Stocker *et al.*, 2013). N_2O, the primary focus of this dissertation, is responsible for 6.2% of the anthropogenically induced global warming (IPCC, 2014). It is also responsible for ozone depletion (Ravishankara *et al.*, 2009). The concentration of N_2O in the atmosphere has increased by 20% since 1750 (Hartmann *et al.*, 2013). This trend is set to continue, with models forecasting a further 40% increase from 2000 to 2050 (Bouwman *et al.*, 2013). This is concerning, as the global warming potential of N_2O is 265 times that of CO_2 and approximately 9 times that of CH_4 over a 100-year time frame (Myhre *et al.*, 2013). N_2O also has an atmospheric lifetime of 131 ± 10 years (Prather *et al.*, 2012).

Globally, agriculture accounts for 56–81% of total anthropogenic N_2O emissions (Davidson and Kanter, 2014). Emissions include direct loss from nitrogen (N) fertilisers, soil disturbance, and animal waste (Mosier *et al.*, 1998). N_2O emissions in soil originate from microbial transformations, which are largely dependent on oxygen supply (or soil water content), organic carbon (OC), N substrate supply (soil mineral N), and temperature, and to a lesser extent, soil pH and salinity (Dalal *et al.*, 2003; Oertel *et al.*, 2016). These processes are discussed in more detail below. Most of our understanding of N_2O emission processes comes from studies in temperate regions (Bouwman, 1996). However, tropical soils are now recognised as greater contributors of N_2O compared with temperate soils, as warm and humid conditions favour N_2O production (Granli and Bockman, 1995; Veldkamp and Keller, 1997; Zhu *et al.*, 2015; Wang *et al.*, 2016a). Yet, tropical agricultural soils still remain underrepresented in global N_2O emission studies (Albanito *et al.*, 2017). Emissions from tropical fruit orchards are of particular concern, with large emission factors of approximately 2% of applied mineral N lost as N_2O – highlighting the need to investigate abatement strategies in these systems (Gu *et al.*, 2019).

The principal method of reducing N_2O emissions is to better match crop N needs with N supply (Dalal *et al.*, 2003; Davidson and Kanter, 2014). Lack of synchronization between applied fertiliser N and plant N uptake has resulted low N use efficiency of crops, which is generally

considered to be less than 50% (Reay *et al.*, 2012). For that reason, the amount, type (form), and timing of N fertiliser applied to soil also has an important impact on the amount and rate of N_2O emissions (Bouwman, 1996; Stehfest and Bouwman, 2006). The form of N fertiliser most commonly applied to crops is urea, which is almost immediately available for plant uptake, but also highly mobile and often applied in excess.

Enhanced efficiency fertiliser (EEFs), such as controlled release fertilisers and fertilisers containing nitrification inhibitors, have been promoted as a potential strategy to mitigate N_2O emissions and improve N use efficiency in agricultural soils (Chen *et al.*, 2008; Qiao *et al.*, 2015; Gu *et al.*, 2019). EEFs attempt to alter the amount and/or form of N available in soil, thereby reducing the amount available for environmental losses. The efficacy of EEFs depends on crop type, soil, climate, and management factors (Chen *et al.*, 2008). Little is understood about their efficacy in hot tropical conditions, and studies to date (primarily sub-tropical rather than tropical) have also shown mixed responses (e.g. Scheer *et al.*, 2014; Scheer *et al.*, 2016; Wang *et al.*, 2016a; Wang *et al.*, 2016b; Rose *et al.*, 2017), highlighting the need for further investigations in these environments.

Ground covers, such as mulches and living vegetative ground covers, have important implications for N_2O production in soils. Ground covers can alter soil water content and nutrient availability, which may consequently influence microbial activity and hence N_2O production (Gu *et al.*, 2019). The impact is dependent on mulch material and species of cover crop, along with crop management (Gu *et al.*, 2019). As such, various studies have indicated mixed responses to ground cover practices. For example, reductions of N_2O emissions due to mulching have been found in maize (Tanveer *et al.*, 2014; Wu *et al.*, 2018) and apples (Fentabil *et al.*, 2016), whereas plant residues in sugarcane have been found to increase emissions (Wang *et al.*, 2016b; Fracetto *et al.*, 2017; Gonzaga *et al.*, 2018). Therefore, it is necessary to individually assess the consequences of specific ground covers on N_2O emissions within the crop of interest.

Banana and mangoes are tropical Australia's largest horticultural industries, with a combined value of >$8,000 million yr^{-1} (ABCG, 2017; HIA, 2017) and covering 23,915 ha (FAO, 2017; HIA, 2017). Globally, there is an estimated 5.7 million ha of mangoes (aggregated with mangosteens and guavas) and 6 million ha of bananas (FAO, 2017). These industries primarily use conventional forms of fertiliser (e.g. urea) in warm and wet conditions, a combination with potential to produce high N_2O emissions (Dalal *et al.*, 2003). However, limited studies have been conducted

in banana cropping (Veldkamp and Keller, 1997; Zhu *et al.*, 2015; Bass *et al.*, 2016) and none have explored the impact of nitrification inhibitors (independently) or ground cover on greenhouse gas emissions. Less studies exist for mangoes, with only one unfertilised trial which did not explore ground covers (Huang *et al.*, 2012).

1.2 Aims of study

The overarching aim of this study was to determine if several alternative management practices reduce N_2O emissions in mango and banana fields, compared with conventional management practices. The primary focus was on N_2O emissions, however CH_4 emissions were also assessed in bananas.

The aims of this study were to:

1) Determine whether N_2O emissions are affected by N fertiliser rate and type (conventional urea vs urea plus nitrification inhibitor vs polymer-coated urea);

2) Determine whether N_2O emissions are affected by soil surface management (conventional bare soil vs mulched/living vegetative ground cover); and

3) Determine the main environmental drivers (e.g. soil water content, temperature and/or mineral N content) that affect N_2O emissions.

These aims were achieved by establishing replicated trials on 1) a commercial mango farm on a Yellow Chromosol soil, 2) a commercial banana farm on a Red Ferrosol soil, and 3) a banana plot on a research station on a Brown Dermosol soil, in tropical north-eastern Australia (Figure 1. 1).

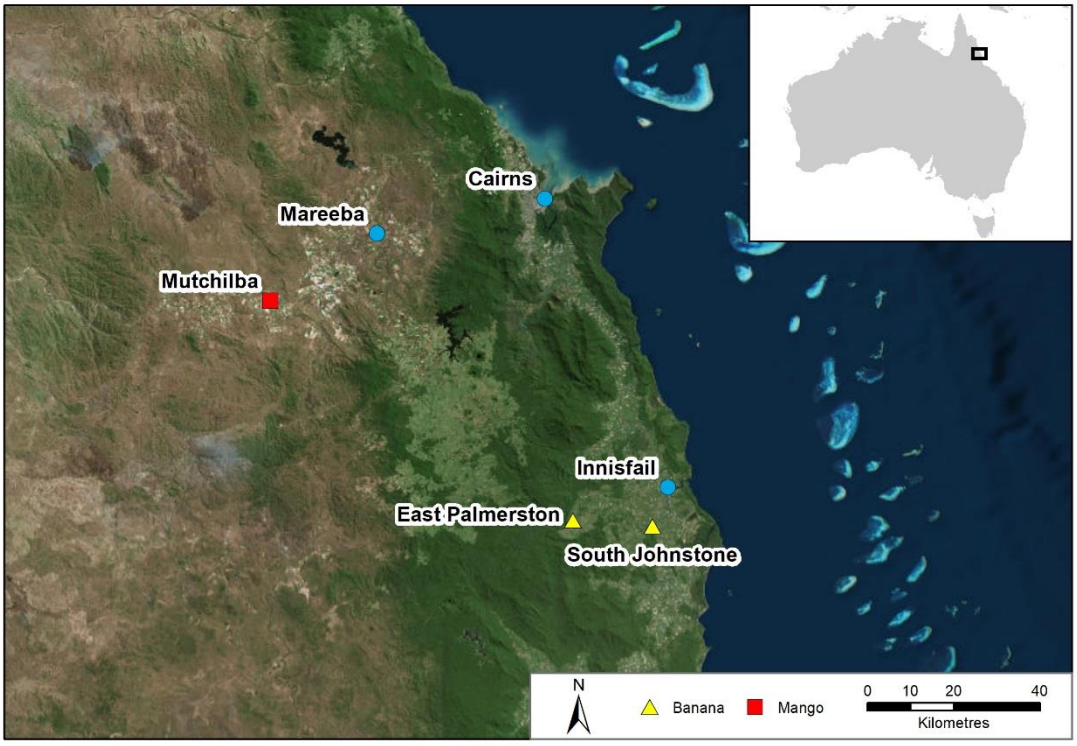

Figure 1. 1. Regional map indicating the location of all study sites. Large towns (Cairns, Innisfail and Mareeba) are included for context. Inset: map of Australia with the main map region outlined in black.

1.3 Thesis outline

The outline of this thesis is as follows:

The remainder of this chapter provides an overview of the literature concerning gaseous N loss from agricultural soils, and the environmental conditions that favour these processes – with a particular emphasis on the microbial process of denitrification. Because the processes that result in N_2O production can also produce di-nitrogen (N_2) and nitric oxide (NO), these and other N gases evolving from agricultural soils are discussed.

Chapter 2 investigates the use of EEFs and ground cover practices, including hay mulch, in a tropical mango orchard. It provides an overview of N_2O emissions from a typical growing year. It also presents the potential implications of mulching practices on soil OC stores.

Chapter 3 examines the impact of N fertiliser rate, a nitrification inhibitor and vegetative ground covers on N_2O emissions in two tropical bananas fields. CH_4 emissions were also measured. This

study focused on emissions occurring during the wet season and discusses N_2O emissions in relation to the primary environmental drivers.

Chapter 4 summaries the major findings of this study, with particular regard to the differences between N_2O emissions in mango and banana fields. This section focuses on the primary environmental drivers of N_2O and management practices in each crop and how EEFs and groundcover practices may influence N_2O emissions. Future research directions and opportunities for improvement are also outlined.

Throughout this thesis important facts and definitions are repeated between the introduction sections of each chapter. This is because it is intended for Chapters 2 and 3 to be published as separate papers, so they need to stand alone.

1.4 Loss of N_2O from tropical agricultural soils

Nitrogen is a constituent of amino and nucleic acids, and hence is essential to life. It is therefore one of the most important nutrients for plant growth. The N cycle is regulated in part by the stability of the triple bond in N_2 gas, which constitutes 78% of the earth's atmosphere and most of the earth's N. To obtain N from the atmosphere, plants and animals rely on the biological fixation of N_2 by bacteria, and to some degree the N fixation caused by lightning in thunderstorms (Schumann and Huntrieser, 2007). However, the invention of the Haber-Bosch process paved the way for the abiotic reduction of N_2 to ammonia (NH_3), allowing the industrial-scale production of synthetic N-based fertilisers since 1913 (Modak, 2011). In the following decades this resulted in a major increase in the amount of N applied to soils, often in quantities in excess of plants' ability to take it up (Reay *et al.*, 2012). This excess N has acidified soils, leached into waterways causing eutrophication, or been lost back to the atmosphere in gaseous forms as a by-product of microbial processes (Vitousek *et al.*, 1997). One gas of particular concern produced by these microbes is the greenhouse gas N_2O.

The following section reviews the processes of N_2O production in agricultural soils, and the environmental conditions that favour these processes, with a particular emphasis on the microbial process of denitrification. The processes that result in the production of N_2O can also produce N_2 and NO. The production of these and other N gases evolving from agricultural soils is discussed.

1.4.1 Nitrogenous gas loss from soil

There are four main nitrogenous gases produced in soil: N_2, NH_3, NO (nitric oxide or nitrogen monoxide) and N_2O (nitrous oxide or di-nitrogen oxide). Of these, only N_2O is a greenhouse gas, but loss of the other gases may contribute to reduced fertiliser N use efficiency in an agricultural setting. N_2 is lost from soil by the process of denitrification (explained in detail below). NH_3 can be lost to the atmosphere by volatilisation from recently applied fertilisers and manures (Schlesinger and Hartley, 1992). It can later re-deposit onto landscapes or waterways elsewhere, contributing to acidification or eutrophication (Fangmeier *et al.*, 1994; Galloway, 1995) or the 'indirect' emission of N_2O (Lam *et al.*, 2017). NO is a ubiquitous molecule which is an important intermediate for oxidant regulation in the troposphere (Bouwman, 1998). It is the precursor to nitric acid, which causes acid rain. It also quickly oxidises in the atmosphere to form nitrogen dioxide (NO_2), which forms photochemical smog (Pilegaard, 2013). Furthermore, both NO and NO_2 are also ozone depleting substances (Crutzen, 1979). NO is also produced through combustion of fossil fuels (Pilegaard, 2013) and is a natural by-product of lightning strikes (Schumann and Huntrieser, 2007).

Overall, N_2 and N_2O are the dominant forms of N gases produced in agricultural soil, with cumulative losses generally accounting for 0–20 kg N ha^{-1} yr^{-1}, but in some cases up to 239 kg N ha^{-1} yr^{-1} have been recorded (Barton *et al.*, 1999). N_2O emissions are also highly variable for a wide range of N fertiliser types and application rates (Bouwman, 1996). Less is understood about NO losses and more research and model development is needed to quantify losses (Pilegaard, 2013). The loss of N in gaseous forms originating from plant-available N in soil also represents a financial loss to the farmer. Therefore, minimising the loss of each of these gases is important for maintaining nutrient use efficiency in agricultural systems.

1.4.2 Production of N_2O and N_2 in soil

In agricultural systems, N_2O is primarily produced during the microbial processes of nitrification, denitrification, and dissimilatory nitrate (NO_3^-) reduction to ammonium (NH_4^+), also known as nitrate ammonification or DNRA (Figure 1. 2; Stevens and Laughlin, 1998; Dalal *et al.*, 2003; Pilegaard, 2013). Nitrification is an aerobic process whereby soil microbes obtain energy by converting (oxidising) NH_4^+ into nitrite (NO_2^-) then into NO_3^-, producing N_2O and NO as by-products. In contrast, denitrification and DNRA generally occur in anoxic conditions when soil microbes use NO_3^- for respiration, producing N_2O when NO_3^- is reduced to N_2 and NH_4^+, respectively. There is some evidence that DNRA can take place in aerobic conditions, under

which it can still produce N_2O (Venterea and Rolston, 2000). However, despite both processes primarily occurring in anaerobic conditions, denitrification and DNRA differ in their ultimate end products. Denitrification produces N_2 when conditions are sufficiently anoxic for N_2O to be further reduced to N_2 via the reactions:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2 \quad \text{(Equation 1)}$$

Whereas the ultimate product of DNRA is NH_4^+ rather than N_2:

$$NO_3^- \rightarrow NO_2^- \rightarrow NH_4^+ + N_2O \quad \text{(Equation 2)}$$

Hence multiple microbial processes can produce to N_2O under both aerobic and anaerobic soil conditions, but only one pathway produces N_2: denitrification, which exclusively occurs under anaerobic conditions.

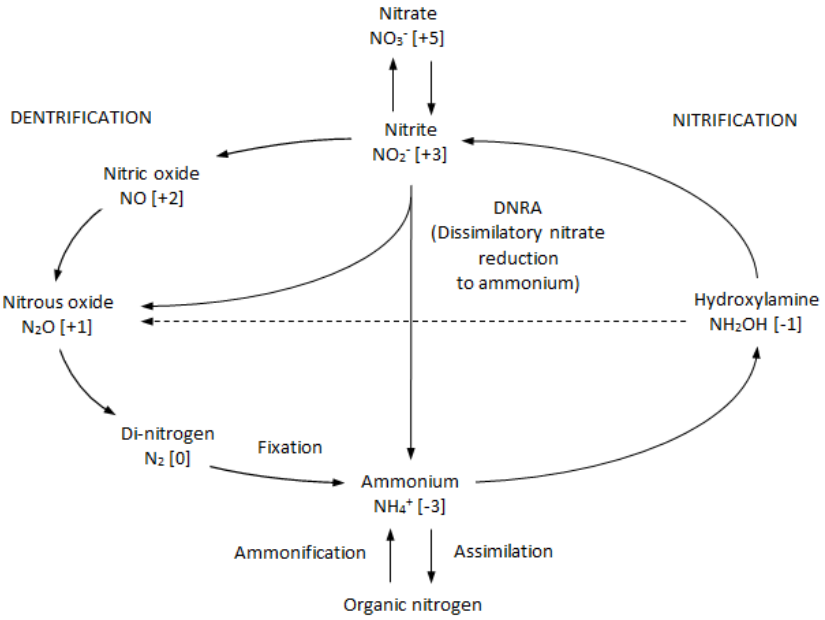

Figure 1. 2. The microbiological nitrogen cycle in agricultural soils

(Adapted from Thomson *et al.*, 2012)

Note: Oxidation states of N given in parentheses

It is worth noting that another important source of N_2 is the microbial process of anaerobic ammonium oxidation (abbreviated as anammox), which involves the conversion of NO_2^- and NH_4^+ to N_2 (Strous *et al.*, 1999). This has not been included in the list above as is it most important in marine systems rather than terrestrial systems (Devol, 2003).

N_2O can also be produced during assimilatory reduction of NO_3^- to NH_4^+ by microbes (Dalal *et al.*, 2003). In this process, the microbes use the reduced NH_4^+ for the production of amino acids, although this constitutes <6% of total NO_3^- reduction in soil. It is considered of minor importance, as low concentrations of NH_4^+ in the soil profile usually serve as an immediate supply that meets microbial needs, precluding use of the assimilatory reduction pathway (Dalal *et al.*, 2003).

Finally, N_2O and N_2 are also produced by the *abiotic* process of chemo-denitrification. Chemo-denitrification involves the reduction of NO_2^- to N_2O, with the assistance of reductants (e.g. ferrous iron) and organic matter (Stevens and Laughlin, 1998; Dalal *et al.*, 2003). In general, concentrations of NO_2^- in soil are usually too low for this process to be favoured, as NO_2^- is an intermediate in nitrification, denitrification and DNRA, and is therefore quickly consumed. Therefore, chemo-denitrification contributes less N_2O and N_2 than these other processes in agricultural soils (Bremner, 1997). However, chemo-denitrification is an important source of N_2O and N_2 in acidic conditions (soil bulk pH <5 or on acidic microsites in soils with bulk pH >5) and may occur in aerobic and anaerobic conditions (Chalk and Smith, 1983). NO_2^- can accumulate in acidic conditions, presumably due to the inhibition of microbial NO_2^- oxidation (Venterea and Rolston, 2000). Chemo-denitrification has been implicated in large N_2O losses from a sugarcane site with acid sulphate subsoils (Thorburn *et al.*, 2013).

Of these processes, denitrification is likely to be the primary source of N_2O in soils (Bouwman *et al.*, 2013), and only denitrification and chemo-denitrification lead to the production of N_2. Nitrification is also recognised as a significant contributor of N_2O from aerobic soils (Bremner, 1997). In soils where there is a mix of aerobic and anaerobic zones, it is likely nitrification may also contribute to the production of N_2 by supplying NO_3^-, hence fuelling denitrification. Furthermore, DNRA can then enhance nitrification through the production of NH_4^+ (Stevens and Laughlin, 1998).

1.4.3 Environmental factors

Nitrification and denitrification in soil depend on several key environmental factors including: soil oxygen and water content, temperature, organic carbon, available soil N, the abundance and composition of microbial organisms, and soil properties such as pH and salinity (Granli and Bockman, 1995; Dalal *et al.*, 2003; Stehfest and Bouwman, 2006; Giles *et al.*, 2012). The environmental drivers of DNRA are similar, but our understanding of them is limited (Giles *et al.*, 2012). The following outline covers each of these driving factors in more detail, with the exception of soil pH and salinity, which are considered secondary drivers and are therefore not discussed here. An overview of the effects of pH and salinity can be found in Dalal *et al.* (2003).

1.4.3.1 Soil oxygen and water content

Soil oxygen and water content are directly linked, as moisture levels in soil affect soil aeration. Soil water content is therefore an important factor mediating nitrification and denitrification, as it directly impacts aeration and therefore microbial activity (Bouwman, 1998; Cosentino *et al.*, 2013). Both nitrifying and denitrifying bacteria respond quickly after wetting dry soil (Davidson, 1992). In general, denitrification rates increase with increasing percentage of water-filled pore space (WFPS; Bouwman, 1998). When soil oxygen (O_2) content is lowered by increasing water content, aerobic respiration becomes limited and microbes use other electron acceptors to derive energy from reduced substrates such as organic matter. Hence, in anoxic conditions, denitrification becomes the dominant N cycling process in place of nitrification. Soil water contents below approximately field capacity result in N_2O production predominantly through nitrification, whereas in soils with water contents above field capacity N_2O is produced predominantly through denitrification (Rudaz *et al.*, 1991). Furthermore, below field capacity the production of NO exceeds that of N_2O, whereas above field capacity the production of N_2O exceeds that of NO (Davidson, 1992).

Bouwman's (1998) model of the relationship between WFPS, nitrification and denitrification describes the ratio of N gases liberated in response to WFPS (Figure 1. 3). In this model, nitrification is most active at 30–60% WFPS, and consequently NO is the dominant gas produced. As WFPS increases to approximately 60% (depending on soil type), denitrification becomes the dominant process. Between 60–80% WFPS, the by-product of denitrification is N_2O. However, over 80% WFPS the N_2O produced is further reduced by denitrification, and N_2 is the end product (Bouwman, 1998). Thus in waterlogged conditions N_2O emissions tend to diminish in favour of

N_2. There has been subsequent field evidence to support this model, with nitrification occurring at >60% WFPS and denitrification occurring when WFPS was 68–80% (Xia *et al.*, 2013).

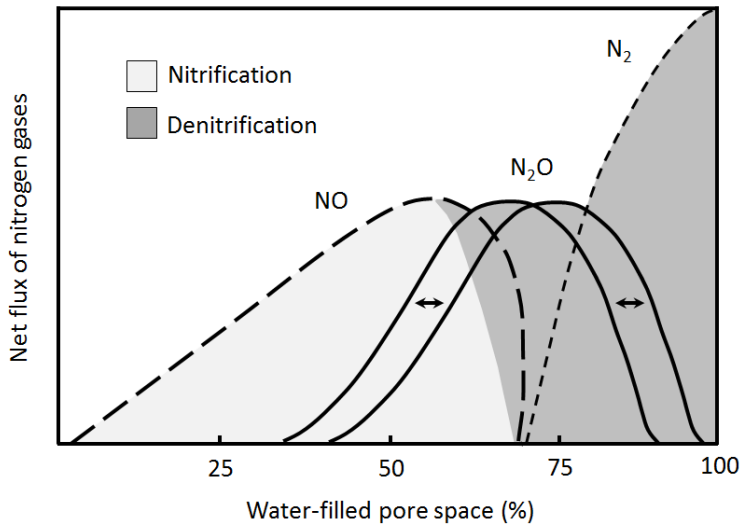

Figure 1. 3. Model of the relationship between water-filled pore space (WFPS) of soils and the relative fluxes of nitrogen gases from nitrification and denitrification (redrawn from Bouwman 1998).

Note: Arrows indicate possible range for N_2O emission

1.4.3.2 Topsoil temperature

Surface soil temperature (e.g. 0–0.1 m) is a primary factor driving nitrification and denitrification rates, with increasing temperature favouring increased gas production, within limits (Keeney *et al.*, 1979; Dobbie *et al.*, 1999; Castaldi, 2000; Cosentino *et al.*, 2013). Therefore, N_2O emissions can fluctuate diurnally and are sensitive to seasonal changes in temperature (Smith *et al.*, 1998; Dobbie *et al.*, 1999; Cosentino *et al.*, 2013). There is also a complex relationship between temperature and WFPS. Numerous studies have demonstrated that temperature and WFPS compete as the key driving variable of N_2O emissions, when available N in soil is not limiting (e.g. Smith *et al.*, 1998; Dobbie *et al.*, 1999; Cosentino *et al.*, 2013). In general, at soil temperatures below 14–15°C N_2O emissions fall significantly as denitrification rates decrease (Keeney *et al.*, 1979; Cosentino *et al.*, 2013). With increasing soil temperature, WFPS can be important, such that emissions from soils at 14–23°C and >59% WFPS are greater than emissions from soils >23°C with <59% WFPS (Cosentino *et al.*, 2013). At soil temperatures above 50°C, chemo-denitrification is likely to be the main process rather than biological denitrification (Keeney *et al.*, 1979).

1.4.3.3 Organic carbon

The capacity of soils to support denitrification increases with increasing organic matter content (Dalal *et al.*, 2003). Organic matter is derived from plant litter, root exudates, manures and incorporation of plant materials, and their subsequent processing by microorganisms (Dalal *et al.*, 2003). It provides soil microorganisms with an energy source for growth and activity (Neff and Asner, 2001). Agricultural practices such as groundcover, mulching and tillage effect OC content of soils. In soil with high OC content and low NO_3^- content, the ratio of N_2 to N_2O production tends to be high (Weier *et al.*, 1993).

In many N_2O emission studies, water soluble OC has been used as a surrogate measure for the labile (or bioavailable) fraction of total OC (e.g. Schipper *et al.*, 1993; Mulvaney *et al.*, 1997; Gagnon *et al.*, 2011). However, the bioavailability of water-extractable OC may not differ substantially from that of other soil OC fractions (Nelson *et al.*, 1994). Permanganate oxidisable OC has been considered an alternative surrogate for determining the bioavailable fraction of OC (Blair *et al.*, 1995; Bell *et al.*, 1998).

1.4.3.4 Available soil nitrogen

The rate of denitrification generally increases with increasing NO_3^- concentration in soil (Barton *et al.*, 1999; Dalal *et al.*, 2003). However, high concentrations of NO_3^- have been shown to inhibit reduction of N_2O to N_2, thus increasing the ratio of N_2O/N_2 (Weier *et al.*, 1993; Dalal *et al.*, 2003). The rate of nitrification can increase with increasing concentration of NH_4^+ in soil (Bremner and Blackmer, 1978; Bremner, 1997; Zhu *et al.*, 2015). Therefore, in agricultural systems the amount, type and timing of N fertiliser applied to soil has an important impact on the timing and magnitude of N_2O and N_2 emissions (Bouwman, 1996; Stehfest and Bouwman, 2006). A survey of N_2O emissions from 180 field experiments demonstrated that anhydrous ammonia and organic N fertiliser, or combinations of organic and synthetic fertilisers, produce higher losses of N_2O than other types of N fertilisers (Bouwman, 1996). However, the dataset was insufficient to determine differences in N_2O emissions according to specific fertiliser composition (i.e. urea, NH_4^+ and NO_3^-). This was partly due to large variations in weather, soil type and management and the interaction between these (Bouwman, 1996).

1.4.3.5 Microbial communities

The abundance and composition of NO_3^- reducing (denitrifying) organisms is important in denitrification processes (Giles *et al.*, 2012). The abiotic environmental drivers (oxygen

availability, temperature, OC, N, pH) and the physiological characteristics of the microbial community affect the amount of denitrification and the ratio of N_2O to N_2 production (Firestone *et al.*, 1980). However, there is limited understanding of how these organisms interact with the abiotic environmental factors (Giles *et al.*, 2012). One study has demonstrated that soil environmental conditions, in particular WFPS, OC and NO_3^-, were the main determinants of denitrification, rather than the abundance and composition of the microbial community (Attard *et al.*, 2011). The study did find partial relationships between denitrification and denitrifier abundance, but not between denitrification and composition of the denitrifier community.

Microbes use enzymes to perform key metabolic processes. The genes for these enzymes are abundant and widely spread across taxonomic groups of soil microorganisms. The successive steps in denitrification (NO_3^- through to N_2) are catalysed by the enzymes NO_3^- reductase, NO_2^- reductase, NO reductase (NOR) and N_2O reductase (N_2OR; Giles *et al.*, 2012). The enzyme N_2OR is responsible for catalysing N_2O to N_2 in the final stage of denitrification, and is the only enzyme known to do this (Thomson *et al.*, 2012). The production of these enzymes can be regulated by environmental signals. Oxygen and NO are known to regulate the expression of genes in bacteria responsible for the enzymes producing and consuming N_2O (Thomson *et al.*, 2012). In most circumstances the primary enzyme involved in N_2O production is NOR. This is found in denitrifying bacteria, as well as some NH_4^+ oxidising (nitrifying) organisms (Thomson *et al.*, 2012). Nitrous oxide, as well as NO, can also be produced by NO_3^- ammonifying (DNRA) bacteria (Streminska *et al.*, 2012).

1.4.4 Summary

In summary, N_2O and N_2 are the dominant N containing gases produced in agricultural soil, with general cumulative losses of up to 20 kg N ha^{-1} yr^{-1}. Loss of N_2O from agricultural soils is of particular concern due to its status as a potent greenhouse gas. Loss of N_2 is not environmentally troublesome, but high losses represents poor nutrient use efficiency. N_2O is primarily produced during the microbial processes of nitrification, denitrification, DNRA and the abiotic process of chemo-denitrification. Only denitrification and chemo-denitrification lead to the production of N_2. These processes are driven by complex relationships among soil WFPS, temperature, available N (NO_3^- and NH_4^+), OC and the size and composition of microbial communities. Denitrification is favoured under anaerobic conditions (>60% WFPS) and adequate amounts of NO_3^- and OC. Nitrification is favoured at <60% WFPS and adequate amounts of available NH_4^+ and OC. N_2O is produced in both of these processes unless WFPS exceeds >80%, at which point

N_2 is the main gas liberated. NO is the main gas produced by nitrification in aerobic conditions. Increasing our understanding of the environmental drivers behind denitrification and nitrification will serve to refine and better target monitoring efforts, as well as identify strategies for mitigating N_2O and N_2 emissions.

This page is intentionally left blank.

Chapter 2: Nitrous oxide emissions and soil carbon in mango orchard soil: the influence of fertiliser type and mulching

2.1 Abstract

Nitrous oxide (N_2O) is the third most important greenhouse gas, accounting for 6.2% of the anthropogenically induced global warming effect. N_2O is a by-product of soil microbial nitrification and denitrification processes, with agricultural soils being the primary source of anthropogenic emissions. There is a lack of research focused on greenhouse gases emitted from soils in tropical tree fruit crops, such as mangoes. In this study, we investigated the impact of nitrogen (N) fertilisers and ground cover practices on N_2O emissions from soil in an established commercial mango orchard (*Mangifera indica*, Kensington Pride variety), in tropical north-eastern Australia. The N fertiliser treatments studied included conventional standard granular urea, and two enhanced efficiency fertilisers (EFFs), being a nitrification inhibitor (3, 4-dimethylpyrazole phosphate, DMPP)-treated urea, and a polymer sulphur-coated (PC) urea mixed with standard urea at a 40/60 ratio. Fertilisers were surface applied to bare soil of the row area only (conventional practice), at 11–25 kg N ha^{-1}. The grassed inter-row was also monitored. Ground cover treatments were hay mulch and bare soil (with standard urea), and hay mulch with DMPP-treated urea (applied at 42 kg N ha^{-1}). Gas emissions were measured using a manual chamber technique. Total organic and labile carbon were measured in soil (0–300 mm) in bare and hay-mulched soils after three years of annual mulch application. The soil type was a Yellow Chromosol and the experiments were factorial designs (randomised block, four replications). N_2O emissions were generally low (<0.34% of fertiliser N applied) and most likely due to nitrification. Low emissions were attributed to low soil water holding capacity and low organic carbon (OC), in addition to low fertiliser N application rates. In general, the greatest N_2O emissions were during the warmer months (February–March) when most rainfall was received and most fertiliser N was applied. The EEF treatments did not have a significant impact on N_2O emissions at the lower N rates applied (<25 kg N ha^{-1}). But at an increased N rate (42 kg N ha^{-1}) and elevated soil water content, DMPP with mulch approximately halved N_2O loss compared to standard urea with mulch. Mulch also reduced N_2O emissions compared to bare soils by approximately half, however sufficient irrigation is required after fertiliser application to mulch to reduce potential volatilisation losses of fertiliser retained in straw and incompletely dissolved. Significant increases in soil OC were not measured in mulched treatments in the three year time-frame of this study. Total soil OC content in the bare row treatments was 14.4 t C ha^{-1} and 16.7

t C ha^{-1} in the mulched rows (0-0.3 m depth). However, the inter-row had significantly greater soil OC content, 22.8 t C ha^{-1}, likely due to 20 years of mulched tree pruning inputs.

2.2 Introduction

Nitrous oxide (N_2O) is the third most important greenhouse gas, accounting for 6.2% of the anthropogenically induced global warming effect (IPCC, 2014), in addition to ozone depletion (Ravishankara *et al.*, 2009). N_2O primarily evolves as a by-product of soil microbial nitrification and denitrification processes (Dalal *et al.*, 2003), with agricultural soils being the primary source due to the application of mineral N fertilisers and animal waste, and soil disturbance (Mosier *et al.*, 1998). As a result, food production contributes 60% of total anthropogenic N_2O emissions world-wide (Syakila and Kroeze, 2011), and emissions are expected to double by 2050 if mitigation action is not taken (Davidson and Kanter, 2014). This is important as the global warming potential of N_2O is 265 times that of CO_2 over a 100-year time frame (Myhre *et al.*, 2013), and it has an atmospheric lifetime of 131 ± 10 years (Prather *et al.*, 2012).

Globally, mangoes are popular tropical fruit grown over an estimated area of 5.7 million ha (aggregated with mangosteens and guavas; FAO, 2017). In Australia, there is approximately 9,894 ha of mangoes under production, with an expected increase of 4% per year by 2021 and onwards, as new trees reach maturity (HIA, 2017). Currently, our understanding of N_2O emissions from mango orchard soils is extremely limited (Huang *et al.*, 2012). Yet, tropical fruit orchards have been identified as significant source of N_2O, highlighting the need for better understanding of N_2O processes and abatement strategies in these systems (Gu *et al.*, 2019).

The production of N_2O in soil is largely dependent on oxygen supply (controlled by soil water content), soil mineral N (ammonium; NH_4^+ and nitrate; NO_3^-), organic carbon (OC), and temperature (Dalal *et al.*, 2003). During nitrification N_2O is liberated when NH_4^+ is oxidised by soil microbes to form NO_3^-. This process requires aerobic conditions. Juxtaposed is the process of denitrification, which occurs in anaerobic conditions, reducing NO_3^- to N_2O, or di-nitrogen (N_2) in persistently wet soils that are highly oxygen deprived.

Enhanced efficiency fertilisers (EEFs), including fertilisers with nitrification inhibitors and controlled-release fertilisers, have been promoted as potential methods of mitigating N_2O emissions (Li and Chen, 2019). As the name suggests, nitrification inhibitors function by reducing the oxidation of NH_4^+, thereby reducing the by-product N_2O and the amount of NO_3^- available

for denitrification. Whereas controlled-release fertilisers have physical coatings, such as polymers and sulfur, that control the rate, pattern, and duration of N release (Shaviv, 2001). The intent is to synchronise the release of N in soils with plant N uptake, consequently improving N use efficiency, whilst maintaining low soil mineral N and reducing environmental losses, such as N_2O. The efficacy of EEFs depends on crop type, soil climate, and management factors (Chen *et al.*, 2008). To date, the impact of these products on N_2O have seldom been tested in tree crops (Olives; Maris *et al.*, 2015) and there have been no studies in mango orchards.

Ground cover management influences N_2O emissions, but various studies have garnered mixed responses to mulching practices. Whilst a reduction in N_2O emissions due to mulching has been found in maize (Tanveer *et al.*, 2014; Wu *et al.*, 2018) and apples (Fentabil *et al.*, 2016), plant residues in sugarcane has been found to increase emissions (Wang *et al.*, 2016b; Fracetto *et al.*, 2017; Gonzaga *et al.*, 2018). In the Australian mango industry, the under-canopy row area is generally maintained with bare soil, or minimal ground cover (Dickinson *et al.*, 2019). This is part of an integrated crop management system approach to reduce fungal diseases in fruit, such as anthracnose (*Colletrotrichum gloeosporiodes*) and stem-end-rots caused by anamorphs of *Botryosphaeria* spp (Akem *et al.*, 2013b). The system also involves annual canopy pruning and fungicide canopy sprays during flowering and fruit development. After pruning, the tree trimmings are raked from beneath the canopy and into the inter-rows, where they are mulched. Most Australian mangoes are grown in areas with seasonally low rainfall, warm temperatures and high evapotranspiration rates (1600+ mm yr^{-1}), with irrigation applied. Organic matter ground cover mulches, such as hay and other plant residues, can improve soil moisture retention and thus improve water use efficiency, root growth, nutrient uptake, and yield (Maurya and Lal, 1981; Chakraborty *et al.*, 2010; Kumar and Dey, 2011). Mulching with organic matter residues can also increase OC sequestration in soil (Lal, 2003). Therefore, mulching practices may be beneficial in mango farming systems. Furthermore, the adoption of post-harvest fungicide hot-dip practices have been shown to successfully control a wide range of fungal diseases in fruit (Akem *et al.*, 2013a), reducing the need for bare soils in mango orchards. However, mulching is not yet commonplace in mango orchards, and the effects on N_2O emissions have not been tested.

The objective of this study was to investigate the impact of N fertiliser type (conventional urea vs EEFs) and ground cover practices (bare soil vs mulching) on nitrous oxide emissions and OC storage in soil, in a mango orchard. Data on soil water-filled pore space (WFPS), soil mineral N

(ammonium-N (NH_4^+-N) and nitrate-N (NO_3^--N)), and soil temperature were measured to help understand the key environmental drivers in the system.

2.3 Materials and methods

2.3.1 Trial site

The field trial was conducted at Mutchilba (17° 08' 08"S 145° 12' 12"E), north Queensland, Australia. The site is at 456 m elevation and characterised by tropical climate with distinct wet and dry seasons. Long-term (1889–2017) annual mean rainfall at Dimbulah (10 km east of Mutchilba) is 778 mm yr^{-1} (Bureau of Meteorology, Australia; Station 31022), with approximately 69% of rainfall occurring in January to March. Peak monthly rainfall is in February (mean 199 mm) and lowest monthly rainfall is in August (mean 4 mm). Mean annual temperature is 22.8°C, with daily maximum temperature being highest (monthly mean 32°C) in November/December and daily minimum temperature being lowest (monthly mean 12°C) in July/August. The soil is a mesotrophic, yellow, Chromosol (Isbell, 2002), with a light-sandy clay loam textured topsoil (0–200 mm) and 0.5% slope. Soil physico-chemical properties near the start of the trial in 2014 are displayed in Table 2. 1.

The trial was superimposed on a commercial mango orchard (*Mangifera indica*, Kensington Pride variety) planted in 1994 at rectangular spacing of 9.7 m (inter-row) x 5.5 m (intra-row) at 198 trees ha^{-1}. Tree canopies were pruned every year to maintain canopy architecture in the shape of a hedge along the tree rows, 5.0 m wide x 4.5 m high. This resulted in a 3.8-m wide vegetated inter-row for vehicle access. The ground in the tree rows (approximately 6 m wide) was kept bare by regular applications of herbicide (glyphosate), and by raking the tree trimmings into the inter-row and mulching there. There was a naturally occurring cryptogamic soil cover in the row, which included an unidentified Bryophyte (moss) with cover ranging from approximately 5 to 90% (among gas sampling chambers). The extent and stage of Bryophyte growth varied through the year, approximately in concert with soil moisture. There was also a variable amount of leaf and flower litter, which varied according to season and management. Irrigation was delivered through under-tree micro-sprinklers to the row area.

Table 2. 1.Soil physico-chemical properties at the Mutchilba Site (December 2013).

Depth (m)	Sand (%)	Silt (%)	Clay (%)	pH	EC (dS m^{-1})	NO_3^--N (mg kg^{-1})	TC (%)
Row							
0.0–0.1	82	12	9	6.7	0.05	4	0.5
0.1–0.2	83	13	8	6.1	0.05	2	0.4
0.2–0.3	81	13	10	6.1	0.07	2	0.3
Inter-row							
0.0–0.1	79	14	10	7.5	0.07	8	1.7
0.1–0.2	80	13	10	7.6	0.04	3	0.4
0.2–0.3	78	12	14	7.6	0.03	3	0.2

Note: EC = electrical conductivity, NO_3^--N = nitrate-N and TC = total carbon. pH was determined with a glass electrode at 25°C in a 1/5 soil/water suspension.

2.3.2 Trial design and treatments

Three experiments were conducted within one field trial. The field trial had a randomised block design with four replicates (blocks). There were three fertiliser and two ground cover treatments in factorial design, resulting in 24 plots. Each plot comprised five mango trees in a single row (three datum trees and two guard trees). The fertiliser treatments were: standard urea (46% N), urea treated with the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP or ENTEC®), and a polymer sulphur-coated (PC) urea mixed with standard urea at a 40/60 ratio, respectively. The PC urea was the product Agrocote® by Everris International (39% N). Fertiliser was applied several times over the course of the trial, with the first application in March 2014. Fertiliser was broadcast over the row at the same rate of N per hectare in all treatments. The groundcover treatments were bare soil in the row (conventional treatment) and mulched ground cover in the row. Mulch was applied as hay at an approximate rate of 2.2 kg dry matter m^{-2} of treated area. The treated area was approximately 55% of the orchard, which equates to an equivalent application rate of 11.9–13.2 t hay ha^{-1}. Hay mulch was applied at 4 occasions over the duration of the trial, the first in February 2014, then August 2014, November 2015 and June 2016. The hay mulch (*Setaria* spp. (grass)) was sourced from local farms and averaged 0.5% N content, with an estimated average contribution of 63 kg N ha^{-1} annually to the soil.

The aim of Experiment 1 was to test the effect of fertiliser type on nitrous oxide emissions from bare soil. Gas sampling and associated measurements were conducted following fertiliser application on 3 March 2014 (25 kg N ha^{-1}; Experiment 1 a.) and 27 August 2014 (11 kg N ha^{-1}; Experiment 1 b.). The treatments selected for this experiment were:

1) Standard urea, no ground cover (U-bare)
2) Urea with DMPP, no ground cover (U+DMPP-bare)
3) PC (40%) and urea (60%) mix, no ground cover (U+PC-bare)

Measurements were also conducted in the unfertilised grassed inter-row, which receives mulch annually from tree trimmings.

The aim of Experiment 2 was to test the effect of mulch, with and without nitrification inhibitor-treated urea, on nitrous oxide emissions. Gas sampling and associated measurements were conducted one year after the first application of mulch, following fertiliser application on 2 February 2015 (42 kg N ha^{-1}). The treatments selected for this experiment were:

1) Standard urea, no ground cover (U-bare)
2) Standard urea, with ground cover (U-mulch)
3) Urea with DMPP, with ground cover (U+DMPP-mulch)

The aim of Experiment 3 was to test the effect of mulch on soil OC content. Soil samples were collected at 1 year 10 months (2 November 2015) and 3 years 2 months (12 April 2017) after first applying mulch. The treatments for this experiment were:

1) Standard urea, no ground cover (U-bare)
2) Standard urea, with ground cover (U-mulch)

Measurements were also conducted in the unfertilised grassed inter-row.

2.3.3 Gas emission measurements

Emission of N_2O from the soil was measured using a manual chamber technique (Parkin and Venterea, 2010). Chamber rings were PVC pipe, 120 mm high and 300 mm in diameter, inserted into soil to approximately 50 mm depth for the duration of the experiments. During measurement, chambers were closed with lids having a rubber seal, septum and a capillary tube 450 mm long with 1 mm internal diameter to equalise the internal chamber pressure with atmospheric pressure. Each plot had four chambers located in the row (fertilised zone) to

proportionally represent the irrigated and non-irrigated zone (Figure 2. 1). In Experiment 1 an additional six chambers were placed in the centre of the grassed inter-row (non-fertilised zone) in each block (replicate).

Measurement duration differed between Experiments 1 and 2. In Experiment 1 (2014), emissions were measured five times in the first week, starting the day before fertiliser application, and then less frequently over the course of the following three months. In Experiment 2 (2015), emissions were measured four times in the first week, starting the day before fertiliser application, and then less frequently over the course of the following 16 days. Gas emissions were measured between 9:00 and 11:00 AM Eastern Standard Time, as emissions during this period approximate the daily mean (Wang *et al.*, 2016a). In Experiment 1 the gas sampling intervals were at 0, 20 and 40 minutes following chamber closure. From August 2014, the syringe was pumped once gently whilst inserted in the chamber, to encourage mixing and to ensure a representative sample was collected from the chamber airspace. This was due to low N_2O emissions encountered during measurements in March to May. In Experiment 2, the intervals were increased to 0, 30 and 60 minutes, as N_2O measures continued to be low throughout the rest of Experiment 1. Samples were immediately injected into evacuated 11-mL plastic vials sealed with a rubber stopper (BD Vacutainer ™ part #364915).

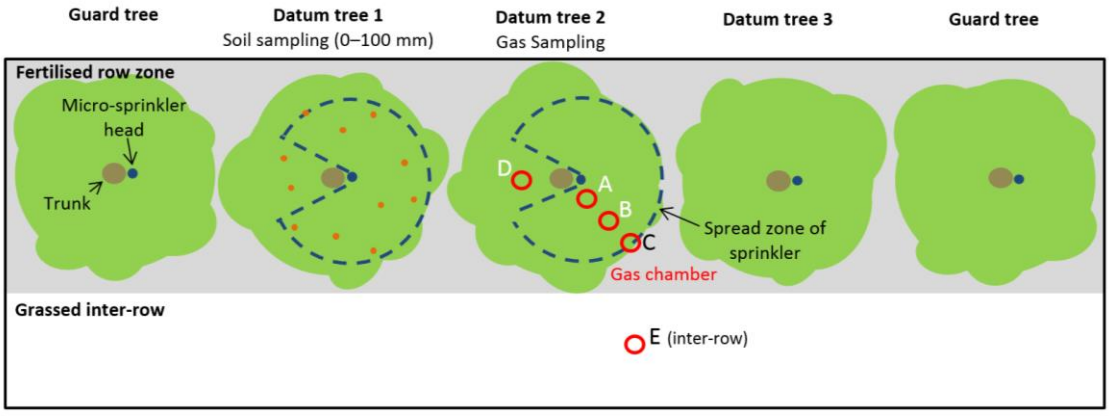

Figure 2. 1. Gas and soil sampling locations within each plot.

Note: Prior to placing the gas chambers within the plots, irrigation distribution measurements were conducted to ensure chamber locations represented the range of soil water contents experienced in the fertilised row zone.

Concentrations of N_2O in the gas samples were measured using a Shimadzu GC-2010 gas chromatograph. Gas separation was effected using a Shincarbon packed column (Serial number C39711-01, length 2.0 m, internal diameter 2.1 mm) at 280°C. The carrier gas was helium, at a

flow rate of 30 mL min^{-1}. N_2O was detected using a ^{63}Ni electron capture detector at 330°C using N_2 as the makeup gas. Peak areas were determined using Shimadzu LabSolutions software and converted to concentrations by calibration against high purity N_2 (zero standard) and two BOC certified standards (1.1 and 10.1 µL L^{-1} N_2O).

The emission rate of N_2O was calculated according to the equation:

$$N_2O \text{ emission rate } (\mu g\ N\ m^{-2}\ h^{-1}) = \frac{28 d V_c}{A_c V_m} \quad \text{Eq. 1}$$

Where 28 is the mass of N per mole of N_2O (g mol^{-1}), *d* is the increase in chamber headspace N_2O concentration per hour at the time the chamber was closed (µL L^{-1} h^{-1}), V_c is the headspace volume (m^3), A_c is the area covered by the chamber (m^2) and V_m is the volume of one mole of ideal gas (m^3), given by the equation:

$$V_m = \frac{RT}{P} \quad \text{Eq. 2}$$

Where R is the gas law constant (8.3145 J mol K^{-1}), *T* is temperature (K) and *P* is pressure (Pa) at the time of measurement.

The rate of increase in chamber N_2O concentration, *d*, was not constant during the period of chamber closure so a quadratic equation was fitted to the data (concentration vs time) and the rate of increase at time zero was estimated using the coefficient of the term *x.*

Nitrous oxide emission values were averaged for each plot (replicate level for the inter-row), and treatment emission means and standard errors were then calculated from the plot values. Total gas emission from each plot over each monitoring period was determined in RStudio version 1.1.383 (RStudio, 2016) by trapezoidal integration between each measurement point ('pracma' package, Borchers, 2017). Total N_2O flux expressed as a percentage of N fertiliser applied was determined as the N_2O flux from the fertilised plots divided by the application rate of N fertiliser (uncorrected for emissions from plots with nil N applied).

2.3.4 Soil and climate measurements

At the time of selected gas emission measurements, soil samples were collected and analysed for mineral N content. Ten soil samples (0–100 mm depth) were collected randomly (proportionally within irrigated zone and non-irrigated zone) under the canopy of one tree in

each treatment plot and combined (Figure 2. 1). Samples collected in the inter-row (2–3 cores near each gas chamber) were combined into one sample (per replicate). Samples were air dried at 40°C in a ventilated oven for 48 h and then ground and sieved to <2 mm. Soil mineral N content (ammonium; NH_4^+-N and nitrate-N; NO_3^--N) was determined by extraction with 2M KCl followed by automated colorimetric analysis (Method No: 7C2; Rayment and Lyons, 2010).

Soil samples collected for soil OC content were analysed for total C and labile C. Initially, samples were taken on 2 November 2015 from 0–25 mm. These samples were collected randomly as outlined above. Samples were also taken on 12 April 2017 to determine C stocks to 0.3 m depth after a 3-year period of mulching. Soil cores were collected at 100-mm depth increments for chemical analysis and bulk density determination. Cores were taken from six points along a diagonal transect of each plot as described by Nelson *et al.* (2015). Cores were bulked for each depth and plot, then dried and sieved as described above. Samples were analysed for total C contents using a LECO TruMac Dumas combustion analyser (Method No: 6B2a; Rayment and Lyons, 2010) and labile C using potassium permanganate oxidation (Method No: 6E1; Rayment and Lyons, 2010). Undisturbed soil cores collected for bulk density determination were dried at 105°C in a ventilated oven for 48 h and weighed.

Soil water content and temperature (0–100 mm depth) were measured approximately 100 mm away from each chamber, mid-way through chamber closure. Soil temperature was recorded using a digital thermometer, and volumetric water content was measured with a HydroSense II® probe (Campbell Scientific). The probe (120-mm length) was inserted on an angle to achieve 100 mm depth. Water filled pore space (WFPS) was determined using the equation:

$$\text{WFPS (\%)} = 100 \times \text{volumetric water content (\%)} / \text{total soil porosity (\%)} \quad \text{Eq. 3}$$

Where total soil porosity = 1 – (soil bulk density/soil particle density) and soil particle density was assumed to be 2.65 g cm^{-3}.

Rainfall, air temperature and soil temperature were measured continuously. Rainfall was measured using a pluviometer fitted with 0.2-mm tipping buckets, located on the farm approximately 200 m from the trial. Air temperature (under canopy) and barometric pressure were recorded using Solinst Barologgers®. Temperature sensors and loggers (Tinytag®) were

used to measure soil temperature (0–50 mm) at 30-minute intervals within the row of a U-bare and a U-mulch treatment plot.

2.3.5 Statistical analysis

The effect of treatments on gas emissions and other variables was determined using one-way analysis of variance (ANOVA) in Genstat (18th Edition, VSN International Ltd., UK). Residuals were checked for normality and no transformations were necessary. Where there was a significant F test (p<0.05) Fisher's 95% protected least significant difference (LSD) was used to make pairwise comparisons between means. Where multiple independent analyses were conducted simultaneously the P value (α) was adjusted by dividing by the number of comparisons made (Bonferroni adjustment), to reduce the possibility of type 1 errors.

2.4 Results

2.4.1 Experiment 1 a.

In March 2014, soil mineral N concentrations in the row increased notably following fertiliser application, irrigation and rainfall, in all treatments (Figure 2. 2). The first soil samples after fertilising were collected 11 days after application, following 5-mm irrigation (applied immediately after fertiliser application) and <2 mm rainfall 8 days later (Figure 2. 3). At this time NH_4^+-N and NO_3^--N concentrations in the row were high in all treatments. NH_4^+-N concentrations in the U+DMPP-bare treatment were higher (14.8 mg kg^{-1}) than in the inter-row (6.1 mg kg^{-1}), but both were similar to the U-bare (9.8 mg kg^{-1}) and U+PC-bare (9.3 mg kg^{-1}) treatments (p<0.05 on 14 March 2014). NO_3^--N concentrations did not differ between treatments (mean 10.7 mg kg^{-1}). Mineral N concentrations then declined over the following two months. Despite no differences in NO_3^--N concentration between treatments there was a clear distinction between the row and the inter-row (p<0.001). The highest NO_3^--N concentration measured in Experiment 1 was 18.8 mg kg^{-1} on 28 March (p<0.001) in the inter-row, following ~42 mm rainfall over several days prior.

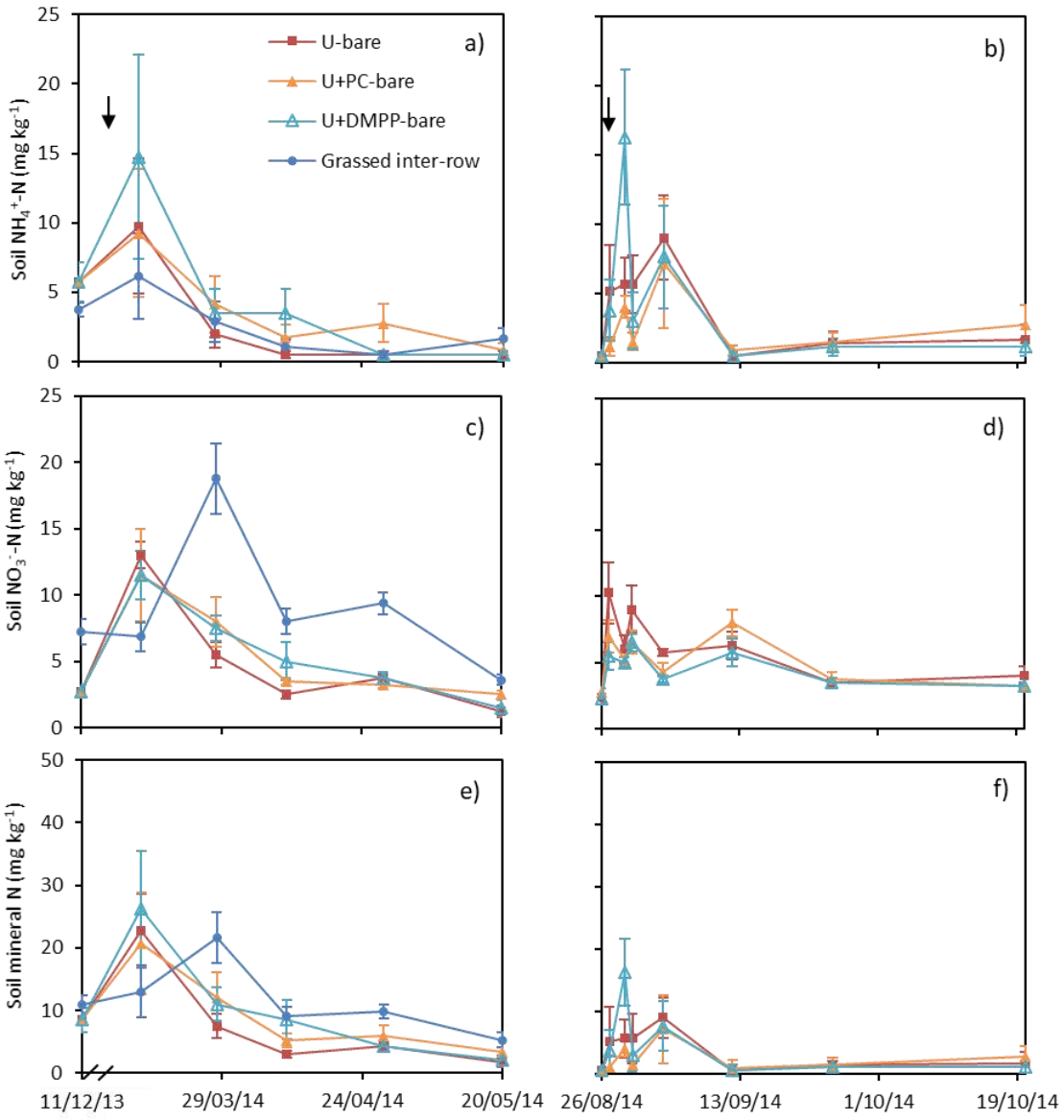

Figure 2. 2. Mean soil ammonium (NH_4^+-N), nitrate (NO_3^--N) and mineral N concentrations in the 0–100 mm layer following fertiliser application in March 2014 (25 kg N ha^{-1}; a, c and e) and in August 2014 (11 kg N ha^{-1}; b, d and f). Arrows in panels a and b indicate time of fertiliser application. The error bars are standard errors of the mean.

Note discontinuity in the timeline represented on the x axis. Only initial measurements were collected from the inter-row for the August monitoring period (26 August 2014) with NH_4^+-N being 2.5 mg kg^{-1} and NO_3^--N 3.4 mg kg^{-1}.

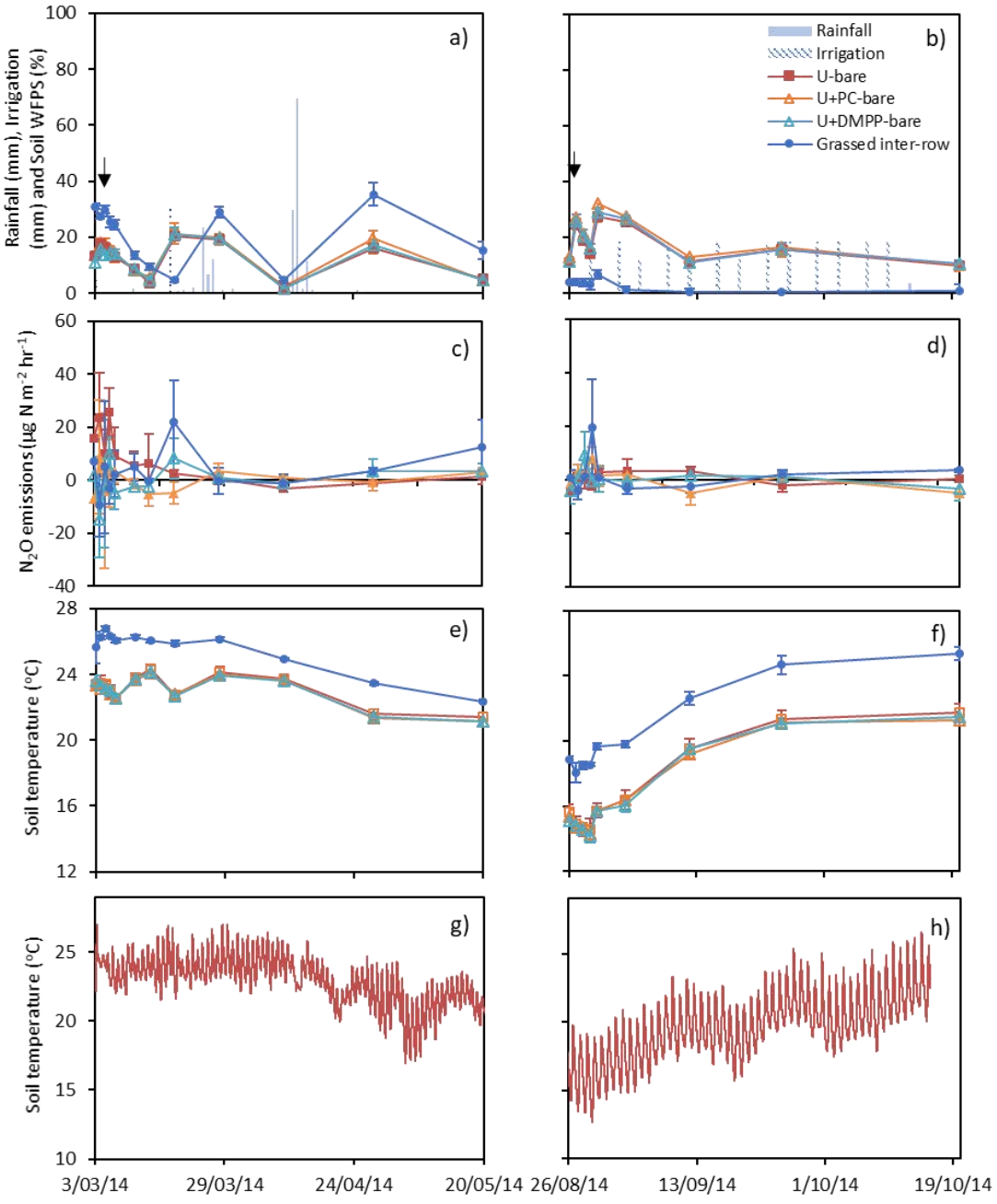

Figure 2. 3. Nitrous oxide emissions and environmental conditions at the Mutchilba site following fertiliser application in March 2014 (25 kg N ha^{-1}) and August 2014 (11 kg N ha^{-1}) showing daily rainfall and soil water filled pore space (a and b; WFPS, 0–100 mm); N_2O emissions (c and d); soil temperature at 0–100 mm depth during chamber closure (e and f); and soil temperature at 0–50 mm depth recorded at 30-minute intervals in the row (U-bare treatment; g and h), last measurement on 15 October 2014. The error bars are standard errors of the mean. Arrows indicate time of fertiliser application.

Soil water content in the rows fluctuated with irrigation and rainfall, ranging from 2 to 21% WFPS (Figure 2. 3). The day after fertiliser application soil water content in the rows averaged 13% WFPS and average temperature was 23°C (Figure 2. 3). On average, soil in the inter-row was 7% greater (p<0.001) and 1.4°C warmer than in the row (p<0.001). Mean daily air temperature was 23.2°C and ranged from 6.3–41.9°C.

N_2O emissions were highly variable before and after fertiliser application, for all treatments, in both the row and the inter-row (Figure 2. 3). As a result, differences between treatments were not discernible. Although not significant, there were generally higher N_2O emissions from the U-bare treatment, peaking at 26 µg N m^{-2} hr^{-1} three days after fertiliser application before declining over the following month. In the other treatments N_2O emissions were low or frequently negative. Negative N_2O emissions continued throughout most of the monitoring period for most treatments and the inter-row. The grand mean emission for the monitoring period was 3 µg N m^{-2} hr^{-1}.

Overall, total N_2O emission did not differ between treatments, or the grassed inter-row. Total N_2O flux was 9, 3, 2 and 0.3 mg N m^{-2} for the grassed inter-row, U+DMPP-bare, U-bare and U+PC-bare treatments, respectively. N_2O flux as a percentage of N fertiliser applied over the observation period was 0.07, 0.06, and 0.01% of fertiliser N for U+DMPP-bare, U-bare and U+PC-bare, respectively.

2.4.2 Experiment 1 b

In August 2014, soil mineral N concentrations in the row increased following fertiliser application and irrigation, for all treatments (Figure 2. 2). Irrigation was applied immediately after fertilising and then regularly (11–19 mm per irrigation) at approximately 3–4 day intervals (Figure 2. 3). Overall, there were no significant effects of treatments on soil NH_4^+-N or NO_3^--N concentration, despite the notable peak in NH_4^+-N for the U+DMPP-bare treatment (16.3 mg kg^{-1}) on the third day after fertiliser application (29 August 2014, p=0.08, Figure 2. 2). NH_4^+-N concentrations were generally elevated for the first 8 days after fertiliser application, before declining over the remaining 7 weeks. NO_3^--N concentrations were elevated for a month after fertilising. During this sampling period soil was collected from the grassed inter-row only on 26 August 2014 with NH_4^+-N and NO_3^--N being 2.5 and 3.4 mg kg^{-1}, respectively.

Soil water content and temperature differed between rows and grassed inter-rows. Soil water content was higher in the rows (p<0.001) due to the regular irrigation (Figure 2. 3). Soil water content was 10–32% WFPS in the rows and <1–7% WFPS in the inter-rows. The highest water contents in the row were reached in August when soil temperatures were cooler (<16^{o}C) than those later in October (22^{o}C; Figure 2. 3). The inter-row was consistently 3^{o}C warmer than the row. In general, despite this period having cooler temperatures than the first monitoring period in March to May, the diurnal range in temperature was greater in August to October (Figure 2. 3). Mean daily air temperature was 22.0^{o}C and ranged from 3.0–42.5^{o}C.

N_2O emissions were low and variable for all treatments, including the inter-row, consistent with the cool and dry conditions (Figure 2. 3). N_2O emissions averaged 0.5 µg N m^{-2} hr^{-1} for all treatments and negative emissions continued regularly. Total N_2O flux was 1.2, 0.6, 0.1 and -1.5 mg N m^{-2} for the grassed inter-row, U-bare, U+DMPP-bare and U+PC-bare treatments, respectively. N_2O flux as a percentage of N fertiliser applied over the observation period was 0.03, 0.01 and -0.08% of fertiliser N for U-bare, U+DMPP-bare and U+PC-bare, respectively.

2.4.3 Experiment 2

Soil mineral N concentrations in the row increased markedly following fertiliser application and rainfall, in all treatments (Figure 2. 4). Concentrations of NH_4^+-N peaked the day after fertiliser application and a ~2.5 mm rainfall event, and then declined over the following two weeks. The highest NH_4^+-N concentrations were reached in the U-bare treatment, peaking at 36.3 mg kg^{-1} (p<0.01 on 3 February 2015). During that time concentrations were similar in the mulched treatments, at 10.8 and 15.8 NH_4^+-N mg kg^{-1} for treatments with and without DMPP, respectively. The U-bare treatment retained the highest NH_4^+-N concentrations for three days after application, after which concentrations and treatment differences diminished over the following two weeks. NO_3^--N concentrations increased during the week after fertiliser application and then stabilised. The highest NO_3^--N concentrations (mean 9.6 mg kg^{-1}) were reached 8 days after fertiliser application (10 February 2015). There were no significant differences between treatments, despite the lower mean concentrations in the U+DMPP-mulch treatment in the latter part of the monitoring period. Prior to fertiliser application there was no significant difference in soil NH_4^+-N or NO_3^--N concentration between treatments (mean 1.9 and 1.6 mg kg^{-1} respectively), despite mulching for 12 months (Figure 2. 4). At the beginning of the experiment fine roots were observed in the surface soil immediately under the mulched treatments, but not in the bare soil treatment.

N_2O emissions increased following fertiliser application and rainfall in all treatments (Figure 2. 4). N_2O emissions peaked 8 days after fertiliser application and after 93 mm of rainfall (over three days). The highest N_2O emissions were reached in the U-bare treatment, peaking at 109 µg N m^{-2} hr^{-1} (p<0.01 on 10 February 2015). At this time N_2O emission rates in the mulched treatments were 14 and 45 µg N m^{-2} hr^{-1} for treatments with and without DMPP, respectively, and soil water content was the highest for the study period (41% WFPS) across all treatments. However, during drier days mulched plots maintained greater soil water content than bare soil (p<0.01 on 4–6 February 2015). After the peak, N_2O emissions declined in all plots, together with soil water content, despite the elevated NO_3^--N concentrations.

N_2O flux over the whole 16-day period was greatest from the U-bare treatment (23 mg N m^{-2}) and much less for the mulched treatments, being 10 mg N m^{-2} for U-mulch and 4 mg N m^{-2} for U+DMPP-mulch (p<0.001). N_2O flux as a percentage of N fertiliser applied over the observation period was 0.34, 0.15 and 0.05% of fertiliser N for U-bare, U-mulch and U+DMPP-mulch respectively.

Soil temperature averaged 24.8°C across all treatments (at time of gas chamber closure) and was an average of 0.3°C warmer under mulched ground cover than without (p<0.05, data not shown). The greatest temperature difference between treatments was 0.8°C on 10 February 2015, at the time of greatest soil water content. The diurnal range in temperature appeared to be greater in bare soil than mulched soil (Figure 2. 4), but the observations were not replicated, so the effect is uncertain. Mean daily air temperature was 25.2°C and ranged from 15.0–42.1°C.

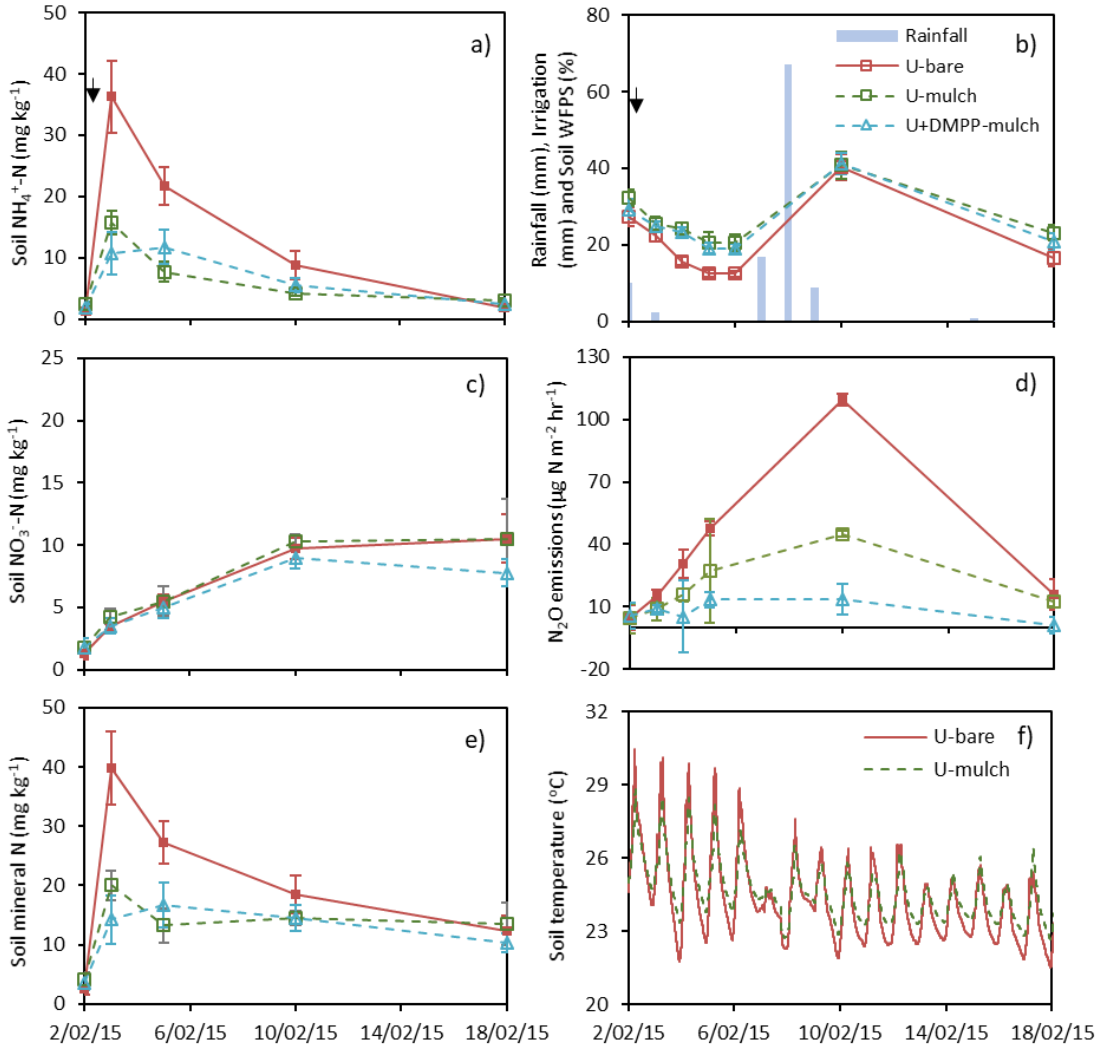

Figure 2. 4. Soil mineral N, nitrous oxide emissions and environmental conditions at the Mutchilba site following fertiliser application in February 2015 (42 kg N ha^{-1}) showing mean: soil ammonium (NH_4^+-N; a), nitrate (NO_3^--N; c) and mineral N (e); concentrations in the 0–100 mm layer of the row; daily rainfall and soil water filled pore space (WFPS, 0–100 mm; b); N_2O emissions (d); and soil temperature in the 0–50 mm layer of soil recorded at 30 minute intervals in two locations in the row (within the chamber; f). The error bars are standard errors of the mean. Arrow indicates time of fertiliser application.

2.4.4 Experiment 3

There was no significant difference in total soil C content (0–300 mm) between the mulched (U-mulch) and non-mulched (U-bare) treatments 3 years and 2 months after application of hay commenced, with mean values of 16.7 and 14.4 t C ha^{-1}, respectively (Table 2. 2). The soil C content in the mulched row area did not differ significantly from that of the inter-row area (22.8 t C ha^{-1}), which was mulched annually with tree clippings and maintained with grass. Overall, differences in soil C content between the row treatments and the inter-row were detected only in the surface soil (0–25 and 0–100 mm), and declined down the profile (Table 2. 2). This was evident for both total and labile forms of organic C.

Table 2. 2. Mean total organic C and labile C content of the row and inter-row at the Mutchilba site (n = 4 for each treatment).

Depth	Labile carbon (g kg^{-1})	Total OC (%)
*0–25 mm**		
Non-mulched row (U-bare)	0.99 a	0.82 a
Mulched row (U-mulch)	0.90 a	0.73 a
Mulched and grassed inter-row	13.70 b	9.14 b
Significance	$p<0.001$	$p<0.001$
l.s.d. (5%)	1.151	0.877
0–100 mm		
Non-mulched row (U-bare)	0.75 a	0.53 a
Mulched row (U-mulch)	1.17 a	0.73 a
Mulched and grassed inter-row	2.13 b	1.20 b
Significance	$p<0.05$	$p<0.01$
l.s.d. (5%)	0.78	0.32
100–200 mm		
Non-mulched row (U-bare)	0.36	0.32
Mulched row (U-mulch)	0.34	0.25
Mulched and grassed inter-row	0.35	0.32
Significance	n.s.	n.s.
l.s.d. (5%)	0.13	0.15
200–300 mm		
Non-mulched row (U-bare)	0.20	0.18
Mulched row (U-mulch)	0.23	0.22
Mulched and grassed inter-row	0.44	0.15
Significance	n.s.	n.s.
l.s.d. (5%)	0.55	0.91
0–300 mm		**Total OC (t C ha^{-1})**
Non-mulched row (U-bare)		14.4 a
Mulched row (U-mulch)		16.7 ab
Mulched and grassed inter-row		22.8 b
Significance		$p<0.05$
l.s.d. (5%)		6.13

*The 0–25 mm layer was sampled 22 months after treatments commenced whereas all other layers were sampled 38 months after treatments commenced.

2.5 Discussion

2.5.1 N_2O emissions and regulating factors

Overall, the low N_2O emissions in this study were primarily a consequence of low soil water content (Figure 2. 3 and Figure 2. 4). Soil water content is the most important soil parameter controlling gas emissions due to the influence on microbial activity (Oertel *et al.*, 2016). Soil texture plays an important role in soil water content and therefore in N_2O emission potential. N_2O emissions in fine-textured soils can have 2–5 times larger emission factors (uncorrected for background emissions) than medium- and coarse-textured soils (Gu *et al.*, 2019). In our study, low WFPS (mean 17%) was due to the low water holding capacity of the permeable sandy soil, coupled with the low OC content, and was well below optimum for microbial nitrification (~60% WFPS; Linn and Doran, 1984). The dominant form of gas produced by nitrification below approximately 60% WFPS is nitric oxide, rather than N_2O, which is favoured between approximately 60–80% WFPS (Bouwman, 1998). However, nitric oxide production was also likely to be very low at this site, as production quickly drops off towards and below 10% WFPS (Bouwman, 1998).

N_2O emissions fluctuated seasonally, as found in other tree crops including lychee (Rowlings *et al.*, 2013), apples and cherries (Swarts *et al.*, 2016). In general, N_2O flux responds to seasonal changes in temperature (Smith *et al.*, 1998; Dobbie *et al.*, 1999; Cosentino *et al.*, 2013), with a significant reduction experienced in soil temperatures below 14–15^{o}C (Keeney *et al.*, 1979; Cosentino *et al.*, 2013). In our study, the greatest N_2O emissions were during the warmer wet season months (February–March) associated comparatively high soil temperatures, mineral N, and WFPS. However, mean soil water content in the row was higher in the cooler dry season months (August–October), due to regular irrigation. But, during this time low soil temperatures (14–16^{o}C), in combination with a low soil mineral N (in particular NH_4^+) would have resulted in reduced nitrification rates. Furthermore, in addition to seasonal variations, there is likely substantial variation in annual emissions. There was a considerable difference in the amount of wet season rainfall between the two years, as well as the amount of fertiliser applied, resulting on a 4-fold difference in peak N_2O emission. Rainfall variability has been found to drive inter-annual variation in N_2O (Rowlings *et al.*, 2015). Therefore, in order to improve N_2O estimates long-term continuous measurements may be important to appropriately assess inter-annual variations in this system (Rowlings *et al.*, 2015).

Our study had lower N_2O emissions than the unfertilised mango study by Huang *et al.* (2012), which was conducted on a Dermosol (Isbell, 2002) in Nambour, in sub-tropical Australia. In our study, mean N_2O emissions from the row ranged from 0.4 g N ha^{-1} day^{-1} in 2014, to 1.1 g N ha^{-1} day^{-1} with 2015 measurements included (bare treatments only). In contrast, the Nambour study N_2O emissions averaged 4.6 g N ha^{-1} day^{-1}. This disparity in emissions is likely due to greater soil water and OC contents at the Nambour site. Average volumetric soil water content at the Nambour site was 25%. Given the reported bulk density of density of 1.3 g cm^{-3} this would be equivalent to a WFPS of 51%. The soil water content at Mutchilba was much lower. Furthermore, soil OC content was also higher at the Nambour site being 2.6%, compared to 0.53% at the Mutchilba site. Greater soil moisture and OC availability supports increased microbial activity and greater turnover of soil nitrogen pools, and hence greater nitrification rates (Dalal *et al.*, 2003). Soil temperatures during each study was similar, with an average of 21.1°C at Nambour and an average of 20.5°C at Mutchilba.

N_2O emissions in our study (<0.34% of N fertiliser applied) were lower than those found in other horticultural crops. A review of N_2O emissions from the fruit orchard literature showed that compared to other regions tropical orchards had large emission factors (approximately 2%; Gu *et al.*, 2019). The Intergovernmental Panel on Climate Change estimate direct N_2O emission from mineral fertilisers in the Tier 1 calculations based on a default emission factor of 1% (IPCC, 2006). The Australian national inventory for greenhouse gas emissions uses a country specific (Tier 2) emission factor of 0.85% (ANGA, 2018). This value was based on an assigned fertiliser rate of 246 kg ha^{-1} yr^{-1} for horticultural crops. However, in comparison to other horticultural crops mangoes are also considered to have lower N requirements, with Australian industry applying approximately 50–79 kg N ha^{-1} yr^{-1} (DAF, 2015). Therefore, mango orchards and other horticultural tree crops with low N requirements potentially warrant a separate classification in the Australian inventories.

N_2O emissions from fruit orchards have been shown to range widely, from -0.116 to 26 kg N ha^{-1} per year or growing season, increasing linearly with N fertiliser input rates on a global basis (Gu *et al.*, 2019). However, as demonstrated by our study, and by Huang *et al.* (2012), the total N application rate is not always the key determinate of N_2O emissions. In the study by Huang *et al.* (2012), two other crops were also assessed, pineapple and custard apple. The pineapple crop had lower annual N_2O losses (1.16 kg N_2O-N ha^{-1}) than the unfertilised mango orchard (1.59 kg N_2O-N ha^{-1}), despite the application of 445 kg N ha^{-1}, which was spread over 20 applications (8–

54 kg N ha^{-1} each). The custard apple crop received only one application of 92 kg N ha^{-1} and had the greatest N_2O emissions overall (2.04 kg N_2O-N ha^{-1}). The emission factor was 0.26% for pineapple and 2.22% for custard apple. In comparison, N_2O emissions from sub-tropical lychees had emissions factors ranging from 1.10% in autumn to 2.44% in spring, from a split application of 265 kg N ha^{-1} (Rowlings *et al.*, 2013). Total N_2O loss was 7.6 kg N_2O-N ha^{-1} yr^{-1}, however without fertiliser applied the losses were still 1.7 kg N_2O-N ha^{-1} yr^{-1}. The previously measured values closest to ours were from temperate apples (0.3 kg N_2O-N ha^{-1} yr^{-1}) and cherries (0.74 kg N_2O-N ha^{-1} yr^{-1}) from annual applications of 40 and 150 kg N ha^{-1}, respectively (Swarts *et al.*, 2016; no emission factor provided).

Forty percent of N_2O emissions in Experiment 1 were negative (Figure 3), both in the row and the inter-row. This may have been due to errors at low concentrations and emission rates. Due to the low emissions our chamber sampling interval timeframes were increased between Experiment 1 and 2. During Experiment 2, fewer negative emissions were measured. However, a coincident increase in N fertiliser applied in this experiment also lead to greater increases in soil mineral N and subsequently greater N_2O emissions. This may have also masked any natural underlying N_2O consumption processes. Chapuis-lardy *et al.* (2007) found negative N_2O emissions in the range -0.0014 to -484 mg N m^{-2} h^{-1} in the literature and highlighted that this process occurs in both agricultural and natural environments, yet with little investigation or explanation. Denitrification is the main biological process known to consume N_2O in soil (Firestone and Davidson, 1989). However, at this site soil water contents were not sufficient to achieve the anoxic conditions (>60% WFPS) required for denitrification. Some studies have shown N_2O consumption in anoxic microsites throughout the soil profile (Parkin, 1987; Frasier *et al.*, 2010). Whilst this was not specifically investigated in our study these microsites are usually associated with OC, which is low in this soil. It is plausible N_2O consumption was occurring in these mango soils, but apparently by processes other than denitrification.

Other possible N_2O reducing processes involve the ability of NH_4^+-oxidising bacteria to denitrify (nitrifier denitrification), and aerobic denitrification (Chapuis-lardy *et al.*, 2007). One possibility is that the cryptogamic layer on the soil surface of the row was consuming N_2O. In a study of mature beech trees the photoautotrophic organisms living on the bark (lichens, mosses and algae) were shown to have N_2O consumption rates of 2.4 to 3.8 µg N m^{-2} hr^{-1} (Machacova *et al.*, 2017). However, in our experiment a cryptogamic layer was identified only in the row.

Considering the amount of negative N_2O emissions measured in this study, further investigation is warranted.

2.5.2 Effects of N fertiliser type on N_2O emission

The efficacy of the EEFs to reduce N_2O emissions depended on the amount of N fertiliser applied. At lower N rates (11 to 25 kg N ha^{-1}) DMPP and the PC urea mix did not significantly decrease N_2O emissions (Figure 2. 3). This is presumably due to the already minimal N_2O production in soil at this site, in addition to the highly variable nature of the emissions. At the highest N fertiliser rate (42 kg N ha^{-1}) a larger N_2O response occurred and DMPP had significantly lower emissions compared to standard urea, when applied with mulch (Figure 2. 4). DMPP was not tested on bare soil at the higher rate, nor was the PC urea mix tested at the higher rate on mulched or bare soil. DMPP has been shown to reduce N_2O emissions in olives (5–35%; Maris *et al.*, 2015), barley, maize, wheat (41–53%; Weiske *et al.*, 2001), and grain sorghum (83%; Scheer *et al.*, 2016). Moreover, PC urea products have also shown reduced N_2O emissions in grain sorghum (70%; Scheer *et al.*, 2016) and sugarcane (31%; Wang *et al.*, 2016b). But in some cases PC urea products have also been shown to increase N_2O emissions (50%; Wang *et al.*, 2016b). In general, our findings suggest that DMPP might play a role in mitigating N_2O emissions when higher N rates are applied, but further investigation on both EEFs is needed.

In soil, both EEFs appeared to influence mineral N contents as intended, despite the lack of consistent treatment differences in N_2O. The PC urea mix generally maintained initially lower soil mineral N, with higher contents at 1–2 months after application, compared to standard urea. Whereas at the lower N rates, DMPP treatments had generally greater NH_4^+ and lower NO_3^- concentrations shortly after application. This was not statistically significant, but this suggests that DMPP may be effectively reducing the NH_4^+ oxidation in this soil. The ability of DMPP to inhibit nitrification is influenced by soil texture, with greater efficacy in sandy soils than loamy soils (Barth *et al.*, 2001), therefore conditions at this site were considered suitable for DMPP. Despite this, at the higher fertiliser rate, the DMPP and mulch treatment had the least NH_4^+ in soil. This may have been a result of ammonia (NH_3) volatilisation from within the mulch, in addition to volatilisation from the soil. This may have consequently influenced N_2O emissions. More recently, nitrification inhibitors have been shown to increase volatilisation of NH_3, due to the preservation of NH_4^+ in soil (Qiao *et al.*, 2015; Lam *et al.*, 2017). This is discussed in further detail in the next section.

There may be other reasons to warrant the application of EEFs in mangoes, regardless of the mixed N_2O results. It is possible that the main environmental loss pathway for N in this soil type is via leaching of NO_3^-, rather than gaseous loss via nitrification. The permeable sandy soil, seasonally high rainfall, and substantial amounts of irrigation could favour NO_3^- movement down the soil profile. Consequently, NO_3^- in groundwater systems may lead to indirect N_2O emissions (Tian *et al.*, 2019). Substantial NO_3^- losses of 8–10% of N applied were measured under a Cashew crop in a Red Chromosol, approximately 12 km from our study site (O'Farrell *et al.*, 2010). Both DMPP and PC urea products may reduce NO_3^- leaching due to reduction of soil NO_3^- content (Zerulla *et al.*, 2001; Qiao *et al.*, 2015; Di Bella *et al.*, 2017). Given that 60–70% of annual N fertiliser is applied during peak vegetative growth in summer, when the highest rainfalls can occur, this maybe the most appropriate time to consider an EEF in this system.

2.5.3 Effects of ground cover mulch on N_2O emission

The significantly lower N_2O emission from mulched treatments compared to bare soil treatments (Figure 2. 4) was likely caused by improved N uptake by tree roots, in addition to possible N loss via ammonia volatilisation. Soil condition under the hay-mulch layer was more favourable for surface root development, with increased soil moisture and buffered soil temperature, which has also been observed in other studies (Kumar and Dey, 2011; Xing *et al.*, 2012). This was evident even though mulch treatments had been *in-situ* for only one year. Root biomass measurements conducted by Dickinson *et al.* (2019) at our trial three years after the first mulch application showed that mulched treatments had significantly higher root weights (<4 mm diameter) at 0–50 mm depth. This greater surface root network would increase nutrient uptake and reduce the available NH_4^+ in soil for nitrification, thereby reducing N_2O emissions. Other studies have also documented reduced N_2O emissions due to mulch ground cover (Tanveer *et al.*, 2014; Fentabil *et al.*, 2016; Wu *et al.*, 2018).

It is also conceivable the reduction in N_2O emissions with mulch was partly a result of greater initial N loss via NH_3 volatilisation in mulched treatments. This may have contributed to the reduced NH_4^+ concentration in soil. NH_3 emission was not measured in this study. But volatilisation was suspected, as the smell of NH_3 was noted the day following fertiliser application. It is probable that some fertiliser granules applied to hay mulch were not fully dissolved and did not wash through the straw and into the soil – although no granules were visible the day after application. Fertiliser application was followed by only a small rainfall event, as the irrigation system was not operational on the day. Therefore, the urea-based fertilisers

could have remained suspended in the straw, experienced rapid hydrolysis, then subsequent volatilisation of NH_3 directly from the mulch (Pinheiro *et al.*, 2018). This issue should be alleviated by application of sufficient irrigation immediately after fertiliser application. Urease inhibitors might also help reduce volatilisation in situations where urea is surface-applied to mulch, by allowing it to move into the soil before hydrolysis (Chen *et al.*, 2008).

Long-term mulching may increase N_2O emissions. Mulching has led to increased N_2O emission in other tropical crops, such as sugarcane (Wang *et al.*, 2016b; Fracetto *et al.*, 2017; Gonzaga *et al.*, 2018). This has been attributed to favourable conditions for microbial activity created by sugarcane leaf residue, including increased OC supply, release of inorganic N through mineralisation, and increases in soil water content. Over time, increases in soil OC due to hay mulch application in mangoes may increase microbial activity and soil water holding capacity of the soil. However, it is highly unlikely that soil OC content could be raised sufficiently in this sandy soil to increase water holding capacity above the 60% WFPS necessary to raise N_2O emissions (Minasny and McBratney, 2018). Given the various uncertainties outlined here, the reduction of N_2O emissions due to mulching practices needs to be substantiated.

2.5.4 Effects of ground cover mulch on soil OC

Mulching did not significantly increase soil OC contents (labile or total OC) in the time-span of this study (Table 2. 2). However, the inter-row had up to 8.4 t C ha^{-1} more stored C than the bare or mulched treatments in the row. Assuming the paddock had relatively spatially uniform OC content prior to farming activities, this indicates an overall net gain of OC storage, or conversely a decline in the row area. The inter-row has been mulched with tree pruning residues annually for 20 years. A study by Zhao *et al.* (2015) found that when tree pruning material was returned to the system, mango orchards were C sinks, with a net C emission (sequestration) of -0.54 t C ha^{-1} y^{-1} for an 'intensive' (1,000 tree ha^{-1}) mango orchard. However, when pruning material was not returned, net C emissions were 0.64 and 0.72 t C ha^{-1} y^{-1} for intensive and 'sparse' (444 tree ha^{-1}) mango orchards, respectively. In our study, tree pruning material was returned to the inter-row and hay mulch was sourced from offsite, and was therefore additional C contributed to the system.

2.5.5 Implications for management

Fruit yields were increased by mulching and not affected by fertiliser type in this trial (Dickinson *et al.* (2019). Dickinson *et al.* (2019) found that the mulched treatments in our study had 10%

greater mean fruit weights and 11% greater fruit yields per tree, during the three study period. Fruit quality was not compromised due to mulching when standard fungicide management treatments were used. However, disease levels were higher with no post-harvest fungicide treatment. Mulching also reduced soil temperature variability and increased soil water holding capacity, surface root biomass, canopy leaf area, and leaf tissue potassium concentration.

Decomposition of hay mulch in the row would have contributed to soil mineral N. However, the N contribution from hay mulch (a maximum of ~63 kg N ha^{-1} yr^{-1}) was not detected in soil mineral N concentrations, presumably due to gradual mineralisation and rapid uptake. Considering the amount of N that hay mulch could deliver to soil, and the similar annual amounts of N applied to mangoes as fertiliser (50–79 kg N ha^{-1} yr^{-1}) there may be opportunity to lower, or potentially avoid, N fertiliser application where mulch is applied. However, in the third year of the study by Dickinson *et al.* (2019) the N content of leaves in the mulched treatments were significantly lower (p<0.05) than in bare soil treatments. This was attributed to potential N draw-down, due to higher microbial activity in the mulched plots (Dickinson *et al.*, 2019). Therefore, N cycling where mulch is applied in mangoes may require further investigation.

Based on the findings of our study and Dickinson *et al.* (2019) the adoption of mulching practices in mango orchards would increase orchard productivity and lower N_2O emission, without detrimental effects on fruit quality. Whilst the use of EEFs did not negatively impact yields, they did not result in consistently lower N_2O reduction. Furthermore, considering the generally negotiable N_2O emissions in this soil type, and the additional cost of EEFs, there appears to be little justification for N_2O mitigation measures with EEFs.

2.6 Conclusions

N_2O emissions were generally low (<0.34% of fertiliser N applied) and most likely due to microbial nitrification. Low emissions were attributed to low field capacity, low soil OC content and low fertiliser N application rates. The highest N_2O emissions occurred during the warmer months (February–March) when most rainfall was received and most fertiliser N was applied. The EEF treatments did not have a significant impact on N_2O emissions at the lower N rates applied (<25 kg N ha^{-1}). But at a higher N rate (42 kg N ha^{1}) and soil water content the nitrification inhibitor, DMPP, approximately halved N_2O loss. However, in general there appears to be little justification for N_2O mitigation measures with EEFs on this soil type due to low emissions.

Mulching had multiple benefits, including reduced N_2O emissions, improved soil moisture retention, and increased root mass and fruit yield. Significant increases in soil OC were not measured in mulched treatments in the three-year time-frame of this study. However, soil OC was significantly greater in the grassed inter-row. This area had been receiving mulch due to routine farming activities for two decades, indicating that increases of soil OC maybe achievable over a longer timeframe. It was also identified that sufficient irrigation is required after fertiliser application to mulch to limit volatilisation losses from fertiliser granules suspended in straw and incompletely dissolved. The reduction of N_2O emissions due to mulching needs to be substantiated over the longer-term.

This page is intentionally left blank.

Chapter 3: Greenhouse gas emissions from banana fields: influence of nitrogen rate, a nitrification inhibitor and vegetative ground cover

3.1 Abstract

In banana cropping systems, where high rates of nitrogen (N) fertiliser, primarily urea, are applied in wet and warm conditions, methods are required to reduce the production of the potent greenhouse gas nitrous oxide (N_2O) originating from nitrification and denitrification in soil. This study aimed to determine the effects of N fertiliser (urea) application rate, a nitrification inhibitor (3, 4-dimethylpyrazole phosphate, DMPP) and ground cover (conventional bare soil versus vegetative ground cover, including Pinto peanut (*Arachis pintoi*)) on N_2O emissions from soil in banana fields in North Queensland, Australia. Emissions of N_2O and methane (CH_4) were measured using a manual chamber technique. The experiments were conducted in the warm wet season months, during the plant stage of the crop cycle, at two sites, one with a Red Ferrosol and the other with a Brown Dermosol. The experiments were factorial designs (randomised block, four replications) with two monthly fertiliser rates ('low N' at 12 kg N ha^{-1} and 'high N' at 18 to 54 kg N ha^{-1}). The DMPP treatment was paired with the low N rate at both sites. The vegetative ground cover treatment was paired with the high N rate on the Brown Dermosol only. At both sites, N_2O emissions occurred as pulses of less than 2–8 days duration following the first substantial increase in soil water filled-pore space (WFPS) shortly after fertilising. The low N rate treatments had consistently lower N_2O emissions than the high N rates, but N_2O emissions increased for all treatments when fertiliser was applied during persistently wet conditions (>68% WFPS). Overall, total N_2O flux as a percentage of applied N was 0.20 to 1.14%. Urea treated with DMPP had approximately half the N_2O emissions than the equivalent N rate with untreated urea on the Brown Dermosol, but did not significantly reduce emissions on the Red Ferrosol. The vegetative ground cover reduced N_2O emissions compared to bare soil during wet conditions and higher N rates, presumably due to greater N uptake by the vegetative ground cover and thus less available soil mineral N. Overall, the primary drivers of N_2O emissions were soil water content, soil mineral N concentration and time since fertiliser application. Our results demonstrated that N_2O emissions can be reduced by avoiding high levels of soil mineral N in wet soils through lower fertiliser rates, use of DMPP and appropriate timing of fertiliser application with respect to rainfall and irrigation.

3.2 Introduction

Tropical agricultural soils have been identified as significant sources of the greenhouse gas, nitrous oxide (N_2O; Veldkamp and Keller, 1997; Crill *et al.*, 2000; Zhu *et al.*, 2015; Wang *et al.*, 2016a). This needs attention, as the global warming potential of N_2O is 265 times that of carbon dioxide (CO_2) and approximately 9 times that of methane (CH_4) over a 100-year time frame (Myhre *et al.*, 2013). Furthermore, N_2O is responsible for ozone depletion (Ravishankara *et al.*, 2009) and has an atmospheric lifetime of 131 ± 10 years (Prather *et al.*, 2012). The primary source of N_2O in agricultural soil is the application of nitrogen (N) as mineral fertiliser or animal manure, in addition to soil disturbance (Mosier *et al.*, 1998). In Australia, agricultural soil is responsible for 59% of N_2O emissions (Commonwealth of Australia, 2018). During the last 30 years atmospheric N_2O concentrations have increased by 0.73 ± 0.03 ppb yr^{-1} (IPCC, 2014). It is anticipated that without targeted reduction strategies N_2O emissions will double by 2050 (Davidson and Kanter, 2014).

In soil, N_2O is primarily produced during the microbial processes of nitrification, denitrification, and dissimilatory nitrate (NO_3^-) reduction to ammonium (NH_4^+), known as DNRA (Stevens and Laughlin, 1998; Dalal *et al.*, 2003; Pilegaard, 2013). Nitrification produces N_2O as a by-product during the oxidation of NH_4^+ to NO_3^- in aerobic conditions. Whereas, denitrification and DNRA produce N_2O by reductive processes in anoxic conditions. Denitrification differs from DNRA in that it reduces NO_3^- to N_2O, and if anoxic conditions persist N_2O is further reduced di-nitrogen (N_2). The amount, type and timing of N fertiliser applied to soil has an important impact on the amount and rate of N_2O and N_2 emissions (Bouwman, 1996; Stehfest and Bouwman, 2006). However, the flux is moderated by soil water content (a surrogate for oxygen availability), temperature, and OC contents (Weier *et al.*, 1993; Veldkamp *et al.*, 1998; Gagnon *et al.*, 2011).

Globally there is an estimated 6 million ha of bananas (FAO, 2017). The industry has rapidly expanded in the last 20 years with the area under production increasing by 1.4 million ha (FAO, 2017). In Australia there is approximately 14,000 ha of bananas under production (FAO, 2017). Most Australian bananas are grown in hot and humid regions, with high rainfall, rates of N fertiliser and irrigation, creating ideal conditions for N_2O production (Veldkamp and Keller, 1997; Zhu *et al.*, 2015). The mean annual fertiliser N rate for the industry was 310 kg ha^{-1} in 2012, down from 520 kg ha^{-1} in 1995 (Armour *et al.*, 2013). In terms of N uptake and efficiency, banana plants are one of the most inefficient crops next to paddy rice (Chen *et al.*, 2008), with only 15% recovery of N from applied fertilisers measured in Australia in the 1990s (Prasertsak *et al.*, 2001).

The rest of the applied N is lost to volatilisation, leaching, denitrification, or remains in the soil (Prasertsak *et al.*, 2001). Banana fields require frequent N application throughout the year, typically in the form of urea (Prasertsak *et al.*, 2001; Armour *et al.*, 2013). The repeated top-dressing of urea results in frequent pulsing of N_2O emissions (Zhu *et al.*, 2015).

Urea and NH_4^+-based fertilisers augmented with nitrification inhibitors can potentially improve N recovery in plants and reduce N_2O emissions (Qiao *et al.*, 2015). Nitrification inhibitors are designed to impede the activity of NH_4^+ monooxygenase, the bacterial enzyme responsible for the first step of nitrification, thereby hampering the oxidation of NH_4^+ in soil (Ruser and Schulz, 2015). The reduction in nitrification consequently reduces the production of N_2O and the amount of NO_3^- available for denitrification. A meta-analysis of the literature shows an average 73% reduction in N_2O emissions where nitrification inhibitors were used (Gu *et al.*, 2019). The nitrification inhibitor, DMPP (3,4-dimethylpyrazole phosphate) has been shown to be one of the most effective of the commercially available products (Chen *et al.*, 2008). Furthermore, due to improved N use efficiency when DMPP is used, the rate of N applied can be reduced (Zerulla *et al.*, 2001). However, DMPP does not consistently reduce N_2O emissions (Nauer *et al.*, 2018). Importantly, DMPP might be less effective in warmer tropical climates (Chen *et al.*, 2008) and to date it has not been trialled in bananas.

Ground cover management has important implications for the sustainability banana cropping systems. Inter-rows may be grassed, but most commercial banana farms keep soil bare in the row. However, living vegetative ground cover around the base of the plant (row area) have recently been shown to improve soil microbial activity, hence providing greater resilience to soil-borne diseases, such as *Fusarium* wilt (Pattison *et al.*, 2014; McBeath *et al.*, 2018). Furthermore, increasing ground cover may reduce soil erosion, which has been identified as a significant source of sediment in surface water runoff entering the Great Barrier Reef marine park on the east coast of Australia (Kroon *et al.*, 2016). Ground covers in fruit orchards modify the availability of soil water and nutrients, and hence the processes that govern N_2O production (Gu *et al.*, 2019). To date, no studies have investigated the impact of living vegetative ground covers on N_2O emissions in bananas.

The objective of this study was to assess the effect of 1) urea application rate, 2) urea augmented with DMPP, and 3) ground cover management (bare soil versus living vegetative ground cover at base of plants) on N_2O emissions from soils in banana fields at two sites.

3.3 Materials and methods

3.3.1 Trial sites

Experimental trials were conducted in two banana fields in north Queensland, Australia in 2015–2016. One was in East Palmerston (17° 35’ 33”S 145° 49’ 57”E) and the other 18 km east in South Johnstone (17° 36’ 19”S 145° 59’ 55”E). The region is characterised by a wet tropical climate. Long-term (1889–2017) annual mean rainfall at South Johnstone is 3,370 mm yr^{-1} (Bureau of Meteorology, Australia; Station 32037), with approximately 50% of rainfall occurring between January and March. Peak monthly mean rainfall is in March (624 mm) and lowest monthly mean rainfall is in September (82 mm). Mean annual temperature is 23.6°C, with daily maximum temperature being highest in January (monthly mean 31°C) and daily minimum temperature being lowest in July–August (monthly mean 15°C). Both sites had similar textured light-medium clay topsoil (0–200 mm). The soil at East Palmerston is a well-drained Red Ferrosol (Isbell, 2002), formed on basalt and with an 8% slope. The 0–100 mm layer had 40% sand, 27% silt, 33% clay, 2.3% total carbon (TC), pH 7.2 and a cation exchange capacity (CEC) of 15 cmol+ kg^{-1} at the start of the trial. The soil at South Johnstone is a moderately well-drained Brown Dermosol (Isbell, 2002) on an alluvial plain with <1% slope. The 0–100 mm layer had 47% sand, 20% silt, 33% clay, 1.7% TC, pH 5.9 and CEC of 7.8 cmol+ kg^{-1} soil at the start of the trial.

The two sites had different cultivars and management regimes. The East Palmerston trial was established on a commercial banana plantation in November 2014. Bananas (cv. Williams, Cavendish *Musa* spp. AAA group) were planted in single rows on 4 November 2014, with 3.5 m between rows and 2.0 m between plants (1,666 plants ha^{-1}). Prior to planting, canola (*Brassica napus*) had been grown for four months, preceded by a two-year fallow of Rhodes grass (*Chloris gayana*). The South Johnstone trial was established in March 2015 at the South Johnstone Research Facility. Bananas (cv. Highgate and Hom Thong Mokho, *Musa* spp. AAA group) were planted in single rows on 24 March 2015, with 5 m between rows and 1.5 m between plants (1,333 plants ha^{-1}). There was no preceding managed fallow; planting occurred two months after the previous banana crop.

3.3.2 Fertiliser and ground cover treatments

Both trials had the same fertiliser treatments, plot size and a randomised block design with four replicates. Each plot comprised 12 banana plants in a single row (10 datum plants and two guard plants). There were three fertiliser treatments: a high rate of urea, a low rate of urea, and a low rate of urea treated with the nitrification inhibitor DMPP (ENTEC®). The high rate was based on local farmer practice, and the low rate was based on the predicted rate of N uptake by the plant (Armour *et al.*, 2013). Fertiliser treatments were applied once per month, as granules to the surface of the row. Both sites were irrigated using under-tree micro sprinklers.

The East Palmerston trial had 12 plots (three fertiliser treatments x four replicates) and no groundcover in the rows. The rows were kept bare with an application of the herbicide glufosinate-ammonium every two months. In the inter-rows, grass was allowed to grow. Urea rates for the 12 months from planting were 180 kg N ha^{-1} for the low N treatment (based on 150 kg N ha^{-1} for a 10 month plant crop growth period; Armour *et al.*, 2013) and 370 kg N ha^{-1} for the high N treatment, based on local farmer practice of 350 kg N ha^{-1} (Figure 3. 1). Depending on stage of plant growth monthly rates ranged from 4 to 25 kg N ha^{-1} for the low N treatment, and 12 to 54 kg N ha^{-1} for the high N treatment, with the N dose increasing as plants grew larger. Potassium (K) rates were adjusted to suit N rates, with the target rate being 300 kg K ha^{-1} for the low N treatment and 650 kg K ha^{-1} for the high N treatment. Potassium was applied as potassium sulphate (41% K and 17% S). Other fertilisers were applied at uniform rates across the treatments. Phosphorus was applied as mono-ammonium phosphate (22% P and 10 % N) on 10 December 2014 at 20 kg P ha^{-1} (includes 10 kg N ha^{-1}). Lime (80% calcium carbonate + 20% magnesium oxide) was applied on two occasions (28 July 2014 and 16 January 2015) at 1 t ha^{-1} each time. Measurements were conducted following fertiliser application on 2 March 2015, in the plant phase of the crop. The treatments for this trial (with rate of fertiliser application) were:

1) Low N rate (12 kg N ha^{-1}), no ground cover (LN-bare)
2) Low N rate (12 kg N ha^{-1}) with DMPP, no ground cover (LN+DMPP-bare)
3) High N rate (54 kg N ha^{-1}), no ground cover (HN-bare)

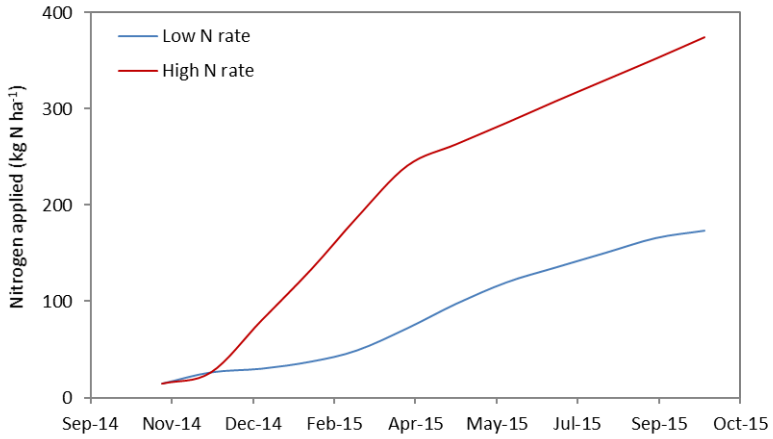

Figure 3. 1. Nitrogen application rates for low and high treatments at the East Palmerston site.

The South Johnstone trial had three fertiliser treatments, two ground cover treatments (for one fertiliser treatment only) and four replicates, resulting in 16 plots. The target urea rates for the 12 months from planting were 190 kg N ha^{-1} for the low N treatment and 350 kg N ha^{-1} for the high N treatment, and applied in similar method to the East Palmerston site. Monthly rates ranged from 2 to 30 kg N ha^{-1} for the low N treatment, and 18 to 43 kg N ha^{-1} for the high N treatment. Ground cover treatments were bare soil versus vegetative ground cover in the row. Vegetative ground cover consisted primarily of Pinto peanut (*Arachis pintoi*), which was planted as runners between banana plants. Other species were allowed to grow, and the groundcover was mowed every two months to maintain low growth. Mowed plant residues were left *in-situ*. Bare soil treatments were maintained the same as the East Palmerston site. In the inter-row, grass was allowed to grow. The target rate for K was 370 kg K ha^{-1} for the low N treatment and 690 kg K ha^{-1} for the high N treatment. Potassium was applied as potassium sulphate. Nitrophoska® special (12% N, 5.2% P and 14.1% K) was applied at planting at a rate of 48 kg N ha^{-1}, 21 kg P ha^{-1} and 56 kg K ha^{-1} across all treatments. Lime was applied every 6 months from March 2015 at 1 t ha^{-1} (75% calcium carbonate and 25% magnesium carbonate). Measurements were conducted following fertiliser applications on 15 February and 14 March 2016, in the plant phase of the crop. The treatments for this trial (with rate of fertiliser in each of the two applications) were:

1) Low N rate (12 & 12 kg N ha^{-1}), no ground cover (LN-bare)
2) Low N rate (12 & 12 kg N ha^{-1}) with DMPP, no ground cover (LN+DMPP-bare)
3) High N rate (18 & 43 kg N ha^{-1}), no ground cover (HN-bare)
4) High N rate (18 & 43 kg N ha^{-1}), vegetative cover (HN-veg)

3.3.3 Gas emission measurements

Emissions of N_2O and CH_4 from the soil were measured using a manual chamber technique (Parkin and Venterea, 2010). Chamber rings were PVC pipe, 120 mm high and 300 mm in diameter, inserted into soil to approximately 50 mm depth for the duration of the trials. At the time of sampling, chambers were closed with lids having a rubber seal, septum and a capillary tube 450 mm long with a 1-mm internal diameter, to equalise the internal chamber pressure with atmospheric pressure. Emissions were measured four times in the first week, starting the day before fertiliser application, and then less frequently over the course of the following month. Each plot had four chambers located in the row (fertilised zone). An additional two chambers were placed in the centre of the grassed inter-row (non-fertilised zone) in each block (replicate). Gas emissions were measured between 9:00 and 11:00 AM Eastern Standard Time, as emissions during this period approximate the daily mean (Wang *et al.*, 2016a). Gas samples were extracted with a syringe and needle via the rubber septum at 0, 30 and 60 minutes after chamber closure. The syringe was pumped once gently whilst inserted in the chamber, to encourage mixing and to ensure a representative sample was collected from the chamber airspace. Samples were then injected into evacuated 12-mL glass Exetainer vials sealed with butyl rubber stoppers lined with Teflon (Labco Ltd part # 6RK9W, UK).

Concentrations of N_2O and CH_4 in the gas samples were measured using a Shimadzu GC-2010 gas chromatograph. Gas separation was effected using a Shincarbon packed column (Serial number C39711-01, length 2.0 m, internal diameter 2.1 mm) at 280°C. The carrier gas was helium, at a flow rate of 30 mL min^{-1}. CH_4 was detected using a flame ionisation detector at 300°C supplied with air (450 mL min^{-1}) and H_2 (10 mL min^{-1}). The methaniser was set at 390°C, using H_2 as makeup gas (35 mL min^{-1}). N_2O was detected using a ^{63}Ni electron capture detector at 330°C using N_2 as the makeup gas. Peak areas were determined using Shimadzu LabSolutions software and converted to concentrations by calibration against high purity N_2 (zero standard) and two BOC certified standards (1.1 µL L^{-1} N_2O and 4.1 µL L^{-1} CH_4; 10.1 µL L^{-1} N_2O and 41.6 µL L^{-1} CH_4).

The emission rate of N_2O was calculated according to the equation:

$$N_2O \text{ emission rate } (\mu g\ N\ m^{-2}\ h^{-1}) = \frac{28 d V_C}{A_C V_m} \quad \text{Eq. 1}$$

Where 28 is the mass of N per mole of N_2O (g mol^{-1}), *d* is the increase in chamber headspace N_2O concentration per hour at the time the chamber was closed (µL L^{-1} h^{-1}), V_c is the headspace volume (m^3), A_c is the area covered by the chamber (m^2) and V_m is the volume of one mole of ideal gas (m^3), given by the equation:

$$V_m = \frac{RT}{P} \quad \text{Eq. 2}$$

Where R is the gas law constant (8.3145 J mol K^{-1}), *T* is temperature (K) and *P* is pressure (Pa) at the time of measurement.

The rate of increase in chamber N_2O concentration, *d*, was not constant during the period of chamber closure so a quadratic equation was fitted to the data (concentration vs time) and the rate of increase at time zero was estimated using the coefficient of the term *x*. CH_4 emissions were determined in the same way as described above and reported as µg C m^{-2} hr^{-1}.

Chamber gas emission values were averaged for each plot, and treatment emission means and standard errors were then calculated from the plot values. Total gas emission from each plot over each monitoring period was determined in RStudio version 1.1.383 (RStudio, 2016) by trapezoidal integration between each measurement point ('pracma' package, Borchers, 2017). Total N_2O flux expressed as a percentage of N fertiliser applied was determined as the N_2O flux from the fertilised plots divided by the application rate of N fertiliser (uncorrected for emissions from plots with nil N applied).

3.3.4 Soil and climate measurements

At the time of gas emission measurements, soil samples were collected and analysed for C and N content and pH (pH at South Johnstone only). Ten soil samples (0–100 mm depth) were collected randomly across each plot and bulked before air drying at 40°C in a ventilated oven for 48 h. Samples were then ground and sieved to <2 mm. Soil mineral N content (ammonium; NH_4^+-N and nitrate-N; NO_3^--N) was determined by extraction with 2M KCl followed by automated colorimetric analysis (Method No: 7C2; Rayment and Lyons, 2010). Samples were analysed for total C contents using a LECO TruMac Dumas combustion analyser (Method No: 6B2a; Rayment

and Lyons, 2010). Soil pH was determined with a calibrated electrode at 25°C in a 1/5 soil/water suspension (Method No: 4A1; Rayment and Lyons, 2010). At the start of the South Johnstone experiment soil samples were also analysed for labile C using potassium permanganate oxidation (Method No: 6E1; Rayment and Lyons, 2010).

Soil water content and temperature (0–100 mm depth) were measured approximately 100 mm away from the chamber mid-way through chamber closure. Soil temperature was recorded using a digital thermometer, and volumetric water content was measured at with a hand-held HydroSense II® probe (Campbell Scientific). The probe (120 mm length) was inserted on an angle to achieve 100 mm depth. Water filled pore space (WFPS) was determined using the equation:

$$\text{WFPS (\%)} = 100 \times \text{volumetric water content (\%)} / \text{total soil porosity (\%)} \quad \text{Eq. 3}$$

Where total soil porosity = 1 – (soil bulk density/soil particle density) and soil particle density is assumed to be 2.65 g cm^{-3}. Bulk density was measured at 0–100 mm in the row of each plot at both sites, and values averaged for each treatment. Bulk density in the inter-row was measured only at East Palmerston. Bulk densities from the row at East Palmerston (mean 1.14 g cm^{-3}) were similar to South Johnstone (mean 1.08 g cm^{-3}), therefore the inter-row value from East Palmerston (1.26 g cm^{-3}) was used for the inter-row at South Johnstone.

Rainfall, air temperature and soil temperature were measured continuously in both trials. Rainfall was measured by pluviometers fitted with a 0.2-mm tipping buckets. Air temperature (under canopy) and barometric pressure were recorded using Solinst Barologgers®. At South Johnstone, temperature sensors and loggers (Tinytag®) were used to measure soil temperature (0–50 mm) at 30-minute intervals inside three chambers close to each other in the centre of the trial, one in each of the following treatments: vegetated soil (HN-veg), bare soil (LN-bare) and the inter-row. At East Palmerston, sensors were located inside two LN-bare chambers, one near the south west corner and one near north east corner of the trial.

3.3.5 Statistical analysis

The effect of treatments on gas emissions and other variables was determined using one-way analysis of variance (ANOVA) in Genstat (18th Edition, VSN International Ltd., UK). Data were checked for normality and no transformations were necessary. Where there was a significant F test (p<0.05) Fisher's 95% protected least significant difference (LSD) was used to make pairwise

comparisons between means. Where multiple independent analyses were conducted simultaneously the P value (α) was adjusted by dividing by the number of comparisons made, to reduce to possibility of type 1 errors.

A generalised additive mixed model (GAMM) was used to assess the influence of environmental variables on N_2O emissions across the full study duration at both sites using the *MuMIn* package in R. Fixed variables in the model were WFPS, soil temperature, and soil mineral N. Time since fertiliser application (in days) was included as a fixed variable to account for temporal dependency in the dataset (i.e. repeated measures). All fixed variables demonstrated non-linear relationships with N_2O emissions and were therefore fitted with smoothers (i.e. penalised regression spline smooth functions with smoothing parameters selected using a restricted maximum likelihood (REML) approach). Site and replicate (nested within site) were included as random factors to account for any spatial dependency in the data (Eq. 4). Results from the inter-row and any results with negative N_2O emissions were excluded from the model. N_2O emissions were natural log transformed to improve model fit. A model selection approach using both the Akaike Information Criterion (AIC) and the Bayesian Information Criterion (BIC) was used to simplify the model down to the most influential environmental variables. Variables describing spatial and temporal dependency (site, replicate, and time since application) were kept throughout the model selection process. Equations are not provided for the smoothers as they are unspecified functions, having been fitted using a "scatterplot smoother" (Hastie and Tibshirani, 1986).

$$\begin{aligned}\ln(\gamma_{N2O}) = \propto &+ f_1\,(WFPS) \\ &+ f_2\,(Soil\ temperature) \\ &+ f_3\,(Soil\ mineral\ N) \\ &+ f_4\,(Time\ since\ fertiliser\ application) \\ &+ (1 + Replicate \mid Site)\end{aligned} \qquad \text{Eq. 4.}$$

3.4 Results

3.4.1 East Palmerston site

Soil mineral N concentrations in the row increased markedly following fertiliser application and rainfall, in all treatments (Figure 3. 2). Concentrations of NH_4^+-N peaked two days after fertiliser application and one day after a 5.5-mm rainfall event, and then declined over the following three weeks. The highest NH_4^+-N concentrations were reached in the HN-bare treatment, peaking at 48 mg kg^{-1} (p<0.01 on 4 March 2015). During that time concentrations were similar in the low N

treatments, peaking at 15.3 and 17.0 NH_4^+-N mg kg^{-1} for treatments with and without DMPP, respectively. After the peak in NH_4^+-N concentrations had passed, concentrations in the rows were similar to the unfertilised grassed inter-row. Concentrations of NO_3^--N peaked later, four days after fertiliser application (and a total of 50 mm rainfall), and remained elevated for a fortnight for all treatments (in the row). The highest NO_3^--N concentrations were reached in the HN-bare treatment, peaking at 56.5 and 47.3 mg kg^{-1} on 6 March 2015 and 10 March 2015 (p<0.01), respectively. The LN+DMPP-bare treatment had marginally lower NO_3^--N concentration (19.3 mg kg^{-1}) than the equivalent treatment rate without DMPP (23.3 mg kg^{-1}), but this difference was not statistically significant. For the second half of the month all NO_3^--N concentrations in the row remained similar to the inter-row.

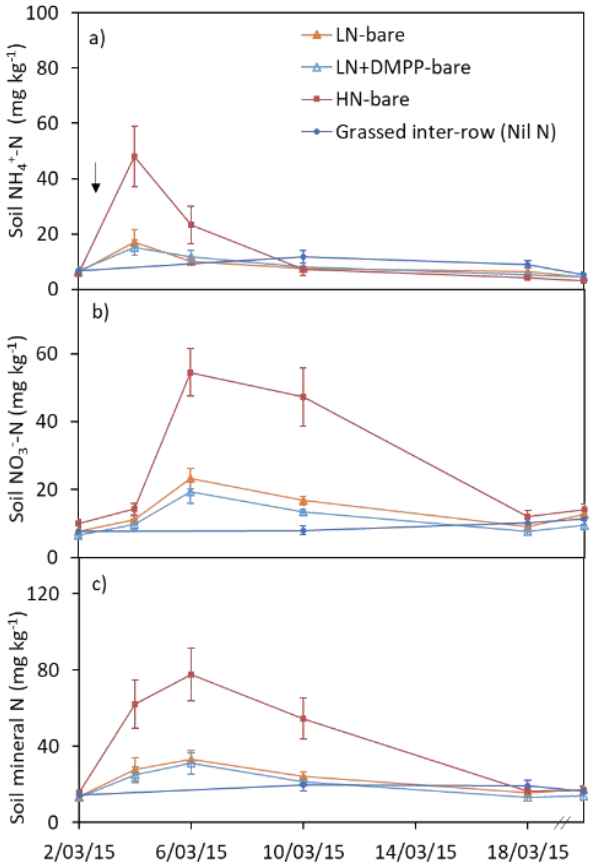

Figure 3. 2. Mean a) soil ammonium (NH_4^+-N), b) soil nitrate (NO_3^--N) and c) soil mineral N concentrations in the 0–100 mm layer at the East Palmerston Site. Arrow in a) indicates time of fertiliser application. The error bars are standard errors of the mean.

Note discontinuity in the timeline represented on the x axis of a), b) and c) (final date 1 April 2015), and lesser number of sampling times in the inter-row.

N_2O emissions occurred as a pulse following fertiliser application and rainfall in all treatments (Figure 3. 3). N_2O emissions peaked three days after fertiliser application and one day after a 44.5-mm rainfall event, and then declined over the following fortnight, regardless of further rainfall throughout this period. During the peak in emissions, soil water content in the rows averaged 39% WFPS. This was in contrast to the relatively dry soil conditions (17% WFPS) on the day of fertiliser application (Figure 3. 3). The highest N_2O emissions were reached in the HN-bare treatment, peaking at 389 µg N m^{-2} hr^{-1} (p=0.001 on 5 March 2015). At this time N_2O emissions in the low N treatments were similar at 117 and 121 µg N m^{-2} hr^{-1} for treatments with and without DMPP, respectively. In comparison, the emissions in the unfertilised grassed inter-row were lowest at 28 µg N m^{-2} hr^{-1}, although N_2O emissions in the inter-row peaked the day prior (58 µg N m^{-2} hr^{-1} on 4 March 2015) after the initial 5.5-mm rainfall event.

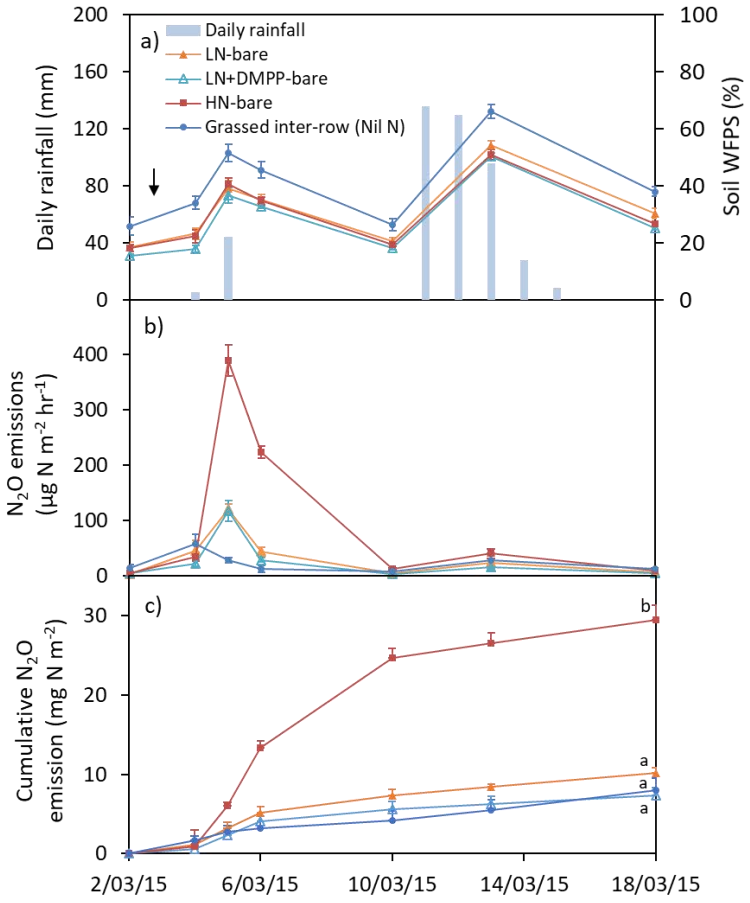

Figure 3. 3. Nitrous oxide emissions and environmental conditions at the East Palmerston site, showing a) daily rainfall, irrigation and soil water filled pore space (WFPS, 0–100 mm); b) mean N_2O emissions; and c) cumulative N_2O emissions. Arrow in a) indicates time of fertiliser application. The error bars are standard errors of the mean. Letters in c) indicate significant differences between emissions for each treatment at the end of the period (p<0.001).

LN and HN treatments had N application rates of 12 and 54 kg N ha^{-1}, respectively.

In order to estimate total N_2O flux for the month of March, N_2O emissions at the end of the month were estimated. During the last fortnight a total of 56 mm rainfall was recorded and on 1 April 2015 the soil was noted as dry when collecting samples for mineral N analysis. Based on these conditions, low mineral N and previous measurements, N_2O emissions were assumed to have remained constant from 18 March 2015 (<11 µg N m^{-2} hr^{-1}) to the end of the month. Overall, total N_2O flux was greatest from the HN-bare treatment (Figure 3. 3; p<0.001), and estimated to be 38 mg N m^{-2} for the month. The low N treatments and inter-row had lower fluxes, estimated to be 15, 11 and 15 mg N m^{-2} for LN-bare, LN+DMPP-bare and the inter-row, for the month, respectively. Based on this, total N_2O flux as a percentage of applied fertiliser N was 0.20, 0.36 and 0.25% for HN-bare, LN-bare and LN+DMPP-bare treatments, respectively.

CH_4 emissions from soil ranged from -12.0 to 9.9 µg C m^{-2} hr^{-1} (data not shown). There was no statistical difference between treatments, with a mean of -2.9 µg C m^{-2} hr^{-1}, or -0.71 g C ha^{-1} day^{-1}. There was no relationship between CH_4 emission rates and any of the environmental variables measured.

Temperatures were high throughout most of the study period. During the pulse in N_2O emissions the soil temperature averaged 25.7°C (Figure 3. 4). However, soil temperatures frequently peaked between 35 and 45°C in the afternoons. Mean daily air temperature was 26.2°C and ranged from 17.9 to 43.9°C.

Total C content of soil did not differ significantly between the bare rows or grassed inter-row, averaging 2.2% for all treatments (data not shown).

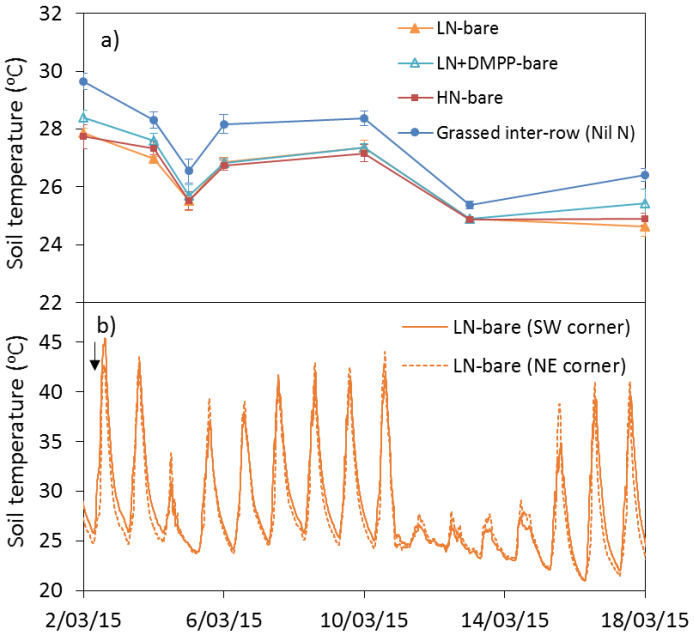

Figure 3. 4. Soil temperature at the East Palmerston site, in the a) 0–100 mm layer of soil during chamber closure, and b) 0–50 mm layer of soil recorded at 30 minute intervals in two locations in the row. Arrow in b) indicates time of fertiliser application. The error bars are standard errors of the mean.

3.4.2 South Johnstone site

Soil mineral N concentrations in the row increased markedly following fertiliser application and irrigation or rainfall, in all treatments (Figure 3. 5). Concentrations of NH_4^+-N peaked within 24 h of initial irrigation or rainfall, whereas NO_3^--N concentrations peaked at three to six days. NO_3^--N concentrations remained elevated for at least two weeks compared to NH_4^+-N, which tended to decline to similar concentrations as in the inter-row within a fortnight. NO_3^--N concentrations did not return to similar levels as the inter-row, with all treatments higher in concentration at the end of each month. This was most evident in the HN-bare treatment, which had significantly higher NO_3^--N concentration (p<0.001) than the other treatments, at the end of the second monitoring period (17.3 mg kg^{-1} on 11 April 2016).

Concentrations of NH_4^+-N following the first fertiliser application and 30 mm of irrigation in February were highest in the LN+DMPP-bare (30.5 mg kg^{-1}) and HN-bare (22.8 mg kg^{-1}) treatments, but there was no significant difference between treatment means. Following the second fertiliser application with 9 mm rainfall in March, concentrations of NH_4^+-N were highest in the HN-bare treatment (70.8 mg kg^{-1}) and HN-veg (64.3 mg kg^{-1}) treatments. This increase in concentration from the first month followed the increase in N application rate for the high N treatments. During the first month NH_4^+-N and NO_3^--N concentrations in HN-bare and HN-veg

treatments were similar, however during the second period concentrations in the HN-veg treatment declined faster for both NH_4^+-N (p<0.01 on 20 March 2016) and NO_3^--N (p<0.001 on 20 March 2016 and 29 March 2016). Throughout both months NO_3^--N concentrations in the LN+DMPP-bare treatment were marginally lower than the equivalent treatment rate without DMPP, however this difference was not statistically significant.

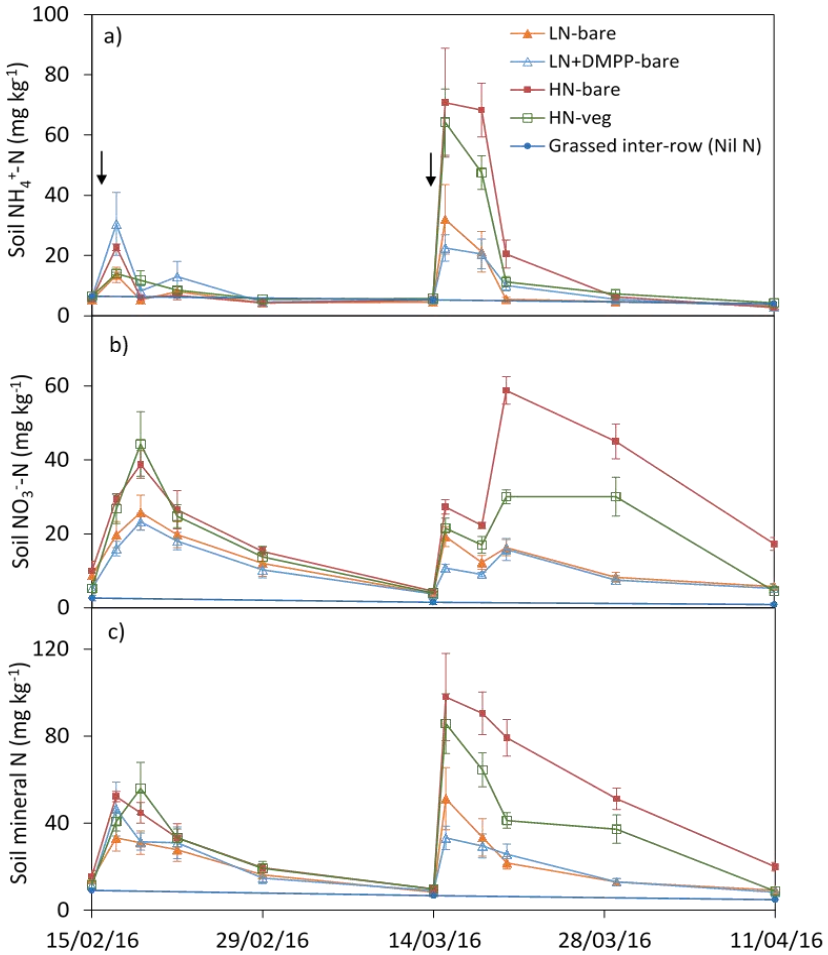

Figure 3. 5. Mean soil ammonium (NH_4^+-N; a), nitrate (NO_3^--N; b) and mineral N (c) concentrations in the 0–100 mm layer of the row treatments at the South Johnstone site. Arrows in a) indicate time of fertiliser application. The error bars are standard errors of the mean.

Note lesser number of sampling times in the inter-row.

N_2O emissions occurred as pulses coincident with the first substantial increase in soil water content after applying fertiliser, whether via rainfall or irrigation (Figure 3. 6). The magnitude of the emissions was governed by soil mineral N content and WFPS. The pulses were 2–8 days long, with their duration corresponding with the duration of elevated soil water content. Treatment effects were most evident during these pulses. The pulses finished when soil water content

subsided, even though soil NO_3^--N concentration remained elevated. In the following weeks emissions tended to remain fairly low, irrespective of increases in soil WFPS, due to the steady decline of soil mineral N concentration.

Overall, the highest N_2O emissions occurred in March and in the HN treatments, peaking at 513 and 514 µg N m^{-2} hr^{-1} for treatments with and without vegetative cover, respectively (p<0.001 on 18 March 2016). At this time emissions were lower in the LN treatments, peaking at 210 and 75 µg N m^{-2} hr^{-1} for LN-bare and LN+DMPP-bare, respectively. Emission from the LN+DMPP-bare was not significantly different to that in the inter-row (-1.3 µg N m^{-2} hr^{-1}).

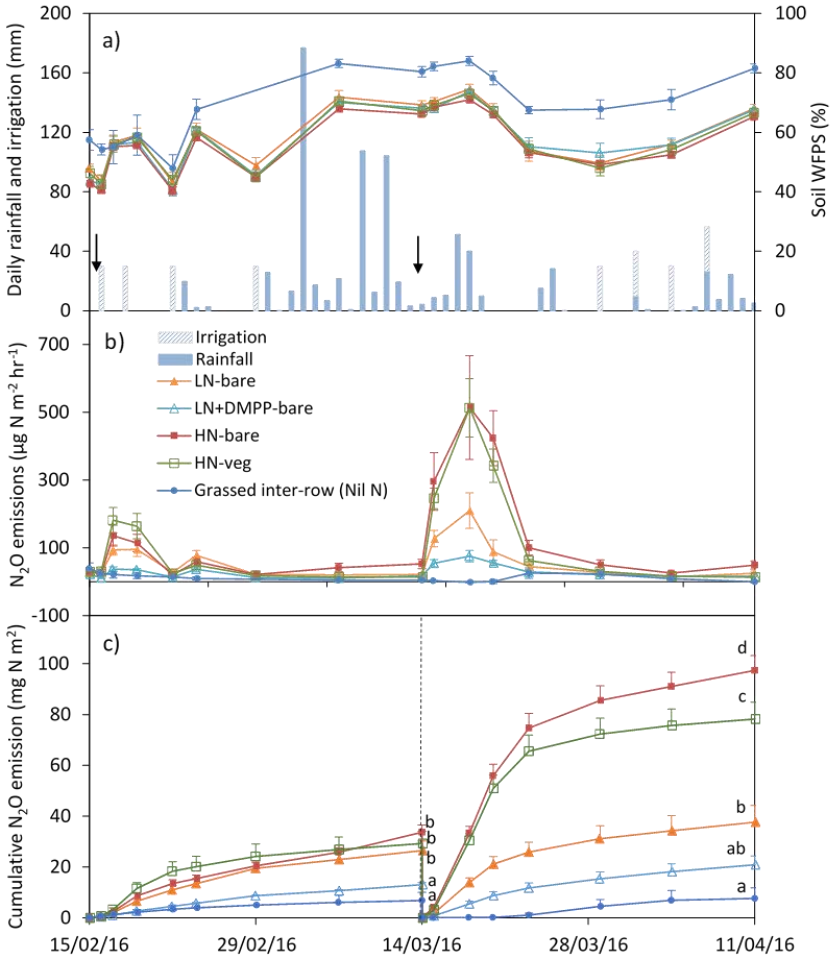

Figure 3. 6. Nitrous oxide emissions and environmental conditions at the South Johnstone site, showing a) daily rainfall, irrigation and soil water filled pore space (WFPS, 0–100 mm); b) mean N_2O emissions; and c) cumulative N_2O emissions. Arrows in a) indicate time of fertiliser application. The error bars are standard errors of the mean. Letters in c) indicate significant differences between emissions for each treatment at the end of the period (p<0.001). LN and HN treatments represent N application rates of 12 and 18 kg N ha^{-1} in February, and 12 and 43 kg N ha^{-1} in March, respectively.

Total N_2O flux for the first month following fertiliser application was greatest in the HN-bare (34 mg N m^{-2}), HN-veg (29 mg N m^{-2}) and the LN-bare (27 mg N m^{-2}) treatments, whilst the lowest emissions were from the LN+DMPP-bare treatment (13 mg N m^{-2}) and the un-fertilised grassed inter-row (7 mg N m^{-2}, p<0.001; Figure 3. 6). In the second month, the HN treatments significantly increased in total N_2O flux compared to the LN treatments (p<0.001), being 97 mg N m^{-2} in HN-bare and 78 mg N m^{-2} in HN veg, compared with 38 and 21 mg N m^{-2} in LN-bare and LN+DMPP-bare, respectively. This increase in N_2O flux from the first month reflected the increase in fertiliser N applied (18 to 43 kg N ha^{-1}). However, the HN-veg treatment was significantly lower than the HN-bare treatment, unlike the preceding month (Figure 3. 6). N_2O flux as a percentage of N fertiliser applied over both observation periods was 0.40–0.63% (LN+DMPP-bare), 0.80–1.14% (LN-bare), 0.68–0.82% (HN-bare) and 0.59–0.66% (HN-veg) of N applied in February and March, respectively.

The lowest N_2O emissions in the row were in the LN+DMPP-bare treatment, whilst the lowest emissions overall were in the unfertilised grassed inter-row (Figure 3. 6). Use of DMPP approximately halved N_2O emission compared with the equivalent rate of urea without DMPP, in both months. However, during the second month emissions from the LN+DMPP-bare were statistically similar to both the LN-bare and the inter-row.

In general, N_2O emissions were greater following rainfall on wet soil compared to irrigation on drier soils (Figure 3. 6). At the time of fertiliser application in February the soil had a moderate water content of 45% WFPS, which rose to 56% following irrigation. In contrast, at the time of fertiliser application in March the soil had a higher water content of 68% WFPS, which increased to 73% WFPS following rainfall. As a result of the increase in soil water content, N_2O emissions for LN treatments were 1.6-fold (p=0.07) and 1.4-fold (p=0.06) higher in March than in February for LN+DMPP-bare and LN-bare, respectively. This change occurred even though the fertiliser application rate was the same (12 kg N ha^{-1}) each month.

CH_4 emissions from soil ranged from -14.9 to 22 µg C m^{-2} hr^{-1} for all treatments (data not shown). There was no statistical difference between treatments, with a grand mean of 5.5 µg C m^{-2} hr^{-1}, or 1.46 g C ha^{-1} day^{-1}. There was no relationship between CH_4 emission rates and the environmental variables measured.

Soil temperature throughout the monitoring period ranged from 23 to 35°C (Figure 3. 7). The diurnal range in soil temperature appeared to be lower in vegetated soil than bare soil, but the observations were not replicated, so the effect is uncertain (Figure 3. 7). Mean daily air temperature was 26.6°C and ranged from 18.5 to 44.4°C.

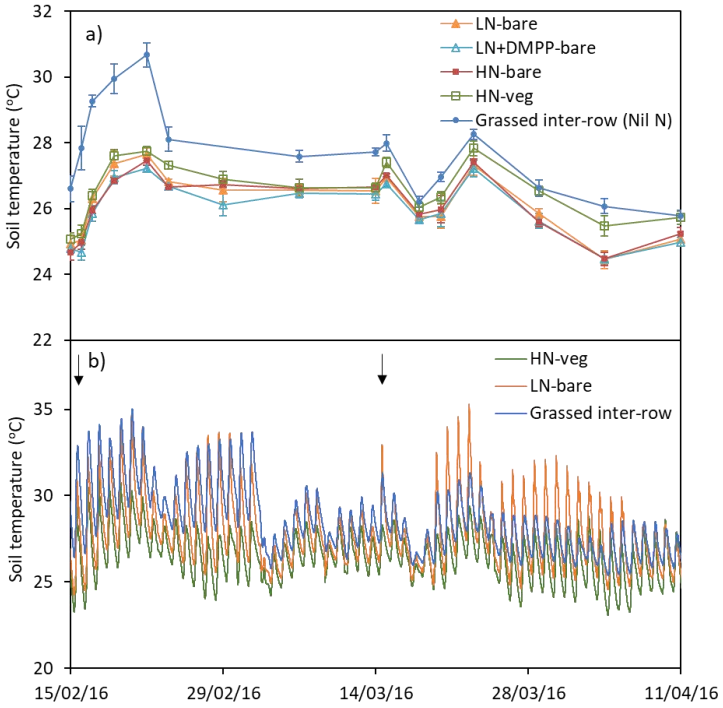

Figure 3. 7. Soil temperature at the South Johnstone site, in the a) 0–100 mm layer during chamber closure (between 9 and 11 am), and b) 0–50 mm layer recorded at 30 minute intervals in a LN-bare and HN-veg row treatment plot and the grassed inter-row. Arrows in b) indicates time of fertiliser application. The error bars are standard errors of the mean.

Soil pH decreased with increasing N rate (Figure 3. 8). Fertilised treatments generally had lower soil pH than in the unfertilised grassed inter-row (p=0.001 on 15 February 2016). Overall, the HN-bare treatment had the lowest soil pH, with a mean of 4.9. The HN-veg (mean pH 5.1) was not significantly different from the HN-bare treatment or either LN treatment (5.3; p>0.05). However, at times soil pH in the HN-bare was distinctly lower than in the HN-veg treatment (p<0.001 on 20 March 2016).

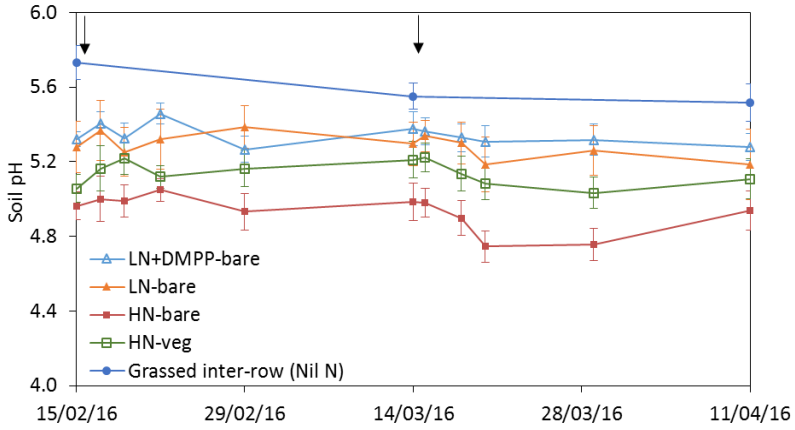

Figure 3. 8. Mean soil pH in the 0–100 mm layer of the row at the South Johnstone site. Arrows indicate time of fertiliser application. The error bars are standard errors of the mean.

Total soil C content did not differ significantly between treatments, although the mean tended to be greater in treatments with vegetated ground cover than those without, with means of 1.93 and 1.97 g kg^{-1} for LN-bare and HN-bare, 1.99 g kg^{-1} for the grassed inter-row and LN+DMPP-bare, and 2.01 g kg^{-1} HN-veg, respectively. A similar result was true for soil labile C concentrations, with means of 1.17, 1.25, 1.27, 1.28 and 1.30 g kg^{-1} for LN-bare, HN-bare, HN-veg, the grassed inter-row, and LN+DMPP-bare, respectively (data not shown).

3.4.3 Environmental drivers of N_2O emissions

The final model describing the effect of measured environmental variables on log-transformed N_2O emissions contained time since fertiliser application, soil WFPS and soil mineral N concentration. All predictor variables were non-linearly related to log-transformed N_2O emissions and were highly significant (p<0.001). The model R^2 was 0.758.

Using soil mineral N concentration instead of soil NH_4^+-N and NO_3^--N separately improved model fit. Subsequent backward stepwise regression indicated that soil temperature did not contribute to the overall model and could be discarded. The effect of the two strongest drivers on measured N_2O emissions shows that a large range of WFPS and soil mineral N concentrations were encountered across the banana sites (Figure 3. 9).

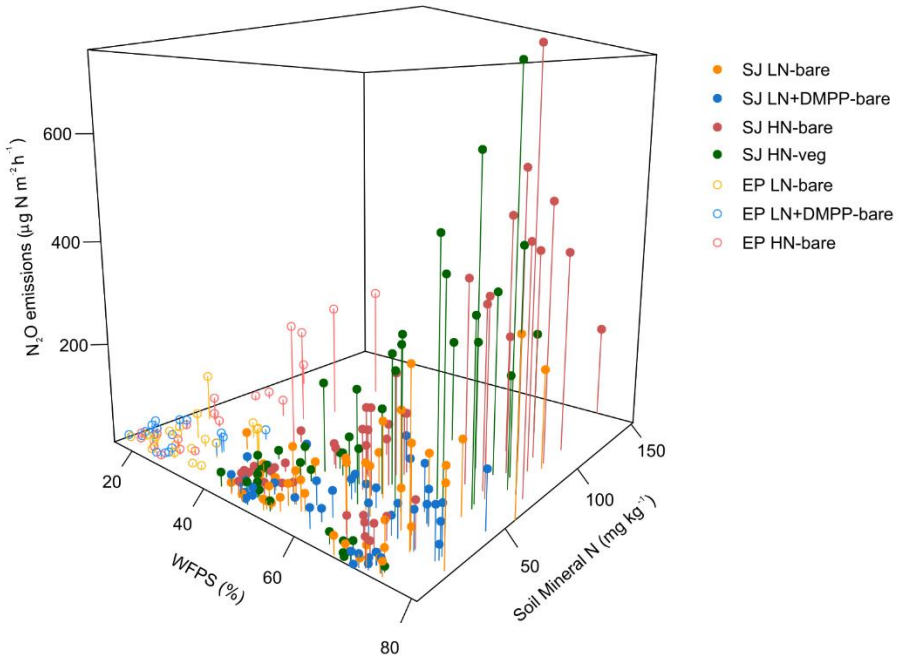

Figure 3. 9. N_2O emission as a function of soil water-filled pore space (WFPS) and soil mineral N concentration, across both study sites and the entire study period. Filled points represent South Johnstone (SJ) measurements and hollow points represent East Palmerston (EP) measurements.

Note inter-row emissions excluded.

3.5 Discussion

3.5.1 N_2O emissions and regulating factors

In this study, soil mineral N concentration and water content were the primary environmental drivers of N_2O emissions (Figure 3. 9), as found by several others (Veldkamp and Keller, 1997; Crill *et al*., 2000). Soil temperature was not so important, unlike other studies (Zhu *et al.*, 2015; Wang *et al.*, 2016a). Because measurements were confined to the warmer wet season months the variation in soil temperature was small, but the variation in soil water content was high, thereby reducing the influence of temperature as a driving factor. These results emphasise the importance of rate and timing of N fertiliser application with respect to rainfall or irrigation when managing loss of N_2O, which is frequently underscored in the literature.

Emissions of N_2O appeared to originate from both nitrification and denitrification, depending on conditions. Following the application of fertiliser and rainfall/irrigation, soil NH_4^+-N peaked within 1–2 days indicating rapid hydrolysis of applied urea, and then declined within 3–4 days of application, giving way to a predominance of soil NO_3^--N. This was consistent with previous investigations into the fate of urea in banana fields (Prasertsak *et al.*, 2001). There was an

exception following the fertiliser application in March at South Johnstone, when nitrification appeared to stall and NH_4^+ concentrations remained elevated for 6 days. In this situation an extended period of rainfall led to soil water contents of 67–73% WFPS, which indicates reasonably anoxic conditions. Nitrification requires aerobic conditions, which peak around 60% WFPS (Linn and Doran, 1984; Bouwman, 1998). Therefore, during this wet period nitrification presumably declined in favour of denitrification. Denitrification generally produces N_2O in favour of N_2 at WFPS between approximately 60 and 80% (Bouwman, 1998). Consequently, denitrification would have been responsible for a major proportion of N_2O in the peak of this event, as there was also an ample supply of NO_3^-. Contributions of N_2O from both nitrification and denitrification may explain why the model of environmental drivers was best represented by soil mineral N, rather than either NH_4^+-N or NO_3^--N. In studies were nitrification is the main source of N_2O emissions, soil NH_4^+-N content has been found to be a primary explanatory variable (e.g. Zhu *et al.*, 2015).

N_2O emissions in the unfertilised grassed inter-row differed between sites. At South Johnstone during the denitrification event outlined above there was briefly net consumption of N_2O (negative emission) in the inter-row (Figure 3. 6). In this situation of low mineral N concentrations (mean 5.8 mg N kg^{-1}) and high WFPS (>81%) it appears that denitrification was reducing N_2O to N_2 so rapidly that N_2O concentrations in the soil dropped below those in the atmosphere (Blackmer and Bremner, 1976; Chapuis-lardy *et al.*, 2007). Negative N_2O fluxes did not occur in the inter-row at East Palmerston. To the contrary, emissions rose after the first rainfall. This rise was likely due to the sufficient soil mineral N content (mean 17.5 mg N kg^{-1}) and suitable soil water content (66% WFPS). The East Palmerston site had recently come out of fallow with Rhodes grass, which has been found to improve soil condition (Anderson *et al.*, 1966). In contrast, the soils at South Johnstone had been under banana production for many years.

N_2O emissions were higher on the Dermosol at South Johnstone than the Ferrosol at East Palmerston. This was presumably the result of greater soil water content on the Dermosol, ranging from 40 to 73% WFPS, compared to 16 to 54% WFPS on the sloping Ferrosol. N_2O emissions increase with increasing soil water content, peaking at approximately 60–80% WFPS (Bouwman, 1998). South Johnstone received more rainfall and irrigation. Furthermore, the highest WFPS occurred shortly after fertilising, unlike at East Palmerston, where the highest WFPS occurred later in the month when soil mineral N concentration was lower. Irrespective of

rainfall received, Ferrosols also have high permeability throughout the profile (Bell *et al.*, 2005) which reduces soil water content at the surface, as demonstrated by the moderate water content (54% WFPS) immediately following 362 mm of rainfall over three days (Figure 3. 2).

On the whole, the initial soil water content and amount of rainfall or irrigation received in the five days after fertilising was largely responsible for the differences in N_2O emissions, given the same N rate. Over the study period the total amount of rainfall and irrigation within five days of the three fertiliser applications studied was 50 mm rainfall at East Palmerston, compared to 60 mm (2 x 30-mm irrigation) at South Johnstone in February and 121 mm rainfall at South Johnstone in March. In that same order, WFPS at the time of fertiliser application was 17, 45 and 68%. Consequently, total N_2O loss from the LN-bare treatments (12 kg N ha^{-1}) treatments during those events was 15, 27 and 38 mg N m^{-2}, respectively. To put this in context, the greatest N_2O loss event of the study was at South Johnstone in March, after fertiliser was applied on wet soil following 515 mm of rainfall in the previous fortnight, followed by 121 mm rainfall in the subsequent 5 days. This demonstrates the risk of N_2O loss when applying fertiliser in the wet season in a "lull" between rainfall events. In situations where scheduled fertiliser applications have been consistently delayed due to wet conditions it would be more desirable to avoid fertiliser application, or to catch up with smaller N applications to minimise risk of N_2O emissions, reserving higher N rates for periods of lower soil water content and lower rainfall. Furthermore, when possible, irrigation scheduling could be managed to apply less water in the week after fertilising (without limiting plant growth), and to increase applications later in the month, if rainfall is insufficient. This active management of the soil water deficit would minimise elevated soil water content at peak soil mineral N concentration, and hence reduce N_2O emissions.

3.5.2 Effect of fertiliser N application rate

N_2O emissions consistently increased with increasing fertiliser application rate (Figure 3. 2 and Figure 3. 6). In context, the high N rates applied in this study reflect Australian industry standard of 350 kg N ha^{-1} yr^{-1} for both plant and ratoon (DAFF, 2016). The low N rates reflect estimated plant crop requirements (150 kg N ha^{-1} $crop^{-1}$), which has previously been demonstrated to maintain yield and lower NO_3^- leaching losses during root establishment (Armour *et al.*, 2013). The range of N rates assessed in this study (12–54 kg N ha^{-1} $month^{-1}$) could be applied within fertiliser regimes aimed at any annual target. Our results demonstrate that adjusting to lower N rates during the wet season would reduce the risk of N_2O loss. Less urea applied in wet

conditions would also minimise N losses via leaching and other gaseous pathways. Leaching of NO_3^- in bananas can represent a substantial portion of the N applied with a range of 24–63% reported in other studies (Prove *et al.*, 1997; Armour *et al.*, 2013). NO_3^- in soil water and groundwater systems may consequently be exposed to denitrifying bacteria (Wakelin *et al.*, 2011), and eventually discharged into drains, rivers and the sea (Rasiah *et al.*, 2010). In surface soil, volatilisation of ammonia (NH_3) gas is also possible, as Prasertsak *et al.* (2002) showed that up to 17% of urea can be volatilised in the 9 days following fertiliser application to wet soil, compared to 3% on dry soil. Furthermore, high nitric oxide (NO) emissions have also been found following urea application to wet soil in banana fields, at a ratio of 1/1 for N_2O/NO at 75% WFPS, though the mechanism for this loss is not fully understood (Veldkamp and Keller, 1997). Nitric oxide emissions are primarily associated with nitrification in drier conditions (<60% WFPS; Bouwman, 1998).

N_2O emissions in our study (0.02 to 1.14% of applied N) were lower than those found in other cropping studies in the tropics. In China, a banana study by Zhu *et al*. (2015) reported emission factors of 1.76 to 2.31%, with N application rates of 312–623 kg N ha^{-1} for a sandy loam textured soil, whilst in Cost Rica Veldkamp and Keller (1997) reported a range of 1.26 to 2.92% for 360 kg N ha^{-1} for bananas in a clay and a loam textured soil, respectively. Similar to the Zhu *et al*. study (2015) our percent losses did not increase proportionally with increasing N rate. In comparison to another tropical crop, studies in sugarcane indicate emission factors are between 1.0% and 6.7%, but with exceptional situations of higher losses of up to 21% (Allen *et al.*, 2010; Denmead *et al.*, 2010; Wang *et al.*, 2016a; Wang *et al.*, 2016b). Annual rates of N fertiliser application in sugarcane are typically 130–160 kg N ha^{-1}, approximately half those in bananas. A review of N_2O emission factors from tropical and sub-tropical agricultural systems found that on a regional basis mean emission factors were lower for Australia (0.9%) compared with Africa (1.4%), Central & South America (1.3%), and Asia (1.1%; Albanito *et al.*, 2017). Currently, global N_2O emission estimates by the Intergovernmental Panel on Climate Change in the Tier 1 calculations are based on a default emission factor of 1% (IPCC, 2006) and assume a linear response to N loading.

One of the possible reasons for the difference in N_2O emissions between our study and previous studies could be the frequency of emission measurements and fertiliser applications. Our study determined N_2O emissions over the course of each period of application (monthly) with an intensive event-based sampling regime, whilst the other studies sampled less frequently (e.g.

10-day or monthly interval) and incorporated the seasonal variations across the year. Furthermore, the frequency of fertiliser application by Zhu *et al*. (2015) was lower. Urea was applied at 40–60 day intervals resulting in high N dosing, in some instances 100–199 kg N ha^{-1} in one application. This less frequent application regime results in higher soil mineral N contents in excess of short-term plant demand, and consequently increases the potential for N_2O production. The intensive sampling regime used in the timeframe of our study captured the temporal variation inherent in N_2O emissions (Veldkamp and Keller, 1997). However, it did not account for the likelihood of lower emissions in the dry season (Veldkamp and Keller, 1997).

Another reason our banana study differs from the others is planting density and concentration of the fertiliser zone. Veldkamp and Keller's study (1997) more closely resembled our study with planting densities of 1,800 plants ha^{-1}, compared to 2,400 plants ha^{-1} in Zhu *et al*.'s (2015). Similar to our study, Veldkamp and Keller (1997) surface-applied fertiliser on a monthly basis (constant rate of 27.7 kg N ha^{-1}). However, fertiliser was placed in an area covering a half circle under each plant, where the sucker was growing. This resulted in a more concentrated application than in our study, in which fertiliser granules were spread over the row area. Zhu *et al*. (2015) also applied fertiliser in more concentrated zones; they buried fertiliser in circular trenches approximately 0.3 m away from each banana plant and then applied drip irrigation to those points. The more concentrated the application the higher the NH_4^+ concentration and pH around fertiliser granules, which reduces nitrification rates (Janke *et al.*, 2019). Overall, these banana studies highlight the considerable variation in fertiliser management (rate, frequency, placement and timing) and soil type experienced in banana cropping. Therefore, emphasising the need for more regionally focused N_2O studies to adequately assess differences in environmental conditions and specific management practices.

The low soil pH experienced in the high N treatment may also be contributing to higher N_2O production, as N_2O emission factors increase significantly with decreasing soil pH (Wang *et al.*, 2018). Increasing soil pH with lime may be a viable abatement strategy were high N rates are used (Shaaban *et al.*, 2015). By increasing soil pH the complete reduction of N_2O to N_2 is encouraged, thereby decreasing the ratio of N_2O/N_2 (Focht, 1974). In our study, lime was applied to all treatments at both sites on a 6 monthly basis at 1 t ha^{-1}, however this regime may need refining for higher N rates.

3.5.3 Efficacy of nitrification inhibitor

DMPP-treated urea approximately halved N_2O emissions at South Johnstone, but did not significantly lower emissions at East Palmerston. Similar variations in the effect of DMPP have been shown previously. For example, reductions in N_2O emissions have been found in barley, maize, and wheat (41–53%; Weiske *et al.*, 2001), grain sorghum (83%; Scheer *et al.*, 2016) and broccoli (75% during the crop phase only; Scheer *et al.*, 2014), but N_2O emissions were not consistently reduced in sugarcane (Wang *et al.*, 2016a; Wang *et al.*, 2016b). Soil temperature and water content are important factors influencing the efficacy of DMPP in soil (Menéndez *et al.*, 2012; Barrena *et al.*, 2017). Soil temperature at East Palmerston peaked between 40–45^{o}C over several afternoons, which may have accelerated the degradation of DMPP. This is well above the range of temperatures typically examined in laboratory studies (5–35^{o}C) (e.g. Suter *et al.*, 2010; Menéndez *et al.*, 2012; Mahmood *et al.*, 2017; Guardia *et al.*, 2018). At the time of this study, the plants at East Palmerston had yet to establish a full canopy and the bare soil of the row was unprotected by leaf residues due to the early stage of crop development. In comparison, the soil temperatures at South Johnstone were much lower as N_2O emissions were measured around bunch development and a full canopy.

Other studies investigating DMPP and N losses in Red Ferrosols, like that at East Palmerston, have found mixed results. Koci and Nelson (2016) found DMPP did not significantly impact N_2O emission in tropical dairy pasture. They postulated that DMPP may be inactivated by sorption on oxides, which are abundant in Ferrosols. They ruled out high soil temperature as a potential cause, but temperature was measured only at the time of gas measurements (morning), and not through the course of the day. Therefore the influence of temperature in their study is not clear. But they also acknowledged the study may have lacked a sufficient number of chambers to detect treatment effects, which is plausible given the highly variable nature of N_2O emissions (Chadwick *et al.*, 2014). In contrast, Suter *et al.* (2010) found in an incubation study, that DMPP was more effective at reducing N_2O emissions in a Red Ferrosol than three other soils, at 25^{o}C and 35^{o}C. DMPP was also found to effectively reduce N_2O emissions during the summer season of a sub-tropical wheat-maize cropping system in a Brown Ferrosol (De Antoni Migliorati *et al.*, 2014). Yet, in another study in a Red Ferrosol of cool temperate Australia, DMPP did not reduce NO_3^- concentration or leachate flux in potatoes, despite evidence of reduced NH_4^+ oxidation (Eyles *et al.*, 2018). Considering the conflicting results of the above studies, further investigations of the behaviour of DMPP in Ferrosols is warranted.

DMPP was less effective at mitigating N_2O emissions in wet soil than dry soil, despite having the lowest N_2O losses of each treatment. At the South Johnstone site, following irrigation on relatively dry soil, DMPP reduced N_2O emission by 51%. Under these conditions nitrification was likely the main source of emissions. In comparison, following fertiliser application to wet soil, DMPP reduced N_2O emission by only 44%. In this situation, denitrification would also have contributed to emissions. This difference in efficacy may be due to multiple reasons. Firstly, denitrification creates more N_2O (or N_2) per mole of N than nitrification. Therefore the reduction of NO_3^- in wet conditions may have led to greater N_2O emissions than the oxidation of NH_4^+ in drier soils. Secondly, DMPP may impact microbial activity differently at different soil water contents. A study by Barrena *et al.* (2017) showed that at a WFPS of 40% DMPP decreased NH_4^+-oxidising bacteria gene abundance (amoA), as well as denitrifying bacteria abundances (narG, nirK and nosZ gene) – which was assumed to be an indirect effect. Whereas at 80% WFPS, DMPP did not affect amoA gene abundance and increased the non-target denitrifying gene abundances. This suggests that DMPP may be more effective at lower soil water content when nitrification is the main process.

Whilst nitrification inhibitors have been found to decrease N_2O emissions, they have recently been found to increase volatilisation of NH_3, due to the preservation of NH_4^+ in soil (Qiao *et al.*, 2015; Lam *et al.*, 2017). Deposition of NH_3 in other systems can consequently lead to indirect emissions of N_2O (Lam *et al.*, 2017). Soils with low pH, high clay content, or high cation exchange capacities favour NH_4^+ sorption, but soils with high pH favour NH_3 volatilisation (Chin and Kroontje, 1963). Microscale studies of urea and DMPP by Janke *et al.* (2019) and Xu *et al.* (2019) demonstrated that high concentrations of NH_4^+ can result in elevated pH and aqueous NH_3 concentrations in the zone surrounding the N fertiliser. This influence is likely to be lower when fertiliser is broadcast rather than applied in a concentrated zone. However, considering losses of up to 17% as NH_3 with standard urea surface applied in bananas with soils of pH 4.5 (Prasertsak *et al.*, 2002), further investigation is merited. Pairing nitrification inhibitors with urease inhibitors may be an option to reduce ammonia losses (Lam *et al.*, 2017).

The efficacy of nitrification inhibitors in tropical crops differs between compounds and may be limited by high temperatures. The most commonly available nitrification inhibitors are nitrapyrin, dicyandiamide (DCD) and DMPP (Zerulla *et al.*, 2001). In tropical China, DCD combined with a urease inhibitor reduced N_2O emissions by 65.4% and increased banana yields by 4.5% (Zhu *et al.*, 2015). However, in this study soil temperature was <36.5^oC and the effect of

DCD cannot be isolated. A review by Chen *et al.* (2008) suggests DMPP is more effective than DCD and can be applied at lower concentrations, but it may be required in slightly higher concentrations in warmer climates. In our study the addition of DMPP was as a pre-treated granular fertiliser (ENTEC®). At this stage urea treated higher concentrations of DMPP is not available. Applying liquid DMPP at higher concentrations is a possible alternative, but may not be practical in banana cropping during wet conditions. However, another nitrification inhibitor, 4-amino-1,2,4-triazole (ATC), has been shown to be more effective than DMPP and DCD at reducing NH_4^+ oxidation in soil incubated at 35°C (Mahmood *et al.*, 2017). In that study DMPP and DCD reduced NH_4^+ oxidation for 1 week, compared to ATC, which was effective for up to 4 weeks. But ATC is not commercially available and has not been tested in bananas.

On both soil types DMPP tended to decrease nitrification rates, resulting in marginally lower NO_3^- in soil, but the effect was not statistically significant. On the Dermosol there was also generally higher NH_4^+ content, although again not significant. Even though not statistically significant, these small differences were enough to reduce nitrification and therefore N_2O emissions at the South Johnstone site. This is likely because influences on soil biotic and abiotic processes occur at the microscale in immediate proximity to the fertiliser, and diminish with increasing distance (>200 mm) away from the site of application (e.g. Janke *et al.*, 2019; Xu *et al.*, 2019). Therefore, significant differences may not be detectable at the scale of our sampling (plot scale).

In our study, DMPP-treated urea did not influence CH_4 emissions. Previous studies have shown mixed results in regards to the impact of DMPP on CH_4 emissions. In a laboratory-based study Menéndez *et al.* (2012) found no impact of DMPP on CH_4. Contrary to this, DMPP was found to reduce both CH_4 emissions in cereals (Weiske *et al.*, 2001) and an intensively managed olive orchard (Maris *et al.*, 2015).

3.5.4 Effect of ground cover

Lower N_2O emission from soil with vegetative ground cover than from bare soil was the apparent result of increased competition between plants and microorganisms for soil mineral N. Peak N_2O emissions shortly after fertilising were similar for both bare and vegetative treatments. However, total N_2O loss corresponded with a faster decline of soil mineral N following the highest rates of application (43 kg N ha^{-1}) and high rainfall, which would have accelerated plant growth rates in the warm conditions. Lower soil NH_4^+ and NO_3^- concentrations would

consequently reduce nitrification and denitrification rates, respectively. In general, vegetative ground covers do not appear to be as effective and consistent a method of N_2O mitigation as lower N rates. It is also possible that additional fertiliser N maybe required to compensate for increased competition for nutrients, which would likely offset the reduction in N_2O.

It is likely mowing the vegetative ground cover in the row and inter-row may have a minor influence on N_2O emissions, as plant residues would mineralise quickly in the hot and wet conditions. A grassland study found that N_2O emissions after defoliation were in the same order of magnitude as fertilising with 20 kg ha^{-1} (Calanca *et al.*, 2001). In our study, this may explain the initial high N_2O response in vegetative ground cover treatments after irrigating in February.

The generally larger amount of OC introduced into the soil in the vegetated treatments might be expected to increase sequestration of soil C in the longer term. Increases in soil total OC were not significant in the timeframe of this study (~1 year), however significant increases can be achieved over a 5-year timeframe (e.g. Johns, 1994).

The impact of banana leaf residues as ground cover was not assessed in this study, as there was less opportunity for leaf matter accumulation in the plant stage. In ratoon crops, surface cover of banana leaf residue is considerable and may impact nitrification and denitrification processes through contribution of organic matter, shading of soil, and the interception of fertiliser and irrigation water. This would be an important aspect to assess in future studies.

3.5.5 Implications for management

There is a trade-off between economic return on fertiliser investment and N_2O emissions. The lower N rate (standard urea) and vegetative ground cover led to lower N_2O emissions than high N rates on bare soil. However, they also increased bunch emergence times (DAWR, 2017; Pattison *et al.*, 2018). Vegetative ground cover treatments at East Palmerston also had lower average bunch weights. Bunch weight results at South Johnstone were uncertain due to a significant loss of bunches due to strong winds collapsing plants (DAWR, 2017; T.Pattison pers comm.). However, another study also found reduced bunch weights with Pinto peanut ground covers in bananas (Johns, 1994). It also seems the Pinto peanut legume did not contribute the additional N required to compensate for the increased demand of the plant and vegetative ground cover. N fixation by legumes is diminished when fertilised (Xie *et al.*, 2015; Pampana *et*

al., 2018). Increased bunch emergence times mean lower economic returns, as well as increased harvesting window timeframes that further reduce farming efficiency (Pattison *et al.*, 2018).

The agronomic response to DMPP was mixed. The DMPP-treated urea at the low N rate had significantly (p<0.05) reduced fruit bunch weight compared with low and high urea treatments at East Palmerston (Pattison *et al.*, 2018). However, in the following ratoon fruit bunch weights increased and were similar between fertiliser treatments. Bunch weight results for South Johnstone were again uncertain (DAWR, 2017; T.Pattison pers comm.). But leaf N concentrations were similar between the DMPP treatment and both the low and high N treatments (DAWR, 2017). DMPP is generally more effective at increasing crop yield in alkaline soils (Yang *et al.*, 2016), which may also explain the overall lack of consistent yield response.

The yield decline experienced in the low N treatments (and vegetative ground cover treatments) of our study maybe due to the trial design. Both experimental trials in this study were fertilised by surface broadcast on a monthly basis year round. But 36% greater N use efficiency can be achieved by fertigation (estimated by the ratio of the mass of fruit produced per unit of applied N) compared with surface broadcasting (Teixeira *et al.*, 2011). The low N rate used in this trial was based on fertigation. Similar fruit production can be achieved with 20% less N by fertigation compared conventional application (Teixeira *et al.*, 2007). In the Australian banana industry, fertigation is typically used to deliver N unless conditions are excessively wet. Therefore, broadcasting generally occurs only during the wet season. Had our trial been designed to accommodate a similar regime, the decline in yield with low N rate may have been avoided. Furthermore, this highlights the need to assess the impact of fertigation practices on N_2O production.

3.6 Conclusions

In this study, soil mineral N, water content and time since fertiliser application were the primary environmental drivers of N_2O emissions. Emissions occurred as pulses coincident with the first substantial increase in soil water content after applying fertiliser, whether via rainfall or irrigation. The greatest losses occurred with high rainfall shortly after fertiliser was applied to wet soils at high N rates. Lower losses occurred on comparatively drier soils following irrigation. The low N rate of 12 kg N ha^{-1} $month^{-1}$ (urea) had total N_2O emissions of 0.36–1.14% (percent applied N), compared to 0.20–0.82% in the high N rates of 18 to 54 kg N ha^{-1} $month^{-1}$. DMPP treated-urea approximately halved N_2O emissions on the Brown Dermosol, but lower emissions

on the Red Ferrosol were not significant. Vegetative ground covers in the row also reduced N_2O losses in wet conditions, possibly due to greater uptake of soil mineral N. However, this reduction is less than that resulting from lower N rates. Our results demonstrated that a reduction of N_2O emissions can be achieved by avoiding high levels of soil mineral N in wet soils through lower fertiliser rates, use of DMPP and appropriate timing of fertiliser application in respect to rainfall and irrigation. Further research is required to validate the efficacy of DMPP in Red Ferrosols and in hot soil temperatures (above 35^{o}C). Overall, our findings demonstrate that different N rates for the plant and ratoon stages might be warranted. The N rate representing 150 kg N ha^{-1} crop^{-1} had lower N_2O losses compared with the industry standard of 350 kg N ha^{-1} crop^{-1}.

Chapter 4: General Discussion

4.1 Comparison of experimental sites

This study was undertaken within two contrasting horticultural crops, bananas and mangoes, in tropical north east Queensland, Australia. Two banana trials were located on the coastal lowlands where annual rainfall is >3,000 mm annually, whereas the mango trial was situated on the tablelands at 456 m elevation where rainfall is <800 mm annually and there is a long dry season. The soils at the banana sites were a Ferrosol and a Dermosol, both characterised by moderate clay contents (33%; 0–0.1 m, respectively), whilst the soil at the mango site was a Chromosol with low topsoil clay content (<10%; 0–0.1 m). Fertiliser treatments were applied by surface broadcasting to the row only at all sites. The principal aims of this study were to 1) determine whether N_2O emissions were affected by N fertiliser rate and type (conventional urea vs enhanced efficacy fertilisers (EEFs)); 2) determine whether N_2O emissions are affected by soil surface management (standard bare soil vs mulched/living vegetative ground cover); and 3) determine the main environmental drivers (e.g. soil water content, temperature and/or mineral N content) that affect N_2O emissions. Based on the scientific literature, there was a general expectation that lower N rates and EEFs would reduce N_2O emissions. With this in mind, a balance with plant N and yield requirements is also necessary. The efficacy of EEFs depends on crop type, soil climate, and management factors (Chen *et al.*, 2008) and there has been limited investigation of these products in these tropical horticultural crops. The nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP or ENTEC®), was the only EEF applied in both crops. There is also limited understanding of how ground cover managements practices within these systems would impact N_2O emissions, also warranting further investigation.

4.2 Comparison of N_2O emissions in bananas and mangoes

Overall, nitrous oxide (N_2O) emissions were greater in the banana field than in the mango orchard. N_2O emissions in bananas were up to 1.14% of fertiliser N applied, whereas in the mango orchard they were <0.34%. The maximum N_2O emissions were 514 µg N m^{-2} hr^{-1} in bananas and 109 µg N m^{-2} hr^{-1} in mangoes. The amount of nitrogen (N) applied in each fertiliser application was similar in the two crops, being 12–54 kg N ha^{-1} in bananas, and 11–42 kg N ha^{-1} in mangoes. In bananas however, there were approximately 12 applications per year, resulting in a total application of 350 kg N ha^{-1} yr^{-1} (DAFF, 2016) compared to only 2–3 applications and 50–79 kg N ha^{-1} yr^{-1} in mangoes. This would result in repeated elevation of soil mineral N

concentrations and therefore greater opportunity for N_2O emissions in bananas (Dalal *et al.*, 2003; Zhu *et al.*, 2015), compared to mangoes. Measurements of N_2O emissions were carried out only in the wet season in bananas, but in both the wet and dry seasons in mangoes. It is plausible that N_2O emissions in the dry season are lower in bananas. However, even when this is considered, overall total N_2O flux would still be higher in bananas due to the substantially larger annual N application rate and wetter soil conditions.

The main reason for differences in N_2O emission between bananas and mangoes was the soil water content, which was primarily driven by soil type (texture) and rainfall. The Dermosol and Ferrosol soils in bananas consistently maintained greater soil water contents than the Chromosol in mangoes. Soil water contents in bananas ranged from 17 to 73% water filled pore space (WFPS), whereas in mangoes the range was 2–41% WFPS. The field capacity of the permeable sandy soil at the mango site was much lower, and in addition to lower rainfall, resulted in less soil water availability. Both crops were irrigated during drier periods, but the resultant soil water contents were lower in mangoes than bananas. N_2O production in soil peaks around 60% WFPS (Linn and Doran, 1984; Bouwman, 1998). Below this value soil conditions are considered to be primarily aerobic, and microbial nitrification is the dominant N_2O production process. Above 60% WFPS soil conditions are considered increasingly anaerobic, and therefore denitrification is the dominant process producing N_2O. But, as the value increases above 80–100% N_2O is further reduced to di-nitrogen (N_2) (Bouwman, 1998). Therefore, N_2O production in mangoes was low and presumably primarily a result of nitrification. Whereas in bananas, N_2O production was greater, and both nitrification and denitrification processes are likely to have been sources, due to the range of aerobic and anaerobic conditions experienced.

The nitrification inhibitor DMPP (3, 4-dimethylpyrazole phosphate) had mixed effects on N_2O emissions in both crops. Where DMPP did reduce N_2O emissions the average emission was approximately half that with standard urea at the same N rate. No statistically significant response was measured at low N application rates in mangoes (<25 kg N ha^{-1}), which was attributed to the already minimal N_2O emission from soil at that site, in addition to the highly variable nature of the emissions. Furthermore, there was no statistically significant response on the Ferrosol soil in bananas. Two conflicting environmental variables may be responsible for that result, including soil temperature and soil type. Soil temperature in the Ferrosol peaked between 40 and 45^{o}C over several afternoons, which may have accelerated the degradation of DMPP. However, Koci and Nelson (2016) also postulate that DMPP may be inactivated by sorption on

oxides, which are abundant in Ferrosols. In general, findings suggest that selected management and environmental conditions warrant the use of DMPP augmented urea, whereas other conditions do not, and further research is needed to increase our understanding of its efficacy and limitations. In mangoes, use of DMPP might be only justified during the wet season, when 60–70% of annual N fertiliser is applied, and when the highest rainfalls can occur. There is no justification to apply in the cooler winter months, when application rates are lower and soil temperatures are ~14–16^{o}C.

Groundcover (living or hay mulch) in the row area reduced N_2O emissions compared to bare soil by reducing available soil mineral N in both crops, but via different mechanisms. Ground cover in mangoes facilitated greater N uptake from soil, whereas living ground cover in bananas competed with the crop for soil mineral N. The application of hay mulch in mangoes created a favourable environment for surface roots to grow and hence facilitated greater uptake of soil mineral N. This consequently reduced N_2O emissions to approximately half those from bare soil. In comparison, the maintenance of living vegetative ground cover around the base of banana plants reduced the amount of soil mineral N available due to increased demand by the banana plant, ground cover, and soil microbes. This subsequently reduced available N for nitrification and denitrification. Overall, mulching in mangoes reduced N_2O and increased fruit yields, whereas living ground cover in bananas reduced fruit yield, but did not consistently reduce N_2O emissions. Moreover, the additional N required to supply bananas and groundcover may increase N_2O emissions, offsetting any mitigation potential of groundcover. Therefore, whilst vegetative ground covers may have other environmental benefits, such as reduced erosion and disease resistance to *Fusarium* wilt (Pattison *et al.*, 2014; McBeath *et al.*, 2018), they do not appear to be a suitable method for mitigating N_2O emission in bananas.

4.3 General conclusions

In this dissertation the effect of fertiliser N rates, EEFs (particularly DMPP) and ground covers on N_2O emissions in soil were examined in mango and banana fields. The management factors examined influenced soil mineral N, water content, temperature and possibly OC, all of which played important roles in determining total N_2O emissions in both crops. Banana fields had greater N_2O emissions due to greater soil water content and higher N rates, compared with mangoes, which had low soil water contents and lower N rates. N_2O emissions in banana fields probably originated from both denitrification and nitrification. In the mango field nitrification

was probably the primary source of N_2O, however persistent negative emissions suggested the presence of unidentified consumptive processes.

In banana fields, adapting to lower N rates and DMPP-augmented urea during wet conditions will reduce N_2O losses. Yet, vegetative ground covers do not appear to reliably mitigate N_2O emissions, and any reduction maybe offset by the additional N required to compensate for competition between the groundcover and the bananas. But the long-term impact of vegetative cover and N cycling was not assessed. In mangoes the most benefit would be gained from mulching. However, further research is required to substantiate the N_2O reduction of hay mulch over the longer term. Mitigation of N_2O emissions in mangoes does not seem as necessary as in bananas, as they are quite low. However, reductions can be made with DMPP, which would be best utilised during the wet season when higher N rates are applied.

On the whole, more study is required into possible reduced efficacy of DMPP in Red Ferrosols and during hot conditions (35–45^{o}C). Finally, the PC urea product in this study needs to be tested in conditions more favourable to denitrification (higher N rate and soil water content) in order to more appropriately assess its impact on N_2O production.

4.4 Future research directions and opportunities for improvement

The aim of this project was to assess the impact of the imposed treatments (fertilisers and ground covers) on N_2O emissions, rather than to determine N_2O emission factors. Whilst total N_2O flux as a percentage of applied N was calculated, and provided useful information, it did not incorporate the range of seasonal and management conditions experienced throughout the year. This is particularly true for bananas, as measurements were conducted only during the wet season. Measurements throughout the dry season would also need to include fertigation (and irrigation) practices, which is becoming the dominant method of N application in the Australian banana industry (outside of the wet season). Further to this, our study determined N_2O emissions only in the plant stage of the crop. Soil conditions in the ratoon are different. In ratoon crops there is considerable surface cover of banana leaf residue from mature plants, which may impact nitrification and denitrification though contribution of organic matter, shading of soil, and the interception of fertiliser and irrigation water. Finally, the planting density of banana plants in this study (1,333 to 1,666 plants ha^{-1}) was low compared to industry standard (1,680 to ~1,800 plants ha^{-1}). This was because plants were planted in single rows to allow increased sunlight penetration for vegetative ground covers. The industry standard is dual rows of banana

plants, which may have different impacts on N_2O production. Therefore, in order to obtain representative N_2O emission factors continual measurements across the year are required, with planting densities similar to industry standards. The inclusion of a nil N treatment would also be necessary to determine background emissions. This would provide improved estimates for country-specific (Tier 2) emission factors for the Australian national inventory of greenhouse gas emissions.

Negative N_2O emissions within the mango soil were frequent (40% of measurements) and intriguing. Other than denitrification, there has been little investigation or explanation of N_2O consumption processes in soil (Chapuis-lardy *et al.*, 2007). More research and understanding of the mechanisms behind natural N_2O consumptive processes may provide insights for new mitigation methods of N_2O emissions in agricultural soils.

More research on controlled release fertilisers and their impact on N_2O emission is needed. In this study, the range of environmental conditions required to induce N_2O emissions (high soil water content, soil mineral N, etc.) were not sufficient to test the efficacy of the polymer coated product tested (in mango soils). Furthermore, polymer sulphur coated urea products, such as the one tested in this study (Agrocote®) have already mostly been superseded by purely polymer coated products such as AgroMaster tropical® (also by Everris International; S.Stacey, pers comm. 2015). Independent research should keep abreast of product development in the fertiliser industry. Additionally, there are environmental concerns for the long term consequences of polymer application to soil (i.e. microplastic pollution), and further exploration in this area needs to be considered if these products are utilised as N_2O mitigation methods.

It is possible that the polymer coated urea does not pair well with a hay mulch system, although it was not tested in this study. The polymer coating prevents immediate dissolution. Therefore, it is possible that the fertiliser granules may remain physically suspended in the mulch layer after surface broadcast application, resulting in increased volatilisation over the time of release. Therefore, further investigation is warranted.

A greater understanding of the DMPP and its impact on N_2O emission over a range of conditions, soil types and crops is required. In particular, this study highlighted the need to investigate DMPP use at high soil temperatures (35^oC+) and in Ferrosol soils. Furthermore, recent research has shown nitrification inhibitors can increase volatilisation of ammonia (NH_3), due to the

preservation of ammonium in soil (Qiao *et al.*, 2015; Lam *et al.*, 2017). Pairing nitrification inhibitors with urease inhibitors may be an option to reduce NH_3 losses (Lam *et al.*, 2017) and should also be considered in future research. This may be particularly relevant when applying together with organic matter mulches, and when irrigation is not available (i.e. on bare soils in wet conditions that do not permit irrigation).

The long term use of hay mulch in mangoes needs to be evaluated to substantiate the reduction of N_2O and to understand the possible consequences for NH_3 volatilisation within mulch (as detailed for the EEFs above). Furthermore, understanding the cycling of N within the plant-soil system is also necessary, as the N concentration in mango leaf tissue was lower in mulched treatments than bare soil treatments after three years (p<0.05) (Dickinson *et al.*, 2019). This was attributed to N draw-down, due to higher microbial activity in the mulched plots, however the cause was unknown.

References

ABCG, 2017. The Australian Banana Industry. Australian Banana Growers' Council Incorporated. https://abgc.org.au/our-industry/key-facts/ (accessed May, 2019)

Akem, C., MacManus, G., Lakhesar, D., Boccalatte, P., Stockdale, K., 2013a. Comparison of fungicide dips efficacies for the control of mango postharvest diseases. International Society for Horticultural Science (ISHS), Leuven, Belgium, pp. 385-392.

Akem, C.N., MacManus, G., Lakhesar, D., Boccalatte, P., Stockdale, K., 2013b. Re-thinking mango disease management in Austrlia; the rationale and approach. International Society for Horticultural Science (ISHS), Leuven, Belgium, pp. 355-367.

Albanito, F., Lebender, U., Cornulier, T., Sapkota, T.B., Brentrup, F., Stirling, C., Hillier, J., 2017. Direct Nitrous Oxide Emissions From Tropical And Sub-Tropical Agricultural Systems - A Review And Modelling Of Emission Factors. Scientific Reports 7, 44235.

Allen, D.E., Kingston, G., Rennenberg, H., Dalal, R.C., Schmidt, S., 2010. Effect of nitrogen fertilizer management and waterlogging on nitrous oxide emission from subtropical sugarcane soils. Agriculture, Ecosystems & Environment 136, 209-217.

Anderson, G.D., Houston, B.G., Northwood, P.J., 1966. Effects of Soil, Cultivation History and Weather on Responses of Wheat to Fertilizers in Northern Tanzania. Experimental Agriculture 2, 183-200.

ANGA, 2018. Australian National Greenhouse Accounts National Inventory Report 2016. In: Department of the Environment and Energy (Ed.), http://www.climatechange.gov.au/emissions (accessed April 2019).

Armour, J.D., Nelson, P.N., Daniells, J.W., Rasiah, V., Inman-Bamber, N.G., 2013. Nitrogen leaching from the root zone of sugarcane and bananas in the humid tropics of Australia. Agriculture, Ecosystems and Environment 180, 68-78.

Attard, E., Recous, S., Chabbi, A., De Berranger, C., Guillaumaud, N., Labreuche, J., Philippot, L., Schmid, B., Le Roux, X., 2011. Soil environmental conditions rather than denitrifier abundance and diversity drive potential denitrification after changes in land uses. Global Change Biology 17, 1975-1989.

Barrena, I., Menéndez, S., Correa-Galeote, D., Vega-Mas, I., Bedmar, E.J., González-Murua, C., Estavillo, J.M., 2017. Soil water content modulates the effect of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) on nitrifying and denitrifying bacteria. Geoderma 303, 1-8.

Barth, G., von Tucher, S., Schmidhalter, U., 2001. Influence of soil parameters on the effect of 3,4-dimethylpyrazole-phosphate as a nitrification inhibitor. Biology and Fertility of Soils 34, 98-102.

Barton, L., McLay, C.D.A., Schipper, L.A., Smith, C.T., 1999. Annual denitrification rates in agricultural and forest soils: A review. Australian Journal of Soil Research 37, 1073-1093.

Bass, A.M., Bird, M.I., Kay, G., Muirhead, B., 2016. Soil properties, greenhouse gas emissions and crop yield under compost, biochar and co-composted biochar in two tropical agronomic systems. Science of The Total Environment 550, 459-470.

Bell, M.J., Bridge, B.J., Harch, G.R., Orange, D.N., 2005. Rapid internal drainage rates in Ferrosols. Soil Research 43, 443-455.

Bell, M.J., Moody, P.W., Connolly, R.D., Bridge, B.J., 1998. The role of active fractions of soil organic matter in physical and chemical fertility of Ferrosols. Australian Journal of Soil Research 36, 809-819.

Blackmer, A.M., Bremner, J.M., 1976. Potential of soil as a sink for atmospheric nitrous oxide. Geophysical Research Letters 3, 739-742.

Blair, G.J., Lefroy, R.D., Lisle, L., 1995. Soil carbon fractions based on their degree of oxidation, and the development of a carbon management index for agricultural systems. Australian Journal of Agricultural Research 46, 1459-1466.

Borchers, H.W., 2017. R Package 'pracma': Practical Numerical Math Functions, version 2.1.1. R CRAN.

Bouwman, A.F., 1996. Direct emission of nitrous oxide from agricultural soils. Nutrient Cycling in Agroecosystems 46, 53-70.

Bouwman, A.F., 1998. Environmental science - Nitrogen oxides and tropical agriculture. Nature 392, 866-867.

Bouwman, A.F., Beusen, A.H.W., Griffioen, J., Van Groenigen, J.W., Hefting, M.M., Oenema, O., Van Puijenbroek, P.J.T.M., Seitzinger, S., Slomp, C.P., Stehfest, E., 2013. Global trends and uncertainties in terrestrial denitrification and N_2O emissions. Philosophical Transactions of the Royal Society B: Biological Sciences 368.

Bremner, J.M., 1997. Sources of nitrous oxide in soils. Nutrient Cycling in Agroecosystems 49, 7-16.

Bremner, J.M., Blackmer, A.M., 1978. Nitrous-oxide- Emission from Soils during Nitrification of Fertiliser Nitrogen. Science 199, 295-296.

Calanca, P., Neftel, A., Fuhrer, J., 2001. N Management of European Grasslands: Can the Exchange of Gaseous N Species Be Influenced at the Operational Level? The Scientific World Journal 1, 652-657.

Castaldi, S., 2000. Responses of nitrous oxide, dinitrogen and carbon dioxide production and oxygen consumption to temperature in forest and agricultural light-textured soils determined by model experiment. Biology and Fertility of Soils 32, 67-72.

Chadwick, D.R., Cardenas, L., Misselbrook, T.H., Smith, K.A., Rees, R.M., Watson, C.J., McGeough, K.L., Williams, J.R., Cloy, J.M., Thorman, R.E., Dhanoa, M.S., 2014. Optimizing chamber methods for measuring nitrous oxide emissions from plot-based agricultural experiments. European Journal of Soil Science 65, 295-307.

Chakraborty, D., Garg, R.N., Tomar, R.K., Singh, R., Sharma, S.K., Singh, R.K., Trivedi, S.M., Mittal, R.B., Sharma, P.K., Kamble, K.H., 2010. Synthetic and organic mulching and nitrogen effect on winter wheat (Triticum aestivum L.) in a semi-arid environment. Agricultural Water Management 97, 738-748.

Chalk, P.M., Smith, C.J., 1983. Chemodenitrification. In: Freney, J.R., Simpson, J.R. (Eds.), Gaseous Loss of Nitrogen from Plant-Soil Systems. Springer Netherlands, pp. 65-89.

Chapuis-lardy, L., Wrage, N., Metay, A., Chotte, J.L., Bernoux, M., 2007. Soils, a sink for N_2O? A review. Global Change Biology 13, 1-17.

Chen, D., Suter, H., Islam, A., Edis, R., Freney, J.R., Walker, C.N., 2008. Prospects of improving efficiency of fertiliser nitrogen in Australian agriculture: a review of enhanced efficiency fertilisers. Soil Research 46, 289-301.

Chin, W.-t., Kroontje, W., 1963. Urea Hydrolysis and Subsequent Loss of Ammonia. Soil Science Society of America Journal 27, 316-318.

Commonwealth of Australia, 2018. National Inventory Report 2016 Volume 1, Commonwealth of Australia Canberra, p. 356.

Cosentino, V.R.N., Figueiro Aureggui, S.A., Taboada, M.A., 2013. Hierarchy of factors driving N_2O emissions in non-tilled soils under different crops. European Journal of Soil Science 64, 550-557.

Crill, P.M., Keller, M., Weitz, A., Grauel, B., Veldkamp, E., 2000. Intensive field measurements of nitrous oxide emissions from a tropical agricultural soil. Global Biogeochemical Cycles 14, 85-95.

Crutzen, P.J., 1979. The role of NO and NO2 in the chemistry of the troposphere and stratosphere. Annual review of earth and planetary sciences, Vol. 7, 443-472.

DAF, 2015. Food for Fruit - Nutrition managment of mangoes. Department of Agirculture and Fisheries, Queensland. DAF, Brisbane, Australia, 99 pp. https://www.industry.mangoes.net.au/resource-collection/food-for-fruit-nutrition?rq=food%20for%20fruit (accessed January, 2019).

DAFF, 2016. Banana Best Management Practices. Environmental Guidelines for the Australian Banana Industry. Queensland Department of Agriculture, Fisheries and Forestry, South Johnstone, p. 141.

Dalal, R.C., Wang, W., Robertson, G.P., Parton, W.J., 2003. Nitrous oxide emission from Australian agricultural lands and mitigation options: a review. Soil Research 41, 165-195.

Davidson, E.A., 1992. Sources of nitric oxide and nitrous oxide following wetting of dry soil. Soil Science Society of America Journal 56, 95-102.

Davidson, E.A., Kanter, D., 2014. Inventories and scenarios of nitrous oxide emissions. Environmental Research Letters 9, 105012.

DAWR, 2017. Validation of greenhouse gas reduction methods in banana and mango tree crops across tropical Queensland, Northern Territory and Western Australia. Action on the

Ground Round 2, Report AOTGR2-0076. Department of Agriculture and Water Resources, Australia.

De Antoni Migliorati, M., Scheer, C., Grace, P.R., Rowlings, D.W., Bell, M., McGree, J., 2014. Influence of different nitrogen rates and DMPP nitrification inhibitor on annual N2O emissions from a subtropical wheat–maize cropping system. Agriculture, Ecosystems & Environment 186, 33-43.

Denmead, O.T., Macdonald, B.C.T., Bryant, G., Naylor, T., Wilson, S., Griffith, D.W.T., Wang, W.J., Salter, B., White, I., Moody, P.W., 2010. Emissions of methane and nitrous oxide from Australian sugarcane soils. Agricultural and Forest Meteorology 150, 748-756.

Devol, A.H., 2003. Nitrogen cycle: Solution to a marine mystery. Nature 422, 575-576.

Di Bella, L.P., Armour, J., Moody, P., Royle, M., Ibanez, M., Le Bris, M., 2017. The assessment of enhanced efficiency Fertilisers (EEFS) in a glasshouse experiment to investigate nitrogen loss pathways in sugarcane. Proceedings of the Australian Society of Sugar Cane Technologists Conference 39, 263-273.

Dickinson, G.R., O'Farrell, P.J., Ridgway, K.J., Bally, I.S.E., Masters, B., Nelson, P., Pattison, A., 2019. Nitrogen and carbon management in Australian mango orchards to improve productivity and reduce greenhouse gas emissions. Acta Horticulturae 1244, 49-60.

Dobbie, K.E., McTaggart, I.P., Smith, K.A., 1999. Nitrous oxide emissions from intensive agricultural systems: Variations between crops and seasons, key driving variables, and mean emission factors. Journal of Geophysical Research: Atmospheres 104, 26891-26899.

Eyles, A., Ives, S., Hardie, M., Corkrey, R., Boersma, M., 2018. Impact of enhanced efficiency fertilizers on potato productivity in a temperate cropping system. Soil Use and Management 34, 439-448.

Fangmeier, A., Hadwiger-Fangmeier, A., Van der Eerden, L., Jäger, H.J., 1994. Effects of atmospheric ammonia on vegetation-A review. Environmental Pollution 86, 43-82.

FAO, 2017. FAOSTAT Online Database. http://faostat.fao.org/ (accessed April, 2019).

Fentabil, M.M., Nichol, C.F., Jones, M.D., Neilsen, G.H., Neilsen, D., Hannam, K.D., 2016. Effect of drip irrigation frequency, nitrogen rate and mulching on nitrous oxide emissions in a semi-arid climate: An assessment across two years in an apple orchard. Agriculture, Ecosystems & Environment 235, 242-252.

Firestone, M.K., Davidson, E.A. (Eds.), 1989. Microbiological basis of NO and N_2O production and consumption in soil. Wiley, New York, NY.

Firestone, M.K., Firestone, R.B., Tiedje, J.M., 1980. Nitrous Oxide from Soil Denitrification: Factors Controlling its Biological Production. Science 208, 749-751.

Focht, D.D., 1974. The effect of temperature, pH, and aeration on the production of nitrous oxide and gaseous nitrogen – A zero-order kinetic model. Soil Science 118, 173-179.

Fracetto, F.J.C., Fracetto, G.G.M., Bertini, S.C.B., Cerri, C.C., Feigl, B.J., Siqueira Neto, M., 2017. Effect of agricultural management on N_2O emissions in the Brazilian sugarcane yield. Soil Biology and Biochemistry 109, 205-213.

Frasier, R., Ullah, S., Moore, T.R., 2010. Nitrous Oxide Consumption Potentials of Well-drained Forest Soils in Southern Québec, Canada. Geomicrobiology Journal 27, 53-60.

Gagnon, B., Ziadi, N., Rochette, P., Chantigny, M.H., Angers, D.A., 2011. Fertilizer source influenced nitrous oxide emissions from a clay soil under corn. Soil Science Society of America Journal 75, 595-604.

Galloway, J.N., 1995. Acid deposition: Perspectives in time and space. Water, Air, and Soil Pollution 85, 15-24.

Giles, M., Morley, N., Baggs, E.M., Daniell, T.J., 2012. Soil nitrate reducing processes - Drivers, mechanisms for spatial variation, and significance for nitrous oxide production. Frontiers in Microbiology 3, 1-16.

Gonzaga, L.C., Carvalho, J.L.N., Oliveira, B.G.d., Soares, J.R., Cantarella, H., 2018. Crop residue removal and nitrification inhibitor application as strategies to mitigate N_2O emissions in sugarcane fields. Biomass and Bioenergy 119, 206-216.

Granli, T., Bockman, O.C., 1995. Nitrous oxide (N_2O) emissions from soils in warm climates. Fertilizer Research 42, 159-163.

Gu, J., Nie, H., Guo, H., Xu, H., Gunnathorn, T., 2019. Nitrous oxide emissions from fruit orchards: A review. Atmospheric Environment 201, 166-172.

Guardia, G., Marsden, K.A., Vallejo, A., Jones, D.L., Chadwick, D.R., 2018. Determining the influence of environmental and edaphic factors on the fate of the nitrification inhibitors DCD and DMPP in soil. Science of the Total Environment 624, 1202-1212.

Hartmann, D.L., Klein Tank, A.M.G., Rusticucci, M., Alexander, L.V., Brönnimann, S., Charabi, Y., Dentener, F.J., Dlugokencky, E.J., Easterling, D.R., Kaplan, A., Soden, B.J., Thorne, P.W., Wild, M., Zhai, P.M., 2013. Observations: Atmosphere and Surface. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K.Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Hastie, T., Tibshirani, R., 1986. Generalized Additive Models. Statistical Science 1, 297-310.

HIA, 2017. Mango Industry Strategic Investment Plan 2017-2021. Horticulture Innovation Australia, Canberra, Australia, 14pp.

Huang, X., Grace, P., Weier, K., Mengersen, K., 2012. Nitrous oxide emissions from subtropical horticultural soils: A time series analysis. Soil Research 50, 596-606.

IPCC, 2006. 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme, Eggleston H.S., Buendia L., Miwa K., Ngara T. and Tanabe K. (eds). Published: IGES, Japan.

IPCC, 2013. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

IPCC, 2014. Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland, 151 pp.

Isbell, R.F., 2002. The Australian Soil Classification (Revised Edition). Australian Soil and Land Survey Handbooks Series 4. CSIRO Publishing, Collingwood.

Janke, C.K., Fujinuma, R., Moody, P., Bell, M.J., 2019. Biochemical effects of banding limit the benefits of nitrification inhibition and controlled-release technology in the fertosphere of high N-input systems. Soil Research 57, 28-40.

Johns, G., 1994. Effect of Arachis pintoi groundcover on performance of bananas in northern New South Wales. Australian Journal of Experimental Agriculture 34, 1197-1204.

Keeney, D.R., Fillery, I.R., Marx, G.P., 1979. Effect of Temperature on the Gaseous Nitrogen Products of Denitrification in a Silt Loam Soil. Soil Science Society of America Journal 43, 1124-1128.

Koci, J., Nelson, P.N., 2016. Tropical dairy pasture yield and nitrogen cycling: Effect of urea application rate and a nitrification inhibitor, DMPP. Crop and Pasture Science 67, 766-779.

Kroon, F.J., Thorburn, P., Schaffelke, B., Whitten, S., 2016. Towards protecting the Great Barrier Reef from land-based pollution. Global Change Biology 22, 1985-2002.

Kumar, S., Dey, P., 2011. Effects of different mulches and irrigation methods on root growth, nutrient uptake, water-use efficiency and yield of strawberry. Scientia Horticulturae 127, 318-324.

Lal, R., 2003. Offsetting global CO_2 emissions by restoration of degraded soils and intensification of world agriculture and forestry. Land Degradation & Development 14, 309-322.

Lam, S.K., Suter, H., Mosier, A.R., Chen, D., 2017. Using nitrification inhibitors to mitigate agricultural N_2O emission: a double-edged sword? Global Change Biology 23, 485-489.

Li, S., Chen, G., 2019. Contemporary strategies for enhancing nitrogen retention and mitigating nitrous oxide emission in agricultural soils: present and future. Environment, Development and Sustainability.

Linn, D.M., Doran, J.W., 1984. Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. Soil Science Society of America Journal 48, 1267-1272.

Machacova, K., Maier, M., Svobodova, K., Lang, F., Urban, O., 2017. Cryptogamic stem covers may contribute to nitrous oxide consumption by mature beech trees. Scientific Reports 7.

Mahmood, T., Ali, R., Lodhi, A., Sajid, M., 2017. 4-Amino-1,2,4-triazole can be more effective than commercial nitrification inhibitors at high soil temperatures. Soil Research 55, 715-722.

Maris, S.C., Teira-Esmatges, M.R., Arbonés, A., Rufat, J., 2015. Effect of irrigation, nitrogen application, and a nitrification inhibitor on nitrous oxide, carbon dioxide and methane emissions from an olive (Olea europaea L.) orchard. Science of The Total Environment 538, 966-978.

Maurya, P.R., Lal, R., 1981. Effects of different mulch materials on soil properties and on the root growth and yield of maize (Zea mays) and cowpea (Vigna unguiculata). Field Crops Research 4, 33-45.

McBeath, A.V., East, D.J., Wright, C.L., Pattison, A.B., 2018. Monitoring microbial functional and structural diversity for management of disease-suppressive soils. Acta Horticulturae, pp. 121-128.

Menéndez, S., Barrena, I., Setien, I., González-Murua, C., Estavillo, J.M., 2012. Efficiency of nitrification inhibitor DMPP to reduce nitrous oxide emissions under different temperature and moisture conditions. Soil Biology and Biochemistry 53, 82-89.

Minasny, B., McBratney, A.B., 2018. Limited effect of organic matter on soil available water capacity. European Journal of Soil Science 69, 39-47.

Modak, J.M., 2011. Haber process for ammonia synthesis. Resonance 16, 1159-1167.

Mosier, A., Kroeze, C., Nevison, C., Oenema, O., Seitzinger, S., van Cleemput, O., 1998. Closing the global N_2O budget: nitrous oxide emissions through the agricultural nitrogen cycle - OECD/IPCC/IEA phase II development of IPCC guidelines for national greenhouse gas inventory methodology. Nutrient Cycling in Agroecosystems 52, 225-248.

Mulvaney, R.L., Khan, S.A., Mulvaney, C.S., 1997. Nitrogen fertilizers promote denitrification. Biology and Fertility of Soils 24, 211-220.

Myhre, G., D., Shindell, F.-M., Bréon, W.C., J. Fuglestvedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, T. Takemura, H. Zhang, 2013. Anthropogenic and Natural Radiative Forcing. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Nauer, P.A., Fest, B.J., Visser, L., Arndt, S.K., 2018. On-farm trial on the effectiveness of the nitrification inhibitor DMPP indicates no benefits under commercial Australian farming practices. Agriculture, Ecosystems and Environment 253, 82-89.

Neff, J.C., Asner, G.P., 2001. Dissolved organic carbon in terrestrial ecosystems: Synthesis and a model. Ecosystems 4, 29-48.

Nelson, P.N., Banabas, M., Goodrick, I., Webb, M.J., Huth, N.I., O'Grady, D., 2015. Soil sampling in oil palm plantations: a practical design that accounts for lateral variability at the tree scale. Plant and Soil 394, 421-429.

Nelson, P.N., Dictor, M.C., Soulas, G., 1994. Availability of organic carbon in soluble and particle-size fractions from a soil profile. Soil Biology and Biochemistry 26, 1549-1555.

O'Farrell, P.J., Armour, J.D., Reid, D.J., 2010. Nitrogen use for high productivity and sustainability in cashew. Scientia Horticulturae 124, 19-28.

Oertel, C., Matschullat, J., Zurba, K., Zimmermann, F., Erasmi, S., 2016. Greenhouse gas emissions from soils—A review. Chemie der Erde - Geochemistry 76, 327-352.

Pampana, S., Masoni, A., Mariotti, M., Ercoli, L., Arduini, I., 2018. Nitrogen fixation of grain legumes differs in response to nitrogen fertilisation. Experimental Agriculture 54, 66-82.

Parkin, T.B., 1987. Soil Microsites as a Source of Denitrification Variability. Soil Science Society of America Journal 51, 1194-1199.

Parkin, T.B., Venterea, R.T., 2010. GRACEnet Sampling Protocols: Chapter 3. Chamber-Based Trace Gas Flux Measurements. In: Follett, R.F. (Ed.), GRACEnet Sampling Protocols. U.S. Department of Agriculture, Agricultural Research Service, pp. 3-1 to 3-39.

Pattison, A.B., East, D., Ferro, K., Dickinson, G., 2018. Agronomic consequences of vegetative groundcovers and reduced nitrogen applications for banana production systems. Acta Horticulturae, pp. 155-162.

Pattison, A.B., Wright, C.L., Kukulies, T.L., Molina, A.B., 2014. Ground cover management alters development of Fusarium wilt symptoms in Ducasse bananas. Australasian Plant Pathology 43, 465-476.

Pilegaard, K., 2013. Processes regulating nitric oxide emissions from soils. Philosophical transactions of the Royal Society of London. Series B, Biological sciences 368, 20130126.

Pinheiro, P.L., Recous, S., Dietrich, G., Weiler, D.A., Giovelli, R.L., Mezzalira, A.P., Giacomini, S.J., 2018. Straw removal reduces the mulch physical barrier and ammonia volatilization after urea application in sugarcane. Atmospheric Environment 194, 179-187.

Prasertsak, P., Freney, J., Denmead, O., Saffigna, P., Prove, B., Reghenzani, J., 2002. Effect of fertilizer placement on nitrogen loss from sugarcane in tropical Queensland. Nutrient Cycling in Agroecosystems 62, 229-239.

Prasertsak, P., Freney, J.R., Saffigna, P.G., Denmead, O.T., Prove, B.G., 2001. Fate of urea nitrogen applied to a banana crop in the wet tropics of Queensland. Nutrient Cycling in Agroecosystems 59, 65-73.

Prather, M.J., Holmes, C.D., Hsu, J., 2012. Reactive greenhouse gas scenarios: Systematic exploration of uncertainties and the role of atmospheric chemistry. Geophysical Research Letters 39.

Prove, B.G., Moody, P.W., Reghenzani, J.R., 1997. Nutrient balances and transport from agricultural and rainforest lands., Sugar Research and Development Corporation Final Report. Queensland Department of Natural Resources and BSES.

Qiao, C.L., Liu, L.L., Hu, S.J., Compton, J.E., Greaver, T.L., Li, Q.L., 2015. How inhibiting nitrification affects nitrogen cycle and reduces environmental impacts of anthropogenic nitrogen input. Global Change Biology 21, 1249-1257.

Rasiah, V., Armour, J.D., Cogle, A.L., Florentine, S.K., 2010. Nitrate import-export dynamics in groundwater interacting with surface-water in a wet-tropical environment. Australian Journal of Soil Research 48, 361-370.

Ravishankara, A.R., Daniel, J.S., Portmann, R.W., 2009. Nitrous Oxide (N_2O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century. Science 326, 123-125.

Rayment, G.E., Lyons, D.J., 2010. Soil chemical methods - Australasia. CSIRO Publishing, Melbourne.

Reay, D.S., Davidson, E.A., Smith, K.A., Smith, P., Melillo, J.M., Dentener, F., Crutzen, P.J., 2012. Global agriculture and nitrous oxide emissions. Nature Climate Change 2, 410-416.

Rose, T.J., Morris, S.G., Quin, P., Kearney, L.J., Kimber, S., Van Zwieten, L., 2017. The nitrification inhibitor DMPP applied to subtropical rice has an inconsistent effect on nitrous oxide emissions. Soil Research 55, 547-552.

Rowlings, D.W., Grace, P.R., Scheer, C., Kiese, R., 2013. Influence of nitrogen fertiliser application and timing on greenhouse gas emissions from a lychee (Litchi chinensis) orchard in humid subtropical Australia. Agriculture, Ecosystems & Environment 179, 168-178.

Rowlings, D.W., Grace, P.R., Scheer, C., Liu, S., 2015. Rainfall variability drives interannual variation in N_2O emissions from a humid, subtropical pasture. Science of The Total Environment 512-513, 8-18.

RStudio, 2016. RStudio: Integrated Development for R. RStudio, Inc., Boston, MA

Rudaz, A.O., Davidson, E.A., Firestone, M.K., 1991. Sources of nitrous oxide production following wetting of dry soil. FEMS Microbiology Letters 85, 117-124.

Ruser, R., Schulz, R., 2015. The effect of nitrification inhibitors on the nitrous oxide (N_2O) release from agricultural soils-a review. Journal of Plant Nutrition and Soil Science 178, 171-188.

Scheer, C., Rowlings, D.W., De Antoni Migliorati, M., Lester, D.W., Bell, M.J., Grace, P.R., 2016. Effect of enhanced efficiency fertilisers on nitrous oxide emissions in a sub-tropical cereal cropping system. Soil Research 54, 544-551.

Scheer, C., Rowlings, D.W., Firrel, M., Deuter, P., Morris, S., Grace, P.R., 2014. Impact of nitrification inhibitor (DMPP) on soil nitrous oxide emissions from an intensive broccoli production system in sub-tropical Australia. Soil Biology and Biochemistry 77, 243-251.

Schipper, L.A., Cooper, A.B., Harfoot, C.G., Dyck, W.J., 1993. Regulators of denitrification in an organic riparian soil. Soil Biology and Biochemistry 25, 925-933.

Schlesinger, W.H., Hartley, A.E., 1992. A global budget for atmospheric NH3. Biogeochemistry 15, 191-211.

Schumann, U., Huntrieser, H., 2007. The global lightning-induced nitrogen oxides source. Atmospheric Chemistry and Physics 7, 3823-3907.

Shaaban, M., Peng, Q.-a., Hu, R., Wu, Y., Lin, S., Zhao, J., 2015. Dolomite application to acidic soils: a promising option for mitigating N_2O emissions. Environmental Science and Pollution Research 22, 19961-19970.

Shaviv, A., 2001. Advances in controlled-release fertilizers. Advances in Agronomy. Academic Press, pp. 1-49.

Smith, K.A., Thomson, P.E., Clayton, H., McTaggart, I.P., Conen, F., 1998. Effects of temperature, water content and nitrogen fertilisation on emissions of nitrous oxide by soils. Atmospheric Environment 32, 3301-3309.

Stehfest, E., Bouwman, L., 2006. N_2O and NO emission from agricultural fields and soils under natural vegetation: Summarizing available measurement data and modeling of global annual emissions. Nutrient Cycling in Agroecosystems 74, 207-228.

Stevens, R.J., Laughlin, R.J., 1998. Measurement of nitrous oxide and di-nitrogen emissions from agricultural soils. Nutrient Cycling in Agroecosystems 52, 131-139.

Stocker, T.F., D. Qin, G.-K. Plattner, L.V. Alexander, S.K. Allen, N.L. Bindoff, F.-M. Bréon, J.A. Church, U. Cubasch, S. Emori, P. Forster, P. Friedlingstein, N. Gillett, J.M. Gregory, D.L. Hartmann, E. Jansen, B. Kirtman, R. Knutti, K. Krishna Kumar, P. Lemke, J. Marotzke, V. Masson-Delmotte, G.A. Meehl, I.I. Mokhov, S. Piao, V. Ramaswamy, D. Randall, M. Rhein, M. Rojas, C. Sabine, D. Shindell, L.D. Talley, D.G. Vaughan, S.-P. Xie, 2013. Technical Summary. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Streminska, M.A., Felgate, H., Rowley, G., Richardson, D.J., Baggs, E.M., 2012. Nitrous oxide production in soil isolates of nitrate-ammonifying bacteria. Environmental Microbiology Reports 4, 66-71.

Strous, M., Fuerst, J.A., Kramer, E.H.M., Logemann, S., Muyzer, G., Van De Pas-Schoonen, K.T., Webb, R., Kuenen, J.G., Jetten, M.S.M., 1999. Missing lithotroph identified as new planctomycete. Nature 400, 446-449.

Suter, H., Chen, D., Li, H., Edis, R., Walker, C., 2010. Reducing N_2O emissions from nitrogen fertilisers with the nitrification inhibitor DMPP. 19th World Congress of Soil Science, 1–6 August 2010, Brisbane, Australia (International Union of Soil Science).

Swarts, N., Montagu, K., Oliver, G., Southam-Rogers, L., Hardie, M., Corkrey, R., Rogers, G., Close, D., 2016. Benchmarking nitrous oxide emissions in deciduous tree cropping systems. Soil Research 54, 500+.

Syakila, A., Kroeze, C., 2011. The global nitrous oxide budget revisited. Greenhouse Gas Measurement and Management 1, 17-26.

Tanveer, S.K., Zhang, J., Lu, X., Wen, X., Wu, W., Liu, Y., Liao, Y.C., 2014. Effect of corn residue mulch and N fertilizer application on Nitrous Oxide (N_2O) emission and wheat crop productivity

under rain-fed condition of loess plateau China. International Journal of Agriculture and Biology 16, 505-512.

Teixeira, L.A.J., Natale, W., Martins, A.L.M., 2007. Nitrogen and potassium application on banana plant by fertirrigation and conventional fertilization-nutritional status of banana plants and fruit production. Revista Brasileira de Fruticultura 29, 153-160.

Teixeira, L.A.J., Quaggio, J.A., Mellis, E.V., 2011. Enhancing nutrient use efficiency in banana tree under irrigation and fertigation. Revista Brasileira de Fruticultura 33, 272-278.

Thomson, A.J., Giannopoulos, G., Pretty, J., Baggs, E.M., Richardson, D.J., 2012. Biological sources and sinks of nitrous oxide and strategies to mitigate emissions. Philosophical Transactions of the Royal Society B: Biological Sciences 367, 1157-1168.

Thorburn, P.J., Biggs, J.S., Macdonald, B.C.T., Allen, D.E., Denmead, O.T., 2013. What causes nitrous oxide emissions from some sugarcane crops to be so high. 35th Annual Conference of the Australian Society of Sugar Cane Technologists 2013, ASSCT 2013, pp. 110-117.

Tian, L., Cai, Y., Akiyama, H., 2019. A review of indirect N_2O emission factors from agricultural nitrogen leaching and runoff to update of the default IPCC values. Environmental Pollution 245, 300-306.

Veldkamp, E., Keller, M., 1997. Nitrogen oxide emissions from a banana plantation in the humid tropics. Journal of Geophysical Research-Atmospheres 102, 15889-15898.

Veldkamp, E., Keller, M., Nunez, M., 1998. Effects of pasture management on N_2O and NO emissions from soils in the humid tropics of Costa Rica. Global Biogeochemical Cycles 12, 71-79.

Venterea, R.T., Rolston, D.E., 2000. Mechanisms and kinetics of nitric and nitrous oxide production during nitrification in agricultural soil. Global Change Biology 6, 303-316.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecological Applications 7, 737-750.

Wakelin, S.A., Nelson, P.N., Armour, J.D., Rasiah, V., Colloff, M.J., 2011. Bacterial community structure and denitrifier (*nir*-gene) abundance in soil water and groundwater beneath agricultural land in tropical North Queensland, Australia. Soil Research 49, 65-76.

Wang, W., Park, G., Reeves, S., Zahmel, M., Heenan, M., Salter, B., 2016a. Nitrous oxide emission and fertiliser nitrogen efficiency in a tropical sugarcane cropping system applied with different formulations of urea. Soil Research 54, 572-584.

Wang, W.J., Reeves, S.H., Salter, B., Moody, P.W., Dalal, R.C., 2016b. Effects of urea formulations, application rates and crop residue retention on N_2O emissions from sugarcane fields in Australia. Agriculture, Ecosystems & Environment 216, 137-146.

Wang, Y., Guo, J., Vogt, R.D., Mulder, J., Wang, J., Zhang, X., 2018. Soil pH as the chief modifier for regional nitrous oxide emissions: New evidence and implications for global estimates and mitigation. Global Change Biology 24, 617-626.

Weier, K.L., Doran, J.W., Power, J.F., Walters, D.T., 1993. Denitrification and the dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate. Soil Science Society of America Journal 57, 66-72.

Weiske, A., Benckiser, G., Herbert, T., Ottow, J.C.G., 2001. Influence of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in comparison to dicyandiamide (DCD) on nitrous oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated application in field experiments. Biology and Fertility of Soils 34, 109-117.

Wu, X.H., Wang, W., Xie, X.L., Yin, C.M., Hou, H.J., 2018. Effects of rice straw mulching on N_2O emissions and maize productivity in a rain-fed upland. Environmental Science and Pollution Research 25, 6407-6413.

Xia, Z., Xu, H., Chen, G., Dong, D., Bai, E., Luo, L., 2013. Soil N_2O production and the $\delta^{15}N–N_2O$ value: Their relationship with nitrifying/denitrifying bacteria and archaea during a growing season of soybean in northeast China. European Journal of Soil Biology 58, 73-80.

Xie, K., Li, X., He, F., Zhang, Y., Wan, L., David, H., Wang, D., Qin, Y., Gamal, F., 2015. Effect of nitrogen fertilization on yield, N content, and nitrogen fixation of alfalfa and smooth bromegrass grown alone or in mixture in greenhouse pots. Journal of Integrative Agriculture 14, 1864-1876.

Xing, Z., Toner, P., Chow, L., Rees, H.W., Li, S., Meng, F., 2012. Effects of Hay Mulch on Soil Properties and Potato Tuber Yield under Irrigation and Nonirrigation in New Brunswick, Canada. Journal of Irrigation and Drainage Engineering 138, 703-714.

Xu, J., Zhu, T., Xue, W., Ni, D., Sun, Y., Yang, J., Xu, L., Chen, X., Li, H., Liu, M., 2019. Influences of nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) and application method on nitrogen dynamics at the centimeter-scale. European Journal of Soil Biology 90, 44-50.

Yang, M., Fang, Y., Sun, D., Shi, Y., 2016. Efficiency of two nitrification inhibitors (dicyandiamide and 3, 4-dimethypyrazole phosphate) on soil nitrogen transformations and plant productivity: a meta-analysis. Scientific Reports 6, 22075.

Zerulla, W., Barth, T., Dressel, J., Erhardt, K., Horchler von Locquenghien, K., Pasda, G., Rädle, M., Wissemeier, A., 2001. 3,4-Dimethylpyrazole phosphate (DMPP) – a new nitrification inhibitor for agriculture and horticulture. Biology and Fertility of Soils 34, 79-84.

Zhao, M., Li, M., Shi, Y., 2015. Effects of plantation ages, densities and management strategies on carbon sequestration in tropical mango and wax apple orchard ecosystems. Fresenius Environmental Bulletin 24, 817-824.

Zhu, T., Zhang, J., Huang, P., Suo, L., Wang, C., Ding, W., Meng, L., Zhou, K., Hu, Z., 2015. N_2O emissions from banana plantations in tropical China as affected by the application rates of urea and a urease/nitrification inhibitor. Biology and Fertility of Soils 51, 673-683.