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Movement of nitrogen through a riparian forest in a tropical, agricultural landscape

Thesis submitted by

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(under a cotutelle agreement)

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STATEMENT OF THE CONTRIBUTION OF OTHERS

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ABSTRACT

Riparian zones have been widely reported to function as effective buffers, removing nitrate (NO_3^-) from groundwater before it is discharged into adjacent streams. This is particularly important in agricultural catchments where additional nitrogen (N) from fertilisers may be leached into groundwater. On coastal plains, NO_3^- in groundwater discharged into streams can potentially enrich coastal waters. The permanent removal of NO_3^- through denitrification can improve water quality, however incomplete denitrification produces nitrous oxide (N_2O), a greenhouse gas.

Despite copious research in temperate regions, little study has been conducted on the capacity of riparian zones to remove NO_3^- from groundwater in the tropics. In agricultural areas of the Australian humid tropics, annual rainfall is high, around 3000 mm, and wet and dry seasons are clearly defined. Wet seasons are characterised by rainfall of high intensity and duration, followed by a dry season producing sporadic small amounts of rainfall.

The overarching questions of this thesis are: in an agricultural landscape in the humid tropics, is NO_3^- in groundwater removed as it enters a forested riparian zone and is transported towards the stream? And, are there temporal and spatial differences in patterns of N_2O emissions produced from the riparian forest?

This research is focused on a forested riparian zone 150 m wide, located amongst sugarcane fields, on the coastal plain adjoining the World-Heritage listed Great Barrier Reef lagoon, in the Australian humid tropics.

To gain an understanding of the movement of groundwater through the riparian site, the hydrology of the riparian zone was characterized using measurements of soil water content and water table depth (13 piezometers). In the wet season the system was highly dynamic with large fluctuations in water table levels and long-term inundation of low lying areas. Rapid water table rises were attributed to high in-situ recharge, low air-filled pore space (unsaturated zone), air entrapment and occasional recharge from the creek, and the rapid falls to the steep local hydraulic gradients. The dry season was characterised by a slow moving system with depth to watertable up to 4 m at high locations.

Groundwater entering the riparian zone was found to have low concentrations of NO_3^- (mean <0.03 mg NO_3-N L^{-1} over both seasons), however, concentrations increased (by up to 50 fold) as groundwater progressed through the riparian zone, suggesting the riparian zone was a potential source of NO_3^- to the adjacent creek. The addition of NO_3^- was attributed to nitrification in riparian surface soils, driven by large net primary productivity, including large amounts of litterfall (12.19 Mg ha^{-1} y^{-1}). Nitrate generated in riparian soil was subsequently leached into groundwater in the wet season during rainfall events. Nitrate was also derived from nitrification in groundwater and, potentially, from the mixing of deeper groundwater of higher NO_3^- concentrations.

The tropical riparian forest is a large emitter of N_2O, with soil emissions ranging from -24 to 657 µg N_2O-N m^{-2} h^{-1}. Emissions were highest in the wet season but not significantly different between sites of high and low elevation. Similarly, there was no effect on emissions from differing amounts of leaf litter accumulated on the soil surface. Based on differences in soil water content, N_2O emissions were attributed to both

denitrification and nitrification. Nitrous oxide was also produced at depth, within the unsaturated zone, with concentrations in soil air ranging from. 0.7 to 157 µg N_2O-N L^{-1}. Dissolved N_2O concentrations in groundwater were greatest at 1.5 m depth and correlated well with NO_3^- concentrations in groundwater. Laboratory experiments determined that riparian surface soils were clearly a source of N_2O, and that soils had limited capacity to further reduce N_2O to dinitrogen (N_2). Denitrification potential was up to 20 times greater in surface soils than in soils at 0.5 m depth.

This study has demonstrated that groundwater leaving cultivated land does not always have high concentrations of NO_3^- and that NO_3^- concentrations are not necessarily reduced during the passage of groundwater through riparian forest. Nitrate generated within the riparian zone, on the other hand, was leached into groundwater during heavy rain events and became a potential source of NO_3^- to the creek at our site. Similarly, nitrification and denitrification processes within the forested riparian zone contributed substantial N_2O emissions to the atmosphere, similar in range to emissions reported for other tropical forests. Although there are many environmental benefits to having healthy riparian forest, this study in a humid tropical environment did not show any water quality benefits.

RÉSUMÉ

Les zones riveraines sont connues pour fonctionner comme des tampons efficaces, capable d'éliminer les nitrates des eaux souterraines avant leur rejet dans les ruisseaux adjacents. Ce rôle de tampon est particulièrement important dans les bassins versants agricoles où, l'azote supplémentaire, provenant des engrais, peut être lessivé dans les eaux souterraines. Sur les plaines côtières, les nitrates présents dans les eaux souterraines puis déchargés dans les ruisseaux peuvent potentiellement enrichir les eaux côtières. La transformation des nitrates par le processus de dénitrification permet d'améliorer la qualité de l'eau, cependant, la dénitrification incomplète produit du protoxyde d'azote (N_2O), un gaz à effet de serre.

Bien qu'un grand nombre de recherches aient été menées dans les régions tempérées, peu d'études ont été conduites dans les régions tropicales sur la capacité des zones riveraines à éliminer les nitrates des eaux souterraines. Dans les zones agricoles de la région tropicale humide en Australie, les précipitations annuelles sont élevées, autour de 3000 mm, et les saisons humides et sèches sont clairement définies. La saison humide se caractérise par des précipitations de forte intensité et de longue durée, suivie par une saison sèche définie par de faibles précipitations sporadiques.

Les questions fondamentales de cette thèse sont les suivantes: dans un paysage agricole tropical humide, les nitrates contenus par les eaux souterraines, sont-ils éliminés lors de leur passage dans une zone boisée riveraine avant d'être transportés vers le ruisseau ?

Observe- t-on des différences temporelles et spatiales des flux de N_2O émis par les sols de la forêt riveraine ?

Cette étude se focalise sur une zone riveraine boisée, d'une largeur de 150 m, située au milieu des champs de canne à sucre, sur la plaine côtière adjacente à la lagune de la Grande Barrière de corail (inscrite au patrimoine mondial), localisée dans la région tropicale humide d'Australie.

Pour acquérir une compréhension du mouvement des eaux souterraines sur le site riverain, l'hydrologie de la zone a été caractérisée par des mesures de la teneur en eau du sol et par la profondeur de la nappe phréatique (13 piézomètres). Durant la saison humide, le système était très dynamique, avec de grandes fluctuations des niveaux de la nappe phréatique et, à long terme, l'inondation des zones basses. Les rapides hausses de la nappe phréatique ont été attribuées à une recharge *in situ* élevée, au faible volume d'air contenu dans les pores (zone non saturée), au piégeage de l'air et à la recharge occasionnelle de la crique. Les baisses rapides de la nappe phréatique ont été attribuées aux importantes différences de hauteur au sein de la zone riveraine, différences dues, partiellement, à la topographie vallonnée du site. La saison sèche a été caractérisée par un système lent, avec une profondeur de nappe phréatique pouvant atteindre 4 mètres dans certains endroits.

Les eaux souterraines arrivant dans la zone riveraine contenaient de faibles concentrations de nitrates (moyenne <0.03 mg NO_3- N L^{-1} durant les deux saisons). Cependant, les concentrations ont augmenté (jusqu'à 50 fois) lors de la progression des eaux souterraines à travers la zone riveraine, suggérant que la zone riveraine était une source de nitrates pour le

ruisseau adjacent. L'augmentation de nitrates a été attribuée à la nitrification ayant lieu dans les sols riverains de surface, processus favorisé par une importante productivité primaire nette, notamment de grandes quantités de litière (12.19 Mg ha^{-1} an^{-1}). Par la suite, les nitrates générés par le sol riverain ont été lessivés dans les eaux souterraines par les précipitations, durant la saison humide. Ainsi, les nitrates dans les eaux souterraines proviennent de la nitrification et, potentiellement, du mélange avec des eaux souterraines profondes ayant des concentrations supérieures en nitrates.

La forêt tropicale riveraine est potentiellement une source importante de protoxyde d'azote, avec des flux allant de -24 à 657 µg N_2O-N m^{-2} h^{-1}. Les émissions ont été plus élevées durant la saison humide, mais aucune différence significative n'a été observée entre les sites situés à haute ou basse altitude dans le paysage. De même, il n'a pas eu effet significatif, sur les émissions de N_2O, des différentes quantités de litière de feuilles accumulées sur la surface du sol. Basé sur les différences de teneur en humidité du sol, les émissions de N_2O ont été attribuées à la fois à la dénitrification et à la nitrification. Le N_2O a également été produit en profondeur, au sein de la zone non saturée, avec des concentrations de l'air du sol variant de 0.7 à 157 mg N_2O-N L^{-1}. Les concentrations de N_2O dissous dans les eaux souterraines ont été les plus élevées à 1,5 m de profondeur et bien corrélées avec les concentrations de nitrates des eaux souterraines. Des expériences menées en laboratoire ont permis de déterminer que les sols de surface riverains agissaient clairement comme une source de N_2O, et que, ces sols ont une capacité limitée à réduire le N_2O en N_2. La dénitrification potentielle était jusqu'à 20 fois plus élevée dans les sols de surface que dans ceux situés à 0.5 m de profondeur.

Cette étude a démontré que les eaux souterraines provenant des terres cultivées ne se caractérisent pas toujours par de fortes concentrations en nitrates et que les concentrations en nitrates ne sont pas nécessairement réduites lors du passage de l'eau souterraine à travers la forêt riveraine. Par ailleurs, sur notre site, les nitrates générés dans la zone riveraine sont lessivés dans les eaux souterraines au cours des fortes pluies, devenant une source de potentiel de nitrates pour le ruisseau. De même, les processus de nitrification et de dénitrification dans la zone boisée riveraine contribuent de façon considérable aux émissions de N_2O dans l'atmosphère, avec des émissions comprises dans la gamme de celles mesurées pour les forêts tropicales. Bien qu'il existe de nombreux avantages environnementaux justifiant le maintien en bonne santé des forêts riveraines, cette étude, menée dans un environnement tropical humide, n'a pas montré de bénéfices des forêts riveraines sur la qualité des eaux.

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Chapter 1.   Introduction

1.1   Rationale for study

Riparian zones may be defined as the vegetated strip adjoining a river or stream. Much of the research into riparian zones and their ability to remove nutrients from ground and surface water has been driven by growing concerns about nutrient contamination of ground, surface and inshore coastal waters as a result of agricultural runoff. In particular, much attention has been directed towards the removal of NO_3^-, one of the most widespread inorganic groundwater contaminants in the world (Hallberg and Keeney, 1993).

Riparian zones have been widely recognised for their capacity to remove nutrients, in particular NO_3^-, from groundwater. The retention or restoration of riparian zones has been identified as an effective means of improving water quality caused by nutrient loss from agricultural areas (Cey *et al.*, 1999; Hill, 1996). Riparian zones are known to attenuate NO_3^- through various means. The effectiveness of a riparian zone in doing this depends upon its ability to capture NO_3^- from groundwater as it moves through the riparian zone, before it discharges into the stream. Despite much research undertaken in temperate regions, the effectiveness of riparian zones to remove NO_3^- from groundwater in agricultural areas of the humid tropics has received very little attention.

Denitrification is recognised as the principal process for permanently removing NO_3^- from the soil-water system. Denitrification is a biogeochemical process in which N is converted to a gaseous form, entering the atmosphere as N_2O or dinitrogen (N_2). Dinitrogen, comprising 78% of air, is a harmless, inert gas. Nitrous oxide, on the other hand, is an

effective greenhouse gas of increasing environmental concern (Seitzinger, 2008). Increased emissions of N_2O are believed to be a result of a global surge in the use of N fertilisers in agriculture (Bouwman, 1998). Many studies have measured N_2O emissions from various landscapes, but very few studies have looked at emissions from riparian forests in agricultural environments on tropical coastal plains.

The Great Barrier Reef (GBR) is a World Heritage-listed site of exceptional environmental, social and economic value, sustaining a range of ecosystem services (Furnas, 2003; Stoeckl *et al.*, 2011). It is located along the coast of north east Queensland. Commercial and recreational activities and livelihoods supported by the GBR are valued in excess of $5 billion per year (Access Economics, 2007). Over the last 150 years the fertile coastal floodplains of GBR catchments have been extensively cleared. Large-scale cropping has been introduced in its place (Brodie and Mitchell, 2005). Sugarcane cropping occupies approximately 180,000 ha of the 'Wet Tropics' region of north east Queensland and horticultural crops approximately 40,000 ha (McDonald and Weston, 2004). Such changes in land use have been associated with a decline in water quality in these coastal catchments (Brodie *et al.*, 2008). Fertiliser inputs from sugarcane farming have been found to impact upon water quality in GBR catchments (Hunter and Walton, 2008; Mitchell *et al.*, 2009). Nitrogen based fertiliser application in the Wet Tropics region is around 140 kg N ha^{-1} (Armour *et al.,* 2012). High concentrations and loads of N in streams draining sugarcane production areas in the Wet Tropics have been reported (e.g. Bainbridge, *et al.,* 2009), with water eventually being discharged into the GBR lagoon. In response to this, the Reef Water Quality Protection Plan (Reef Plan) was introduced by the Australian federal government and the Queensland state government in 2003 (Queensland

Government, 2003). The aim of the plan is to improve the quality of water discharging into the GBR lagoon. Nitrogen (in both dissolved and particulate forms) is considered one of the main nutrient pollutants of concern in this region. The two key objectives of Reef Plan are to: 1) reduce the amount of pollutants entering the waterways and, ultimately, the GBR lagoon, and 2) promote protection and improvement of natural filters, such as riparian zones and wetlands, that can intercept these pollutants prior to them entering the marine environment. Riparian degradation has been highlighted as a significant impairment to the health of freshwater ecosystems (Brodie *et al.*, 2008). Hence, one of the goals of Reef Plan is to improve the condition and extent of riparian zones by 2013. Natural resource management bodies, Landcare and industry groups are actively promoting the restoration of riparian zones in GBR catchments (e.g. Smith, 2008). Through Reef Plan, the Australian federal government has offered Reef Rescue Water Quality Grants, a component of the Caring for our Country initiative, to fund activities such as riparian restoration.

In light of these initiatives, there is a need to understand the functioning of riparian zones within an agricultural landscape on humid tropical floodplains. For example, how much N is removed from groundwater flowing through a given width of riparian forest, and in what parts of the landscape are riparian zones most effective? Such information would assist in optimising the effectiveness of Reef Rescue Plan investments.

1.2   Aims of the study

The aims of this study were to:

1) determine the effectiveness of a forested riparian zone within an agricultural landscape of the humid tropics in removing NO_3^- from groundwater as it is transported towards the stream,

2) infer the most significant biogeochemical processes involved, and

3) assess the magnitude of the N_2O emissions associated with N cycling processes in the riparian zone.

To achieve these aims, a field study was undertaken at a forested riparian site in the Australian humid tropics, referred to locally as the 'Wet Tropics' of north Queensland. The riparian site was located amongst sugarcane fields, on the coastal plain, adjoining the World-Heritage listed GBR lagoon. A site with a wide strip of healthy riparian forest was chosen for the study. The use of a wide riparian zone would maximise the chances of detecting water quality changes. This would allow us to scale-down results to predict effects in narrower riparian zones which are more common in this landscape.

1.3   Thesis outline

The outline of this thesis is as follows:

The remainder of this chapter provides an overview of the literature concerning the principal areas covered by this study.

Chapter 2 describes the hydrology of the riparian study site, in particular the groundwater dynamics and groundwater-surface water interactions. It provides a year-round picture of the movement of water throughout the site based on field measurements during two wet seasons and the intervening dry season. An understanding the movement of water through the riparian zone provides a template for the movement of N and other solutes. Similarly, groundwater movement and soil wetness dictate the oxidation state of riparian soils. These, in turn, influence the spatial and temporal distribution of biogeochemical processes that occur within the site.

Chapter 3 examines the chemistry of groundwater moving through the riparian zone, from the sugarcane fields towards the creek. Nitrate was the focus of the study, and the aim was to determine if, and by how much, NO_3^- concentrations diminish during the passage of groundwater through the riparian zone. Creek water chemistry, soil chemistry and litterfall were also examined in order to gain an understanding of their roles in N cycling.

Chapter 4 assesses emissions of N_2O from the soil surface during wet and dry seasons at high- and low-elevation sites within the riparian forest. Several additional experiments were conducted to help interpret results of the field measurements. One field experiment examined the influence of leaf litterfall on N_2O emissions. Nitrous oxide concentration was also measured at different depths within the soil profile to determine its depth distribution in relation to soil water content and water table depth. Laboratory experiments were performed to test the riparian soils for potential denitrification capacity and capacity to reduce N_2O to N_2.

Chapter 5 integrates and summarises the major findings of the study, and ends with conclusions to this research.

Chapter 6 discusses the implications of this research and recommends areas for further investigation.

1.4   Literature review

1.4.1 Role of riparian zones in N removal

Due to their unique, low-lying position in the landscape, located between terrestrial and aquatic environments, riparian zones are ideally placed to receive and process NO_3^- transported via groundwater from agricultural areas towards rivers and streams (Groffman *et al.*, 2000; Hill, 1996; Lowrance *et al.*, 1984; Osborne and Kovacic, 1993). Riparian zones or 'buffers' are believed to be an effective means of protecting aquatic ecosystems from excessive inputs of N from anthropogenic sources (Verhoeven *et al.*, 2006).

A number of mechanisms have been identified that effectively remove N from groundwater flowing through riparian zones. These include: denitrification, a microbially mediated process (Groffman *et al.*, 1992; Lowrance, 1992), plant uptake (Dhondt *et al.*, 2003), microbial immobilization (Hill, 1996) and dissimilatory NO_3^- reduction to NH_4^+ (DNRA) (Davis *et al.*, 2008). Some disagreement exists as to which of these processes are mostly responsible for the attenuation of NO_3^- concentrations in groundwater as it moves through the riparian zone. However, denitrification appears to be the most widely cited and accepted mechanism (Hill, 1996). Denitrification reduces NO_3^- to N_2 (Figure 1.1). Since N_2 is unavailable for use by most organisms, denitrification is considered the only

mechanism capable of permanently removing N from the plant-soil-water system (Burgin and Hamilton, 2007). Where the denitrification process is incomplete, however, N_2O is produced. The other removal mechanisms listed above store or recycle N within the riparian zone, either in the soil, immobilised in microorganisms, or in plants. However, whilst nitrification in the unsaturated zone converts ammonium to NO_3^-, a proportion of N is also removed through the emission of N_2O. Although denitrification has been established as the principal mechanism to remove N, the relative importance of each of the other N removal processes is still not fully understood (Dhondt *et al.*, 2003; Dhondt *et al.*, 2006).
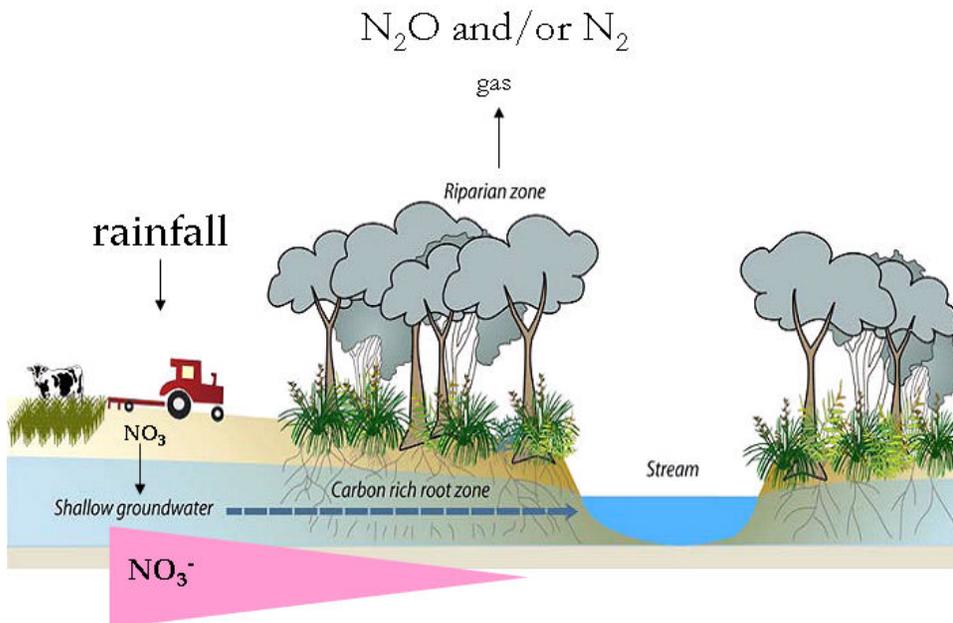
Figure 1.1 Conceptual diagram showing the process of NO_3^- removal from shallow groundwater by denitrification as groundwater flows laterally through a riparian zone towards a stream. (Adapted from Hunter *et al.* (2006)).

The effectiveness of a riparian zone to remove NO_3^- is often defined as the decrease in NO_3^- concentration in groundwater as it passes through the riparian zone, presented as a proportion of NO_3^- concentration measured in groundwater entering the riparian zone. Many riparian zones have been reported as effective in removing NO_3^- from incoming groundwater in temperate regions (Table 1.1). However, in a few cases, riparian zones have also been found to be ineffective. In these cases, riparian conditions have resulted in a net increase in NO_3^- concentrations in groundwater (e.g. Sabater *et al.*, 2003). This has been attributed to N saturation of riparian zones or to high hydraulic conductivity of riparian soils, the latter resulting in minimal residence time for groundwater within the riparian zone, thereby limiting the time for removal processes to take effect.

Table 1.1. Effectiveness of forested riparian zones at removing NO₃- from subsurface water (extracted from Mayer *et al.* (2007)).

Riparian zone width	NO₃⁻ concentration		NO₃⁻ removal effectiveness	Source
(m)	(mg L⁻¹⁾		(%)	
	Influent	Effluent		
50	26	11	58	Hefting *et al.* (2003)
200	11	4	64	Spruill (2004)
10	6.29	1.15	82	Schoonover and Williard (2003)
14	0.02	0.02	0	Sabater *et al.* (2003)
30	0.02	0.01	50	Sabater *et al.* (2003)
50	0.49	0.76	−55	Sabater *et al.* (2003)
15	28.64	35.84	−25	Sabater *et al.* (2003)
20	1.14	0.7	39	Sabater *et al.* (2003)
20	0.12	0.43	−258	Sabater *et al.* (2003)
15	3.23	0.72	78	Sabater *et al.* (2003)
20	6.4	1.44	78	Sabater *et al.* (2003)
55	–	–	83	Lowrance *et al.* (1984)
85	7.08	0.43	94	Peterjohn and Correll (1984)
204	29.4	1.76	94	Vidon and Hill (2004b)
50	13.52	0.81	94	Lowrance (1992)
60	8	0.4	95	Jordan *et al.* (1993)
16	16.5	0.75	95	Osborne and Kovacic (1993)
16	6.6	0.3	95	Haycock and Pinay (1993)
15	–	–	96	Hubbard and Sheridan (1989)
165	30.8	1	97	Hill *et al.* (2000)
50	6.26	0.15	98	Hefting and de Klein (1998)
220	10.8	0.22	98	Vidon and Hill (2004b)
50	7.45	0.1	99	Jacobs and Gilliam (1985)
10	13	0.1	99	Cey *et al.* (1999)
100	5.6	0.02	100	Spruill (2004)
30	1.32	nd	100	Pinay and Decamps (1988)
100	12	nd	100	Spruill (2004)
60	–	–	27	Groffman *et al.* (1996)

Despite the attention received by riparian zones in temperate climes, relatively little research has been carried out on the effectiveness of riparian zones to improve water quality in the tropics. In the sub-tropics of Australia, Lamontagne, Herczeg *et al.* (2005) reported that reducing conditions within the riparian zone were effective in removing NO₃⁻

from groundwater. Woodward *et al.* (2009) concluded that a riparian zone adjacent to an ephemeral stream was effective in removing added NO_3^- under experimental conditions. Similarly, comparing the hydrology of riparian zones adjoining ephemeral and perennial streams in a sub-tropical region of south east Queensland, Rassam *et al.* (2006) concluded that the extent to which NO_3^- removal was likely depended upon the individual characteristics of the sites. McJannet *et al.* (2012) conducted a study on the ability of wetlands to filter sediments and nutrients through a wetland in the Australian humid tropics, and they found little evidence of significant removal of N. This was attributed to the very short residence time of water passing through the wetland during large rainfall events and the low N concentrations in groundwater in the dry season, despite longer dry season residence times.

McKergow *et al.* (2004a; 2004b) studied the effectiveness of riparian zones in the humid tropics at trapping sediment and nutrients transported in surface waters. They concluded that the position of the riparian buffer zone in relation to cropped fields was important in trapping sediment. At the height of the wet season, however, the riparian zone was severely limited in its ability to trap sediments or nutrients due to the high volumes of runoff.

Studies of riparian zone function (with reference to N removal) in other humid tropical regions of the world have mainly been conducted in undisturbed, upland forested catchments in the Americas.   Authors have observed a decrease in NO_3^- concentrations as groundwater passed through the riparian zone (e.g. Brandes *et al.*, 1996; Chestnut and McDowell, 2000; McClain *et al.*, 1994; McDowell *et al.*, 1992; Saunders *et al.*, 2006; Williams *et al.*, 1997). In a small Amazonian catchment, McClain *et al,.* (1994) reported

dramatic shifts in concentrations and compositions of dissolved inorganic N (DIN) at the boundaries between the upland and the riparian zone and between the riparian zone and the stream. Nitrate was the dominant form of dissolved N in groundwater in the uplands but was replaced by NH_4^+ as groundwater entered the riparian zone. The greatest reduction in DIN concentrations (85%) was observed at the stream bank as groundwater crossed the riparian-stream margin. This was later confirmed by Brandes *et al.* (1996) at the same site. In an undisturbed catchment of the Luquillo Experimental Forest in Puerto Rico, Chestnut and McDowell (2000) calculated that groundwater discharging from the riparian zone could potentially increase stream NO_3^- concentrations by 84%. However, it was also concluded that significant N retention had to be occurring at the riparian-stream margin since stream water concentrations did not reflect the calculated inputs of N from groundwater discharge. Comparing the transport of N through two sub-catchments in the same forest in Puerto Rico, McDowell *et al.,* (1992) found that DIN concentrations diminished as groundwater flowed from the uplands towards the stream. However, spatially, N transformation processes were notably different between the two catchments. This was attributed to differences in the physical characteristics of the two sites.

Hence, the limited number of studies that have focussed on the tropics are in general agreement that riparian zones are effective in removing N from incoming groundwater. These studies highlight the importance of N processing at the riparian-stream-bank interface and the influence of individual site characteristics on N cycling processes.

Despite the contribution of these tropical studies, little is still known about the movement of N through riparian zones on tropical coastal plains, where agriculture is often the predominant land use. What is more, only studies by McKergow *et al*., (2004a; 2004b) have been undertaken in the Australian humid or "Wet" tropics where annual rainfall is very high (between 2000 and 8000 mm a year) and is concentrated in only a few months of the year (Bonell and Callaghan, 2008). This high intensity of rainfall can deliver up to 2 orders of magnitude more rainfall in the Wet Tropics compared to humid temperate zones in North America and Western Europe (Bonell and Callaghan, 2008), where most riparian zone studies have been conducted . Hence, during the wet season, processes within a riparian zone in the Australian Wet Tropics would be expected to be affected by large pulses of water flowing through the riparian zone, potentially affecting their capacity to remove N from shallow groundwater.

1.4.2 Role of riparian hydrology in nitrate attenuation

Nitrogen removal efficiency of riparian zones is closely linked to riparian hydrology. This, in turn, is regulated by the position of the riparian zone in the catchment in relation to surface and groundwater flows. Results from studies across different landscape settings in Ontario, Canada (Devito *et al.*, 2000; Vidon and Hill, 2006) and across a climatic gradient in Europe (Sabater *et al.*, 2003), suggest that hydrogeology/landscape setting has a greater control over NO_3^- removal than climate, at least in temperate regions. Knowledge of groundwater dynamics and ground and surface water interactions occurring in this near-stream environment, and how these factors interact with biogeochemical processes, is important when evaluating the effectiveness of the riparian zone for its potential to remove N (Burt and Pinay, 2005). Cirmo and McDonnell (1997) emphasised the need to link

predictions of N dynamics to seasonal (i.e. "long-term" temporal), hydrologic event (i.e. "short-term" temporal), and spatial (i.e. microtopographic or hydrogeomorphic) variations in the environment. For example, changes in reduction and oxidation (redox) states in riparian soil are influenced by water table fluctuations (themselves regulated by landscape position, topography, lithology and hydrology). Water table fluctuations, in turn, influence the rates of biological processes such as ammonification, nitrification and denitrification (Clément *et al.*, 2002; Reddy *et al.*, 1984). These processes are controlled by differences in oxygen (O_2) concentrations in the groundwater – soil environment. Hydrologic flowpaths and soil characteristics can impact upon the rate and magnitude of subsurface NO_3^- removal. For example, riparian zones characterised by a shallow impermeable layer, forcing groundwater to move laterally through shallow root zones and organic-rich soil, are considered ideal for NO_3^- attenuation (Burt *et al.*, 1999; Hill, 1996). Hill (1996) suggested that the majority of studies showing effective NO_3^- removal share these hydrogeologic characteristics. Where groundwater flow by-passes the root zone (Bohlke and Denver, 1995; Burt *et al.*, 1999; Speiran, 2010), or where groundwater flows through organically-poor soil (Robertson and Schiff, 2008), riparian zones are likely to be less efficient at removing NO_3^-. Most of the studies indicating effective retention of NO_3^- in the riparian zones of small agricultural watersheds have focused on groundwater fluxes during times of stream baseflow. Fewer studies have evaluated N concentrations in groundwater in riparian zones during stormflow conditions (Cooper, 1990; Hill, 1993; Hill *et al.*, 1999; Pionke *et al.*, 1988; Schilling *et al.*, 2006; Schnabel, 1986). Varying degrees of N removal have been observed during stormflow events. For example, Schilling *et al.* (2006) found that elevated concentrations of NO_3^- were observed in groundwater near the stream bank of an incised

riparian zone during a storm event. This was attributed to leaching of NO_3^- from the unsaturated zone into groundwater. It was suggested that the riparian zone could become a source of NO_3^- to the stream. Similarly, during the winter season, Hill and Shackleton (1989) observed soil NO_3^- leaching from a maple stand adjoining a riparian zone in Ontario, resulting in increased NO_3^- concentrations in shallow groundwater and perennial streams.

Mixing of surface water and groundwater within the riparian zone is likely to influence N transport and transformation pathways. Each water body will have different physical and chemical properties; hence, such mixing can influence the chemical properties of the adjacent stream (Hill, 1996). Dilution from rainfall (Maitre *et al.*, 2003) and upwelling groundwater with low N concentrations (Schoonover and Williard, 2003) can result in a decrease in N concentrations in shallow groundwater flowing through the riparian zone. These processes alone, however, do not diminish the N load. The fate or chemical speciation of N in groundwater passing through the riparian zone therefore depends on a number of factors, including the residence time and the biogeochemical environment encountered along the hydrologic flowpath (Cirmo and McDonnell, 1997).

1.4.3 The N cycle in riparian zones

The N cycle is the biogeochemical cycle that describes the transformations of N and N-containing compounds. Spatial and temporal changes in aerobic and anaerobic conditions are important factors influencing N cycling within riparian soil, soil water and groundwater (Figure 1.2). Such changes are highly dependent upon the hydrologic characteristics of the site, including the range of water table fluctuation and the degree of soil wetness (e.g.

Hefting *et al.*, 2004). Where tropical forest vegetation includes N-fixing organisms, N can

be biologically fixed from the atmosphere and stored within plant biomass (Jenny, 1950).

N stored in vegetation will become re-mobilised as organic N when plants and trees

deposit litter and roots. Mineralisation or ammonification is the process whereby inorganic

N is produced by the decomposition of organic N.   Inorganic N may become assimilated

into microbial biomass or absorbed by plants. Here it will become converted to an organic

form such as amino acids or DNA. This assimilation is also referred to as immobilisation.

Mineralisation and immobilisation of N enable a continual biological turnover of N in the

soil-plant-water system (Richards, 1974).   Mineralisation/ammonification and nitrification

rates of N in tropical forest soils are typically higher than those of temperate forests;

subsequently there is the potential for large amounts of NO_3^- to be produced in tropical

forests (Davidson *et al.*, 2000).
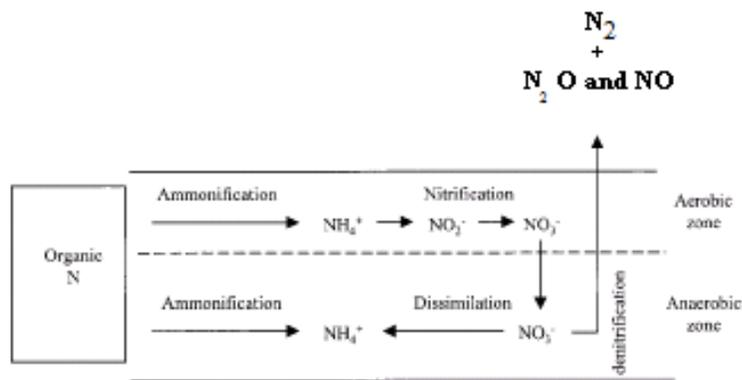
Figure 1.2 The principal components of the N cycle relating to riparian (wetland) soils under aerobic and anaerobic conditions (adapted from Pinay *et al.* (2002)).

Ammonification is the first step of the mineralisation process. Ammonification, which occurs during the decomposition of organic matter by microorganisms, is the conversion of organic N into the inorganic form ammonium (NH_4^+).

Nitrification is the biological oxidation of NH_4^+ with O_2 into nitrite (NO_2^-), followed by the oxidation of NO_2^- into NO_3^-. Nitrification is carried out by nitrifying bacteria under aerobic conditions. The simplified process is shown in equation 1.1.

$$\underset{NH_4^+}{} \xrightarrow{\text{(Nitrosomonas)}} NO_2^- \xrightarrow{\text{(Nitrobacter)}} NO_3^- \qquad \text{Eq. (1.1)}$$
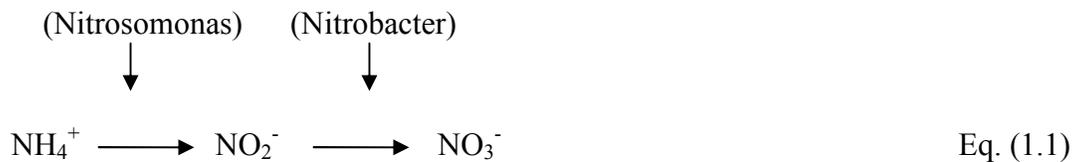
Nitrification can also be a significant source of N_2O. Nitrous oxide is produced when NO_2^- is used as electron acceptor by NH_4^+ oxidising bacteria (with the prefix Nitroso- in their names e.g. *Nitrosomonas*) under oxygen-limited conditions. Nitrite oxiders (bacteria of the genus *Nitrobacter*), on the other hand, are believed to produce little or no N_2O (Goreau *et al.*, 1980).

Biological or respiratory denitrification is a stepwise process undertaken by heterotrophic, facultatively anaerobic bacteria (known as denitrifiers) whereby NO_3^- is reduced from an oxidation state of +5 to 0. Nitrate is first reduced to NO_2^-, which, in turn, is converted to a gaseous phase consisting of the intermediate products nitric oxide (NO), N_2O and, when the process is complete, N_2 (Bowden, 1986; Nommik, 1956) (Equation 1.2).

$(+5)$ $\qquad$ $(+3)$ $\qquad$ $(+2)$ $\qquad$ $(+1)$ $\qquad$ (0)

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2 \qquad \text{Eq. (1.2)}$$
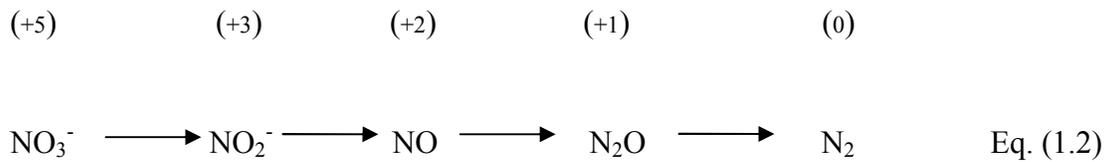
Denitrification in soil is regulated by a number of factors. These include the presence of dentritrifying bacteria, a supply of NO_3^- and organic C and anaerobic conditions or restricted O_2 availability, the latter influenced by soil water content and respiration (Firestone, 1982). The proportion of gases produced through denitrification depends upon the extent to which the regulating factors are fulfilled, although other factors, such as soil temperature, soil pH,   soil texture and structure, also influence the process. Nitrate is the principal substrate for denitrification, however it also acts as an inhibitor for the transformation of N_2O to N_2 (Granli and Bøckman, 1995). Respiratory denitrification derives energy from the oxidation of organic matter (Reddy and Patrick, 1984) whereby organic C acts as an electron donor. Tiedje (1988) suggested that C as an electron donor rarely limits denitrification in anaerobic habitats. However, it must be noted that organic C is also required for other metabolic processes, such as cellular growth, and by organisms other than denitrifiers. Organic C also has an indirect effect on denitrification, enhancing oxygen consumption by aerobic bacteria, leading to increased partial pressures of CO_2 through respiration and decreased O_2, resulting in anaerobiosis. High availability of organic C enhances denitrification rates. Low availability of organic C may increase the $N_2O{:}N_2$ ratio, hence increasing net N_2O production (Weier *et al.*, 1993). However, other pathways for denitrification exist, including autotrophic denitrification whereby pyrite can be used as an electron donor where organic C is limiting. Here NO_3^- is reduced whilst sulphide and iron become oxidised (Blicher-Mathiesen and Hoffman, 1999). Physical

characteristics of the soil, such as texture and structure can affect denitrification (Arah and Smith, 1989). The ability of a soil to retain water is influenced by its texture. For example, clay soils maintain water content for longer periods than coarser textured soils. Hence, O_2 is likely to be less available in finer textured soils which retain water more effectively, thereby providing conditions conducive for denitrification. Similarly, soil porosity and water content affect the diffusion of gases in soil. As air filled porosity declines, gas diffusion becomes more restricted (Amundson and Davidson, 1990).

Denitrifiers use NO_3^- rather than O_2 as an electron acceptor during respiration, with most denitrifiers undertaking denitrification under anaerobic conditions, i.e. only when O_2 availability is limited (Robertson and Groffman 2007). This occurs when soil water content is high and O_2 diffusion is slowed. Soil water content, often expressed as water filled pore space (WFPS, the volumetric proportion of soil pores filled with water), is considered a useful indicator of the relative potential for aerobic and anaerobic microbial activity in the soil (Linn and Doran, 1984). Denitrification starts to occur when WFPS is 60%, increasing greatly at WFPS >80%.

At low pH, N_2O is the dominant gas produced from denitrification, whilst at pH>7, N_2 production dominates (Weier and Gilliam, 1986). In general, N_2O is emitted as a denitrification end-product under conditions that are sub-optimal for denitrification (Hefting *et al.*, 2003). Under field conditions, however, each of the controlling variables and environmental factors are likely to interact, causing gaseous N emissions to vary in both space and time (Skiba and Smith, 2000). Such interaction often makes it difficult to

determine which circumstances are enhancing and which are limiting N_2O production

(Hefting *et al.*, 2003), but some generalisations can be made (Table 1.2).

Table 1.2. The general effect of several factors on denitrification and on the $N_2O:N_2$ ratio (Castaldi, 2000; Focht and Verstraete, 1977; Granli and Bøckman, 1994; Munch & Velthof, 2007; Weier *et al.*, 1993).

Factors	Effect on denitrification ($N_2O + N_2$ production)	Effect on $N_2O:N_2$ ratio
Increasing NO_3^- supply	+	+
Increasing O_2 content	-	+
Increasing available C	+	+
Increasing temperature	+	-
Increasing pH	+	-

Denitrification is likely to occur readily under conditions typical of most riparian zones. A high water table will reduce O_2 availability in near-surface soils and riparian vegetation can provide a source of organic C from roots and litter. Denitrifying bacteria clearly also need to be present in riparian soil for denitrification to occur.

Other N transformations may also occur within riparian zones. Dissimilatory NO_3^- reduction to NH_4^+ (DNRA), whereby NO_3^- is transformed first to NO_2^- then to NH_4^+, is another anaerobic pathway resulting in NO_3^- loss from soils and water (Burgin and Hamilton, 2007; Rutting *et al.*, 2011). It essentially "short circuits" the N cycle as the direct transformation of NO_3^- and NO_2^- to NH_4^+ bypasses denitrification and N_2 fixation (Cole and Brown, 1980). DNRA decreases the amount of NO_3^- circulating within a system by converting it to NH_4^+; however, N is not permanently removed from the plant-soil-

water system and NH_4^+ could be reconverted to NO_3^- by nitrification. DNRA has been found to occur under more anaerobic conditions than denitrification (e.g. Takaya, 2002). However, DNRA has also been shown to be less sensitive to O_2 concentrations than denitrification (Fazzolari *et al.*, 1998) yet more sensitive to the availability of labile C (Bengtsson and Bergwall, 2000). Many microorganisms conducting DNRA also produce N_2O (Cole, 1988). In a riparian zone in Europe, Dhondt *et al.* (2003) reported that denitrification dominated in riparian soils during the growing season whilst DNRA dominated during dormancy, when riparian plant activity was low.

Nitrite, derived from NO_3^- reduction or ammonium oxidation, can also be converted to N_2 via the 'anammox' pathway (anaerobic NH_4^+ oxidation), involving the simultaneous conversion of NO_2^- and NH_4^+ to N_2 (Jetten, 2001).

Other, less discussed pathways that could remove NO_3^- from riparian zones include nitrifier denitrification (Wrage *et al.*, 2001) and aerobic denitrification. Nitrifier denitrification is the process whereby ammonia (NH_3) is oxidised to NO_2^-, followed by the reduction of NO_2^- to NO, N_2O and N_2 under anaerobic conditions. Aerobic denitrification, on the other hand, requires aerobic conditions and consists of NO_3^- respiration in the presence of O_2 by certain genera of denitrifiers (Carter *et al.*, 1995). Some researchers have suggested that most of the N_2O attributed to nitrification is actually produced by nitrifier denitrification (Poth and Focht, 1985; Wrage *et al.*, 2001). The likelihood of the various denitrification and nitrification processes occurring depends on the availability of C, N and O_2 (Figure 1.3).
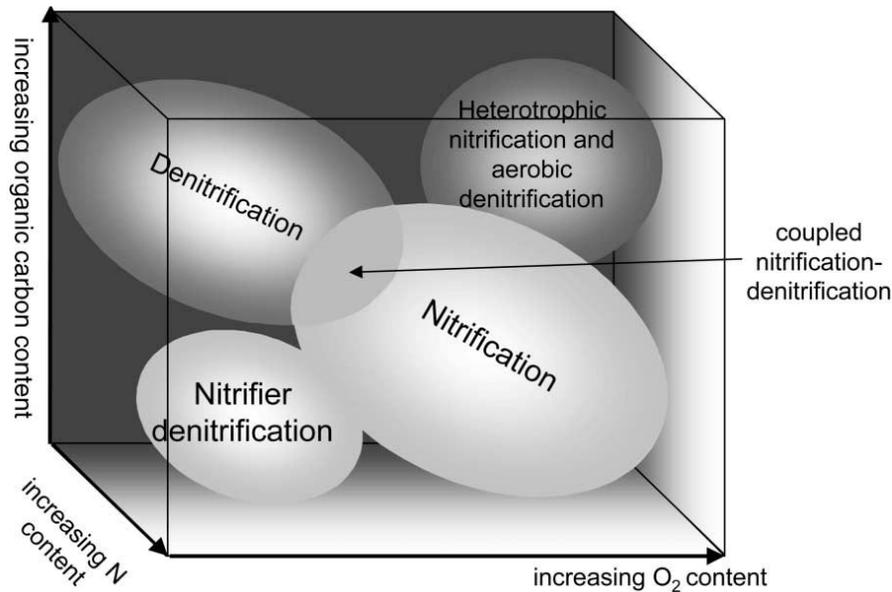
Figure 1.3 Possible ecological niche for nitrification and denitrification processes relative to the amounts of available C, N and O_2 available in fertilised soil. (Source: Wrage *et al.*, 2001).

1.4.4 Nitrous oxide emissions

Nitrogenous gases are the end product of a number of N transformation pathways. Dinitrogen is a harmless, inert gas. Nitrous oxide, on the other hand, is an effective greenhouse gas of increasing environmental concern (Seitzinger, 2008). It is stable in the troposphere for approximately 114 years and has a global warming potential, or heat trapping potential, 298 times that of carbon dioxide over a 100 year time horizon (IPCC, 2001). In the stratosphere it is known to be reactive and a contributing factor to stratospheric ozone destruction (Crutzen, 1970; Johansson et al., 2003). Increased emissions of N_2O are believed to be a result of a global surge in the use of N fertilisers in agriculture (Bouwman, 1990).

The global atmospheric N_2O concentration has increased from a pre-industrial value of about 0.270 μL L^{-1} to 0.319 μ L L^{-1} in 2005, primarily due to agriculture (IPCC, 2007). It is estimated that approximately 57% of the global atmospheric sources of N_2O are related to emissions from soils (Mosier and Kroeze, 1998), predominantly from nitrification and denitrification.

As previously described, soil water content, often expressed as WFPS (the volumetric proportion of soil pores filled with water), affects gaseous emissions by controlling aeration, diffusion of substrate and products, and microbial activity; it is hence a useful indicator of the relative potential for aerobic and anaerobic microbial activity in the soil (Linn and Doran, 1984). Davidson (1991) posited that N_2O production occurring between 30 and 70% WFPS is due to nitrification, with maximum emissions observed at 50%. Nitrous oxide production resulting from denitrification, on the other hand, was reported to occur between 50 and 90% WFPS, with maximum N_2O emission occurring at 70%. Davidson (1991) also noted that N_2 is emitted at water contents above 70% WFPS and becomes the main product of N gas emissions when soil water content exceeds 75% WFPS. The ''hole-in-the-pipe'' model was proposed to explain N_2O emissions from nitrification and denitrification in relation to mineral N content and WFPS (Firestone and Davidson, 1989). This conceptual model assumes that N_2O produced by these two processes is related to the N flow rate and the ''leak'' from those gross rates. It also assumes that N_2O is predominantly produced by nitrification at below 60% WFPS and by denitrification at above 60% WFPS (Bouwman, 1998). Other studies have suggested that maximum N_2O emissions could occur at between 80-85% WFPS (e.g. Veldkamp *et al.*, 1999).

It is clear that riparian zones can provide redox conditions conducive to both nitrification and denitrification, and, where NO_3^- and organic C are available, are likely to constitute potential 'hotspots' for N_2O production. Where the removal of NO_3^- through denitrification is concerned, the question is raised as to whether riparian zones simply swap one form of pollution for another i.e. is NO_3^- removed from soil and groundwater in exchange for emissions of N_2O? A number of studies have measured N_2O emissions from the surface of riparian soils, with a large variation in the range and maximum emissions reported (Table 1.3).

Table 1.3 Maximum surface N_2O emissions measured from riparian zones.

Maximum N_2O emission (μg N_2O-N m^{-2} h^{-1})	Location	Source
392	SE Queensland, Australia; sub-tropical riparian	Hinshaw (2008)
48	Puerto Rico; tropical riparian zone	McSwiney *et al.* (2001)
144	Ontario, Canada; riparian zone	Desimone *et al.* (2010)
	Puerto Rico tropical forest :	Bowden *et al.* (1992)
435	Icacos riparian site	
42	Bisely riparian site	
40	Ohio, USA; constructed riparian wetland	Hernandez and Mitsch (2006)
97	Chesaspeke Bay, USA; stream bank	Weller *et al.* (1994)
720	South Appalachia, USA; riparian zone	Walker *et al.* (2002)
104	Belgium, forested riparian zone	Dhondt *et al.* (2004)
1250	Netherlands, forested riparian zone	Hefting *et al.* (2003)

The profile of N_2O production with depth has been less well studied. A number of researchers have tested riparian soils at depth for potential denitrification (e.g. Dhondt *et al.*, 2004; Ullah and Zinati, 2006), but fewer studies have measured in situ N_2O concentration profiles in soil or groundwater at depth (Table 1.4 and Table 1.5)

Table 1.4 Soil air N_2O concentrations in forested sites (riparian and non-riparian).

N_2O in soil air (μ L N_2O L^{-1})	Location	Source
0.5 - 3	Australia, tropical forest	Kiese and Butterbach-Bahl, (2002)
1 - 10	Puerto Rico, tropical riparian	McSwiney *et al.* (2001)
0.3 - 8	Brasil, tropical forest	Verchot *et al.* (1999)
0.2 - 45	Canada, riparian zone	Desimone *et al.* (2010)

Table 1.5 Dissolved N_2O concentrations (as N) in groundwater at riparian and non-riparian sites.

Dissolved N_2O (μ g N_2O-N L^{-1})	Location	Source
6.5 - 71	German and USA	Well *et al.* (2001)
0 - 10	USA, Oregon, riparian	Davis *et al.* (2007)
0.5 - 8	USA, forest	Davidson and Swank (1990)
6 - 14	USA, Iowa, riparian	Kim *et al.* (2009)
1 - 8	Puerto Rico, tropical riparian	McSwiney *et al.* (2001)
1 - 30	Germany, ex-agricultural land	Weymann *et al.* (2009)

Chapter 2. Hydrology of a forested riparian zone in an agricultural landscape of the humid tropics

Published.

2.1 Introduction

Vegetated riparian buffer zones are widely promoted as a tool for mitigating the transport of nutrients from farms into surface water bodies (Pert *et al.*, 2010), but their role in humid tropical regions is little examined. In temperate regions the role of riparian zones in removing N from groundwater prior to discharge is well documented (Hanson *et al.*, 1994; Hefting *et al.*, 2006; Hill, 1996; Lowrance *et al.*, 1984; Peterjohn and Correll, 1984). The N removal efficiency of riparian zones is closely linked to riparian hydrology and biogeochemical processes (Burt and Pinay, 2005; Tesoriero *et al.*, 2005; Vidon and Hill, 2004a; Vidon and Hill, 2004b). Lateral movement of groundwater, water table rise and fall, downward leaching of rainfall and bank storage are the main pathways of water through riparian zones. In the Australian humid tropics, long duration, high rainfall intensities can produce large volumes of surface and subsurface runoff so water flow through riparian zones can be rapid (Bonell and Callaghan, 2008; McKergow *et al.*, 2004a). Retention times may therefore be too low for NO_3^- reducing processes to have a significant effect on water quality. On the other hand, the saturation of surface soils caused by flooding could be expected to enhance NO_3^--reducing condition; flooding is common on tropical

floodplains due to 'trapping' of water as torrential rain converges with rivers already in spate (Bruijnzeel, 1990). While there is an increasingly good understanding of the hydrology of lowland tropical forests (Bonell and Balek, 1993), there is little data on the flow paths of water through humid tropical riparian zones.

Riparian function in humid tropical catchments is of particular interest worldwide due to large-scale conversion of tropical forested areas to agricultural land over recent years (Drigo, 2005) and the potential impacts on sensitive and biodiverse downstream ecosystems (Todd *et al.*, 2010). The rapid expansion of agriculture has been accompanied by a substantial increase in the use of nitrogenous fertilisers (Matthews, 1994) and potential increased NO_3^- concentrations and loads in streams. Studies of riparian zone function in the tropics have mostly been undertaken in undisturbed forest catchments in the Americas (e.g. Brandes *et al.*, 1996; McClain *et al.*, 1994; McDowell *et al.*, 1992; Saunders *et al.*, 2006) where those authors observed a decrease in NO_3^- concentration as groundwater passed through the riparian zone. Less is known about the hydrology and biogeochemistry of riparian zones in humid tropical plains, particularly where agriculture is the predominant land use. McKergow *et al.* (2004a), reporting on the hydrology of riparian zones receiving runoff from cropped slopes (bananas) in tropical north east Australia, documented high runoff volumes and peak discharges. They found that the effectiveness of riparian zones for reducing sediment and nutrient transport in surface runoff was limited (McKergow *et al.*, 2004b).

In the Australian humid tropics, elevated concentrations of NO_3^- have been observed in groundwater (Rasiah *et al.*, 2005; Thorburn *et al.*, 2003) and groundwater is considered an

important pathway for the transport of N lost from agriculture into streams and eventually the GBR lagoon (Armour *et al.*, 2004; Furnas, 2003; Rasiah *et al.*, 2010; Rasiah *et al.*, 2003). The Australian humid tropics are characterised by high intensity, long duration, seasonal rainfall events and cyclonic activity (Bonell and Callaghan, 2008). There has been substantial degradation or removal of forest from riparian zones in these catchments (Lawson *et al.*, 2007), and that has been linked to water quality decline due to nutrient enrichment (Brodie *et al.*, 2008).

In order to understand and model the effectiveness of forested riparian zones for improving water quality in agricultural regions of the humid tropics, the first step is to understand their hydrology. In this study, we set out to determine the principal flow paths of water through a study site on the coastal plain of north east Queensland, Australia, amidst sugarcane fields, in the catchment of the World Heritage-listed GBR lagoon. The site was typical of the coastal plain of the Australian humid tropics in terms of topography and soil type, but was atypical in terms of vegetation, being a wide (150 m) and relatively undisturbed riparian forest. We were most interested in the direction and speed of groundwater moving through the near-surface layers, where saturated conditions, coupled with abundant supply of organic C, could potentially provide favourable conditions for gaseous loss of N from groundwater (Burt and Pinay, 2005). Therefore the objectives were to determine: how wet is the near-surface riparian zone over the course of a year, and what is the direction, duration and velocity of water movement through that zone?

2.2   Methods

2.2.1 Site description

The study was conducted from November 2008 to March 2010 in the riparian zone of

Behana Creek (145.842° E, 17.122° S) in north east Australia (Figure 2.1).
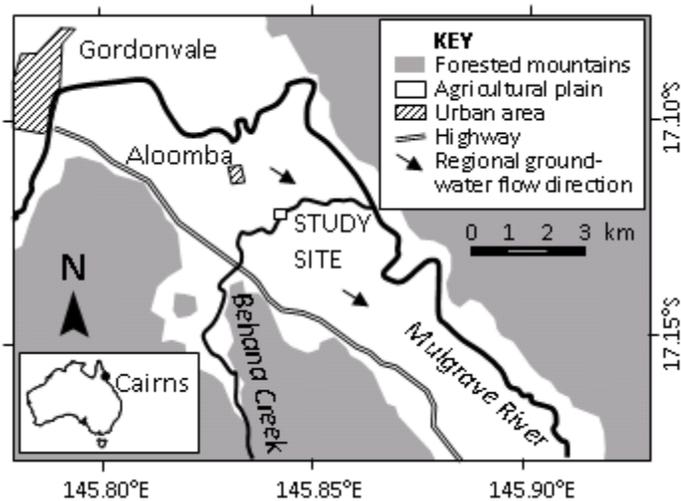
Figure 2.1. Location of study site. Gordonvale, shown on the main map, is 19 km south of the regional centre Cairns, shown on the inset.

Behana Creek is a perennial stream originating in the Bellenden Ker mountain range,

draining into the Mulgrave River and then into the Coral Sea (GBR lagoon). Rainfall in the

catchment ranges from an annual average of approximately 2300 mm on the plain (Leach

and Rose, 1979) to approximately 8000 mm on Mount Bellenden Ker (Australian Bureau

of Meteorology, 2010a). More than 80% of Behana Creek's catchment is comprised of

mountains covered in rainforest. The lower part of the catchment, in the coastal plain, has

been cleared and developed for agriculture, primarily sugarcane. The lower reaches of the

creek are considered ecologically healthy, with better riparian forest cover than similar

streams throughout the region (Arthington and Pearson, 2007). The coastal plain of the Mulgrave catchment, bounded on both sides by granitic and metamorphic mountains, ranges from about 3 to 13 km in width. It is comprised mostly of gravelly to clayey Pleistocene and Holocene alluvium and colluvium (Nott *et al.*, 2001) reaching maximum depth of approximately 80 m and housing an unconfined aquifer (Leach and Rose, 1979). At the study site the depth to bedrock is approximately 42 m (Leach and Rose, 1979). The study site was a forested riparian strip, approximately 150-170 m wide (Figure 2.2) set amongst sugarcane fields on the coastal plain. The forest is relatively undisturbed remnant lowland complex mesophyll vine forest (DERM, 2009b) lying approximately 1-5 m lower in elevation than the surrounding agricultural area. The ground surface topography, surveyed using a Total Station ™, undulates between approximately 2.5 and 7 m above sea level (Australian Height Datum (AHD)). Areas within the study site were classified as 'high' when located between 4.8 and 7 m altitude and 'low' from 2.5 to 4.7 m. A wide depression or gully runs through the study site and is connected to Behana Creek at the north east corner of the site. (The 'gully' was previously the Behana Creek channel, as indicated by cadastral boundaries surveyed in 1883. The deepest point within the gully was at approximately 2.2 m AHD). The sugarcane field adjacent to the riparian zone has rows and furrows aligned slightly off the contour, so that any surface runoff generated therein flows towards a drain. This empties into the riparian zone approximately 100 m to the south west of the study site. During large rain events some of this water moves into the study site through a ditch, towards the gully. A study in the sugarcane field directly upslope of our study site found that deep drainage was 22-37% of rainfall over the 2007-2010 period (Armour *et al.,* 2012).
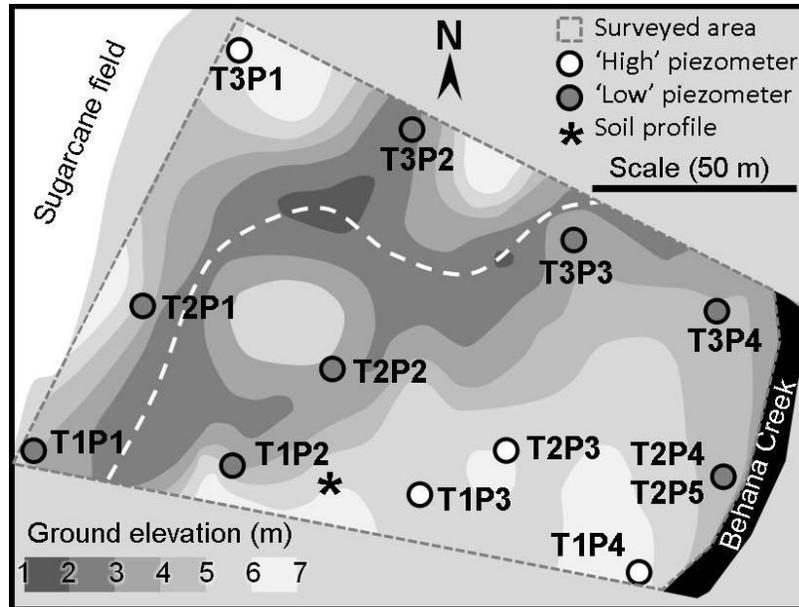
Figure 2.2. Topography of study site (ground surface elevation contours in metres above sea level) and location of sampling points. 'T' refers to transect and 'P' refers to piezometer. The dashed white line is the 'gully' referred to in the text.

2.2.2 Rainfall, reference evapotranspiration and soil water content

Rainfall was measured and recorded daily using a manual rain gauge located approximately 500 m from the study site. Reference evapotranspiration (ET_o) was derived from SILO-Datadrill (DERM, 1998), calculated using the FAO Penman-Monteith formula (Allen *et al.*, 1998).

Soils at the site are mapped as Orthic Tenosols (Murtha *et al.*, 1996) which are formed in recent alluvium. Soil across the site was characterised by measuring field texture and bulk density (50 mm long, 70 mm diameter cores). Saturated infiltration rate was measured at high and low sites using ponded ring infiltrometers. Soil water content was measured at several locations using time domain reflectometry (TDR, uncalibrated CS616-L probes,

CR1000 data logger; Campbell Scientific, Logan, UT). The standard calibration was used as recommended for soils such as those of our study site, with low electrical conductivity, bulk density and clay content. From March 2009 to May 2010 water content at 0.1 m depth was recorded at 10-minute intervals at a low site (T1P2) and high site (T1P3). In December 2009 additional TDR probes were inserted at 0.1, 0.5, 1.0 and 2 m depth into the face of the wall of a soil pit (subsequently back-filled as close to the original bulk density as possible by replacing all of the soil layer by layer) located at an intermediate elevation (soil profile, Figure 2.2). Water content of the soil profile was monitored from 15 December 2009 to 5 May 2010. Total porosity, air- and water-filled porosity were calculated using soil water contents, bulk density and particle density. At 0.1 m depth, soil particle density was calculated at 2527 kg m^{-3}, using an organic matter content of 107 g kg^{-1} (measured mean organic C content of 53.5 g kg^{-1} multiplied by two) and assuming the density of mineral and organic matter fractions were 2650 and 1500 kg m^{-3}, respectively (Brady and Weil, 2008; Mwaikambo and Ansell, 2001).

2.2.3 Water table levels and groundwater flow velocity

In order to determine groundwater flow velocity through the site, 12 piezometers were installed in 3 transects (Figure 2.2). Transects were parallel to the main direction of groundwater flow as noted in previous studies (Bajracharya, 1999; Leach and Rose, 1979). The piezometers, made from 50-mm diameter PVC pipe, were installed to approximately 0.5 m below the water table at the end of the dry season (November 2008). They were slotted from the bottom to 0.4 m below the ground surface, except for an additional piezometer (T2P5). Piezometer T2P5 was installed to 6 m depth, 1 m from T2P4 (which was slotted from 0.4 to 2.5 m depth) and was slotted only from 5.8 to 6.0 m depth. The

hole around all PVC pipes was back-filled with creek sand up to 0.4 m depth, bentonite at 0.2-0.4 m depth and soil to the ground surface. Soil extracted during the augering of each of the piezometers was analysed for field texture (NCST, 2009).

Water table levels were monitored at the four corner piezometers of the grid (T1P1, T1P4, T3P1 and T3P4) throughout the study using capacitance probes (model Z412, Odyssey, Christchurch, New Zealand) calibrated using manual measurements and programmed to log at 10-minute intervals. Additionally, depth to water table in all piezometers was measured manually at least once a month, except when piezometers were submerged and inaccessible. All water table levels were measured from the ground surface and referenced to AHD.

The overall lateral hydraulic gradient across the study site was calculated from

$$i = (i_1^2 + i_2^2) / (i_1 + i_2), \qquad \qquad \text{Eq. (2.1)}$$

where i is the overall gradient, i_1 is the measured absolute gradient parallel to Behana Creek and i_2 is the measured absolute gradient perpendicular to the creek. The hydraulic gradients in those two orthogonal directions were determined using the mean water table elevation and horizontal distance between the T1P1- T3P1 and T1P4 - T3P4 pairs of piezometers in one direction and the T1P1-T1P4 and T3P1-T3P4 pairs in the other. Overall groundwater flow direction was calculated using trigonometry and expressed as degrees in relation to grid north (UTM, WGS84). Vertical hydraulic gradient was calculated from the relative hydraulic heads in nested piezometers T2P4 and T2P5.

Saturated hydraulic conductivity (*K*) of the aquifer was determined using the slug test method (Bedient *et al.*, 2008) over a depth range of 0.4-1.2 m at piezometer T1P1, 2.1-2.2 m at T2P4 and 1.9-3.1 m at T3P1. Results were interpreted using the Hvorslev method (Freeze and Cherry, 1979) which assumes a homogenous, isotropic medium in which soil and water are incompressible.

Groundwater samples were taken at least once per month from all piezometers and analysed for chloride (Cl⁻) for use as a conservative tracer of water flows. Prior to sampling, the piezometers were purged of 3 times the standing volume of water, or until dry, using a manual bailer. After recovery, two -125 mL samples were taken and transported back to the laboratory on ice.

2.2.4 *Plant uptake of groundwater and soil water (unsaturated zone)*

The amount of water taken up from groundwater and its associated capillary zone by the riparian forest was estimated using diurnal variations in the water table level during rain-free periods using the method of White (1932). This method was selected as it is still considered to be the best currently available means of measuring transpirative discharge from the saturated zone during rain-free periods (Loheide *et al.*, 2005). The method assumes that (1) diurnal water table fluctuations at a given point (well) are a product of plant water uptake from around the well and lateral flow into that region from further afield (2) that evapotranspiration and uptake are negligible during the night (3) a constant rate of flow into the near-well region occurs over the entire 24-hour period and (4) that a suitable value for the specific yield (*Sy*) can be determined for the region of interest. It is worth noting that, if lateral inflow rates during the day-time were greater than night-time rates

(due to differences in gradient resulting from uptake), uptake from groundwater will be underestimated in this study. Uptake of groundwater (UGW, mm d^{-1}) was calculated using data from piezometers T1P1 and T3P1 for the period 14 June - 11 July 2009 from

$$UGW = Sy \ (24R + [H_1 - H_2] \qquad\qquad\qquad \text{Eq. (2.2)}$$

where H$_1$ is the highest level of the water table on day 1 (mm), H_2 is the highest level of the water table on day 2 (mm), and R is the mean rate of water table rise (mm h^{-1}) during the nights (19:00 h to 07:00 h) before and after the day of interest. The 19:00 to 07:00 h period was used as the rate of change was constant during that time. An appropriate value for Sy was determined using measurements of the change in soil water content at a particular point over the period immediately after the water table fell past that point, during a period with no rainfall. We used data from the TDR probes in the soil pit and applied a distance of movement (<0.5 m) and time period (12 h) that were appropriate to the measurements of water table fluctuations. Using this approach, $Sy = 0.111$ at 0.1 m depth and 0.053 at 0.5 m depth. As the soil texture at 0.5 m depth in the pit is similar to that over the depths of interest in piezometers T1P1 and T3P1, we used the value 0.053 in the calculations. We used the term UGW rather than ET_G (proposed by Loheide *et al*. (2005) for the same parameter) as uptake on a particular day does not necessarily equal ET, due to capacitance in the trees.

Uptake of water from the 0-0.2 m depth layer of the unsaturated soil zone (USW, mm d^{-1}) was calculated for low, intermediate and high elevation sites (T1P2, soil pit and T1P3, respectively, Figure 2.2) during a rain-free period (2-9 March 2010) using data from the TDR probes at 0.1 m depth. Daily uptake was calculated by the decrease in volumetric soil

water content over a 24-hour period (equation 2.3), subsequently corrected for changes not due to uptake.

$$USW = 200 \ (24C + (\theta_1 - \theta_2)) \hspace{4cm} \text{Eq. (2.3)}$$

where θ_1 is the soil water content at 06:00 h on day 1 ($m^3 \ m^{-3}$), θ_2 is the soil water content at 06:00 h on day 2 ($m^3 \ m^{-3}$) and C is the mean rate of increase in soil water content ($m^3 \ m^{-3} \ h^{-1}$) during the nights (20:00 - 06:00 h) before and after day 1. The rate of increase during the night was usually positive, presumably due to a net gain from water moving upwards from wetter zones or exudation from roots, but occasionally negative (in the wettest soil), presumably due to net loss by drainage. The changes in soil water content not due to uptake were estimated by measuring the change during the night-time and assuming that the rate of change also applied during the daytime. Uptake was assumed to be negligible during the night. During the measurement period, the depth to water table at the intermediate elevation site dropped from 0.98 to 1.53 m below ground.

2.2.5 Deep drainage and in situ recharge of groundwater

Lateral groundwater flows could be estimated from water table gradients. However, in situ deep drainage might also be expected to contribute a significant amount of recharge. A one-dimensional, daily time step, tipping bucket model was devised to estimate the amount of deep drainage and in situ recharge. The model was applied to piezometer T3P1 as this site had the most complete data set. For days during which there was a net rise in water table, the contribution of deep drainage to that rise (RD_2, with length units) was estimated using

$$RD_2 = \frac{\left(\frac{W_1 T_2}{T_1}\right) + P_2 - ET_2 - (\theta_{FC} T_2)}{\varepsilon - \left(\frac{W_1}{T_1}\right)}$$

Eq. (2.4)

in which θ_{FC} is the volumetric field capacity water content and ε is the total porosity of the variably saturated zone (both dimensionless), T_1 and T_2 are the thickness of the unsaturated zone on day one and day two, respectively, W_1 is the amount of water in the unsaturated zone on day one, P_2 is the amount of rainfall reaching the ground on day 2 (measured rainfall - estimated interception) and ET_2 is evapotranspiration on day 2 (all with units of length).

On days when there was a fall in water table level, the amount of water in the unsaturated zone was also calculated, accounting for losses by evapotranspiration and gains from the addition of the previously saturated zone. Total soil porosity was set at 0.57 m^3 m^{-3} based on bulk density measurements. The value of W was constrained by minimum and maximum soil water contents of 0.1 m^3 m^{-3} (the lowest measured in the field) and 0.376 m^3 m^{-3} (field capacity), respectively. Soil water content at field capacity was the mean of values calculated for 0.5 and 1.0 m depth at the soil pit using the method of Vachaud *et al.* (1978). Interception was set at 2 mm d^{-1} for rainy days, which falls within the 4.5-22% of rainfall value found for tropical forests (Bruijnzeel, 1990). Although results are presented using the values above, the sensitivity of deep drainage estimates to parameter values was tested by varying them as follows: ET from 0.5 to 1 times ET_0 , ε and θ_{FC} from 0.8 to 1.2 times the values given above; volumetric air entrapment from 0 to 0.14; and interception from 1-3 mm d^{-1}.

2.3   *Results*

2.3.1 Rainfall, evapotranspiration, infiltration and soil water content

Rainfall for 2009 was 2978 mm, of which approximately 75% occurred in January – April (Figures 2.3 and 2.5). Rainfall was often intense and prolonged; e.g. 617 mm on 10-15 January 2009, and up to 214 mm in one day (12 January 2009). Total ET_0 for 2009 was 1535 mm, leaving at least 1443 mm available for runoff and deep drainage.

Soil porosity and permeability was generally high throughout the site. Soil furthest from the creek tended to have a loam-clay loam topsoil over a sandy clay loam to medium clay horizon, with coarser texture below one or 2-m depth. The gully areas consisted of loose, loamy topsoil underlain by coarse sand to gravel below approximately 1 m. Average soil bulk density at the surface (0-0.05 m depth, excluding gully soils) was 800 kg m^{-3}, with the lowest value, 680 kg m^{-3}, adjacent to the gully. Bulk densities measured at the soil pit were 1210 and 1130 kg m^{-3} at 0.5 and 1.0 m depth, respectively. Infiltrability of the surface soil was $> 1.91 \times 10^{-5}$ m s^{-1} at all sites and Hortonian overland flow was never observed, even during intense rainfall events during the wet season. Therefore, during those times, all rainfall that reached the ground is assumed to have infiltrated. However, saturation overland flow was frequently observed during periods of high in situ rainfall at times and places where the water table breached the soil surface (as indicated by water table measurements being made at the time in nearby piezometers).
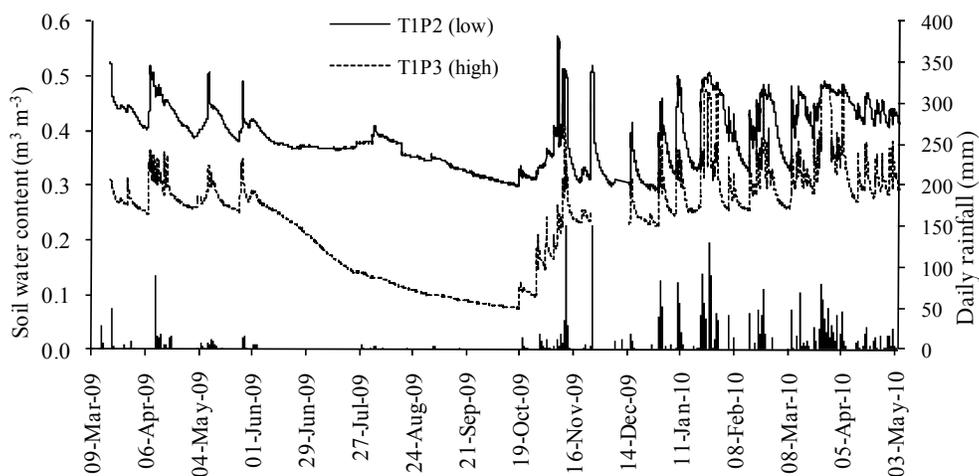
Figure 2.3. Soil water content at 0.1 m depth at sites T1P2 (ground elevation 4.2 m) and T1P3 (ground elevation 5.4 m) and daily rainfall.

Surface (0.1 m) soil water contents at the high and low sites T1P3 and T1P2 are summarised in Table 2.1. Surface soil at the low site (4.1 m elevation) remained moist throughout most of the year (Figure 2.3), maintaining soil water content equivalent to > 60 % WFPS during the wet months, a duration equivalent to approximately 25% of the year (Table 2.1).

Table 2.1. Summary of soil water contents (θ) and the proportion of the year during which water content was > 60% water filled pore space (WFPS) at 0.1 m depth at sites T1P2 and T1P3. Annual values are for the period 19 March 2009 - 19 March 2010.

Site	Minimum θ	Maximum θ	Annual mean θ	Total porosity	θ at 60% WFPS	>60% WFPS
			($m^3 m^{-3}$)			(% of year)
T1P2 (low)	0.29	0.58	0.38	0.690	0.414	24.7
T1P3 (high)	0.08	0.49	0.22	0.625	0.375	1.4

Areas lying at <4 m elevation could be expected to be wet (>60 % WFPS) for a greater portion of the year. These areas, accounting for approximately 40% of the riparian site, consisted predominantly of the gully and gully banks. At the higher location (T1P3), the soil became very dry at the surface during the dry season although it remained wetter below approximately 0.5 m depth (personal observation). It only reached the equivalent of >60% WFPS for very few days of the year, during large rainfall events (

Table **2.1** Table 2.1, Figure 2.3). Soil at the high site was much quicker to drain after rainfall ceased than soil at the lower location, presumably due to the close proximity of the water table at the low site (the water table at this location was never deeper than 1.3 m below the surface).

The influence of the water table on soil water content was observed from the soil profile observations: the water table was <2 m deep throughout the monitoring period; soil at 0.1 and 0.5 m depth wetted up quickly during rainfall and drained rapidly between rainfall events, whereas water content at 1 m depth varied less with time (Figure 2.4). It is interesting to observe that, during periods of water table rise to the ground surface, soil beneath the water table failed to reach a state of complete saturation. Soil between 0.1 m and 1.0 m depth only reached 74-79% of saturation, corresponding to an entrapped air content of 0.14 - 0.15 m^3 m^{-3}. Below the water table, soil water content at a given depth rose when the water table rose (Figure 2.4) possibly due to compression of the entrapped air.
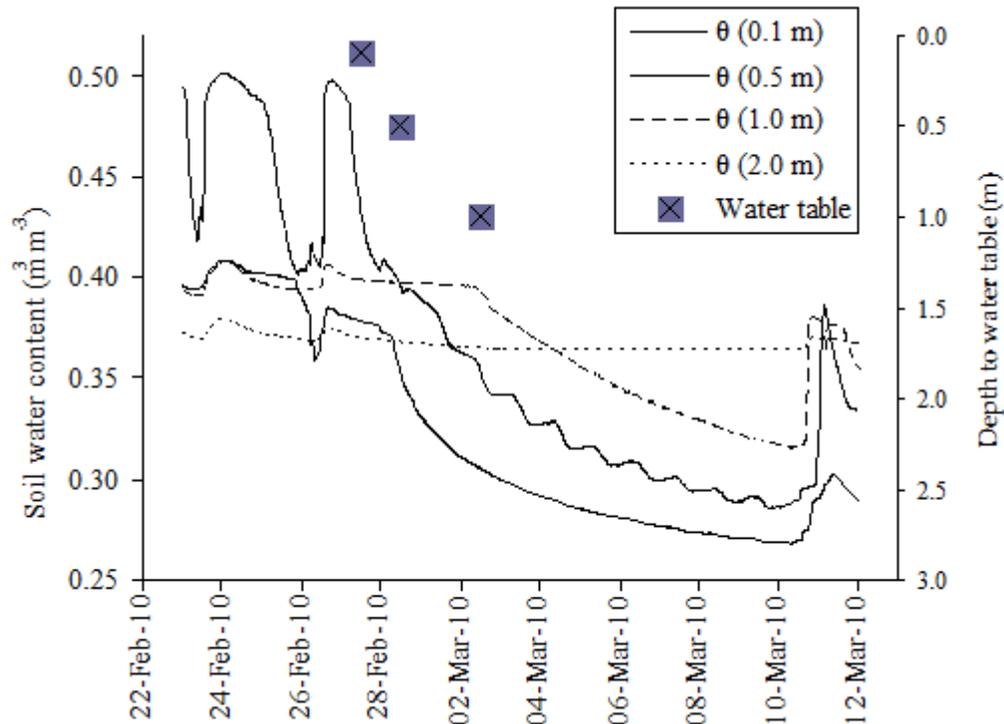
Figure 2.4. Soil water content at several depths at the soil profile site during and after a rainy period, and depth to water table on the days when it dropped past each of the soil water content probes. (The water table did not reach 2 m depth during the period shown).

2.3.2 Water table levels and groundwater flow

Water table dynamics exhibited a clear seasonal pattern (Figure 2.5). Water table elevation fluctuated by up to 4 m during the wet season whereas it remained fairly constant during the dry season. Depth to water table at the higher locations (T1P4, T2P1, T3P1 and T1P3 and T2P3) ranged from 3.2 - 4.0 m during the dry season and 0.5- 3.5 m during most of the wet season. Water table levels at all logged piezometers showed rapid responses to wet season rain events, with a very sharp rising limb. Drainage at high sites was rapid once in situ rainfall had ceased, although the receding limb was less steep than the rising limb. At the lowest-lying locations the water table was 0.5- 1.5 m below ground in the drier months (June to end of October 2009) and above ground through much of the wet season.
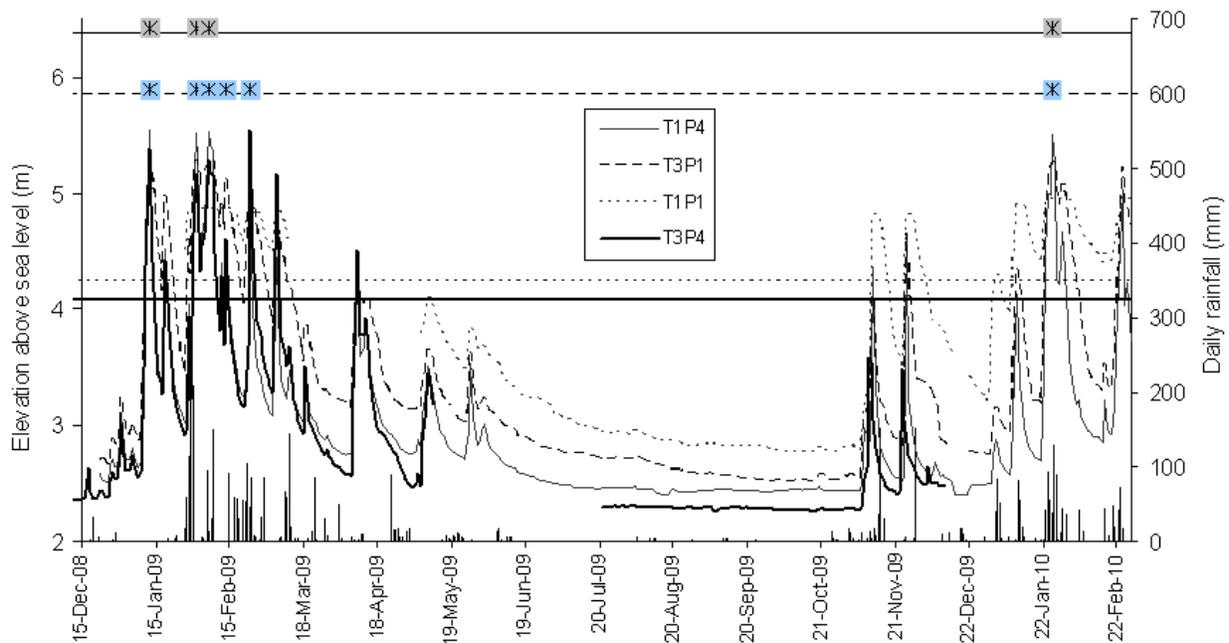
Figure 2.5. Daily rainfall and daily average water table levels for the 4 corner piezometers from December 2008 - February 2010.
Horizontal lines represent ground surface elevations for each piezometer. Asterisks indicate when water levels were higher than the measurement range for >10 h in piezometers T1P4 and T3P1. On these occasions groundwater surfaced. Capacitance probes in piezometers T1P1 and T3P4 were able to measure heights of flood water above-ground at those locations. Missing data are due to technical difficulties.

The study site was partially inundated for most of the wet season. Total inundation occurred for approximately 48 hours on 10-15 January 2009 and 36 hours on 23-27 January 2010, with flood waters reaching a height of approximately 4 m above the ground surface in some parts (data not shown, personal observation). For most of the wet season, the lowest-lying areas remained flooded from the first large rain event (10-15 Jan 2009) until the end of April 2009. Water table levels at the creek-bank piezometers reflected Behana Creek stage levels. The creek rose above ground level at the lower creek-bank piezometers (T2P4 and T3P4) on at least 5 occasions, for periods of 6 hours (10 April 2009) to 11 days (31 January - 10 Feb 2009). At these times creek water moved into the riparian zone.

The overall water table gradient across the riparian zone was between 0.002 and 0.003 during the dry season and 0 to 0.010 during the wet season (Figure 2.6). The maximum gradient recorded between individual logged piezometers was 0.014. The overall direction of groundwater flow through the site was from the sugarcane fields towards the creek for most of the year; in the dry season the flow direction was 60° from grid north, or approximately 45° to the creek, whereas in the wet season it was more perpendicular towards the creek. However, short periods with a high creek stage, associated with large wet season rainfall events in the Behana Creek catchment, resulted in temporary gradient reversal. At these times the overall groundwater flow gradient was from Behana Creek into the riparian zone. Gradient reversals lasted up to ~60 hours, (e.g. 6-9 February 2009 when 360 mm of rain fell in situ over 4 days). The maximum recorded reverse gradient was 0.010 on 24 February 2009. After Behana Creek levels had receded the creek-ward gradient was rapidly re-established. The capacitance probe range was exceeded in one or more of the 4 monitored piezometers in February 2009, which is likely to have resulted in an underestimation of gradients during large rainfall events on 2, 4, 6 9, 14 and 24 February 2009. Using the overall gradients across the riparian zone, calculated lateral groundwater flow rates were low. The measured K value was approximately 7.06×10^{-6} m s^{-1}, resulting in overall lateral groundwater velocity of approximately 1.74×10^{-8} m s^{-1} during the dry season and up to 7.10×10^{-8} m s^{-1} during the wet season.

Although the overall gradients across the site were low, manual measurements of water table depths at non-logged piezometers showed a much more complex pattern of hydraulic gradients than could have been deduced from the 4 corner bores or a simple transect perpendicular to the stream (Figure 2.7). High gradients occurred over short distances

within the riparian zone during the wet season. For example, observations at T3P1 showed a short-range gradient reached approximately 0.1 during a rainfall event in November 2009 (Figure 2.8) corresponding to a velocity of 7.06 x 10^{-7} m s^{-1} using Darcy's law. Hydraulic gradients were largely determined by the location of discharge areas within the riparian zone; the discharge zone expanded and contracted with changes in water table level.
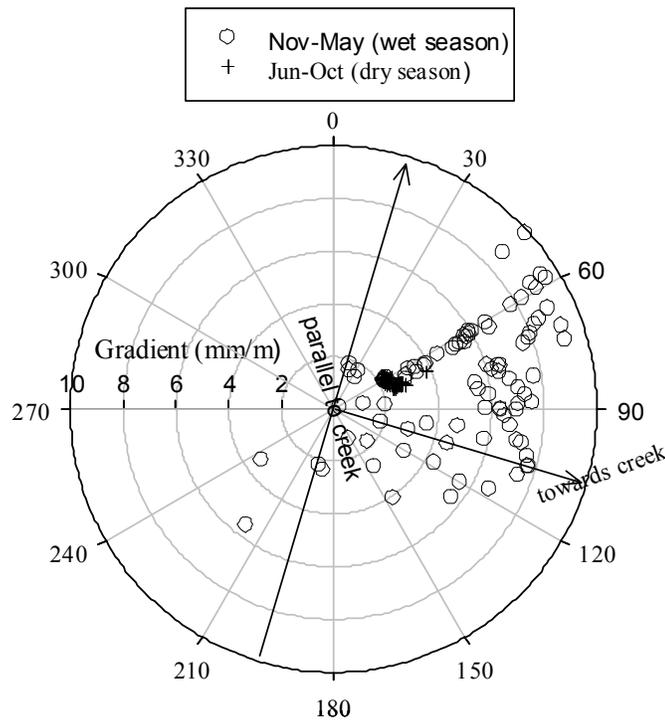
Figure 2.6. Hydraulic gradient and groundwater flow direction (degrees from grid north) over the whole study area over the period 28 January 2009 -12 December 2009.
Values were calculated from water table elevations in the 4 corner piezometers at 12:00 h on every day for which there was data (200 days).

Results from the nested piezometers on the creek bank (T2P4 and T2P5) showed upward gradients most of the time between 2.5 and 5.8 m depth. In the dry season, the overall hydraulic gradient at the creek was approximately 0.056 (vector sum of 0.025 lateral and

0.050 upwards gradients), resulting in a calculated velocity of 3.94×10^{-8} m s^{-1}. During non-rainy periods in the wet season, the overall hydraulic gradient at the creek was approximately 0.078 (0.070 lateral and 0.033 upwards) resulting in a calculated velocity of 5.44×10^{-8} m s^{-1}. There were periods when there was recharge from the creek rather than discharge into the creek, due to high creek stage. Small recharge gradients were observed occasionally in the nested piezometers during the dry season, but the large recharge events that occurred during the wet season were not observed in the nested piezometers due to inaccessibility at those times. There was presumably also an upward component of groundwater flow around the gully discharge zone, but no nested piezometers were installed in this region.
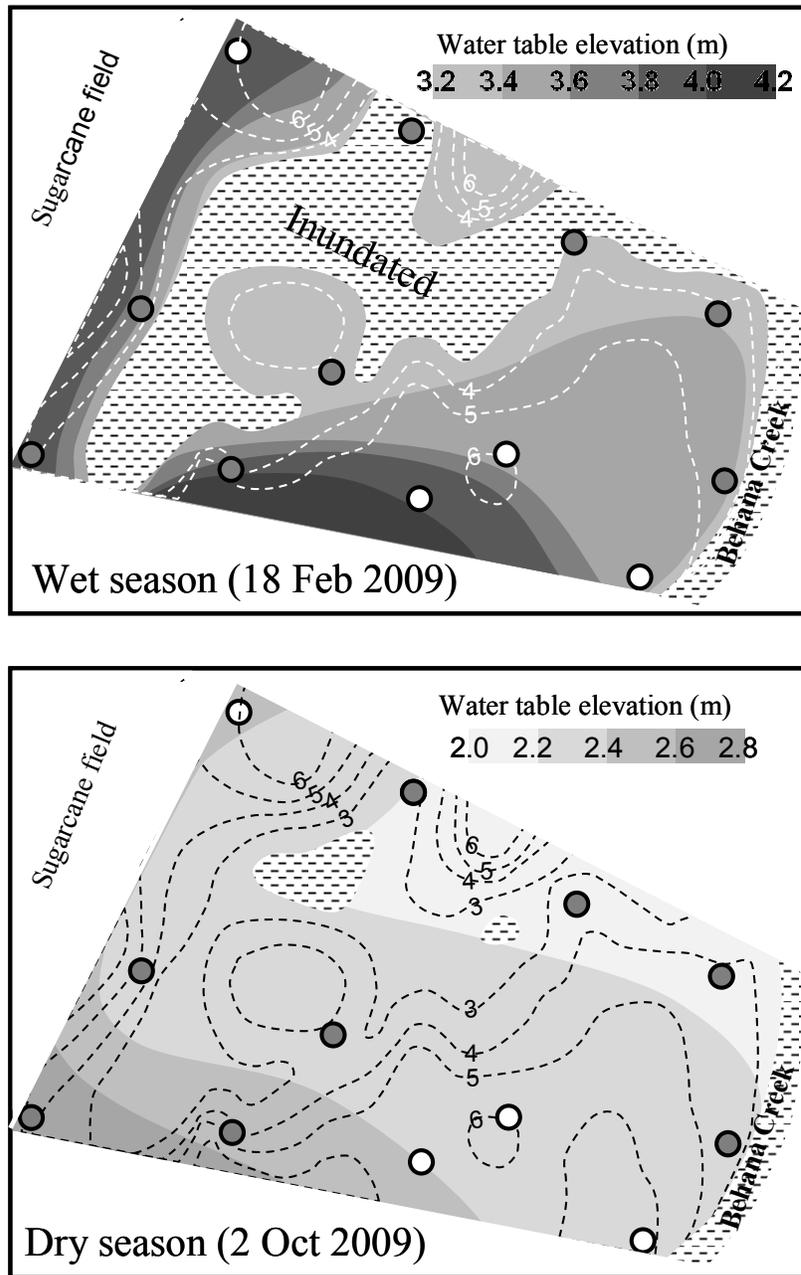
Figure 2.7. Water table contours in the study area on days that represented common conditions during the wet and dry seasons. Ground surface elevation contours are shown as dashed lines.
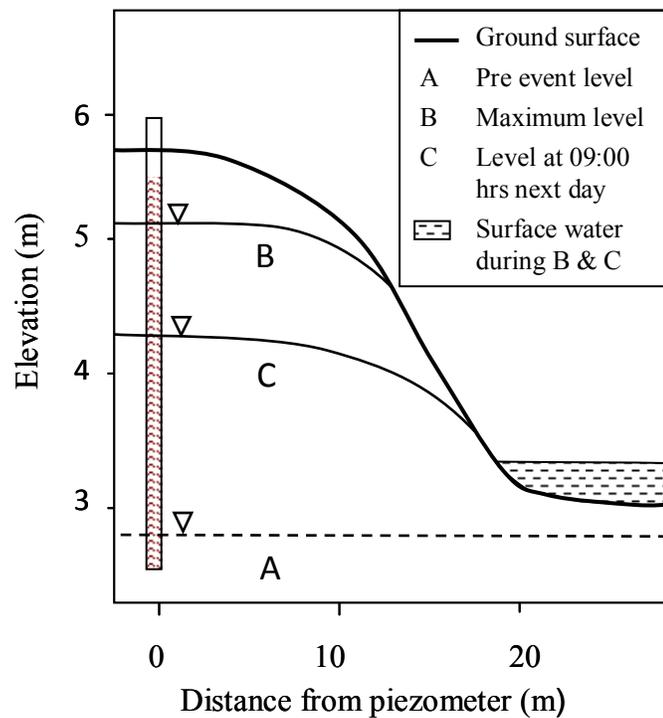
Figure 2.8. Water table levels at T3P1 during and subsequent to a rainfall event on 26 November 2009.

2.3.3 *Plant uptake of groundwater and soil water (unsaturated zone)*

Diurnal water table fluctuations were observed during the dry season where the water table was <1.5 m below ground (T1P1) but not where the water table was close to 3 m depth (T3P1). Diurnal fluctuations in water table level were not observed during the wet season when frequent, large, rapid recharge and discharge events appeared to mask the effects of uptake by riparian vegetation. During the dry season, uptake of groundwater ranged up to 2.5 mm d^{-1} and 50% of ET_0 over the measurement period (Figure 2.9). Uptake was positively correlated with depth to water table (Figure 2.9), but there was no significant relationship between uptake from groundwater and ET_0. Assuming a dry season discharge of 1.7 mm d^{-1} into the creek (creek bank velocity of 3.94 x 10^{-8} m s^{-1} multiplied by porosity

of 0.5) and a wetted creek cross section of 10 m, discharge into the cross section is 0.017 $m^2 \, d^{-1}$ during the dry season. Meanwhile, assuming plant extraction of 1 mm d^{-1} (

Figure 2.9) and a riparian forest cross section of 150 m, extraction of groundwater is 0.15 $m^2 \, d^{-1}$, an order of magnitude higher than discharge into the creek. This difference suggests that uptake by vegetation substantially reduced baseflow to the creek during the dry season resulting in negligible discharge to the creek.
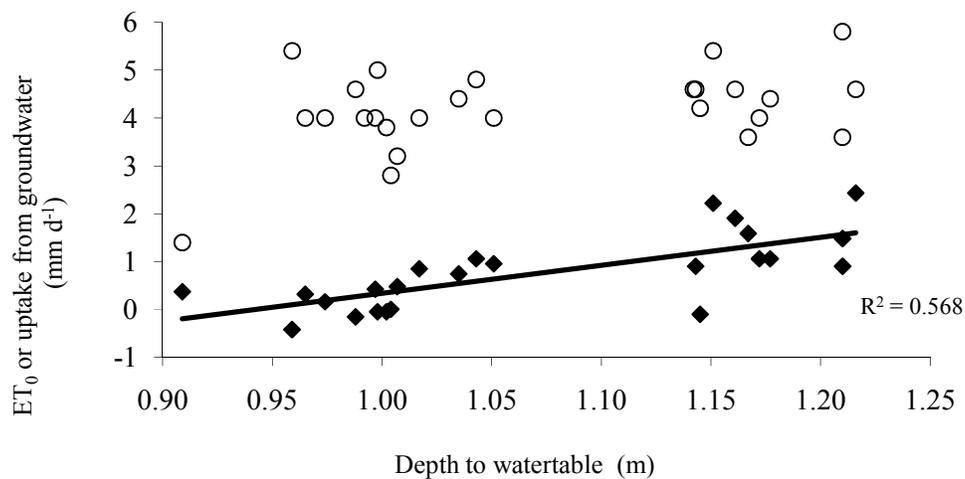
Figure 2.9. Uptake of groundwater at T1P1 in relation to water table depth over the period 14 June -11 July 2009. Daily ET_0 is also shown for those days (open circles).

Uptake of water from the 0- 0.2 m depth layer was closely related to soil water content, ranging from 1.3 mm d^{-1} at the driest site and time to 3.9 mm d^{-1} at the wettest site and time (Figure 2.10). Mean uptake from the 0- 0.2 m depth layer at the high, intermediate and low sites was 1.6, 2.4 and 3.3 mm d^{-1}, corresponding to 39, 60 and 85 % of mean ET_0, respectively. A substantial portion of the water taken up was supplied by capillary rise, as shown by increases in soil water content during the night time at 0.1 m depth (Figure 2.4).

Calculated uptake from deeper layers (from probes at 0.5 and 1.0 m depth) was negligible, possibly masked by rapid capillary rise.
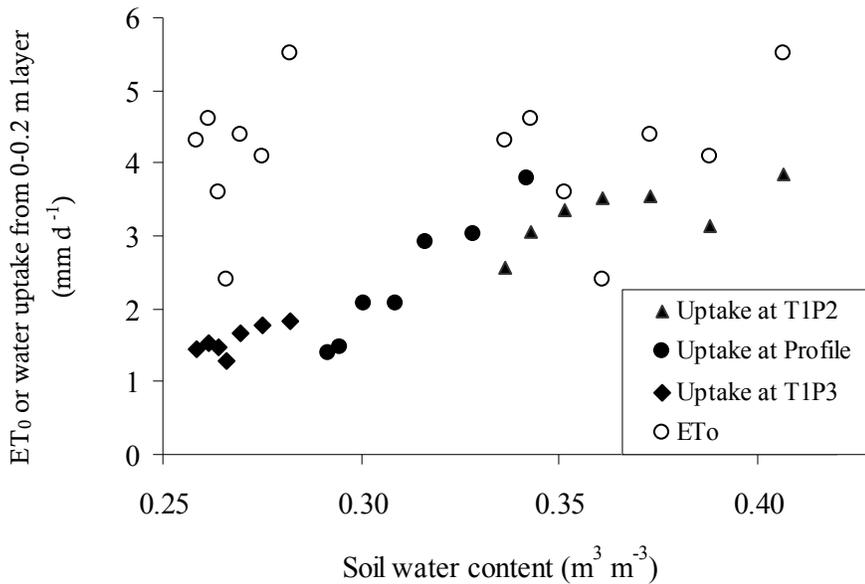
Figure 2.10. Uptake of water from the 0-0.2 m depth layer at three sites at different elevations (T1P2, soil profile and T1P3), over the period 3-9 March 2010. ET_0 is also shown (repeated for the driest and wettest sites).

2.3.4 In situ recharge of groundwater

Results from our recharge model indicated variable contributions of in situ deep drainage to recharge at piezometer T3P1, with the balance of recharge presumably being due to lateral inputs from upslope or occasionally from the gully (Figure 2.11). In situ rainfall made no contribution to water table rise on about half of the days when a rise was observed. On those days the water table was usually deeper than 2 m and the unsaturated zone had sufficient storage capacity to absorb the rainfall, the actual rise came from lateral inputs. At sites high in the landscape and at dry times of the year, rainfall is unlikely to

contribute recharge unless the event is very large. On the other hand, there were occasions when >100% of the recharge was attributed to deep drainage. That overestimation was at least partially due to the rapid rise and subsequent fall of the water table within the 24-hour period used in the model. For example, on one occasion the water table at T3P1 rose by 2.2 m in response to rainfall, but then fell considerably by 09:00 hours the next day, which was the time used in the daily calculations (Figure 2.8). The rapid fall was presumably driven by the steep gradient and proximity to the gully. Changes in the deep drainage model parameters changed the deep drainage estimates, but most combinations resulted in similar conclusions.
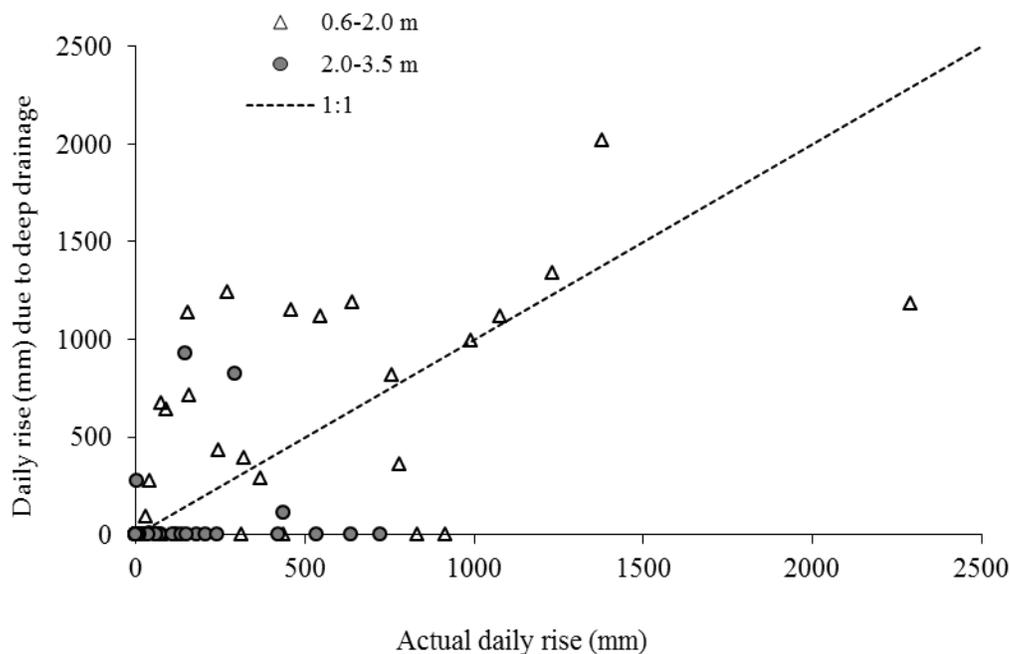
Figure 2.11. Daily rise in water table expected from deep drainage versus measured daily rise, plotted for two ranges of depth-to-water table. For the results shown here, the deep drainage calculation was based on ET = ET$_0$; ε = 0.57 - 0.14 for entrapped air; and θ_{FC} = 0.376.

2.3.5 Chloride concentrations

Concentrations of Cl^- in groundwater were reasonably constant across the riparian zone during the dry season (mean 8.5 mg L^{-1}, S.D. 2.1, no significant differences between piezometers), but were significantly ($p<0.05$) higher than the creek (mean 4.6 mg L^{-1}, S.D. 0.9 mg L^{-1}). During the wet season, groundwater Cl^- concentrations declined significantly from the canefield-riparian edge (mean 10.4 mg L^{-1}, S.D. 5.6) to the creek bank (mean 6.6 mg L^{-1}, S.D 2.8). During the wet season the creek-side concentrations of Cl^- were not significantly different ($p>0.05$) from Cl^- concentrations of creek water (mean 4.6 mg L^{-1}, S.D. 1.0).

These results suggest that, during the wet season, the riparian groundwater was diluted by recharge from in situ rainfall and creek water. The hydraulic data show that the ingress of creek water occurred as overland flood water and as flow through the creek bank on occasions when the creek stage rose higher than the water table level in the riparian zone. Dilution of groundwater was not observed during the dry season.

2.3.6 Summary of water flows through the site

The hydrology of the Behana Creek riparian zone is complex, with large variations in the magnitude and direction of water flows occurring in space and time. The hydrologic behaviour has been conceptualised in Figure 2.12 using four scenarios (A-D) covering the main types of behaviour over the period of a year. The figure shows a vertical plane through the centre of the site, along transect two. For most of the year scenarios A and C operate. In the dry season (scenario A) there is little or no net groundwater flow towards the creek. Surface (0.1 m) soil is dry. The remainder of the unsaturated zone dries

progressively over the duration of the dry season (with the exception of the capillary fringe just above the water table), and uptake and transpiration of groundwater is a significant component of the water balance in regions where there is insufficient water in the unsaturated zone to meet transpiration demand. While the difference between hydraulic heads at the sugarcane and creek edges of the site suggested slow movement towards the creek, manual measurements within the site showed virtually no gradient in that direction, presumably due to the uptake and transpiration by vegetation.
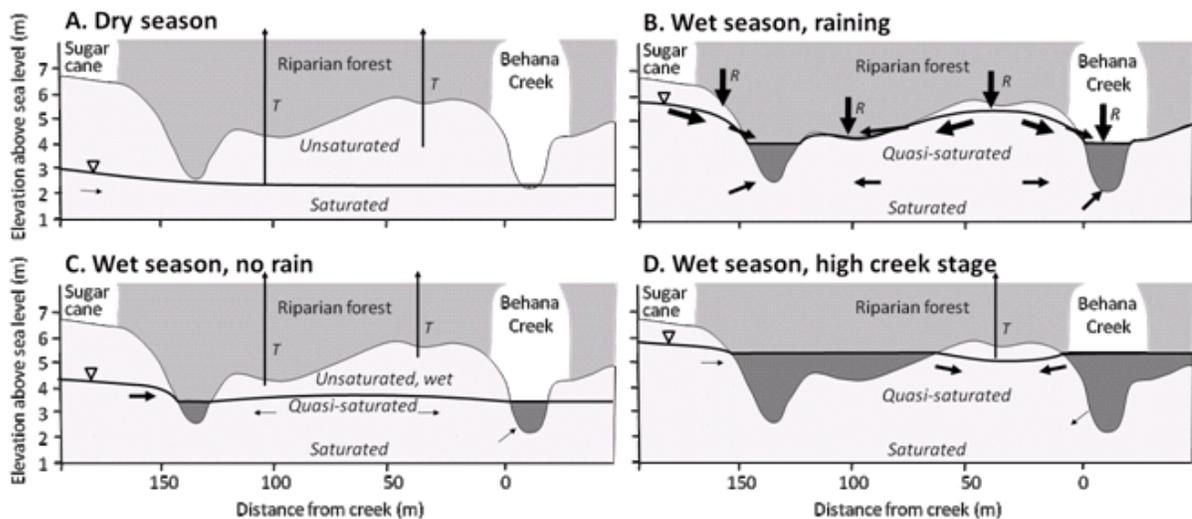
Figure 2.12. Summary of water table levels and water flows through the centre of the site, along transect two. Arrows represent the direction of flows, with their size approximating their relative magnitude. T represents transpiration, R represents rainfall and the other arrows represent groundwater flow. Flows parallel to the creek (perpendicular to the page) are not shown but are discussed in the text.

During the wet season, while it is raining (scenario B), there are large flows of water through the saturated and variably saturated zones. Groundwater flows into the site from the sugarcane fields due to a large hydraulic gradient, and there is substantial deep drainage (approximately 1400 mm y^{-1} in episodic events, Chapter 2) and recharge within the site causing a rising water table, exfiltration and saturated overland flow at lower elevations

and discharge into the creek and gully. Uptake and transpiration of water is deemed to be minimal during rain events due to low atmospheric demand. After rainfall ceases the water table falls and hydraulic gradients decrease (scenario C). However, these gradients still drive groundwater into the site and within the site, towards the inundated discharge zone in the gully and creek, which decreases in size as the water table falls. Uptake and transpiration are predominantly from the unsaturated zone, which is relatively wet. These conditions prevail during most of the wet season.

Finally, there are occasions when a high creek stage is the main driver of water flows (scenario D). This occurs when rainfall in the upper catchment is greater than in situ rainfall. As the creek rises the site becomes inundated by water flowing directly from the creek and through the gully. During these short periods groundwater within the site is recharged by creek water. However, periods of high creek stage usually coincide with high in situ rainfall and recharge, so bank storage is not a major component of the water balance. During the wet season the gully effectively receives discharge from shallow groundwater draining the sugarcane fields, creating a temporary disconnect between upslope and the main Behana Creek channel.

In addition to the flows illustrated in Figure 2.12, there is a substantial component of water flow parallel to the creek, especially through the high area in the middle of the site. Surface water in the gully generally flowed in the same direction as the creek, discharging into it at the downstream edge of the site, but occasionally flowing in the opposite direction, into the riparian zone, when the creek stage was high.

2.4   Discussion

In this coastal plain riparian zone there were large temporal and spatial variations in the water content of the near-surface layers, and in the direction, duration and velocity of water movement through those layers. Hydrology was highly dynamic during the wet season but much more stable during the dry season. One hydrological feature that stood out was the rapidity with which the water table rose and fell. Although such rapid fluctuations have been observed in a nearby upland site (Bonell *et al.*, 1998) they were not expected in this lowland site.

Water content of the near-surface zone ranged from very dry at topographic highs during the dry season to very wet throughout the year at the lowest locations and throughout the site during wet season rainfall events. However, complete saturation of the variably saturated zone was never observed. The presence of entrapped air could be expected to influence the transport and emission of gases produced in the soil, enhancing transport from the quasi-saturated zone into the unsaturated zone (Geistlinger *et al.*, 2010). That would be the case for N_2 produced by denitrification, and N_2O produced by denitrification or nitrification. However, across most of the site, water contents of surface layers were conducive to ammonification and nitrification rather than denitrification for most of the time (<60% water filled pore space, Brady and Weil (2008)). During the dry season in particular, conditions in the thick aerobic unsaturated zone might be expected to favour production of NO_3^- via mineralisation and nitrification, especially in organic-rich surface layers. However, topographic lows in and around the gully, where the organic-rich soil is wet and water table is close to the surface, may provide 'hot spots' for denitrification.

The direction, duration and velocity of water flow through the near-surface zone were relatively stable during the dry season but very dynamic during the wet season. During the dry season groundwater moved slowly through the site, almost parallel to the creek, at depths of 0-4 m below the ground surface. During the wet season the variably saturated zone was frequently flushed by water flowing downward as deep drainage and laterally as the water table rose and fell. This flushing of the variably saturated zone might be expected to mobilise solutes, such as NO_3^- and dissolved organic matter, generated during times when the soil was unsaturated. In addition, the rainfall brings with it dissolved oxygen.

The rapid fluctuations in water table levels implied much faster groundwater velocities through the near-surface region than those calculated using Darcy's law (0 to 7.1×10^{-7} m s^{-1}). The measured aquifer K value could be classified as 'moderate' (Australian Government, 2009) and falls within the range of values for medium sand material (8.9×10^{-8} to 5.0×10^{-5} m s^{-1}). Short-range hydraulic gradients were greater than the values across the whole site, and the distance to the discharge zone was often short due to the undulating topography and gully. However, the traditional Darcian saturated groundwater flow model still appears unlikely to explain the large flows of groundwater through the riparian zone during the wet season. We therefore consider additional mechanisms. They include: near surface lateral flow when the water table rises into permeable topsoils (Rodhe, 1989); preferential flow through macropores or 'pipes' (Anderson and Burt, 1990; Beven and Germann, 1982), near-stream groundwater ridging (Abdul and Gillham, 1989; Ragan, 1968; Sklash and Farvolden, 1979) and air entrapment during water table rise (Tanaka, 1992). From our results, a combination of any of these mechanisms could have been operating.

High permeability of the near-surface soils appeared to influence hydrology of our site in several ways. Firstly, Hortonian overland flow was not observed in our study, corresponding with previous observations in humid forested environments (Bruijnzeel, 1990; Dunne *et al.*, 1975). Secondly, the high permeability of the near-surface soils throughout most of the site would provide a conduit for rapid, shallow, subsurface flow, facilitating a mechanism for rapid water discharge into Behana Creek (Rodhe, 1989). Recent research on overland runoff entering riparian zones from upslope in the Australian humid tropics, found that infiltration within the riparian zone was the most important mechanism for filtering hillslope overland runoff (McKergow *et al.*, 2004a). However, when subsurface flows were large during large rain events, saturation overland flows within the riparian zone significantly hindered infiltration (McKergow *et al.*, 2004a).

The rates of groundwater flow may be enhanced by the existence of interconnected macropores developed by root holes, soil cracks or fauna burrows, producing preferential lines of flow (Beven and Germann, 1982). Furthermore, in alluvial environments, lenses of coarse-grained material can act as preferential flow paths. We did not explicitly investigate the presence of preferential flow paths at our site, but a concurrent study using seepage meters to measure groundwater discharge to Behana Creek found considerable spatial variation in flow rates (J Kinley *pers. comm.*).

During large rainfall events, high in situ recharge resulted in the formation of 'mounds' of groundwater within the riparian zone. Rapid groundwater recharge from rainfall is most likely to occur when the unsaturated zone is shallow and wet, either due to recent rainfall or because the capillary fringe is close the ground surface. Since our in situ recharge model

was run only at a location high in the landscape, it is possible that rainfall contributes more to groundwater recharge at other locations, i.e. in topographic lows. The formation of groundwater 'ridges' or 'mounds' has been described by Sklash and Farvolden (1979). As the 'new' water displaces the 'old' groundwater, the groundwater discharge area is increased and groundwater is preferentially discharged to the creek, either by saturation overland flow or rapid subsurface flow. There has been, and still is, considerable discussion about the conditions under which groundwater ridging occurs and the discharge mechanisms associated with it (e.g. Cloke *et al.*, 2006; Gillham and Jayatilaka, 1998; McDonnell and Buttle, 1998; Szilágyi, 2006) and groundwater ridging is not likely to occur where macropores are present.

Rapid rises in shallow groundwater at our site may also be partially explained by the entrapment of air in soil pores. Soil water content measurements showed that soils between 0.1 and 1.0 m depth failed to reach saturation once they were beneath the water table. At 0.1 - 1.0 m depth entrapped air represented a mean of 14% of bulk soil volume, slightly higher than published values, which range from 6 to 11% (Bower and Rice, 1983; Faybishenko, 1995; Fayer and Hillel, 1986; Sakaguchi *et al.*, 2005).

Although there was considerable discharge of groundwater within the site, saturation overland flow would also have been considerable during times when there was a large saturated area. Based on Freeze's (1974) summary of storm flow generation mechanisms, variable source area saturation overland flow from riparian areas with shallow water tables is likely to deliver runoff from a combination of exfiltrating subsurface flow, return flow, with contributions from direct precipitation onto the saturated area during high rainfall

(Rodhe, 1989). When quantifying the relative contributions of 'new' and 'old' water from catchment runoff, McGlynn and McDonnell (2003) observed that a large proportion of the 'new' water entering a stream was generated within the riparian zone, particularly during the early stages of a rain event. Earlier studies of catchment runoff mechanisms in the Australian humid tropics at South Creek in Babinda, found saturation overland flow and subsurface flow to be the dominant runoff processes (Bonell and Gilmour, 1978). At South Creek, where the riparian zone was both narrow and steep, Bonell *et al*. (1998) concluded that 'new' water originated from both upslope and the riparian zone. The interaction between rainfall intensity, long duration of storms, and the hydraulic properties of the subsoil were important factors in the generation of storm runoff processes at their site. An impeding layer at 0.2 m at the South Creek site prevented the vertical transmission of rain water during storms, producing saturation overland flow and subsurface flow in the root layer (Bonell *et al.*, 1981). In our study a shallow water table resulted in a similar effect.

Uptake by vegetation was a relatively small component of the water balance during the wet season, but a large component during the dry season. Extraction of groundwater by riparian vegetation must have substantially limited the volume of baseflow delivered to the creek during the dry season, similar to observations elsewhere (Gribovszki *et al.*, 2010). However, the values of *UGW* that we determined were at the low end of the range found in other studies (e.g. Schilling and Jacobson, 2009). This is most likely due to two factors. Firstly, the value of *Sy* in our study, 0.053, is low when compared to other studies. For example, Schilling and Jacobson (2009) used a value of 0.15 based on literature values associated with a sandy loam texture as suggested by Loheide *et al.,* (2005). According to Loheide *et al.* (2005) estimation of the value of *Sy* is the largest source of error associated

with *UGW* using the White (1932) method. We obtained an appropriate value of *Sy* by measuring changes in soil water content over scales of time and distance that corresponded to the diurnal fluctuations in water table levels. Secondly, it was clear that riparian vegetation extracted water from where it was most readily available: uptake from the topsoil was high when it was wet but declined as it dried (Figure 2.10), and uptake from groundwater increased during a drying period (Figure 2.9). For much of the dry season, the thick unsaturated zone was likely to have supplied soil water for a substantial portion of plant transpiration needs. This appears to be the case at T3P1, where the unsaturated zone was approximately 3 m thick, and where no diurnal fluctuations in water table depth were observed. Finally, and in common with other studies using the White (1932) method, *UGW* would underestimate actual uptake if day-time lateral inflow rates were greater than those at night.

Observations during installation of the piezometers suggested that there were large numbers of active roots in the zone of water table fluctuation and it is possible that different species at the site employ different water uptake strategies (e.g. obligate, facultative or non-phreatophytes), as discussed by Lamontagne, Cook *et al.* (2005) and McJannet (2008). On many days, uptake of groundwater or topsoil water alone was 39-85% of ET_0 (Figures 2.9 and 2.10), suggesting higher transpiration than values estimated from sapflow measurements in similar forest (McJannet et al., 2007).

2.5   *Conclusions*

Hydrology of this humid tropical coastal plain riparian zone varies greatly in complexity between the wet and dry seasons. Dry season hydrology is predominantly characterised by

deep, slow, lateral groundwater flow. On the other hand, in the wet season, water fluxes are dynamic, with inputs from in situ rainfall playing an important role in groundwater recharge. During times of high rainfall, rapid subsurface stormflow channels groundwater directly towards the discharge zone. The direction and magnitude of these shallow subsurface fluxes is driven by transient water table gradients and the location of discharge zones. The location of discharge zones shifts as their size and shape changes; which, in turn, is determined by the interaction between water table elevation and topography. Surface soils in low-lying areas remained wet throughout the wet season; however, the higher areas were quicker to drain. During the dry season surface soils became very dry at topographic highs, while the lowest lying areas remained moist. The hydrological conditions documented in this study are likely to exert large and variable influences on the transport and transformations of N in this part of the landscape.

Chapter 3.   Movement of nitrogen through soil and groundwater of the forested riparian zone

3.1   Introduction

Elevated concentrations of NO_3^- have been observed in groundwater in some catchments of the Australian humid tropics in north east Queensland, particularly in areas under agriculture where fertilisers are widely used (Rasiah *et al.*, 2005; Thorburn *et al.*, 2003). Groundwater is therefore considered a potentially important pathway for the transport of N lost from agriculture towards streams and rivers (Armour *et al.*, 2004; Rasiah *et al.*, 2010; Rasiah *et al.*, 2003). Groundwater from catchments bordering the Coral Sea will eventually enter the GBR lagoon, either directly (Stieglitz, 2005), or indirectly, by discharging into rivers and streams which, in turn, discharge into the GBR lagoon. There is an assumption that riparian zones in the Australian humid tropics are likely to remove NO_3^- from agricultural groundwater runoff as has been shown by a wide range of studies elsewhere. Hence, a significant investment is underway to promote the restoration of riparian zones in an attempt to improve the quality of water discharging into the GBR lagoon (Queensland Government, 2009).

The aim of this study was to 1) determine the effectiveness of a forested riparian zone, within an agricultural landscape in the humid tropics, at preventing NO_3^- in groundwater from entering the adjacent creek and 2) identify spatial and temporal patterns in the movement and transformations of N moving through the riparian zone.

It was hypothesised that high concentrations of NO_3^- in groundwater would enter the riparian zone at the sugarcane field-riparian boundary, but that these concentrations would be reduced as groundwater moved through the riparian forest towards the creek. The rate of decrease in NO_3^- concentration could be used to predict the width of riparian forest needed to improve water quality by a given amount.

3.2   *Methods*

3.2.1 Groundwater and creek water sampling

Groundwater and creek water samples were collected from the riparian site at Behana Creek between November 2008 and March 2010 using the network of piezometers shown in Figure 2.2 (Chapter 2). Groundwater samples were collected from all 13 piezometers at the site, unless a piezometer was either dry or inaccessible due to flooding. Sampling took place at least once a month and more frequently throughout the wet season, before and after heavy rainfall events, when access to the site was possible. Prior to sampling groundwater, the depth to the water table was measured manually using an electronic measuring device. Piezometers were then emptied of three times their standing water volume (or, on occasions, pumped dry) using a manual bailer. For piezometers experiencing fast recharge, samples were collected immediately. For piezometers with slower recharge rates, samples were collected approximately four hours after pumping, once the water table had returned to approximately its original level. Groundwater samples were collected in the bailer and immediately transferred into two x 125-mL plastic sample bottles. Bottles were subsequently stored on ice until returning to the laboratory, whereupon they were frozen until analysis. Groundwater electrical conductivity (EC), pH

and temperature were measured in the field from a third sample (using a TPS Aqua-CP meter), and dissolved oxygen (DO) concentration (using a Hanna 9143 probe) from a fourth. Creek water was sampled using the grab sampling method and the same physical and chemical parameters were measured as were for groundwater.

3.2.2 Analyses of water samples

All samples were analysed at the Queensland Department of Environment and Resource Management (DERM) laboratories at Indooroopilly (NATA accredited) using procedures described by Rayment and Higginson (1992). Ammonium-N and oxides of N (NO_x-N) were analysed colorimetrically by dissolved, ultra low level flow injection analysis (FIA) (Lachat QuikChem 8000 analyser). Comparison of NO_3-N concentrations using ion chromatography (Metrohm 850 Professional Ion Chromatograph) with NO_x-N concentrations by FIA, showed that NO_2-N concentrations were negligible at this site. Hence, NO_3-N concentrations were effectively equal to NO_x-N concentrations. Since NO_x analysis by FIA had a lower detection limit (0.001 mg L^{-1}) than NO_3-N by ion chromatography (0.1 mg L^{-1}), concentrations of NO_x-N were adopted as a proxy for NO_3-N in this study. Results for inorganic N are expressed as NO_3-N and NH_4-N. Dissolved organic nitrogen (DON) was calculated by subtracting NH_4-N from dissolved Kjeldahl nitrogen (DKN), acquired using a Seal segmented flow analyser. Dissolved organic carbon (DOC) in groundwater was analysed for using the non-dispersive infrared detector (NDIR) method (OI TOC Analyser) using samples filtered through 0.45 μm membrane filter prior to analysis. Cl^- concentrations, analysed by ion chromatography, were measured for use as a conservative tracer to evaluate dilution effects or concentration effects due to evapotranspiration (e.g. Altman and Parizek, 1995; Cey *et al.*, 1999).

3.2.3 Soil sampling

Soil samples were collected from a depth of 0- 0.1 m at least once a month from February 2009 to February 2010 (with the exception of August, September and October 2009). Sampling was concentrated around four piezometer sites, two at 'high' positions (T1P3 and T2P3 at 5.40 and 5.93 m elevation respectively) and two at 'low' positions (T1P2 and T3P3 at 4.12 and 3.89 m elevation respectively). For piezometer positions, refer to Figure 2.2. Six soil samples were taken from within 1.5 m of each piezometer and thoroughly mixed, providing one composite sample per site, per visit. Samples were collected from bare soil after moving leaf litter to one side.

In the laboratory, soil slurries were prepared for testing EC and pH by adding de-ionised water (1:5 soil:water). Slurries were shaken end over end for 1 hour then centrifuged for 10 minutes and the supernatant analysed using a TPS Lab Chem pH and EC meter. A second set of slurries were prepared for extractable NO_3-N and NH_4-N and DOC analysis by adding 0.1M KCl in a 1:5 soil: solution using 7.5 g wet soil, equivalent to 6 g dry soil. These slurries were also centrifuged for 10 minutes and the supernatant extracted and frozen until analysed. Prior to analysis, defrosted extracts were filtered through a 0.45 μm membrane filter. Concentrations of NO_3-N and NH_4-N were determined according to methods described by Rayment and Higginson (1992) using FIA and DOC using NDIR. For measurement of soil total C and N content, sub samples of soil were homogenised, ground, dried and analysed in a Costech elemental combustion system (model: ECS 4010).

3.2.4 Litterfall collection and identification of leguminous species

Litterfall was collected monthly for one year between June 2009 and the end of May 2010. The prominent canopy species at the study site include *Cryptocarya triplinervis* var *riparia, Elaeocarpus grandis, Dysoxylum gaudichaudianum, Melicope elleryana, Syzygium tierneyanum and Castanospermum australe*. Four litter traps were installed at each of the piezometer sites T1P2, T1P3, T2P3 and T3P3 (the same four sites employed for soil sampling) plus four at an additional site which was not associated with a piezometer. The additional site was located in an area of high ground (approximately 6.4 m elevation) where a cluster of large leguminous trees (*Castanospermum australe*) had been identified. Each litter trap consisted of a plastic hoop (constructed from flexible irrigation pipe) measuring 0.7 m in internal diameter (0.38 m^2 collection area). A fine nylon mesh (<2 mm) bag, approximately 0.4 m deep, was attached to each hoop and hoops were supported by 4 wooden stakes approximately 1 m above the ground. The total collection area covered by the 20 individual litter traps was 7.6 m^2.

Litterfall was collected once a month. Any large branches and woody matter > 20 mm diameter was discarded. Litter was oven dried in paper bags at 50° C for 5 days or until constant weight and stored for analysis. Total litter was weighed for each trap. The 4 bags of mixed litter collected for each site were then compounded and sorted into 3 categories: leaves, reproductive structures (which includes seeds, fruits and flowers) and woody matter (consisting of twigs, branches, wood and bark) each month. Each category was weighed separately for each site, each month. The monthly leaf litter component (excluding other litter categories) was then thoroughly mixed by mulching. A sub sample of dried leaf litter

was finely ground and analysed for total C and total N in a Costech elemental combustion system (model: ECS 4010).

A survey was conducted to identify and count all leguminous species within the study site. The extent of canopy cover attributed to leguminous species was measured using their identified locations, aerial photos showing canopies of individual trees, and a geographic information system.

3.2.5 Statistical analyses

Data for groundwater, soil and litterfall were checked for normality of distribution. Where data were not normally distributed they were log transformed (ln). Mean, maximum and minimum concentrations and standard deviations were determined prior to log-transforming the data.

Independent T tests were used to compare differences in parameters for groundwater, soil and litter between wet and dry seasons and between topographic positions (high and low). For the statistical purposes of this study the dry season corresponded to dates between November 2008 and December 2008 and June to October 2009. January to May 2009 and November 2009 to February 2010 were considered the wet season. Differences were deemed to be statistically significant at the $p = 0.05$ level.

Independent sample T tests were used to evaluate differences in groundwater solute concentrations at positions at different distances from the creek during the wet season and the dry season. Paired sample T tests were used to test for differences between NO_3-N and NH_4-N concentrations across the site.

Pearson product-moment correlation was applied to all groundwater and soil variables to explore the interrelationships for both the dry and the wet seasons. The strength of relationships between variables was classified as small (r=0.10 to 0.29), medium (r=0.30 to 0.49) or large (0.50 to 1.0) based on the suggested classification by Cohen (1988, pp. 79-81). These classifications are also expressed as weak, moderate or strong.

All statistical analyses were performed using SPSS for Windows, version 17.0.1 (SPSS, 2008).

3.3   Results

Mean groundwater and creek water parameters are summarized for the wet and dry seasons in **Table 3.1**. Behana Creek water was consistently fresh, with EC values of 15-50 $\mu S\ cm^{-1}$ over the study period. Groundwater EC values covered a wider range (30 to 453 $\mu S\ cm^{-1}$) with higher values (> 200 $\mu S\ cm^{-1}$) occurring at a single piezometer (T1P2). Groundwater pH values ranged from 4.1 to 6.16 throughout the site. Groundwater pH was significantly lower in the wet season than the dry with the lowest values occurring during the first two months of the wet seasons when rainfall was highest. Creek water was less acidic (pH 5.54 - 6.86), with no significant difference in pH between seasons. Groundwater temperature ranged from 21.6 to 29.5 ^{o} C with temperatures significantly higher in the wet season. Temperature of creek water was slightly lower than that of groundwater, ranging from 21.5 to 28.7 ^{o}C, with highest temperatures also in the wet season, although differences were not significant between seasons.

Table 3.1. Summary of groundwater and creek water variables indicating means for dry and wet seasons for samples collected between November 2008 and March 2010. Groundwater samples are combined for all piezometer locations. *p* values are the results from T tests conducted to explore differences between seasons. *n* represents number of samples collected.

			Groundwater				Creek water		
	Season	***n***	**Mean**	**S.E.**	***p* value**	***n***	**Mean**	**S.E.**	***p* value**
pH	Dry	100	5.5	(0.02)	<0.001	9	6.3	(0.11)	0.126
	Wet	147	5.2	(0.03)		9	6.0	(0.12)	
EC (µS cm^{-1})	Dry	100	100.2	(4.13)	0.495	9	39.4	(2.45)	0.615
	Wet	147	104.8	(4.72)		9	37.2	(3.65)	
DO (% Sat.)	Dry	99	22.6	(1.29)	0.421	9	78.9	(4.26)	0.957
	Wet	159	21.2	(1.18)		11	78.7	(2.34)	
Temp (^{o}C)	Dry	99	25.0	(0.13)	<0.001	9	24.7	(0.97)	0.804
	Wet	159	25.8	(0.08)		11	24.9	(0.53)	
DOC (mg L^{-1})	Dry	100	2.60	(0.33)	0.302	10	1.10	(0.19)	0.083
	Wet	169	3.60	(0.76)		12	2.00	(0.41)	
Cl (mg L^{-1})	Dry	100	8.70	(0.19)	0.564	10	4.70	(0.29)	0.950
	Wet	169	8.40	(0.29)		12	4.70	(0.29)	
NH$_4$-N (mg L^{-1})	Dry	100	0.24	(0.03)	<0.001	10	0.01	(0.01)	0.349
	Wet	167	0.08	(0.01)		12	0.06	(0.04)	
NO$_3$-N (mg L^{-1})	Dry	100	0.11	(0.04)	<0.001	10	0.09	(0.01)	0.111
	Wet	169	1.52	(0.27)		12	0.12	(0.01)	
DON (mg L^{-1})	Dry	100	0.24	(0.04)	0.308	10	0.07	(0.01)	0.100
	Wet	140	0.20	(0.02)		11	0.10	(0.02)	

Mean concentrations of solutes in groundwater as a function of distance from Behana Creek are shown in Figure 3.1. Groundwater was generally very low in oxygen throughout the year, conducive to a reducing environment, with a mean DO of 21.9 % saturation over the duration of the study. Areas of more oxygenated groundwater, however, were observed sporadically throughout the site (up to 70% saturation), although no clear spatial or temporal pattern emerged as to the distribution of these more oxygenated areas. Wet season DO values tended to be lower when the water table was closer to the ground surface, likely due to increased microbial activity where groundwater comes into contact with organic C-rich surface soils.   Hence, in the wet season, lower DO values were associated with sites lower in the landscape where the water table was closer to the surface, compared to sites of higher elevation ($p<0.001$).
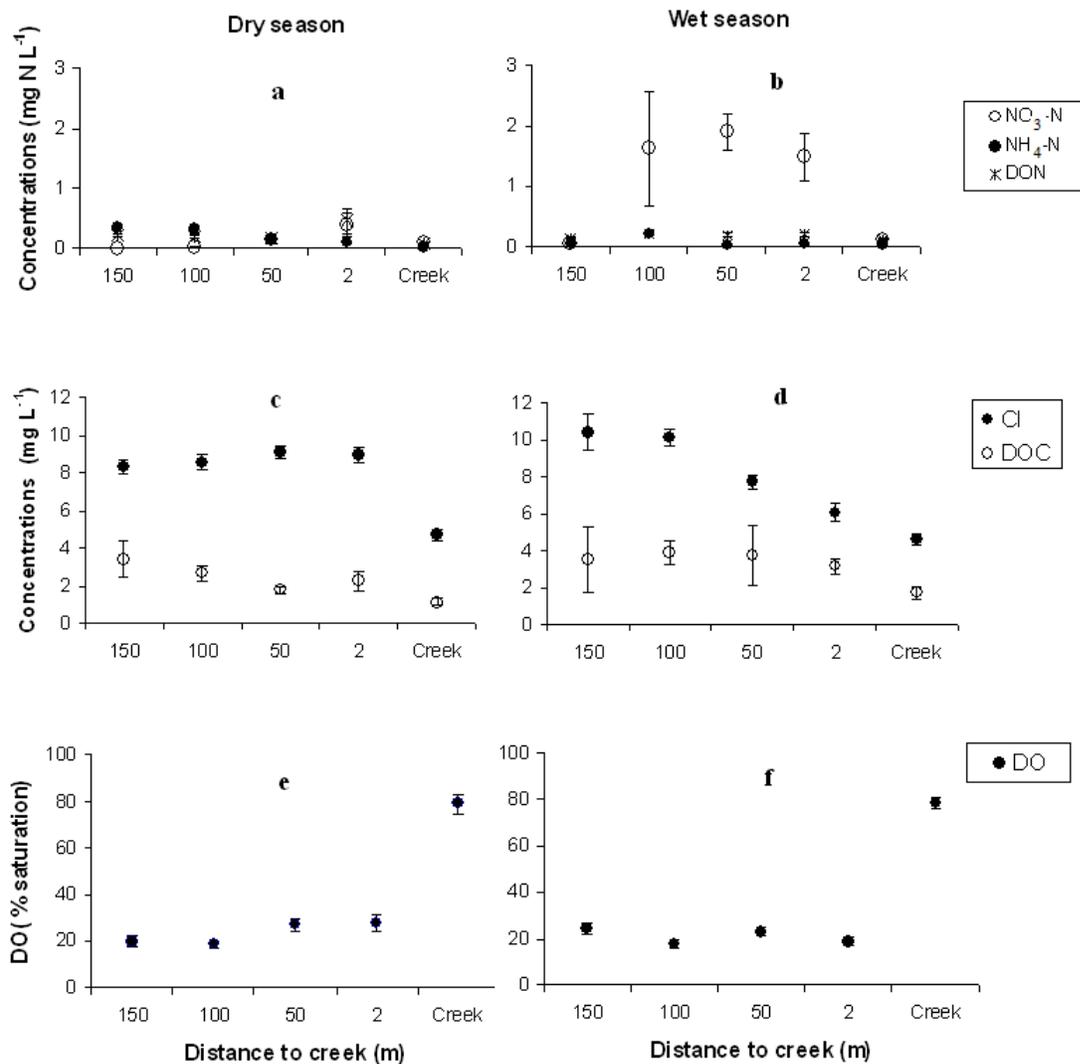
Figure 3.1 . Mean concentrations of solutes in groundwater and creek water for dry and wet seasons showing distance to creek for (a and b) inorganic N and DON, (c and d) DOC and Cl⁻ (e and f) DO. For the wet season, n= 29 at 150m, 37 at 100m, 71 at 50m, 31 at 2m and 11 from creek for inorganic N, DON, DOC and Cl⁻, and for DO n= 29 at 150m, 35 at 100m, 62 at 50m, 31 at 2m and 10 for the creek. For the dry season, n=29 at 150m, 31 at 100m, 22 at 50m, 18 at 2m and 10 for the creek for all solutes. Bars represent SE values.

Dissolved organic C concentrations in groundwater were highly variable in space and time, ranging from 0.7 to 111 mg L^{-1}, with spikes > 10 mg L^{-1} occurring on nine occasions at various times and in various locations. There was no significant difference in DOC concentrations between seasons (p= 0.302, Table 3.1). The overall mean value of DOC in groundwater was 3.3 mg L^{-1}. Concentrations of DOC were significantly higher at low sites than at high sites (p=<0.001) and tended to increase at low sites after large wet season rain events.

The C:N ratio of dissolved organic matter in groundwater had a mean value of 21.6 (mass basis), however this was highly variable, ranging from 0.31 to 555, mainly due to extreme values of up to 111 mg L^{-1} for DOC concentration in groundwater in the wet season months of January and March 2009.

Chloride concentrations were described in Chapter 2 and concentrations of N in groundwater and creek water are presented in detail below.

3.3.1 N in groundwater entering the riparian zone

Groundwater N entering the riparian zone (at 150 m from the creek) in the dry season consisted predominantly of NH_4^+ (mean 0.33 mg N L^{-1}). Nitrate concentrations at the canefield-riparian boundary, on the other hand, often approached the detection limit (0.001 mg N L^{-1}) in the dry season (mean 0.008 mg N L^{-1}). Dissolved organic N, on the other hand, entered the riparian zone with intermediate concentration, (mean 0.21 mg L^{-1}). The proportions of NH_4-N, NO_3-N and DON concentrations in water entering the riparian zone during the dry season were approximately 60, 1 and 39 percent respectively (Figure 3.2).

During the wet season, DON became the dominant form of N in groundwater entering the riparian zone from the canefields (mean concentration 0.15 mg L^{-1}). Mean NH_4^+ concentrations entering the riparian zone decreased to 0.04 mg N L^{-1} whilst NO_3^- concentrations increased to 0.06 mg N L^{-1}, resulting in a shift in species dominance in groundwater entering the riparian zone/leaving the canefields from the dry to the wet season. In the wet season the proportions of NH_4-N, NO_3^- N and DON concentrations entering the riparian zone were 23, 17 and 60 percent respectively: NO_3^-N concentrations continued to be the lowest of the three N species measured (Figure 3.2).
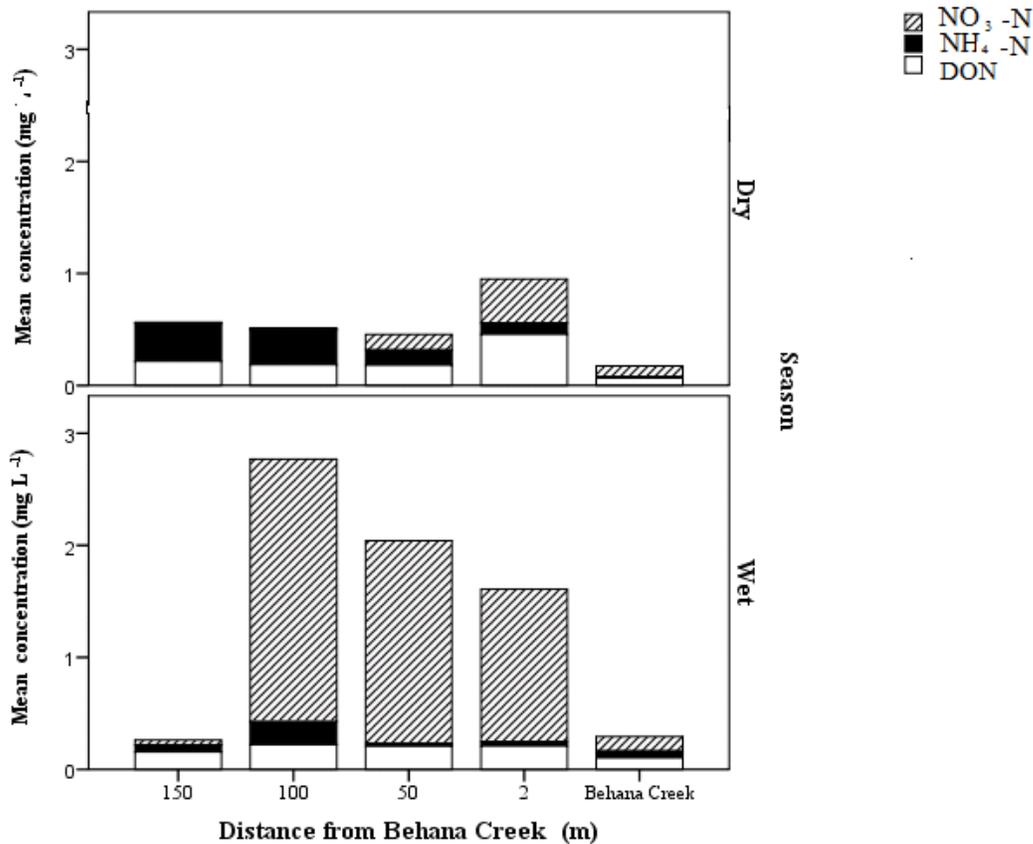
Figure 3.2 Mean concentrations of NO_3-N, NH_4-N and DON in groundwater and creek water at piezometers located at each distance from the creek for dry and wet seasons.
For the dry season, for all three N species: n= 29 at 150 m , 31at 100 m, 22 at 50 m , 18 at 2 m and 10 at Behana Creek. For the wet season, for all three N species: n= 25 at 150 m, 32 at 100 m, 35 at 50 m, 26 at 2 m and 11 at Behana Creek.

3.3.2 N in groundwater within the riparian zone

As groundwater progressed from the canefield-riparian boundary into the riparian zone, NO_3^- became the dominant N species in the wet season (Figure 3.2). Mean NO_3^- concentrations in groundwater were significantly higher in the wet season than they were in the dry ($p<0.001$, Table 3.1). Based on concentrations within the riparian zone (excluding concentrations at the cane field – riparian boundary), NO_3^- concentrations did not differ significantly between groundwater sampled from high and low locations ($p=0.791$). However, both DON and NH_4^+ concentrations in groundwater were significantly higher at the lower sites than at the higher sites ($p<0.001$ and $p=0.008$ respectively), with mean values for NH_4-N at high and low sites being 0.13 mg L^{-1} (+/- 0.02) and 0.16 (+/- 0.01) mg L^{-1} and for DON 0.19 (+/- 0.02) mg L^{-1} and 0.24 (+/- 0.03) mg L^{-1} respectively.

Within the riparian zone, different temporal and spatial patterns were observed in the concentrations of the various N species (Figures 3.1., 3.2 and 3.3).

Dry season

Nitrate concentrations in groundwater were generally low throughout the riparian zone in the dry season (mean 0.11 mg NO_3-N L^{-1}, Figures 3.1, 3.3 and 3.4) in comparison to the wet season. Concentrations tended to increase as groundwater moved through the riparian zone towards the creek (Figures 3.1 and 3.3). The dry season groundwater flowpath followed a direction of approximately 60° from grid north. Following this approximate direction of flow through the riparian grid, mean dry season NO_3^- concentrations showed

an increase from 0.008 mg N L^{-1} at the canefield-riparian boundary to 0.40 mg N L^{-1} over a distance of approximately 140 m (100 m from the canefield-riparian edge). Ammonium concentrations generally showed the opposite pattern to those of NO_3^- with a decrease in NH_4^+ concentrations as groundwater moved towards the creek (Figures 3.1 and 3.3) along the dry season flow path. Ammonium concentrations decreased from a mean of 0.33 mg N L^{-1} at the canefield-riparian edge to a mean of 0.17 mg N L^{-1}, also over a distance of approximately 140 m in the direction of dry season flow. At a distance of 50 m from the canefield riparian boundary, NH_4^+ concentrations were generally higher than those of NO_3^- ($p < 0.001$). However, at 100 m from the canefield-riparian boundary, NO_3^- concentrations began to dominate DIN concentrations (Figure 3.2).

Dissolved organic N concentrations remained fairly stable as groundwater traversed the site (Figures 3.1 and 3.3), (mean of 0.26 mg L^{-1}), although an increase in DON concentrations was observed near the creek edge in November 2008, towards the end of the dry season (Figure 3.3).

a)

b)

c)
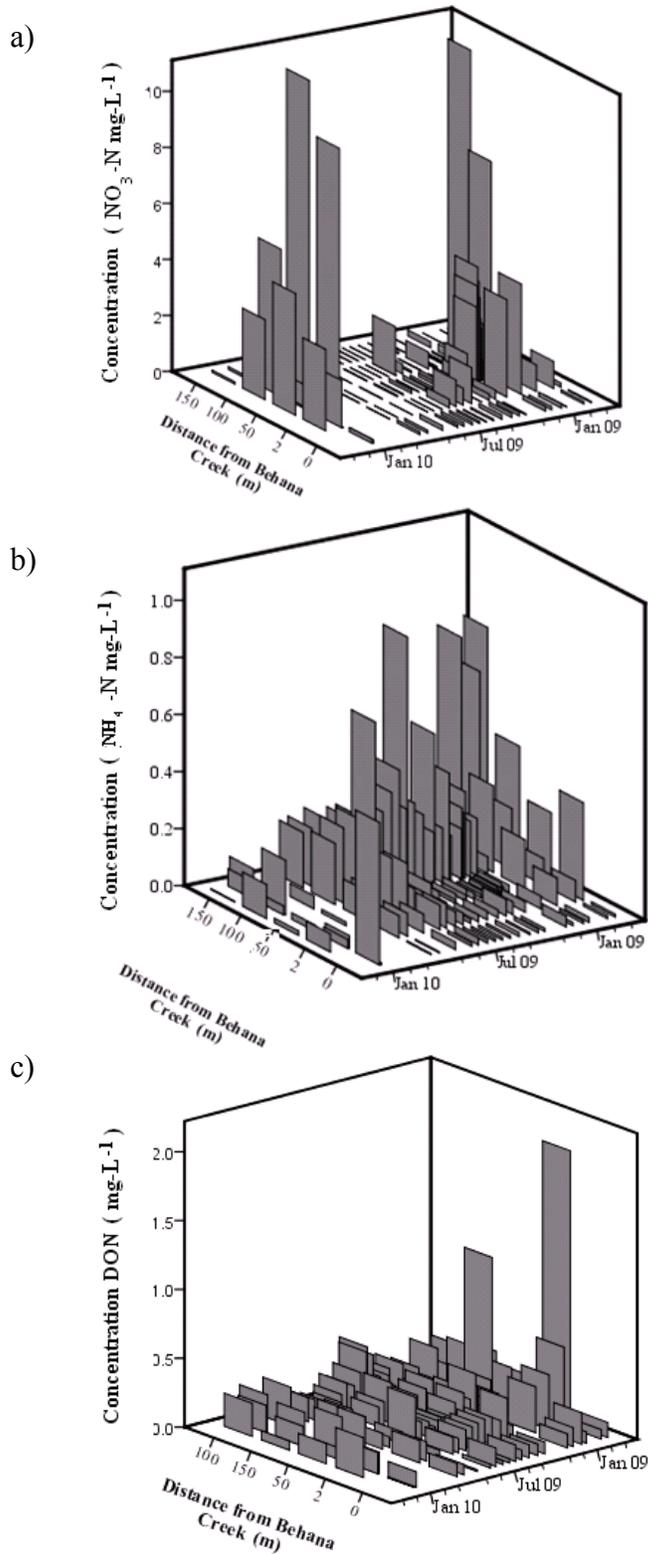
Figure 3.3 Mean monthly groundwater concentrations for (a) NO$_3$-N (b) NH$_4$-N (c) DON expressed as a function of distance and time. Sampling period covers November 2008 to February 2010. Note differences in scale.
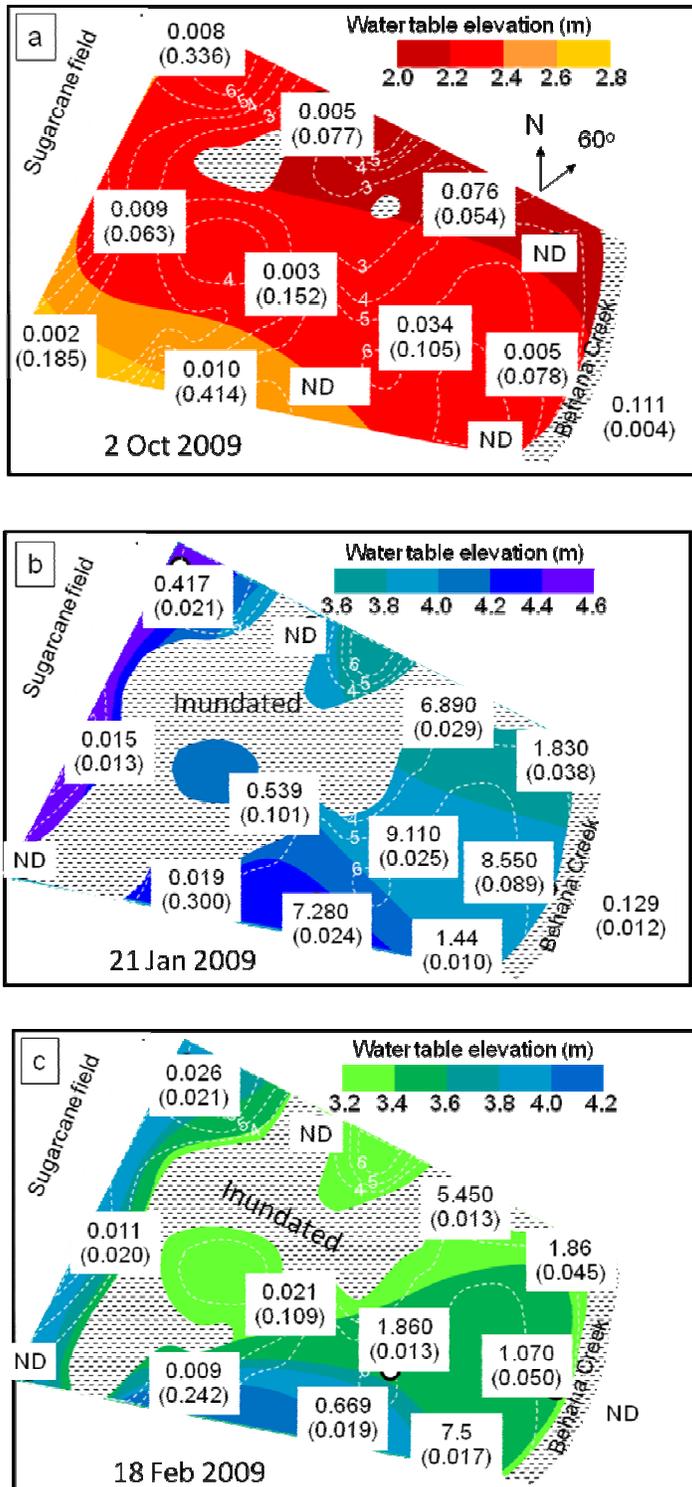
Figure 3.4 Inorganic N concentrations in groundwater on days in the (a) dry season (2 October 2009) (b) the beginning of the wet season (21 January 2009) and (c) wet season after a large rainfall event (18 February 2009). Numbers in boxes represent inorganic N concentrations in mg N L^{-1}.The top line represents NO$_3$-N and the number in parentheses represents NH$_4$-N concentrations. ND signifies no

data available. In the dry season piezometers showing ND were dry; in the wet season they were inundated and in February 2009 conditions were unsafe to collect a creek sample. Dashed contour lines show ground elevation.

Wet season

With the arrival of the first heavy rains of the wet season, in January and November 2009, groundwater NO_3^- concentrations rose dramatically, exceeding 10 mg N L^{-1} at some piezometer locations. A second spike was observed in January 2010 after a relatively dry month throughout December 2009 (Figure 3.3). Nitrate concentrations generally diminished as the wet season progressed, although spikes were observed in individual piezometers, most notably at the beginning of large rainfall events, with concentrations decreasing over the subsequent days of the event. Overall, NO_3-N comprised a mean of 86 % of the total dissolved N in groundwater in the wet season within the riparian zone (from 100 m to the creek bank, excluding concentrations entering from the sugarcane fields), with the remainder being DON (10%) and NH_4-N (5%, Figure 3.2).

Nitrate concentrations increased as groundwater progressed through the riparian zone in the wet season with concentrations generally peaking at 50 m from the creek bank or at the creek bank (Figures 3.1 and 3.4). Mean wet season NO_3^- concentrations closest to the creek (at 2 and 50 m from the bank) were significantly higher than those furthest from the creek (at 100 and 150 m from the creek) (p<0.001). This is despite the occurrence of one exceptionally high value of 31.5 mg NO_3-N L^{-1} observed at 100 m from the creek at piezometer T1P2 in November 2009. Mean NO_3^- concentrations at 50 and 2 m from the creek were, respectively, ~ 40 and 30 times higher than mean concentrations in groundwater entering the riparian zone at the canefield-riparian boundary in the wet season.

Whilst NO_3^- concentrations in groundwater increased with distance into the riparian zone in the wet season, concentrations tended to decrease as groundwater approached the creek bank. Nitrate concentrations in creek water were significantly lower than concentrations in groundwater at 50 m from the creek ($p<0.001$). However, NO_3^- concentrations in groundwater at 2 m from the creek and concentrations in the creek water itself were not significantly different ($p=0.217$). Nonetheless, mean NO_3^- concentrations in creek water over both seasons were higher than those in groundwater entering the riparian zone at the canefield-riparian boundary ($p<0.001$ for wet and dry seasons). This demonstrates that groundwater entered the riparian zone with relatively low concentrations of NO_3^- yet acquired additional NO_3^- as groundwater moved through the riparian zone.

Ammonium concentrations in groundwater were very low throughout the wet season and did not exhibit the large peaks that were observed with NO_3^- (Figures 3.3 and 3.4). Mean wet season NH_4^+ concentrations in groundwater tended to increase over the first 50 m of the riparian zone, then decrease as groundwater flowed towards the creek (Figure 3.2).

3.3.3 Differences in NO_3-N concentrations between deep and shallow groundwater

Samples from shallow and deep groundwater from nested piezometers at the creek bank differed in DIN concentrations. The deeper piezometer (T2P5) was slotted between 5.8 and 6.0 m and the shallow piezometer (T2P4) from 0.4 to 2.5 m depth. Nitrate concentrations in the deeper groundwater were, for the most part, higher than concentrations from shallow groundwater (piezometer T2P4) (Figure 3.5). Differences in NO_3^- concentrations between the deep and shallow water were significant ($p<0.001$ in the dry season and $p=0.041$ for the wet season). During the dry season, NO_3^--N concentrations in groundwater

from the deeper piezometer were consistently higher than those of all other shallow

piezometers (mean deeper groundwater 1.07 (+/- 0.14) mg L^{-1} versus 0.01 (+/-0.004) mg

L-^{1} in shallow groundwater). During the wet season this was reversed. Mean NO$_3$-N

concentrations were higher in the shallow groundwater (1.72 (+/-0.97)) mg L^{-1} than in

deeper groundwater (1.19 (+/- 0.18) mg L^{-1}). Large spikes were observed in NO$_3^-$N

concentrations in shallow groundwater at this time, suggesting additional NO$_3^-$ may have

been leached into shallow groundwater from the soil surface or the unsaturated zone during

in situ rainfall. No such spikes were observed in deeper groundwater.
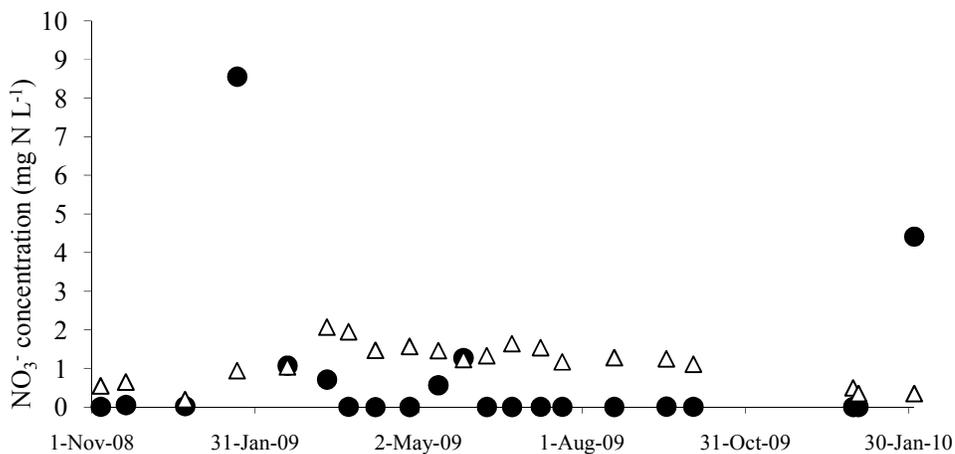
Figure 3.5. NO$_3$-N concentrations in shallow groundwater (0.4 to 2.5 m depth) at piezometer T2P4 (black circles) and deeper groundwater (between 5.8 and 6 m depth) at piezometer T2P5 (clear triangles). Piezometers are nested on the bank at 2 m from the creek.

Ammonium concentrations were higher in shallow groundwater for the dry season (mean

0.1 mg L^{-1} (+/-0.01) for shallow groundwater versus mean 0.02 (+/- 0.01) mg L^{-1} for

deeper groundwater, (p<0.001)) and for   the wet season (mean 0.06 (+/- 0.007) mg L^{-1}

NH$_4^-$ for shallow groundwater versus 0.02 (+/- 0.007) mg L^{-1} for deeper ground water

(p=0.001)). Mean DO concentrations were higher in deeper groundwater (27.3% (+/- 2.2))

than in shallow groundwater (18.5% (+/- 1.2)) over the study period, suggesting

nitrification was not the source of additional nitrate in the deeper groundwater. With

reference to DON there was no significant difference between shallow and deeper

groundwater concentrations for either season (overall mean 0.15 mg L^{-1} (+/- 0.02)).

Chloride concentrations, on the other hand, were higher in shallow groundwater in the dry

season only (mean 9.44 (+/- 0.32) mg L^{-1} versus 7.66 (+/-0.27) mg L^{-1} for deeper

groundwater, p=0.001) with no significant difference in the means of chloride

concentrations between deep and shallow groundwater in the wet season (wet season mean

for both deep and shallow groundwater 7.2 (+/-0.36) mg L^{-1}). This is consistent with the

upward movement of water at the creek bank during the wet season. On the few occasions

when sampling was safely conducted during large wet season rainfall events when the

creek stage was high, Cl^- concentrations in shallow groundwater at 2 and 50 m from the

creek were notably lower than those of deeper groundwater. This suggests that dilution

from the creek water is likely to have occurred at this time.

3.3.4 Relationships between groundwater variables

A significant, medium, negative, relationship was observed between NO_3^- and NH_4^+

concentrations in groundwater over both seasons (Table 3.2). Nitrate and DO

concentrations in groundwater were positively correlated, strongly in the dry season and

moderately in the wet. The relationship suggests that higher NO_3^- concentrations were

associated with more oxygenated groundwater. The opposite relationship was observed

between NH_4^+ and DO, suggesting the more oxygenated the groundwater, the lower the

concentrations of NH_4^+. The dry season relationship between NO_3^- and DO suggests

conditions were conducive to nitrification. No significant relationship, on the other hand, was observed between DON and DO.

Dissolved organic N concentrations were strongly, positively, associated with DOC concentrations in groundwater in both seasons. The relationship between DON and NH_4^+ concentrations was weaker, yet still significant. The relationship between NO_3^- and DOC was non-significant for both seasons.

Electrical conductivity, pH, Cl^-, DON and NH_4^+concentrations were positively correlated with each other in both seasons. However, there was no significant relationship between NO_3^- concentrations and EC or pH.

Table 3.2. Relationships among measured groundwater variables for wet and dry seasons (Pearsons's Product Moment correlation). Correlation was performed on log-transformed data with the exception of pH.

Dry Season	NO$_3$-N (Ln)	NH$_4$-N (Ln)	DON (Ln)	DOC (Ln)	Cl (Ln)	EC (Ln)	pH	Temp. (Ln)	DO (Ln)
NH$_4$	-0.567								
DON	0.102	0.387**							
DOC	-0.154	0.541**	0.898**						
Cl	-0.146	0.440**	0.232*	0.254**					
EC	-0.128	0.466**	0.250*	0.175	0.614**				
pH	-0.177	0.152	0.129	0.092	0.155	0.331**			
Temp.	0.338**	-0.096	0.251*	0.053	0.085	-0.002	-0.429		
DO	0.611**	-0.139	0.12	0.145	-0.154	-0.064	-0.101	0.183	
Distance to water table	0.038	0.017	-0.17	-0.154	0.112	0.098	-0.01	0.206*	0.084

Wet season	NO$_3$-N (Ln)	NH$_4$-N (Ln)	DON (Ln)	DOC (Ln)	Cl (Ln)	EC (Ln)	pH	Temp. (Ln)	DO (Ln)
NH$_4$	-0.419								
DON	-0.033	0.450**							
DOC	-0.039	0.400**	0.862**						
Cl	-0.362	0.444**	0.114	0.158*					
EC	-0.041	0.532**	0.304**	0.360**	0.505**				
pH	-0.446	0.426**	-0.008	0.046	0.225**	0.208**			
Temp.	0.182*	-0.125	0.079	0.005	-0.247	-0.24	-0.457		
DO	0.307**	-0.306	-0.166	-0.198	-0.127	-0.137	-0.209	-0.079	
Distance to water table	-0.033	-0.217	-0.35	-0.200	0.022	-0.242	0.053	-0.06	0.246**

**. Correlation is significant at the 0.01 level (2-tailed).
*. Correlation is significant at the 0.05 level (2-tailed).

3.3.5 Inorganic N in creek water

Creek water NO$_3^-$ concentrations were consistently higher than NH$_4^+$ concentrations (Figure 3.6). It is useful to compare the measured values to Queensland regional guideline values, which, for surface water quality in lowland streams with slightly-to-moderately disturbed conditions in the north Queensland Wet Tropics region, are 0.03 mg oxidised N L^{-1} (for NO$_3$-N) and 0.01 mg N L^{-1} for NH$_4$-N (DERM, 2009a). Concentrations of both N

species in creek water were, for the most part, higher than those specified by the guidelines (up to 6 times for NO_3^- and 4 times for NH_4^+) (Figure 3.6). Ammonium concentrations peaked at times of high rainfall in the wet season, however, no discernible temporal pattern emerged for NO_3^- concentrations in creek water over the study period.
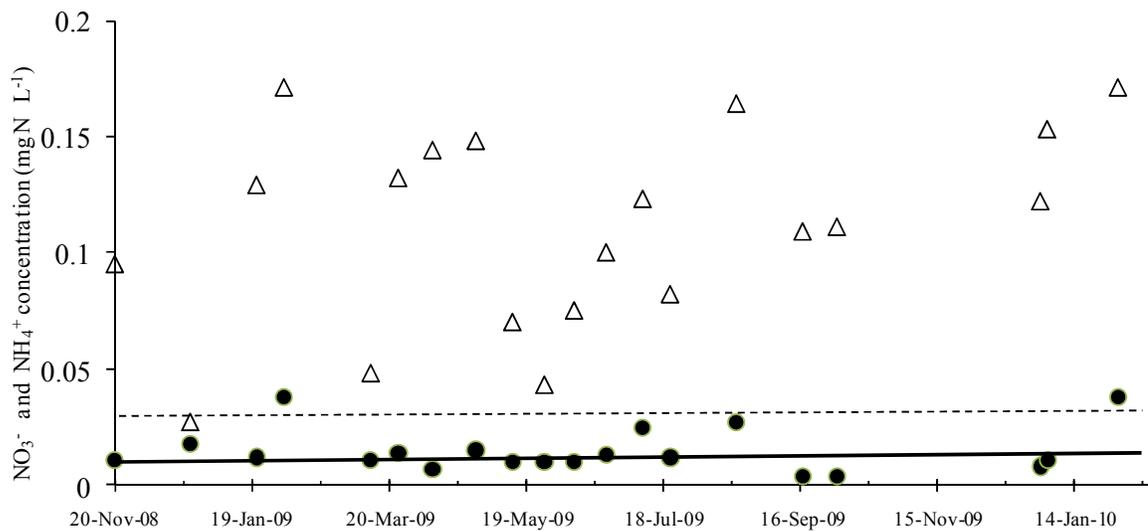
Figure 3.6 Behana Creek NO_3-N (triangles) and NH_4-N concentrations (circles) in stream water. Dashed horizontal line represents Queensland regional water quality guideline value for NO_3-N and solid horizontal line the value for NH_4-N. Guideline values correspond to those determined for slightly-to-moderately disturbed lowland streams in the North Queensland Wet Tropics region (DERM, 2009a).

3.3.6 N and C in soils

Mean values of soil parameters at each sampling site (high and low) for wet and dry seasons are shown in Table 3.3. The soils (0 - 0.05 m depth) had low bulk density, increasing with depth. Soil pH was acidic, ranging between 4.80 and 5.95. Soil NO_3^- concentrations at $0 - 0.1$ m depth exhibited the opposite temporal pattern to NO_3^- concentrations in groundwater: NO_3^- concentrations in soil increased steadily throughout the dry season but abruptly declined at the beginning of the wet season(s), coinciding with

the first of the large wet season rainfall events (Figure 3.7). Soil NO_3^- concentrations

ranged between 0.6 and 50.3 mg N kg^{-1}, with the highest concentrations occurring at the

end of the dry season; concentrations were significantly higher in soils at the higher

locations than at the lower locations (p=0.002). This is likely related to differences in soil

water content.
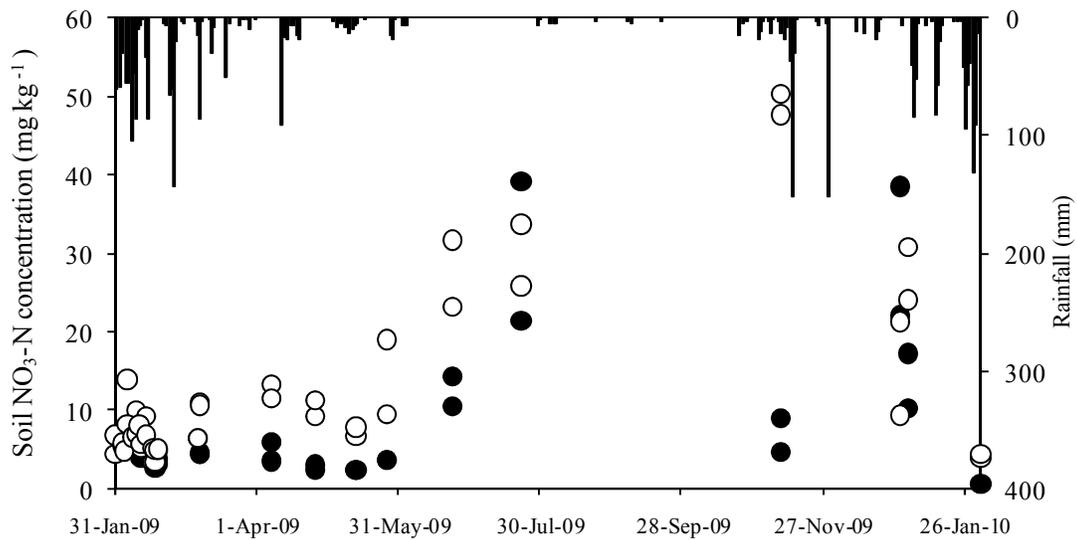
Figure 3.7 . Soil NO_3-N concentrations at 0 – 0.1 m depth (clear circles = high sites, black circles = low sites) and daily rainfall.

Table 3.3 Soil characteristics (0-0.1 m depth unless otherwise indicated) from the four soil sampling sites for wet and dry seasons. Values are the mean for the season and values in parentheses represent standard errors.

	Season	Low				High			
		T1P2	(SE)	T3P3	(SE)	T2P3	(SE)	T1P3	(SE)
Elevation (m AHD)		4.12		3.89		5.93		5.40	
Bulk density (kg m^{-3}) (0 - 0.05 m depth)		680		860		930		860	
Bulk density(kg m^{-3}) (0.10 - 0.15 m depth)		780		1040		970		950	
NH$_4$-N (mg kg^{-1})	Dry	0.57	(0.02)	0.58	(0.02)	0.73	(0.23)	1.74	(0.27)
	Wet	3.23	(0.84)	2.36	(0.74)	2.82	(1.04)	3.73	(1.67)
NO$_3$-N (mg kg^{-1})	Dry	15.97	(5.47)	26.70	(12.38)	24.55	(1.32)	32.67	(1.04)
	Wet	5.65	(1.62)	7.03	(2.51)	11.52	(2.42)	10.26	(2.25)
DOC (mg kg^{-1})	Dry	38.49	(0.56)	48.13	(18.29)	36.89	(5.26)	18.08	(0.00)
	Wet	33.82	(3.54)	33.58	(2.17)	48.93	(3.41)	42.27	(3.00)
C:N ratio (mass)	Dry	15.31	(0.79)	15.35	(1.03)	14.84	(0.69)	13.36	(1.09)
	Wet	15.94	(0.69)	17.27	(0.61)	15.92	(0.52)	16.01	(0.59)
Total C (%)	Dry	5.18	(0.19)	3.97	(0.04)	5.33	(0.05)	5.59	(0.19)
	Wet	5.09	(0.13)	4.51	(0.22)	5.83	(0.14)	5.75	(0.18)
Total N (%)	Dry	0.34	(0.30)	0.26	(0.02)	0.36	(0.02)	0.42	(0.02)
	Wet	0.33	(0.01)	0.26	(0.01)	0.37	(0.01)	0.36	(0.01)
pH	Dry	5.11	(0.05)	5.29	(0.07)	5.28	(0.05)	5.29	(0.04)
	Wet	5.41	(0.06)	5.62	(0.04)	5.53	(0.04)	5.54	(0.05)

Ammonium concentrations in soil exhibited the opposite temporal pattern to NO_3^- concentrations (Figure 3.8), with NH_4^+ concentrations peaking with the arrival of the first significant wet season rains. Soil NH_4^+ content ranged from 0.49 to 35.78 mg N kg^{-1} with no significant difference in concentration between high and low sites, although the two highest concentrations measured (>20 mg N kg^{-1} in January 2010) were both at high sites.
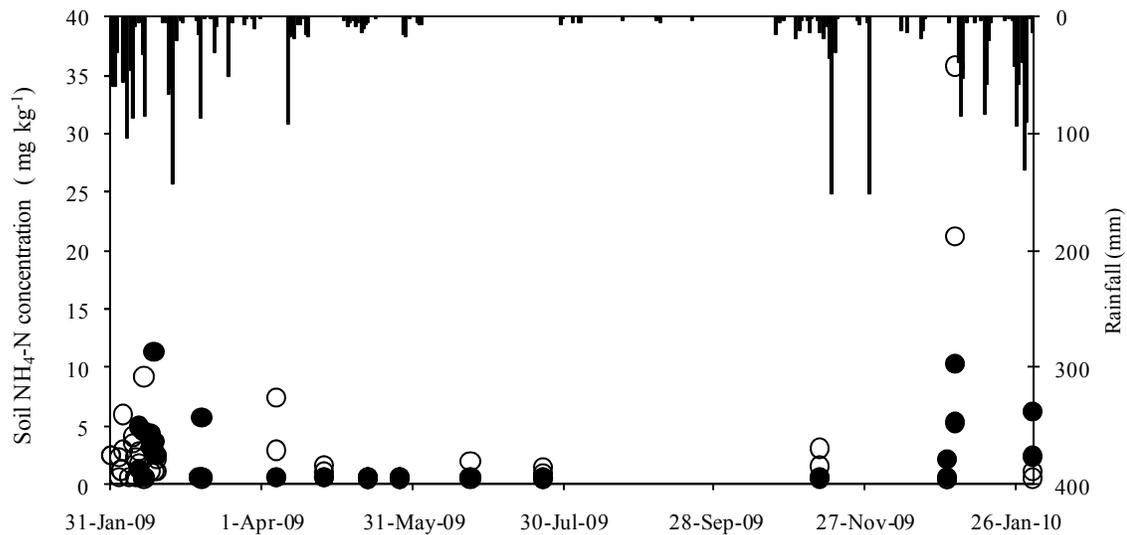
Figure 3.8 Soil NH_4-N concentrations (clear circles = high sites, black circles = low sites) and daily rainfall.

Soil DOC concentrations ranged between 17 and 74 mg kg^{-1}, with concentrations significantly lower at sites lower in the landscape (p=0.001). Mean DOC concentrations were 45 mg kg^{-1} at high sites and 35 mg kg^{-1} at low sites; overall, there was no significant difference in soil DOC concentrations between seasons (p=0.927). Soil C:N ratio (mass basis) ranged between 10.1 and 23.2 with no significant difference between seasons. Sites with the highest mean C:N ratios were T1P3 and T2P3, both located in high positions in

the landscape, although overall there was no significant difference between high and low sites (p=0.256).

3.3.7 Vegetation

N fixing species identified within the riparian zone were: *Castanospermum australe* (black bean tree)*, Millettia pinnata*, *Samanea saman* (rain tree*), Entada phaseoloides* and the common climber, *Derris trifoliata*. Cover from leguminous tree and vine species corresponds to approximately 5 % of the canopy over the study site.

Annual litterfall for the study site was 12.19 Mg ha^{-1}y^{-1}, with leaf litter comprising almost 60% of the total (7.07 Mg ha^{-1}y^{-1}). Total litter fall showed a strong seasonal pattern, with the heaviest falls occurring at the end of the dry season in October 2009 and at the height of the wet season in January 2010 (Figure 3.9). The largest mean monthly litterfall (184 g m^2) corresponded to the month of highest rainfall (870 mm) and storm activity, January 2010, producing the highest monthly fall in leaf and woody material as well as substantial large branch fall (which was not included in the litter collection).
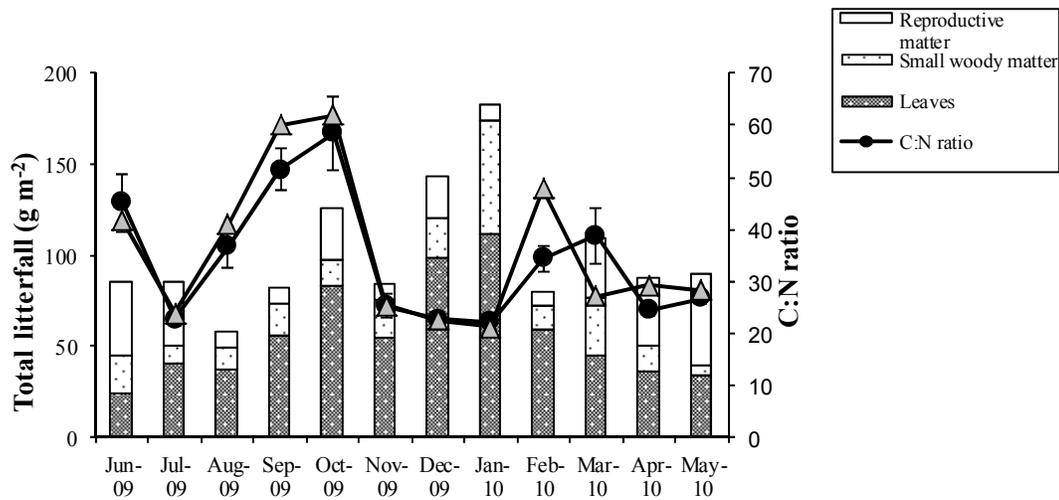
Figure 3.9 Mean monthly litterfall from 5 collection sites showing litter components (leaves, small woody matter and reproductive material. Line with black circles represents mean monthly C:N ratios of leaf litter for 4 sites showing standard error bars. Line with grey triangles represents mean monthly C:N ratio of leaf litter from legume site only.

Reproductive materials consisted predominantly of seed pods from large *Castanospermum australe* trees at the 'legume' site and fruit from *Elaeocarpus grandis* (quandong) at T1P3. The fall of reproductive material was greatest between March and July 2009. Black bean seed pods fell mainly between March and May and quandong fruits between April and July 2009.

Mean foliar C and foliar N concentrations were 43.29 % and 1.39 % respectively over the period of one year. Foliar C:N ratio was significantly higher in the dry season than the wet season (Figure 3.9, dry season mean 43.5 compared to wet season mean 28.0, $p= 0.030$) due to a decrease in N concentration in leaves from all sites in the dry season. However, the C:N ratio did not differ significantly between sites ($p= 0.392$). Based on foliar N concentration of 1.39 % for the leaf component, approximately 169 kg N ha^{-1} y^{-1} would be expected to return to the riparian forest floor in leaf litter. Seasonal trends in N accession

showed N flux in leaf litterfall to be lowest in the dry months and highest in the wet, with the exception of July which had unseasonally high N concentrations in leaf litter. The N content in leaf litter at the legume site did not differ significantly from the other four sites (p=0.580).

The total amount of litterfall was high, in part, due to the large amount of *Castanospermum australe* seed pods collected in the litter traps. A large pod weighed up to 70 g. Excluding the 'legume' site, total litter fall would be 11.4 Mg ha^{-1} y^{-1}, still with ~ 60% leaf litter, but with the contribution of reproductive matter reduced from 22% to 16%. Similarly, excluding the 'legume' site reduces estimated N input from litterfall to 158 kg N ha^{-1}y^{-1}.

3.4   Discussion

It was hypothesised that NO$_3^-$ concentration in groundwater would decrease as groundwater moved from an agricultural landscape, through the riparian zone and towards the creek. This hypothesis was based on the results from a wide range of studies examining the movement of NO$_3^-$ through riparian zones in agricultural catchments (e.g. Dhondt *et al.*, 2006; Haycock and Pinay, 1993; Lowrance, 1992; Peterjohn and Correll, 1984). However, it is clear from our results that this did not occur at our site: NO$_3^-$ concentration was low in groundwater entering the riparian zone from the sugarcane fields, yet tended to increase as groundwater moved through the riparian forest towards the creek. Nitrate concentrations in groundwater generally decreased again before discharge into the creek; however, concentrations in groundwater at 2 m from the bank of the riparian zone were always higher than in groundwater entering the riparian zone. These results clearly suggest

that the forested riparian zone is a source of NO_3^- to groundwater, and potentially to the creek.

Although beyond the scope of this study, the low NO_3^- concentrations in groundwater entering the riparian zone may be attributed to 1) denitrification occurring in groundwater as it moves beneath the sugarcane fields, towards the riparian zone (Wakelin *et al.*, 2011) and/or 2) the efficient use of N fertiliser upslope, with little leaching loss and hence low concentrations in groundwater entering the riparian zone. In a concurrent study, Armour *et al.* (2012) indeed found little leaching loss of NO_3^- from a sugarcane field just upslope of the riparian study site. They attributed the low leaching loss of NO_3^- to appropriate rates of fertiliser application and substantial uptake of N by the crop between fertiliser application and the onset of the wet season. The presence of a cane field drain (approximately 1 m deep) upslope of the study site, approximately 100 m to the south west, is likely to have diverted a portion of surface water from the sugar cane field during, or following high rainfall events. This would have reduced the amount of deep drainage on the field upslope of the riparian zone; at the same time some of this water may have been channelled towards the gully at the study site.

Compared to another tropical riparian study, groundwater NO_3-N concentrations within the riparian zone at Behana Creek were high, yet NH_4-N concentrations were lower. In the Luquillo Experimental Forest in Puerto Rico, in a undisturbed catchment, McDowell *et al.* (1992) compared NO_3 and NH_4 –N concentrations in shallow groundwater from two riparian zones. Nitrate -N concentrations were < 0.2 mg L^{-1} in both of the riparian zones studied. Concentrations of NH_4-N were relatively high in the Icacos riparian zone, up to

2 mg L^{-1}. In the Bisely riparian zone, on the other hand, NH_4-N concentrations were lower, at < 0.1 mg L^{-1}.

Results from our study suggest that high concentrations of NO_3^- accumulated in riparian forest soil throughout the dry season and that this NO_3^- was rapidly displaced into groundwater with the onset of large wet season rainfall events. This produced a rapid reduction in soil NO_3^- concentrations and a corresponding increase in groundwater NO_3^- concentrations, similar to that identified by Bechtold *et al.* (2003). The translocation of NO_3^- from surface soils to groundwater is closely associated with the hydrology and soil characteristics of the site. Nitrate is likely to have been displaced into groundwater through either of the two hydrologic mechanisms: 1) the 'flushing' effect (Creed and Band, 1998; Hornberger *et al.*, 1994) whereby the rising water table flushes the variably saturated zone and NO_3^- becomes incorporated into groundwater, and/ or 2) through deep drainage, whereby NO_3^- is transported downwards to the water table by percolating rainwater. Where NO_3^- is displaced vertically, Wetselaar (1962) found a strong, positive correlation (r=0.946) between the downward movement of NO_3^- and rainfall in two soils in northern Australia. A mean downward rate of movement of NO_3^- of approximately 27.3 mm was calculated for every 25.4 mm of rainfall in a clay loam soil and almost double that for a sandy soil, over a vertical distance of 1.52 m. The relatively high infiltration capacity, low bulk density and high porosity of the Behana Creek riparian soils (Chapter 2) provide conditions conducive to the rapid, downward displacement of NO_3^- through the soil profile during wet season rain events. Nitrate displacement at our site is likely to be substantial with annual deep drainage estimated to be at least 1400 mm y^{-1} in episodic events (Chapter 2).

The accumulation of NO_3^- in tropical forest soils has been previously documented (e.g. Chaves *et al.*, 2009; Greenland, 1958; Markewitz *et al.*, 2004; Wetselaar, 1962). Recent work on montane tropical forests in Central America and the Caribbean, demonstrated that NO_3^- deriving from nitrification in tropical forest soils can be directly exported to streams (Brookshire *et al.*, 2012), implying that NO_3^- removal processes were not effective. Chaves *et al.* (2009) described leaching of NO_3^- from the soil surface to deeper within the profile of Amazonian forest soils. Despite this, groundwater NO_3^- concentrations at their site remained very low, even immediately after leaching events. This was attributed to either denitrification, or to the retention of NO_3^- ions on anion exchange sites deep within the unsaturated zone, before NO_3^- reached the water table. At the Amazonian site there was no low-lying riparian zone per se. Hence, the position of the water table was likely much deeper at the Amazon site than at Behana Creek, where the water table fluctuated between the ground surface and 0.5 - 4 m depth throughout the wet season (depending on the surface elevation). Assuming a deeper water table, groundwater at the Amazonian site would be less likely to interact with surface soil layers and N would need to be displaced over a greater vertical distance before reaching the water table. Longer residence time of NO_3^- within the unsaturated zone would provide a greater opportunity for processes such as denitrification, or uptake by vegetation, to occur. As well as differences in the hydrologic setting of the two sites, differences in soil texture between our site and the Amazonian site could account for the higher concentrations of NO_3^- in groundwater at Behana Creek. Amazonian soils had high clay content. An impeding layer between 0.12 and 0.2 m depth was noted, likely resulting in lower hydraulic conductivity. Alluvial soils at Behana Creek, on the other hand, are coarse and permeable, providing rapid flowpaths to groundwater.

Retention through anion exchange is likely to be minimal in Behana Creek soils as evidenced by low iron oxide content in the soils (personal observation). Hence, the combination of 1) relatively permeable soils 2) minimal retention mechanisms and 3) the rapid and frequent fluctuation of the water table flushing surface layers during wet season rain events, would facilitate the transfer of NO_3^- from the unsaturated zone to the saturated zone at Behana Creek, increasing NO_3^- concentrations in groundwater.

Conditions for denitrification to occur in the top layers of soil (0-0.1 m depth) varied spatially and temporally within the site. The denitrification process demands 1 mole of organic C to 0.8 mole of NO_3^- (Davidsson and Leonardson, 1996); soil DOC: soil NO_3^- in the top 0.1 m of the soil of the riparian zone was consistently > 1: 0.8, suggesting the availability of substrates was conducive to denitrification. It should be noted, however, that organic C is also required for other metabolic processes and by other organisms aside dentitrifiers, hence not all organic C is necessarily available for denitrification. However, assuming the supply of organic C is bio-available and in sufficient quantities to fulfill competing requirements, and that denitrifying organisms are present in riparian soil, denitrification would occur predominantly in the wet season (November to May) when soil water content is highest and, subsequently, O_2 content at its lowest. Soil water content was closely linked to rainfall and the position of the water table which, in turn, was linked to the site topography. Low lying areas closest to the water table sustained higher soil water content. Hence, denitrification in near-surface soils is most likely to occur:

1) During and immediately after high, in situ, wet season rainfall throughout the entire riparian zone when water content is highest. Infiltrating rainfall and a rising water

table raises the soil water content of soils, reducing O_2 availability. Oxygen present in infiltrating rainwater is likely to become rapidly consumed by microbial activity. Denitrification in near-surface soils would likely continue until the water table recedes and soils drain. Nitrate concentrations in near-surface-soils may become depleted or displaced to deeper within the soil profile over the duration of the rainfall event, thus limiting denitrification. Under such conditions, the reduction of N_2O might be favoured, producing N_2. Nitrate is unlikely to be replenished through nitrification during heavy rainfall events due to low O_2 availability in the soil.

2) At topographic highs denitrification in near surface soils is likely limited to times of intense wet season rainfall events. Soils at the high sites were quick to drain once rainfall subsided and WFPS rarely exceeded 60% (Chapter 2).

3) In the lower-lying areas of the riparian zone, denitrification is likely to occur throughout most of the wet season as near-surface soils at low sites exceeded 60% WFPS for ~25% of the year (Chapter 2). Areas in and around the gully (topographic depressions <~4 m elevation) retained high soil water contents throughout most of the year, with the water table remaining close to the ground surface. These areas are likely to constitute denitrification 'hot spots' within the riparian zone, so long as NO_3^- does not become limiting.

Opportunities for denitrification to occur in groundwater, deeper within the soil profile, existed throughout most of the year. Groundwater DOC: NO_3^-N ratios were likely conducive to denitrification and DO levels in groundwater were low (mean DO 21.9%) throughout the year. The hydrology study was unable to quantify the groundwater fluxes occurring during wet season rainfall events. However, large, rapid (sub-daily) water table

fluctuations and short distance water table gradients were measured during times of high in situ rainfall, suggesting that rapid subsurface fluxes channelled water rapidly towards the multiple discharge zones. This would result in short residence time of groundwater within the riparian zone at this time, limiting the interaction of groundwater with riparian soils. A decrease in groundwater NO_3^- concentrations measured over a storm event in February 2009 suggested that denitrification may have been occurring, but dilution of the initial flush of NO_3^- from surface soils may also explain the decrease in concentration.

Nitrate accumulated in surface soils of the riparian forest throughout the dry season. Approximately 40 mg NO_3-N kg^{-1} accumulated in the 0- 0.1 m layer of riparian soil from the end of the wet season to the end of the dry season (Figure 3.7). Assuming a mean soil bulk density of 900 kg m^{-3} over the 0-0.1 m layer, 0.24 kg NO_3-N ha^{-1} would have been generated (nitrified) daily in the 0-0.1 m soil layer in the riparian zone during this time. Accumulation of NO_3^- in the soil was likely the result of sporadic dry season rainfall replenishing soil moisture. This would produce conditions conducive to mineralisation/ammonification and nitrification processes in surface soils. This dry season rainfall, however, was neither intense nor frequent enough to enable NO_3^- to leach into groundwater at this time. Wetselaar (1962) reported that, in the absence of additional rainfall, NO_3^- continued to accumulate in tropical soils in northern Australia for up to 9 and a half weeks after a single wetting event. The longest time without rain during the study period at Behana Creek was 7 and a half weeks. This suggests that nitrification within the top 0.1 m of soil was likely to be continuous throughout the dry season. During times of no rainfall, the formation of early morning dew may have temporarily increased soil water

content, producing an environment suitable for nitrification (e.g. Schimel and Parton, 1986).

Nitrification presumably continued to take place in riparian soils throughout the wet season, as evidenced by increases in NO_3^- concentrations between large rainfall events (Figure 3.7). However, in contrast to the dry season, NO_3^- did not accumulate for long periods in surface soil at this time. Some soil NO_3^- may have become assimilated by riparian vegetation or by microbes between rainfall events, however, NO_3^- became rapidly displaced deeper into the soil profile or incorporated into groundwater with the advent of rainfall and/or a rising water table, as described above. Assuming a similar rate of nitrification in surface soils in the wet season as in the dry season, approximately 88 kg NO_3-N ha^{-1} y^{-1} would have been generated over one year in the 0- 0.1 m layer. Kiese *et al.* (2002) noted that nitrification in lowland tropical soils in north east Queensland was higher in the wet season than in the dry season; thus, 88 kg NO_3-N ha^{-1} y^{-1} is likely an underestimate. Similarly, at a tropical forest site in north east Queensland, Kiese *et al.* (2003) observed leaf litter decomposition to be approximately two-fold higher in the wet season compared to the dry season. This would provide substrate for the nitrification process. The initially high concentrations of NO_3^- in groundwater observed at the beginning of the wet season are likely due to an additional "pulse" of mineralisation and nitrification stimulated by the re-wetting of dry soils (Davidson *et al.*, 1993). Large pulses of biogeochemical activity at a point in time may be attributed to 'hot moments' (sensu McClain *et al.*, 2003).

Whilst NO_3^- accumulated in the soil throughout the dry months, corresponding groundwater NO_3^- concentrations remained low. Decreasing concentrations of NH_4^+ and increasing concentrations of NO_3^- in groundwater throughout the dry season, however, suggests that nitrification was taking place in groundwater as well as in soil. No net change in DIN concentrations (NO_3^- and NH_4^+) was observed in groundwater during the dry season, indicating the conversion of NH_4^+ to NO_3^- via nitrification in groundwater at this time and no removal of NO_3^- through denitrification. This is supported by the strong, positive relationship between concentrations of NO_3^- and DO. Dissolved oxygen in groundwater reached up to 70% saturation in the dry season in some areas of the riparian zone, a condition conducive to nitrification. However, very low hydraulic gradients throughout the dry season, together with transpiration from riparian vegetation, resulted in negligible groundwater flow through the riparian zone at this time. Hence, despite ongoing nitrification in soil and groundwater, it is unlikely that N is delivered to Behana Creek through groundwater at this time.

Increases in groundwater NO_3^- concentrations during the wet season were clearly due to the flushing of soil NO_3^- into groundwater; however, the upwelling of deeper, NO_3^--rich, groundwater may have contributed additional NO_3^- to shallow groundwater. The absence of a confining layer beneath the riparian zone at Behana Creek (in this case, underlain by coarse gravel alluvium), suggests that upwelling from deeper groundwater could occur (e.g. Hill, 1996). The upward gradients observed in deeper groundwater from deep piezometer T2P5, (6 m) at the creek edge (Chapter 2) suggest the mixing of deeper groundwater with shallow groundwater. Hence, a portion of shallow groundwater N concentrations may be supplemented by N from upwelling older, deeper groundwater.

3.4.1 Influence of riparian vegetation on the transport and transformations of N

Riparian vegetation produces a potentially large pool of mineralisable N. Litterfall rates at our site (12.19 Mg ha^{-1} y^{-1}) are high when compared to those of other lowland tropical forests, which range between 5.8 and 11.4 Mg ha^{-1}y^{-1} (Spain, 1984; Vitousek, 1984). High rates of litterfall imply high above-ground net primary production, providing large inputs of organic matter to the forest floor. The estimated input of N from leaf litter (169 kg N ha^{-1} y^{-1}) is higher than the range of values reported for Australian tropical forests (120 -140 kg N ha^{-1} y^{-1}) by Brasell *et al.*(1980), but just within the range for tropical and subtropical forests around the world (e.g. 74-169 kg N ha^{-1} y^{-1}) as reported by Ewel (1976). Below-ground inputs of organic matter or N were not measured in this study, but these would be additional to those in litterfall.

The presence of N- fixing leguminous species is an important source of N to tropical forest soils (e.g. Jenny, 1950). Biological N fixation by leguminous species at our site is likely an important source of N to the riparian forest. Nitrogen fixation, based on acetylene reduction techniques, has been found to contribute up to 243 kg N ha^{-1} y^{-1} to Amazonian floodplain forests (Salati *et al.*, 1982; Sylvester-Bradley *et al.*, 1980). However, Cleveland *et al.* (1999) considered this figure to be a maximum, arguing that this rate would likely be representative of 100% coverage by N-fixing species. The amount of N fixed by legumes at Behana Creek is likely to be closer to 12.2 kg ha^{-1} y^{-1}, as estimated by Cleveland *et al.* (1999), referring to tropical floodplain ecosystems globally, based on a conservative presence of 5% legumes. (In their review, coverage was calculated to represent the average of all cover estimates of leguminous species for each type of ecosystem and accounted for the heterogeneous distribution of symbiotic N fixers, e.g. leguminous species

over large landscapes). In comparison, and based on literature values from other studies in north east Queensland, atmospheric N input is estimated to be around 1.8 kg N ha^{-1} y^{-1} (Hunter and Walton, 2008). In addition to N fixation by legumes, inputs from free-living N fixers can be significant in tropical forests, in the order or 4-60 kg N ha^{-1} y^{-1} (Reed *et al.,* 2011). N inputs in rainfall were assumed to be low; N inputs in rainfall of 0.26 – 1.99 kg ha^{-1} were measured by Armour *et al.* (pers. comm.) in a similar environment, south of the study site, at East Palmerston.

Nitrate concentrations in groundwater have been reported to be significantly higher under forests comprised of leguminous species than under forests comprised of non-leguminous species (e.g. James *et al.*, 1990). At our site, leaf litter analysed from the targeted legume site did not have significantly different N concentration from the other sampling locations. Neither soil nor groundwater was sampled at the legume site, thus potential differences in soil and groundwater N concentrations between legume and non-legume sites were not tested.

Ratios of C:N in leaf litter and soil are likely to influence the decomposition and mineralisation rates of litter. Foliar C:N ratio is often used as an index of the quality of organic matter, with high quality plant tissue associated with C:N ratios <25 and lower quality litter >25. Lower quality litter equates to slower tissue break-down by decomposers (Myers *et al.*, 1994). At Behana Creek foliar C:N ratios were >25 for both seasons. However, as litter starts to decompose, the leaf litter C:N ratio is likely to be rapidly reduced (ie. some C will be lost as CO_2 but N will be retained) providing mineral N to the soil. High wet season rainfall at Behana Creek may also influence leaf litter

decomposition rates. Mass loss rates through litter decomposition were positively correlated with rainfall in a lowland wet tropical forest (Wieder *et al.*, 2009), suggesting faster rates of litter decomposition could occur in the wet season compared to the dry season. Net mineralisation within the soil is most likely to occur at soil C:N ratios of <20 (Alexander, 1977). At soil C:N ratios > 20, NO_3^- is more likely to become immobilised. Mean soil C:N ratios at Behana Creek were consistently <20, (16.4 in the wet season and 14.3 in the dry season, Table 3.3). At C:N ratios of <20, the mineralisation rate of soil organic matter is thus likely enhanced and microbial immobilisation of NO_3^- reduced, conducive to the supply of mineral N to riparian soils.

3.4.2 Uptake of inorganic N by riparian vegetation

Based on measurements available from this study, uptake of inorganic N by riparian vegetation over the period of a year can be estimated at 43 kg N ha^{-1} y^{-1}. This was calculated by partitioning ET into uptake from the top 0-0.1m soil layer (year-round) and uptake from groundwater throughout the wet season, and based on the following assumptions: 1) mean concentrations of inorganic N in soil and groundwater at T2P3 were representative of the whole site, and 2) uptake occurred by mass flow (i.e. no selective uptake or exclusion of N). The estimated uptake of inorganic N by vegetation is likely to be an underestimate as it does not account for uptake from the unsaturated zone below 0.1 m depth. Other studies in temperate regions have reported total N uptake from riparian vegetation to be between 77-84 kg ha^{-1} y^{-1} (e.g. Fail *et al.*, 1986; Peterjohn and Correll, 1984). Fail *et al.* (1987) suggested that riparian forest communities within agricultural environments absorb and retain nutrients lost from agricultural uplands. Our study suggests

that little N is imported from agricultural land upslope of the riparian zone; rather N is fixed by riparian forest and cycled within the riparian zone.

3.4.3 Transport of N towards the creek

The fate of N transported in groundwater through the riparian zone varies between seasons, dependent upon groundwater flowpaths. During the dry season baseflow virtually ceases and creek flow becomes highly diminished. At this time it is unlikely that much N, if any, is delivered to the creek via shallow groundwater. Wet season groundwater hydrology, on the other hand, is much more complex due to increased local hydraulic gradients. Vertical fluxes play an important role in translocating N through the profile at times of intense and frequent rainfall. The low-lying position of the riparian zone, hence short distance to the water table, provides frequent contact between surface soil and groundwater in the wet season. This, in turn, provides an efficient pathway for the exchange of N (in particular NO_3^-) between riparian forest soils and groundwater, providing the opportunity for export of N to the creek. Lateral wet season fluxes constitute complex hydrologic pathways channelling groundwater in multiple directions. This is governed by local groundwater gradients which, in turn, are influenced by the undulating riparian topography (Chapter 2 Figure 2.12). Nitrogen in groundwater subsequently becomes entrained and directed towards the low lying discharge areas, including the gully and the creek.

To calculate the N load exiting the riparian zone it would be necessary to multiply the area of the discharge zone by the velocity of groundwater and the concentration of N in groundwater. Multidirectional groundwater flow complicates the patterns of N moving through the riparian zone in groundwater in the wet season at any one time. Originally, the

discharge zone was anticipated to comprise the creek only. However, the study of groundwater movement in Chapter 2 demonstrated that the discharge zone during the wet season is variable in both time and space, mainly due to the presence of the gully. With regard to groundwater velocity, measurements from the four corner capacitance probes were unable to account for the dynamic, short range fluxes produced within the riparian zone. Neither could they account for the rapid subsurface storm flow that transported groundwater through the riparian zone directly to the discharge zones. Therefore, it is considered to be beyond the scope of this study to calculate the export of N to the creek during the wet season. During the dry season the export of N to the creek must be close to zero.

Our results strongly imply that N that is fixed and cycled within the riparian forest produces an additional source of N to that entering the riparian zone in groundwater from the surrounding agricultural area. Hence, inorganic N generated within the riparian zone becomes incorporated into groundwater and is likely delivered to the creek in the wet season. Other tropical studies have found biogeochemical processes occurring at the interface between the riparian bank and the stream to dramatically reduce the export of inorganic N to streamwater (e.g. Brandes *et al.*, 1996; Chestnut and McDowell, 2000; McClain *et al.*, 1994), At a site in the Brazilian Amazon, by using ^{15}N labelling of NO_3^- and NH_4^+, Brandes *et al.* (1996) showed that most of the dissolved inorganic N approaching the stream via groundwater flowpaths was removed at the riparian-stream interface. However, the data collected by these researchers did not allow for a quantitative explanation for the loss of inorganic N across the riparian-stream channel margin. The hypotheses evaluated included plant uptake, open channel consumption and coupled

nitrification-denitrification, yet no conclusions were drawn. Removal processes may also occur at the creek bank (or in the stream bed) at Behana Creek. However, their effectiveness would still be questionable at times of peak wet season rainfall when groundwater discharge is substantial and rapid. Brandes *et al.* (1996) suggested that remineralisation of organic N within the stream itself may represent a major source of in-stream DIN. Nitrate in creek water at Behana Creek might therefore derive from a combination of: 1) groundwater discharge from the adjacent riparian zone, 2) NO_3^- acquired from upstream discharge, and 3) in-stream N processing.

3.5   Conclusion

Contrary to our hypothesis, and contrary to the results of the majority of riparian zone studies, the riparian zone studied was a source of N to groundwater. Nitrate concentrations in groundwater increased as groundwater moved through the riparian zone at Behana Creek, most notably in the wet season. These concentrations, however, tended to decrease as groundwater approached the creek bank, yet concentrations at the creek bank were always higher than those in groundwater entering the riparian zone at the boundary with sugarcane fields. It is thus likely that, unless removal processes take place at the interface between the riparian zone and the creek, NO_3^- produced in the riparian zone would be exported to the creek. Groundwater discharge was minimal or absent in the dry season; delivery of NO_3^- to the creek at this time would therefore be unlikely. Groundwater NO_3^- within the riparian zone derived from internal N fixation and cycling processes, a product of the highly productive, tropical, riparian forest vegetation. The presence of leguminous N-fixing species likely enhanced N- richness in this tropical lowland riparian forest.

The low lying position of the riparian zone and the undulating topography were important factors in the mobilisation and transport of N through the site. Frequent contact between surface soil and groundwater by a fluctuating water table during the wet season provided a short, efficient pathway for the transfer of N (in particular NO_3^-) from riparian forest soils to groundwater. Steep water table gradients formed during wet season rain events resulted in complex subsurface flowpaths, entraining N in groundwater in various directions towards low-lying discharge zones. After heavy wet season rainfall, the gully filled with water, forming an additional discharge zone and, in effect, splitting the riparian zone into two. Wet season in-situ rainfall conditions were conducive for NO_3^- removal from groundwater by denitrification (low O_2 levels and a substantial source of organic C); however , rapid shallow groundwater fluxes during wet season rain events would have limited the groundwater residence times, limiting the opportunity for dentitrification to occur. On the other hand, denitrification is most likely to have occurred throughout the entire site <u>after</u> in situ wet season rain events. At these times near-surface soils, particularly in low lying sites, retained high soil water contents, yet shallow groundwater fluxes were less dynamic. Hence, groundwater residence times were likely longer and more conducive to the occurrence of denitrification. Conditions in the lowest lying areas, in and adjacent to the gully, were conducive to denitrification throughout the year, as soil water content remained high.

Conditions for nitrification occurred during the dry season and between rainfall events in the wet season, most notably at locations of higher elevation where soil water content was lowest. Patterns in N transformations in the riparian zone can be further investigated by measuring N_2O emissions from soil, together with measurements of soil wetness.

Chapter 4.   Nitrous oxide emissions from the forested riparian zone

4.1   Introduction

Nitrous oxide emissions from soil mainly result from microbiological processes, principally via the aerobic process of nitrification and the anaerobic process of denitrification (Firestone and Davidson, 1989), resulting in a loss of N to the atmosphere. The principal factors influencing N_2O emissions are soil aeration, temperature, NO_3^- concentrations, organic C concentrations (including the quality and bio-availability of the organic C), pH and the characteristics of the microbial community (Dendooven *et al.*, 1996; Granli and Bøckman, 1994; Wrage *et al.*, 2001).

Forested riparian zones are potential "hotspots" for N_2O emissions from denitrification (Groffman *et al.*, 2000; Hefting *et al.*, 2003). This is particularly the case where riparian zones are located within agricultural catchments where NO_3^- loads in groundwater can be elevated due to fertiliser leaching. As low-lying features of the surrounding landscape, riparian zones are generally associated with shallow water tables. This often results in saturated soils, in turn, producing low O_2 environments. Most reports of N_2O emissions from riparian zones have been associated with denitrification. However, where the water table is deeper and climatic conditions dry, soil water content will decrease and aerobic conditions can prevail. Under these conditions, nitrification is a likely source of N_2O (Hefting *et al.*, 2004; Kiese *et al.*, 2008).

Tropical forest soils are important sources of N_2O emissions (Bouwman *et al.,* 1993; Breuer *et al.,* 2000; Butterbach-Bahl *et al.,* 2004; Kiese *et al.,* 2003; Matson and Vitousek,

1990; Werner *et al.,* 2006) although there is large variability in ecological processes and differences in characteristics among tropical forests which may influence their potential to emit N_2O (Jordan, 1985; Vitousek and Sanford, 1986; Werner *et al.*, 2007). Tropical forest soils with high N availability, coupled with high water content, are most likely to emit N_2O (Davidson *et al.,* 2000). As such, we hypothesise that a forested riparian zone in an agricultural region of the humid tropics is likely to be a large emitter of N_2O.

The aims of this study were to: 1) quantify N_2O emissions from the soil surface in the riparian study site, 2) assess spatial and temporal differences in N_2O emissions (between high and low locations, between wet and dry seasons) and in N_2O concentrations within the profile, and 3) infer the source(s) of N_2O from riparian soils over the study period. To gain a more thorough understanding of factors likely to influence N_2O emissions and help interpret the field emission measurements, the following were also examined: 1) the influence of leaf litterfall on N_2O emissions (manipulative experiment in the field) and 2) the denitrification capacity of the riparian zone soils, and their capacity to reduce N_2O to N_2 (laboratory experiment).

4.2 Methods

4.2.1 Nitrous oxide emission measurements

Nitrous oxide and CO_2 emissions were studied in situ at four sites within the riparian zone at Behana Creek, two at 'high locations' (T1P3 at 5.40 m and T2P3 at 5.93 m elevation) and two at 'low' sites (T1P2 at 4.12 m and T3P3 at 3.89 m elevation). At each site, 6 PVC cylinders (chamber collars) (inner diameter 250 mm, height 120 mm) were inserted 20 mm

into the soil at no more than 1.5 m distance from the piezometer. Collars were left in the ground for the duration of the study to avoid soil disturbance, as disturbance can alter soil resistance to gas exchange (Matthias *et al.*, 1980). Collars had a 10 mm diameter hole at ground level to allow surface water to move freely in and out of the chamber. The hole was blocked with a stopper during measurements. Chamber lids were placed on the collars only during measurement periods. A vent comprising a thin nylon tube (inner diameter 1 mm, length 200 mm) was fitted to the removable lid of each chamber to enable air pressure inside the chamber to equilibrate with the outside atmosphere. Each lid was also fitted with a rubber septum for use as a sampling port.

To measure gaseous emissions, a lid was placed on each chamber, and the headspace air was sampled 4 times over one hour (time 0, 20, 40, and 60 minutes). Sampling was conducted by inserting a double-ended needle (Venoject[®], Terumo Europe) into the septum and collecting a sample of the chamber headspace air into a pre-evacuated 12-mL plastic vacutainer [®] (BD, UK). Sampling took place in the afternoon (between 13:00 and 15:00 hours Australian Eastern Standard Time (AEST)) at least once a month between 31 January 2009 and 2 February 2010, with the exception of August, September and October 2009. More intensive sampling was carried out over the course of a wet season rainfall event in February 2009.

Soil volumetric water content was recorded at the end of each sampling round using a hand-held Hydrosense[®] meter with a probe 0.12 m in length (Campbell Scientific). Soil water content was also determined gravimetrically for each site by oven drying a sub-sample of a composite soil sample (comprised of 6 samples per site, taken outside the

chambers) at 105°C. Soil and ambient air temperature were measured using a digital thermometer, 0.1 m in length. Atmospheric pressure at sampling times was accessed from the Australian Bureau of Meteorology (2010b).

The headspace air samples were transported back to the laboratory and analysed using a gas chromatograph (GC) (model: Shimadzu 2010) equipped with a [63]Ni electron capture detector (ECD) for N_2O and a methaniser connected to a flame ionisation detector (FID) for CO_2. The GC was fitted with Haysep T 100/120 and Carbosphere 80/100 packed columns (Alltech Associates, Deerfield, IL). Operating conditions were: column temperature 129 °C; ECD temperature 320 °C, helium carrier gas set at a flow rate of 20 mL min^{-1}, the make-up gas for the ECD was argon, set at 5 mL min^{-1}. Carbon dioxide was converted to CH_4 in the methaniser, set at a temperature of 390 °C with helium as carrier gas set at a flow rate of 20 mL min^{-1}. The FID was set at 300 °C with hydrogen as make-up gas set at a flow rate of 5 mL min^{-1}. Concentrations of N_2O and CO_2 were derived from peak areas determined by the Lab Solutions software package and based on external calibration using 5 standards (2 x replicates) of different concentrations prepared from certified standard gas mixtures.

A sample of a certified standard gas mix was analysed with each batch of 32 samples to calibrate each batch and to detect potential instrument drift. Samples of known N_2O and CO_2 concentrations were stored and concentrations measured over time to test for integrity of the vacutainer septa.

Hourly N_2O emissions (μg N_2O-N m^{-2} h^{-1}) were calculated from the slope of the linear increase in N_2O concentration for either 0 – 40 minutes or 0 – 60 minutes. In most cases the change in concentration was linear ($R^2 > 0.85$). Cases where the slope of the change in concentration presented an R^2 of < 0.85 (linear regression) were generally associated with low fluxes (< 10 μg N_2O-N m^{-2} h^{-1}). For these cases, the shortest time period was used for which flux was maximal.   Emissions were then calculated using air temperature, ambient air pressure (via the ideal gas law) and the ratio of chamber volume to surface area. The resulting emissions were reported as the mean of 6 chambers for each site on each sampling date and expressed as μg N_2O-N m^{-2} h^{-1}.

Carbon dioxide emission was also calculated as above and reported as μmol m^{-2} h^{-1}.

4.2.2 Soil water content and analysis of soil and water samples

In addition to measuring soil water content at the time of sampling, soil water content was monitored continually at 0.1 m depth at one of the high elevation gas sampling sites (T1P3) and one of the low elevation gas sampling sites (T1P2). Data from the TDR probes at T1P2 and T1P3 was used to estimate a continuous record of WFPS for the other two gas sampling sites. Values for sites T2P3 and T3P3 were estimated based on regression of manual measurements at those sites against concurrent TDR data at site T1P3 and T1P2, respectively.

Soil and groundwater samples were collected at each of the four sampling sites on each sampling date as described in Chapter 3. Soil parameters measured included NO_3-N, NH_4-N, DOC, total N, total C, temperature, pH and EC. Groundwater parameters included

NO$_3$-N, NH$_4$-N, DON, DOC, temperature, pH, EC and DO. Analytical methods for all these are described in Chapter 3.

Water filled pore space (WFPS) was calculated according to equations 4.1 and 4.2, assuming a water density of 1000 kg m^{-3} and particle density of 2527 kg m^{-3} (Chapter 2).

WFPS = (Gravimetric water content x soil bulk density)   Eq. (4.1)
                    Total soil porosity

 Porosity = 1 – (soil bulk density / particle density)   Eq. (4.2)

4.2.3 Litter manipulation study: effect on N$_2$O emissions

The effect of litter quantity on N$_2$O emission from the ground surface was assessed in a litter manipulation study in the lowlands of the Daintree rainforest. This site was selected opportunistically to optimise resources. A concurrent litter manipulation study had been established by entomologist Peter Grimbacher to evaluate invertebrate distribution in relation to differing amounts of leaf litter on the rainforest floor.   The Daintree forest site is located approximately 150 km north of the Behana Creek site on the coastal plain near Cape Tribulation (16°17′ S, 145°29′ E). The site is composed of complex mesophyll vine forest, similar to the vegetation assemblage at Behana Creek. The soil at the site is an acidic, dystrophic, Brown Dermosol (Isbell, 2002) with many (20-50%) cobbles and stones throughout the profile. The soil is developed in colluvium from the metamorphic and granitic mountains to the west. Sampling took place in January 2009 on experimental plots (3 x 3 m in size) that had been subjected to 3 treatments for the previous 4 months. Treatments were: 1) litter prevented from reaching the ground using nylon bird netting

(mesh size 20 x 20 mm) suspended above the ground, 2) litter had been added beyond the natural rate (5 monthly additions, each being 60 L plot^{-1}) and 3) litterfall had been allowed to accumulate naturally, with no manipulation. There were 6 replicates, with each replicate being a cluster of plots in a different area to account for variability in the canopy species. Two PVC chambers were placed on each of the 18 plots to measure N_2O and CO_2 emissions, as described in section 4.2.1.

Soil temperature and soil volumetric water content were recorded from inside each individual chamber at the end of the experiment, and air temperature recorded using a digital thermometer. A soil sample (0- 0.05 m depth) was taken from inside each chamber for analysis of total C and N, NO_3-N, NH_4-N and DOC concentrations using the methods described in Chapter 3.

4.2.4 N₂O concentration in soil air and in groundwater at different depths

In December 2009, during a dry period, a pit was dug at the Behana Creek site 2 m deep by 2 m long by 1 m wide at the location shown in Figure 2.2. Equipment was installed to sample soil air and groundwater at depths of 2.0, 1.5, 1.0, 0.5 and 0.1 m. The equipment consisted of soil air sampling ports, TDR and temperature probes, piezometers and ceramic suction cups (Figure 4.1).

The soil air sampling ports consisted of air-permeable membrane at the depths of interest, attached to steel tubes protruding from the soil surface. Each stainless steel tube (3 mm internal diameter) was bent over 0.05 m from the bottom end to form an "L" shape. The "L bend" was connected to an air-permeable yet hydrophobic Teflon$^{®}$ membrane, 0.1 m in

length. To better protect the membrane and to prevent it from becoming flattened under the weight of the soil, it was encased in a perforated steel tube (10 mm i.d.). A rubber septum was fitted into the top of each pipe to allow soil air samples to be extracted.
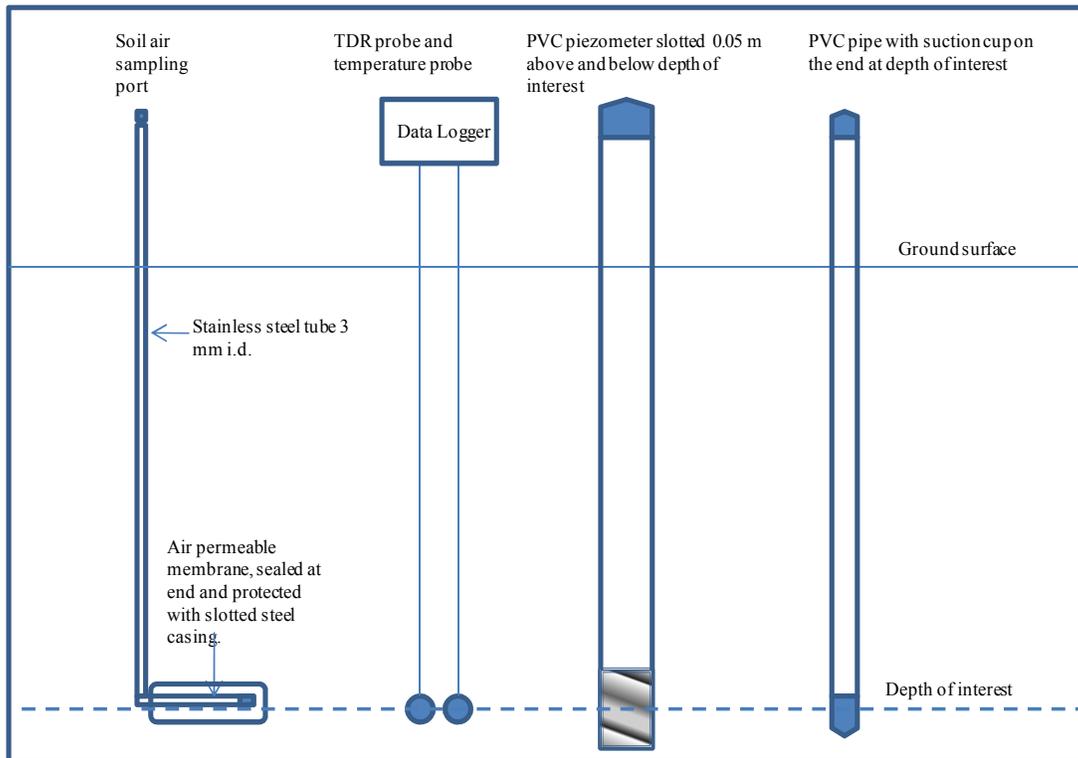
Figure 4.1. Schematic of experimental design for sampling soil air and groundwater in the soil pit at each depth of interest.

The TDR (Campbell Scientific, model: 616) and temperature probes (Campbell Scientific, model: 107) were installed at each depth, except for 1.5 m, and connected to a Campbell Scientific data logger (model: CR1000) installed 5 m above ground level to avoid floods, programmed to log every 10 minutes.

The piezometers, made of 50-mm diameter PVC pipe, slotted over the lower 0.1 m, were installed at each depth to enable measurement of depth to water table and to facilitate

groundwater sampling at the depth of interest. Depth to water table was measured manually.

The ceramic suction cups were installed at each depth to collect soil water from the unsaturated zone. They were attached to 35-mm diameter PVC pipes protruding from the soil surface. Soil water samples were collected using a manually operated suction pump.

Once the equipment had been installed, the pit was carefully back-filled to approximately the original bulk density by replacing all of the soil layer by layer. The soil in the pit was then left undisturbed to equilibrate for 6 weeks. Sampling commenced at the beginning of February 2010 and was carried out on 9 occasions over a 6-week period, leaving a minimum of 3 days between sampling. Sampling took place between 12:00 hours and 15:00 hours AEST.

Groundwater was collected using a manual bailer and decanted in two x 125-mL plastic bottles for analysis of dissolved NO_3-N, NH_4-N, DON and DOC concentrations. Bottles were stored on ice until transported to the laboratory whereupon they were frozen until analysis. Groundwater analyses were performed as described in Chapter 3. Groundwater pH, temperature and EC were measured in the field in a sample of groundwater using a TPS Aqua –CP meter and DO was measured using a Hanna 9143 probe. Another sample of groundwater was collected for analysis of dissolved N_2O. As soon as groundwater was collected, three x replicate 5-mL subsamples were carefully extracted from the bailer using an airtight syringe (Hamilton, USA), taking care not to trap air bubbles and minimizing the possibility of N_2O degassing. The 5-mL subsamples were then injected into

12-mL vacutainers [®] that had been previously flushed with N_2, equilibrated to atmospheric pressure, and from which 5 mL of N_2 had been subsequently removed.

The concentration of N_2O in soil air was measured. Soil air was sampled from all depths on each sampling event, even when the depth of interest was below the water table. Soil air was sampled directly from the sampling ports from the top of the steel pipes using a double-ended needle inserted into an evacuated 12-mL vacutainer[®]. Samples were carefully transported back to the laboratory for analysis. Soil air concentrations were analysed for N_2O using gas chromatography as described above, corrected for soil air temperature and ambient air pressure, and expressed in µg N_2O-N L^{-1} (air).

In order to measure the concentration of N_2O in groundwater, the vacutainers [®] containing groundwater samples were first shaken vigorously at 20 ^oC to equilibrate N_2O concentrations between the gas and liquid phases. The headspace was then sampled and introduced into the gas chromatograph. The total amount of N_2O dissolved in groundwater was calculated using the formula presented by Well and Myrold (1999) (Equation 4.3),

$$M = C\,(V_G + \alpha\,V_L)$$ Eq. (4.3)

in which M is the total volume of N_2O (in µL), C is its concentration in the gas phase (in µL L^{-1}), α is the Bunsen coefficient for N_2O at 20^oC at low salinity (0.632 L L^{-1}, Tiedje, 1994) and V_G and V_L are the respective volumes of gas and liquid inside the sample container. Concentrations of N_2O in groundwater are expressed in µg N_2O-N L^{-1} (water). The concentration of N_2O dissolved in soil water was not measured since the extraction method was conducive to degassing.

4.2.5 Laboratory study: Potential denitrification rates and N₂O reduction capacity of the soils

Soil samples were collected from two depths (0 - 0.1 m and 0.45- 0.55 m) from each of the four gas sampling sites (T1P2, T1P3, T2P3 and T3P3) at the Behana Creek riparian zone in the dry season, in July 2009. Each sample was a composite of 6 samples taken from each site and depth within an area of 1 x 1 m². Soil samples at field water content, equivalent to 50 g of dry soil, were sieved through 5 mm mesh and placed into 565-mL flasks for incubation. For both incubation experiments (potential denitrification and N₂O reduction capacity) all treatments had three replicate flasks, all under anaerobic conditions. Anaerobic conditions were produced by removing air from the flasks using a vacuum pump and replacing it with N₂. This procedure was performed three times in succession to ensure a completely anaerobic environment inside the flasks. No C was added in either experiment, thus natural soil organic matter was the only supply of C for all soils.

Sub samples of the soils were analysed for total C and total N content. The samples were homogenised, ground and dried and then analysed on a Costech elemental combustion system (model: ECS 4010). Results were presented on the basis of oven-dry equivalent weight. Soil pH was measured in a 1:5 soil: water suspension in the laboratory using a TPS Lab Chem pH meter.

The potential denitrification rate of the soils, and their capacity to reduce N₂O, were tested using the methods described by Hénault *et al.* (1998) and Hénault *et al.* (2001). These methods were derived from Tiedje (1982) and Blackmer and Bremner (1978). Potential denitrification was measured by incubating the soil with water and NO_3^- added to all flasks

(50 mL of KNO_3 solution with 100 mg N L^{-1}). The NO_3^- was to serve as an electron acceptor. To half of the sample flasks acetylene (10 mL, approximately 2% of flask volume) was added and to the other half no acetylene was added. The difference in N_2O production between the flasks with and without acetylene was taken to represent N_2 production. Under these experimental conditions N_2O from nitrification was assumed to be negligible given the anaerobic atmosphere, however there is also potential for underestimation of N_2O due to ineffective inhibition of N_2O reduction or inhibition of the earlier reduction step between NO and N_2O.

The N_2O reduction capacity of the soils was measured by incubating 50 g dry soil with 50 mL of water and adding 5 mL of N_2O to each flask. The reduction in N_2O concentration was measured over time in all flasks. In this experiment N_2O served as an electron acceptor. To half of the flasks acetylene was added (10 mL, approximately 2% of flask volume) and to the other half no acetylene was added. The difference between these two treatments enabled the calculation of a soil's potential to reduce N_2O to N_2.

For both incubation experiments, flasks were placed in an oscillating shaker (120 rpm) at 20°C for 8 days. The flask atmosphere was sampled at 0, 24, 48, 72, 144 and 192 hours using 3-mL Terumo vacutainers®. Samples were analysed for N_2O using an MTI P200 gas chromatograph equipped with a thermal conductivity detector, (Microsensor Technology Inc., Fremont, CA, USA) and Porapak Q capilliary column. Oven and detector temperatures were set at 60°C. Dissolved N_2O in the slurries was accounted for by applying Henry's Law (Moraghan and Buresh, 1977).

Potential denitrification and N_2O reduction rates were calculated from the change in N_2O concentration in the flask over time. Potential denitrification rate ($N_2O + N_2$) and N_2O production rates were calculated from the slope of the line of the N_2O concentration versus time in flasks with or without added acetylene, respectively. The rate of N_2 production was taken as the difference between the N_2O+N_2 and N_2O production rates. The rates were calculated for the first 72 hours of the incubation, as constant production rates during this period indicated that no limitations to production had been induced. In most samples that period corresponded to the maximum rate of denitrification, except in the cases of the subsoil from sites T2P3 and T3P3. The N_2O reduction capacity was calculated as the difference between the N_2O concentration decline over time in the flasks with added acetylene and that in the flasks with no added acetylene, expressed as a positive value. The time period used for the calculation was that in which the potential N_2O reduction rate was greatest. That was at either 48-72 hours or 72-144 hours in all samples.

4.2.6 Statistical analyses

Preliminary analyses were conducted to ensure against violation of the assumptions of normality, linearity, multicollinearity and homoscedasticity. N_2O and CO_2 emission data from field chamber measurements were log transformed to obtain a normal distribution. The following soil and groundwater variables were also log transformed using natural log (ln): soil NH_4-N and NO_3- N concentrations, soil temperature, groundwater DOC and DO concentrations.

T tests and ANOVA were performed on individual chamber data to test for differences in mean N_2O emissions and WFPS between seasons, sites and elevation (high versus low

position in the landscape) from the Behana Creek site. Correlation analysis was employed to determine relationships between N_2O emissions, soil and groundwater variables and CO_2 emissions (using the means of 6 replicates per site). Multiple linear regression was performed to determine which variables best predicted N_2O emissions.

For the litter manipulation experiment from the Daintree forest site, ANOVA was used to determine the effects of the treatments on measured variables and correlation analysis was used to determine relationships between N_2O emissions and soil properties. Nitrous oxide emission data, together with soil total C and soil total N data, were log transformed (ln) to obtain a normal distribution.

For the N_2O-at-depth experiment conducted in the soil pit, correlation analysis was used to determine relationships between concentration of N_2O in soil air and dissolved in groundwater and measured groundwater parameters.

For the laboratory incubation experiment, ANOVA was employed to test for the effect of site elevation (high or low) and soil depth (0-0.1 m and 0.45- 0.55 m) on rates of N_2O production.

4.3   Results

4.3.1 N₂O emissions from soil surface

Nitrous oxide emissions from individual chambers were highly variable, ranging from -24 to 657 µg N_2O-N m^{-2} h^{-1} (Figure 4.2).
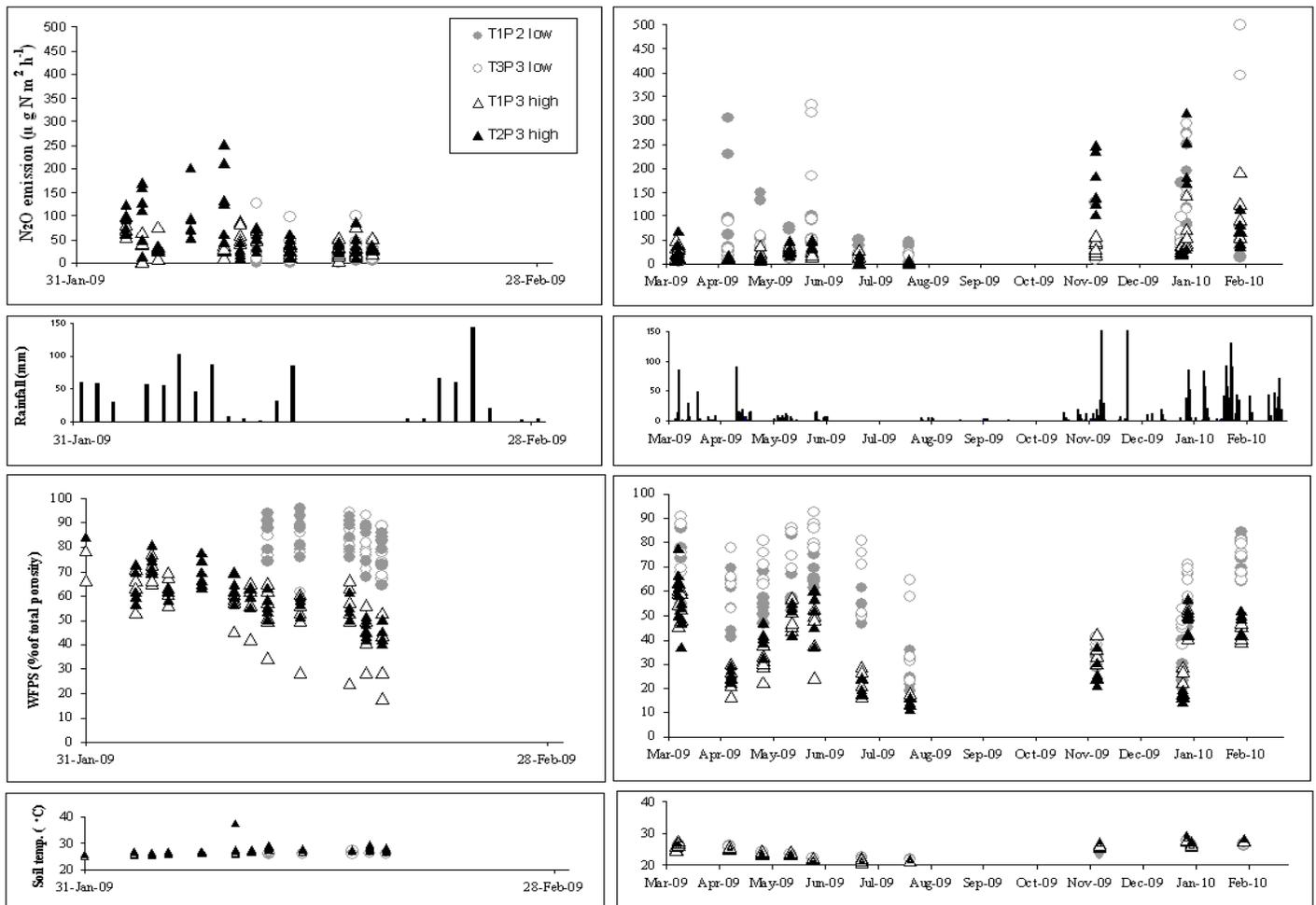
Figure 4.2. N_2O emissions and water filled pore space (WFPS) calculated from manual measurements for individual chambers from January 2009 to February 2010, daily rainfall at Behana Creek and mean soil temperature for each site measured at time of gas sampling.

No sampling occurred between August and October 2009. Two graphs are shown for each parameter so that results for the first month, with high frequency sampling, and subsequent months, with low frequency sampling, can both be displayed clearly.

Table 4.1 Summary of N$_2$O emissions at each site based on values from individual chambers for dry and wet seasons.Coefficient of variation (Cv) was calculated from all values, including negative fluxes.

	Low		High	
	T1P2	T3P3	T2P3	T1P3
Wet season				
Range (μ g N m^{-2} h^{-1})	1 - 305	5 - 657	8 - 507	2 - 192
Mean (μ g N m^{-2} h^{-1})	52	80	65	41
Cv (%)	128	164	112	69
Dry season				
Range (μ g N m^{-2} h^{-1})	-1 - 50	4 - 23	0 - 22	-24 - 30
Mean (μ g N m^{-2} h^{-1})	26	15.6	5.6	3.2
Cv (%)	78	38	120	383

Coefficients of variation (Cv) for N$_2$O emissions for each site were large, ranging between 38 and 383 % for the dry season and 69 and 164 % for the wet season (Table 4.1). The low site T3P3 showed the largest range of N$_2$O emissions in the wet season, from 5 to 657 μg N$_2$O-N m^{-2} h^{-1} (Cv 164%). The site with the lowest mean N$_2$O emission in the dry season, high site T1P3, exhibited the highest variability (Cv 388%). This is likely due to one large negative value of -24 μg N$_2$O-N m^{-2} h^{-1} in June 2009.

Based on all chambers, N$_2$O emissions were higher in the wet season than in the dry season (p<0.001) with the highest emissions occurring in January and February 2010. Emissions in the wet season reached a maximum of 657 μg N$_2$O-N m^{-2} h^{-1} in one individual chamber, whereas dry season emissions reached a maximum of 50 μg N$_2$O-N m^{-2} h^{-1}.

The overall mean emission from the measurements was 54 µg N_2O-N m^{-2} h^{-1}. This, however, is biased towards wet season emissions as more sampling was undertaken in the wet season than the dry. By multiplying the mean emission by the number of hours in one year, a total of 4.65 kg N ha^{-1} y^{-1} would be lost as N_2O. Mean wet and dry season emissions were 58 and 14 µg N_2O-N m^{-2} h^{-1} respectively. Based on seasonal mean emissions and assuming 6 months for each season, the overall loss of N_2O-N from the riparian forest amounts to 2.98 kg N ha^{-1} y^{-1}.

There was no significant difference between emissions from high and low sites when considering the entire data set. However, by further dividing the data into wet and dry seasons, N_2O emissions were higher ($p<0.001$) at the low sites than the high sites during the dry season. No significant difference in N_2O emissions was observed between high and low sites during the wet season.

Water filled pore space was consistently higher at low elevation sites (mean 65 %) than it was at the high elevation sites (mean 47 %) ($p<0.001$) based on manual measurements at the time of sampling. Water was slower to drain at topographic lows and the water table was closer to the ground surface. Mean N_2O emissions were higher where WFPS was >60% (67 µg N_2O-N m^{-2} h^{-1}), than where WFPS was <60% (45 µg N_2O-N m^{-2} h^{-1}). However, some degree of N_2O emission was observed across the spectrum of WFPS, which ranged from 11 to 99% based on individual manual chamber measurements. Soil temperature, measured manually at the time of sampling for N_2O, ranged between 20 and 30°C, with the exception of one high reading (37°C) at high site T2P3 over the study

period. There was no apparent correlation between this high temperature from one individual chamber and the corresponding N_2O emissions.

Over the period 19 March 2009 to 28 February 2010, mean WFPS measurements (per site) fluctuated between ~45 and 80 % at low elevation sites and between 15 and 75 % WFPS at the high elevation sites (Figure 4.3).
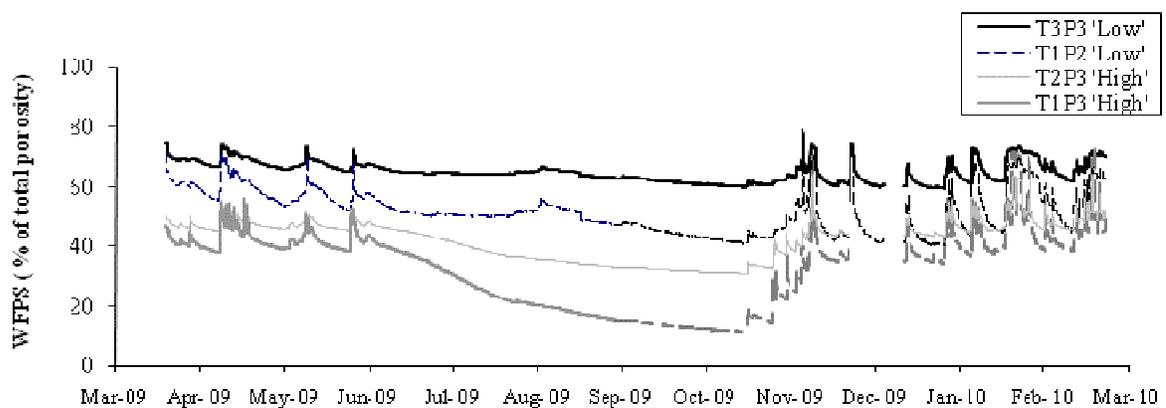
Figure 4.3. Water filled pore space (WFPS) in soil (0.1 m depth) at the 4 gas sampling sites.

Nitrous oxide emissions were highly correlated with CO_2 emissions (Table 4.2). Similarly, although to a lesser degree, soil temperature and soil DOC concentrations were both significantly, positively correlated with N_2O emissions. Nitrate concentrations in groundwater showed a significant, positive correlation with N_2O emissions, but concentrations of soil NO_3^- were not significantly correlated with N_2O emissions. Concentrations of NH_4^+ in either soil or groundwater did not correlate significantly with N_2O fluxes. Similarly, there was little relationship between soil or groundwater pH and N_2O emissions over the study period.

Table 4.2. Relationship between N2O emissions and soil and groundwater (Gw) parameters over the study period (Pearson's Product Moment Correlation). Ln indicates log transformed data.

	CO_2 (Ln)	WFPS	Soil temp. (Ln)	Soil pH	Soil NO_3-N (Ln)	Soil NH_4-N (Ln)	Soil DOC	Gw DOC (Ln)	Gw NO_3-N (Ln)	Gw NH_4-N (Ln)	Gw DO (Ln)
N_2O (Ln)	0.713[**]	0.206	0.362[**]	0.178	-0.181	0.139	0.331[**]	-0.006	0.244[*]	-0.177	0.048

[**]Correlation is significant at the 0.01 level (2-tailed)
[*] Correlation is significant at the 0.05 level (2-tailed).

A review of the relationship between soil DIN species and N_2O emissions for each season revealed that these relationships were stronger in the dry season. The relationship between soil NH_4^+ concentrations and N_2O emissions became significant (r=-0.759, p=0.029), suggesting nitrification in top soil layers was a likely source of N_2O emissions during the dry months.

A significant model emerged from the multiple regression analysis performed using natural log transformed N_2O emissions (mean of 6 chambers) as the dependent variable ($F_{4,73}$ =28.47, $p < 0.001$), producing an R^2 of 0.609 (Table 4.3). In this model, mean CO_2 emissions were considered as an independent variable as were other soil and groundwater parameters.

Table 4.3. Results from multiple linear regression analysis using log transformed N_2O emission as the dependent variable and including log transformed (ln) CO_2 emissions amongst the independent variables. Only variables that produced a significant, unique contribution are shown.

Predictor variable	Beta	p value
CO_2 emission (ln)	0.742	< 0.001
Soil WFPS	0.265	0.001
Soil DOC content	0.224	0.010

The resulting model may be stated as

N_2O (ln) = 7.103 + 1.303 CO_2 (ln) + 0.014 WFPS +0.017 soil DOC   Eq. (4.4)

where N_2O is N_2O emission in μg N_2O-N m^{-2} h^{-1}, CO_2 is CO_2 emission in μmol m^{-2} h^{-1}, WFPS is in % and soil DOC is in mg kg^{-1}.

In this model CO_2 emissions made the highest significant, unique, contribution to the prediction of the magnitude of N_2O emissions although lesser, unique contributions to predicting N_2O emissions were made by WFPS and soil DOC content. Nitrous oxide emissions were plotted against CO_2 emissions and WFPS (Figure 4.4) highlighting the trend that N_2O emissions were generally higher where WFPS was >60%.
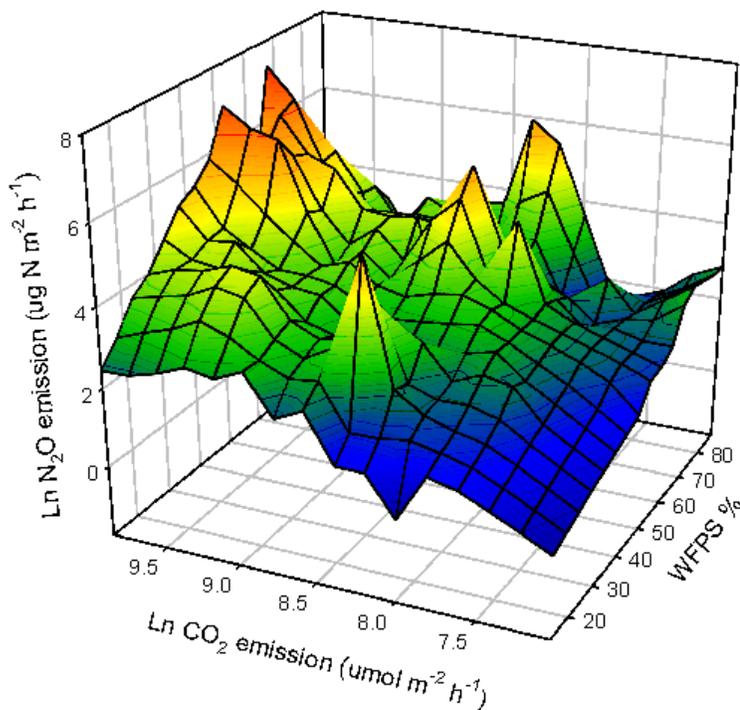
Figure 4.4. Relationship between N_2O (ln) emissions, CO_2 (ln) emissions and soil water filled pore space (WFPS).

The regression model was re-run to include easily measurable field parameters only, this time excluding mean CO_2 emissions (Table 4.4). Without CO_2, the R^2 was reduced to 0.307. The same parameters, i.e. soil DOC and soil water content, emerged as the best predictors of N_2O emissions, together with soil temperature (all measured in the top 0.1 m of soil). Dissolved organic C from the 0-0.1 m soil layer had the greatest influence over N_2O emissions (Beta =0.452) compared to soil temperature and soil water content (Beta values 0.275 and 0.261 respectively) (Table 4.4). According to these models, groundwater parameters did not make significant contributions to N_2O emissions from the forested riparian zone.

Table 4.4. Results from multiple regression analysis using log transformed N_2O emission data as the dependent variable, excluding CO_2 emission data. Only variables that produced a significant, unique contribution are shown.

Predictor variable	Beta	p value
Soil temperature (ln)	0.275	0.024
Soil DOC content	0.452	<0.001
Soil WFPS	0.261	0.020

4.3.2 Litter manipulation study: effect on N_2O emissions

Nitrous oxide emissions at the Daintree forest site ranged between 3 and 80 µg N_2O-N m^{-2} h^{-1} across all litter treatments, with a mean of 18 µg N_2O-N m^{-2} h^{-1} (Figure 4.5, Table 4.5). No significant difference in N_2O emissions was observed between litter treatments (p=0.648). Water filled pore space varied throughout the litterfall experiment site, ranging from 25 to 52%, with a mean of 35% (Table 4.5), and there was no significant difference in WFPS between treatments (p=0.383). Water filled pore space was low, considering that a total of approximately 800 mm rain had fallen in the area over the three weeks prior to

sampling, showing that the soil (or at least the top 0.05 m) was well drained.   Soil total C

and total N contents were significantly lower in the litter excluded treatment than the other

treatments (Table 4.5) but, overall, there was no significant relationship between N_2O

emissions and measured soil parameters (Table 4.6).
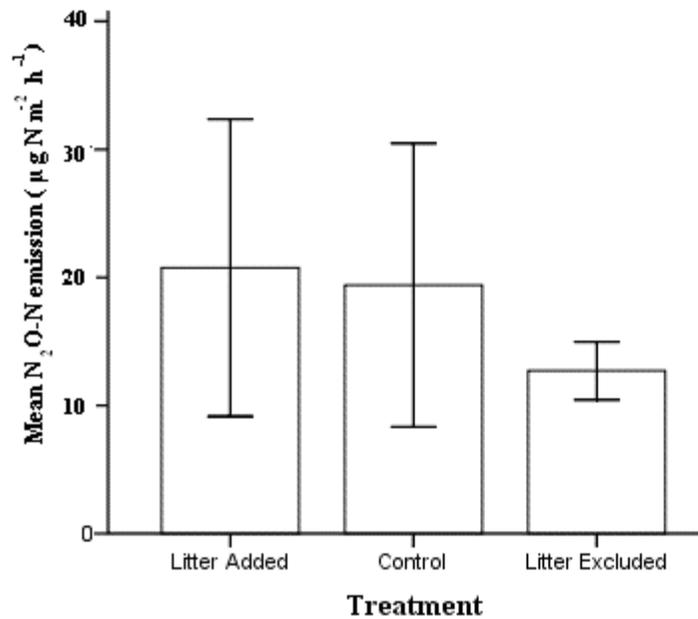
**Figure 4.5. Nitrous oxide emissions from litter manipulation treatments at the Daintree forest.
Error bars represent 2 standard errors of the mean.**

Table 4.5. Summary of mean N_2O emissions and measured soil parameters for manipulated litter treatments at the Daintree forest site. (p values represent results of ANOVA comparing differences between treatments).

	Litter added	(SE)	Control	(SE)	Litter excluded	(SE)	p value
N_2O (μ g N m^{-2} h^{-1})	20.76	(5.80)	19.40	(5.54)	12.71	(3.90)	0.422
WFPS (%)	32.79	(1.37)	36.77	(2.84)	34.48	(1.61)	0.383
Soil NH_4-N (mg kg^{-1})	7.26	(1.48)	9.82	(3.21)	4.18	(1.55)	0.200
Soil NO_3-N (mg kg^{-1})	7.33	(0.63)	7.55	(1.52)	6.41	(0.42)	0.660
Soil DOC (mg kg^{-1})	71.95	(12.37)	104.65	(39.39)	91.60	(40.10)	0.781
C:N	17.86	(0.43)	19.19	(0.62)	17.86	(0.25)	0.031
Total C (%)	5.75	(0.57)	6.36	(0.85)	4.44	(0.26)	0.048
Total N (%)	0.32	(0.03)	0.33	(0.04)	0.25	(0.01)	0.042
pH	5.51	(0.05)	5.40	(0.10)	5.37	(0.09)	0.495
EC (μS cm^{-1})	41.32	(3.73)	39.85	(3.22)	34.95	(3.64)	0.414

Table 4.6. Relationship between N_2O emissions (log transformed) and soil parameters for the litter manipulation experiment at the Daintree forest (Pearson's Product Moment Correlation). None of the correlations were significant at the 0.05 level.

	WFPS	Soil total N (Ln)	Soil total C (Ln)	Soil NH_4-N	Soil NO_3-N	Soil pH	Soil EC	Soil DOC	Soil Temp.
N_2O (Ln)	0.130	0.087	-0.065	-0.283	0.034	-0.019	-0.160	-0.147	-0.024

4.3.3 Depth profile of N_2O concentration

Profiles of N_2O concentration with depth indicated that N_2O production was not limited to the surface soil. Concentrations of N_2O in soil air ranged from 0.7 to 156.7 μg N_2O-N L^{-1} (Figure 4.6), and were always greater than concentrations measured just above the soil

surface at time zero of surface emission measurements (minimum 0.3 μg N_2O-N L^{-1}).   In the unsaturated zone, soil air N_2O concentrations generally increased with depth, forming an upward diffusion gradient towards the soil surface. The highest values were observed at 1.0 m depth, mean 110.7 μg N_2O-N L^{-1} (Table 4.7). This is reflected in the negative, significant correlation between soil air N_2O concentrations and the distance to the water table from the depth of gas sampling (r=-0.466 p=0.001, Table 4.8).   During times of no rainfall (e.g. between 2 March and 9 March 2010), N_2O concentrations in soil air clearly diminished over time, most notably in the shallower layers (Figure 4.6), suggesting N_2O is lost faster than it is produced during dry periods. Loss may consist of emission of N_2O to the atmosphere or consumption of N_2O and subsequent conversion to N_2. There was no significant relationship between N_2O concentrations in soil air and corresponding soil water content or temperature measured within the unsaturated zone (Table 4.8).   It is assumed that N_2O in soil air detected at depths beneath the water table is from either 1) N_2O in entrapped soil air bubbles in the quasi-saturated zone, or, 2) from the diffusion of N_2O dissolved in groundwater through the hydrophobic membrane, or 3) remnant N_2O in the steel pipe having not yet diffused back into the soil/groundwater. Concentrations of N_2O dissolved in groundwater were generally higher than those in soil air beneath the water table at the corresponding depth. Exceptions occurred on 17 March and 9 April 2010 when the water table had risen to around 0.5 m depth (Figure 4.6).
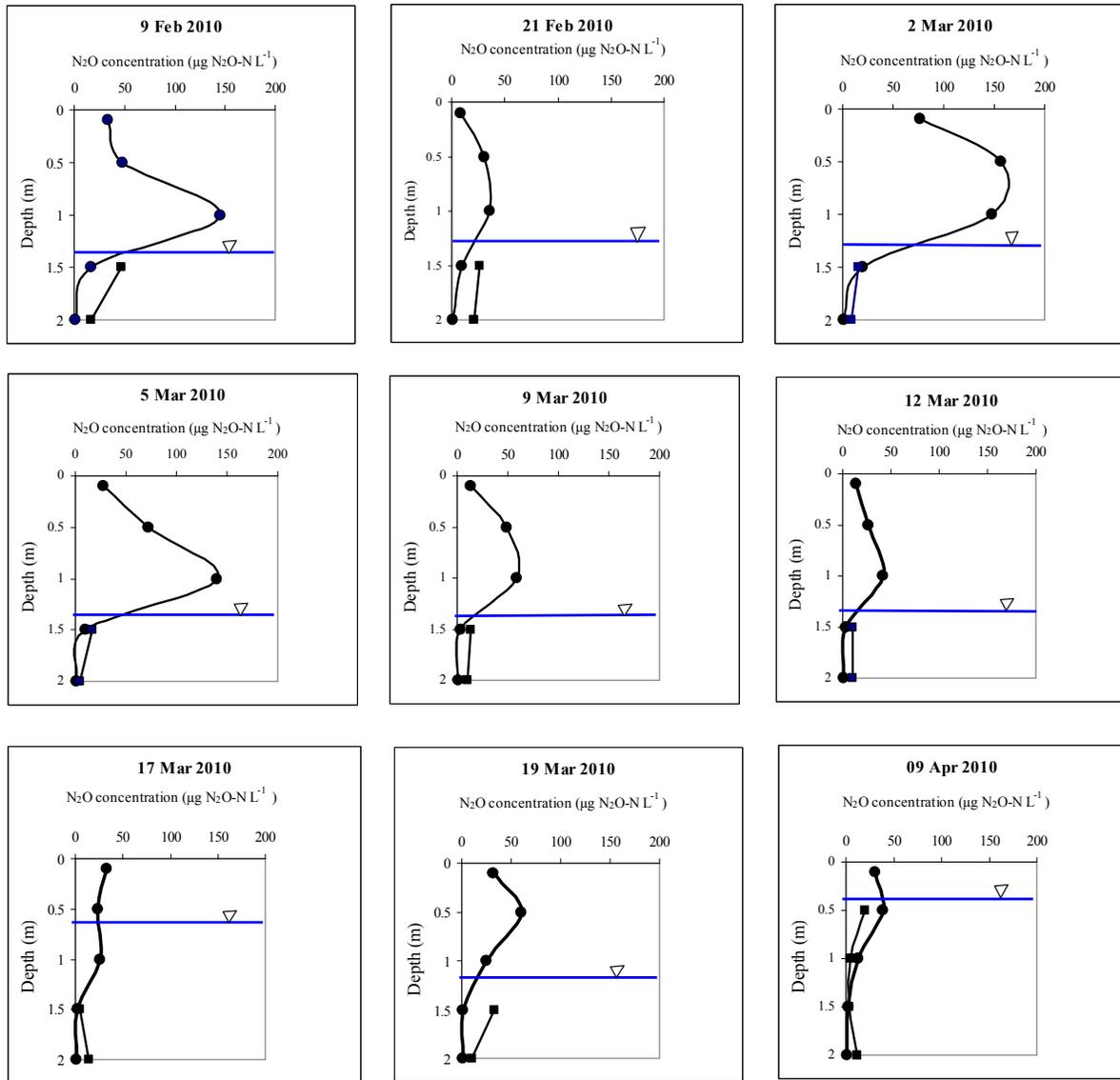
Figure 4.6. Concentrations of N₂O in soil air (circles, in µg N₂O-N L⁻¹ air) in the unsaturated zone and N₂O dissolved in groundwater (squares, in µg N₂O-N L⁻¹ water).
Triangle represents water table level at the time of sampling.
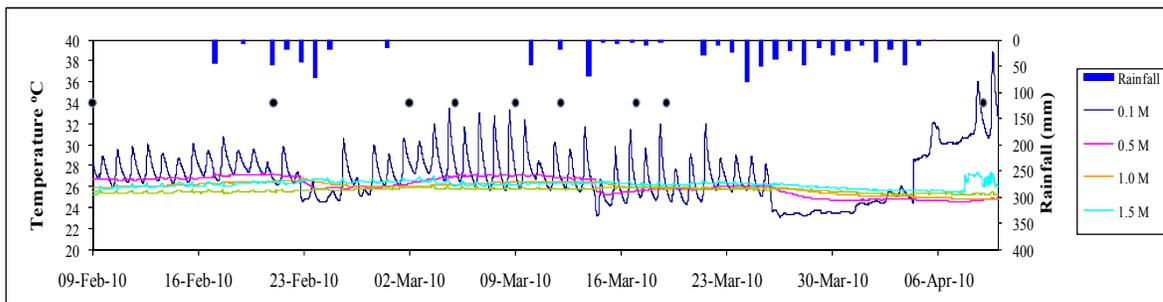
Figure 4.7. Rainfall (daily) and soil temperature at the soil pit during the N₂O depth profile experiment. Circles represent sampling dates.

Table 4.7. Mean values of soil and groundwater (Gw) parameters measured in the soil pit between 9 February and 9 April 2010. 'Gw' parameters corresponding to 0.1 m depth (in bold) are from soil water rather than groundwater. Asterisk denotes n=1.

	Depth (m)									
	0.1	(SE)	**0.5**	(SE)	**1.0**	(SE)	**1.5**	(SE)	**2.0**	(SE)
Soil water content (m^3 m^{-3})	0.34	(0.01)	0.30	(0.01)	0.40	(0.00)	NA	NA	0.36	(0.00)
Soil temp. ($^{\circ}$C)	28.35	(0.71)	26.38	(0.25)	26.0	(0.17)	26.4	(0.08)	25.8	(0.07)
Conc. N$_2$O-N (µg L^{-1} in soil air)	47.26	(10.51)	88.44	(21.34)	110.7	(29.70)	12.2	(3.70)	1.3	(0.06)
Conc. N$_2$O-N (µg L^{-1} in water)			30.78*	(0.00)	18.84	(10.67)	29.71	(7.44)	18.72	(1.81)
Gw NH$_4$-N (mg L^{-1})	**0.06**	**(0.02)**			0.04	(0.01)	0.09	(0.03)	0.24	(0.03)
Gw NO$_3$-N (mg L^{-1})	**1.04**	**(0.93)**			2.30	(2.22)	1.12	(0.45)	1.37	(0.18)
Gw DON (mg L^{-1})	**0.72**	**(0.40)**			0.40	(0.15)	0.55	(0.13)	0.63	(0.10)
Gw DOC (mg L^{-1})	**21.65**	**(16.15)**			3.70	(0.80)	5.29	(0.72)	5.57	(0.54)
Gw pH					4.92	(0.12)	5.62	(0.03)	5.62	(0.04)
Gw EC (µScm^{-1})					82.50	(20.50)	133.10	(6.77)	157.70	(13.67)
Gw DO (% Sat.)					34.00	(6.00)	24.81	(3.57)	20.09	(2.20)

Table 4.8. Relationship between N$_2$O-N concentrations in soil air and other parameters at the corresponding depth (Pearson's Product Moment Correlation).

	Gw N$_2$O-N	Soil temp.	Soil water content	Distance to water table
Soil air N$_2$O-N	0.336	0.063	-0.202	-0.466**

**. Correlation is significant at the 0.001 level (2-tailed).

Table 4.9.   Relationship between concentrations of dissolved N$_2$O-N in groundwater and other parameters at the corresponding depth (Pearson's Product Moment Correlation).

	Gw NH$_4$-N	Gw NO$_3$-N	Gw DO	Soil temp.	Gw DOC	Gw pH	Gw EC	Distance to water table
Gw N$_2$O-N	0.041	0.511*	0.465*	0.062	0.117	0.164	0.332	-0.437*

*. Correlation is significant at the 0.05 level (2-tailed).

Concentrations of N$_2$O dissolved in groundwater were related to the water chemistry and distance from the water table. Nitrous oxide concentrations ranged from 3.2 to 47.2 μg N$_2$O-N L^{-1} (Figure 4.6). The highest concentrations were generally closest to the water table, hence the significant, inverse relationship between dissolved N$_2$O concentrations and distance to the water table (r= -0.437, p=0.047, Table 4.9). Dissolved N$_2$O concentrations showed a significant, positive relationship with both DO and groundwater NO$_3$$^-$ concentrations.   Both DO and NO$_3$$^-$ concentrations tended to increase directly after rainfall, suggesting temporary oxygenation of groundwater by percolating rainwater and displacement of NO$_3$$^-$ from the unsaturated zone to the saturated zone at this time. Nitrate concentrations in groundwater were consistently highest at 1.0 m depth. The highest concentration (8.27 mg NO$_3$-N L^{-1}) was observed on 17 March at 1.0 m depth. This was measured after the water table had risen in response to approximately 80 mm of in situ rainfall over the two days prior to sampling, suggesting the addition of NO$_3$$^-$ to groundwater from the overlying unsaturated zone as a result of deep drainage.

Nitrate concentrations in soil water at 0.1 m depth (on all days when samples could be extracted) were lower than NO$_3$$^-$ concentrations in groundwater. (On days when the soil

was too dry, and soil water could not be extracted, NO_3^- may have accumulated in the soil and concentrations may have increased). Concentrations of DOC, on the other hand, were substantially higher in soil water than in groundwater (Table 4.7). Concentrations of DOC in groundwater ranged from 1.8 to 10.3 mg L^{-1} over all depths. The mass ratio of DOC: NO_3-N was generally > 1.2. The exception to this was at 1.0 m depth on four occasions when groundwater NO_3^- concentrations increased after periods of rainfall. Groundwater pH ranged between 4.6 and 5.9, increasing with depth.

There was no significant relationship between dissolved N_2O concentrations and soil temperature in the (quasi) saturated zone (Table 4.9). Soil temperature in the unsaturated zone in the near-surface layer (0.1 m depth) ranged between 23.2 and 35.7 ^{o}C between 9 February and 9 April 2010 (Figure 4.7). Diurnal temperature fluctuation was clearly identifiable in near-surface soils as was temperature decrease in response to rainfall. Highest temperatures were recorded daily at ~15.00 hours AEST in near-surface soils with the lowest temperatures recorded at ~09.00 hours AEST over the measured period. During periods of no rainfall, temperature in the near-surface soil fluctuated by up to 7.5^{o}C within a 24-hour period. At 0.5 and 1.0 m depths, diurnal fluctuation was minimal (< 0.1 ^{o}C). At depths consistently below the water table, at 1.5 and 2.0 m, temperature fluctuated up to 0.5 ^{o}C within a day during periods without rain. At these depths, maximum temperatures peaked earlier than in near-surface soils, at around 12.00 hours midday AEST. Minimum temperatures, on the other hand, were observed at night, between 22:00 hours and midnight AEST, different to near-surface soils. Direct sunlight accessed the pit location daily between (approximately) 13.00 hours and 15.00 hours AEST during the measuring period (personal observation), through an opening in the canopy. A large rise in near-surface soil

temperature was observed towards the end of the monitoring period, rising 7.9 $^{\circ}$C between 4 April and 9 April 2010 (Figure 4.7). Mean daily ambient temperature corresponding to this period rose only by 3.2 $^{\circ}$C (Australian Bureau of Meteorology, 2010b). No disturbance (e.g. treefall or interference with temperature probes) was noted at the site. It was thus unclear as to why this relatively sharp rise in temperature was recorded. Despite the rise in temperature in near-surface soil at this time, a corresponding rise in N_2O concentration in soil air at 0.1 m depth was not observed, although higher temperatures would be conducive to higher rates of diffusion as well as higher rates of microbial activity.

4.3.4 Laboratory study: Potential denitrification rates and N₂O reduction capacity of the soil

The soils used in this experiment were from two landscape positions and two depths. Soil properties did not differ much between landscape positions, but the shallower soil had higher C and N contents and higher pH than the deeper soil (Table 4.10).

Table 4.10. Characteristics of soil samples used in laboratory experiments.

Depth	Soil parameter	Low		High	
		T1P2	T3P3	T1P3	T2P3
0- 0.1 m	Total C (%)	5.57	4.36	6.27	4.79
	Total N (%)	0.38	0.26	0.39	0.35
	C:N ratio	14.66	16.77	16.08	13.69
	pH	5.10	5.33	5.27	5.29
0.45- 0.55 m	Total C (%)	1.00	0.91	1.06	0.73
	Total N (%)	0.07	0.05	0.08	0.03
	C:N ratio	14.29	18.20	13.25	24.33
	pH	4.45	5.05	4.98	5.10

The mean potential denitrification rate was approximately 20 times higher in surface soils than it was in deeper soils; 1.22 versus 0.06 μg N_2O-N g^{-1} soil h^{-1} based on measurements over 72 hours (Figure 4.8). Surface soils from low sites displayed a fairly constant rate of denitrification over approximately 192 hours, mostly producing N_2O. However, soils from low site T1P2 started reducing N_2O to N_2 after approximately 72 hours. Nitrate-N would have become limiting after about 100 hours in these soils (based on the amount of NO_3^- added). Nitrate-N supply in the surface soils at low site T3P3, on the other hand, would have been non-limiting for at least 170 hours. Surface soils at the low elevation sites showed potential denitrification rates of 0.9 and 0.7 μg N_2O -N g^{-1} soil h^{-1} for T1P2 and T3P3 respectively for the first 72 hours.   The potential denitrification rate over the first 72 hours for surface soils at high locations, on the other hand, was higher at 1.8 and 1.6 μg N_2O -N g^{-1} soil h^{-1} for T1P3 and T2P3 respectively.

In the consumption experiment (Figure 4.9), surface soils at low locations showed a lag phase of approximately 72 hours before rapid consumption of N_2O commenced. N_2O consumption rates for the 72 -144 hour period were of 1.1 and 0.7 μg N_2O -N g^{-1} soil h^{-1} for low sites T1P2 and T3P3 respectively. The N_2O reduction rate was faster in soils from high sites. Between 72 and 144 hours reduction rates were 3.4 and 3.5 μg N_2O -N g^{-1} soil h^{-1} for high sites T1P3 and T2P3 respectively. As demonstrated in the denitrification potential experiment, surface soils at both high sites showed exclusive N_2O production for the first 72 hours (Figure 4.8). After that, added NO_3^- would have been consumed, and all of the N_2O that had been previously produced became rapidly consumed in these soils. This suggests that, under strictly anaerobic conditions, and once NO_3^- becomes limiting, surface soils have the capacity to reduce N_2O to N_2.

Denitrification potential results for deeper soils at low site T1P2 differed from those of other deeper soils. During the first half of the incubation the denitrification rate of soils from T1P2 was fairly constant (0.17 µg N_2O -N g^{-1} soil h^{-1} for the first 72 hours) but started to slow down, presumably as something, other than nitrate, became limiting. Approximately half of the gas produced was attributed to N_2. All other deeper soils produced N_2O only. The potential denitrification rate from other deep soils was slower (mean 0.03 µg N_2O -N g^{-1} soil h^{-1} for the first 72 hours) but tended to accelerate over the incubation period. Results from the N_2O consumption experiment for deeper soils, on the other hand, indicated a much lower N_2O reduction rate (mean rate of 0.31 µg N_2O -N g^{-1} soil h^{-1}) than was observed in surface soils. Also, the N_2O reduction rate in subsoils was slightly greater in soils from the low sites compared to the high sites, which was the opposite case to surface soils.

Under strictly anaerobic conditions and with a non-limiting supply of NO_3^-, the denitrification rate appears to relate to total organic C content. Topsoils had higher Total C content than subsoils and higher denitrification rates. Under these conditions the product of denitrification was exclusively N_2O, except for site T1P2 in which N_2 made a significant contribution both in surface soils and at depth. T1P2 also had the lowest pH which may be related to the ratio of $N_2O{:}N_2$ produced. Under strictly anaerobic conditions, the N_2O reducing capacity of the soils also appeared related to total organic C content, with topsoils showing much greater N_2O reducing capacity than subsoils (Figure 4.9).

Movement of nitrogen through a riparian forest in a tropical, agricultural landscape.
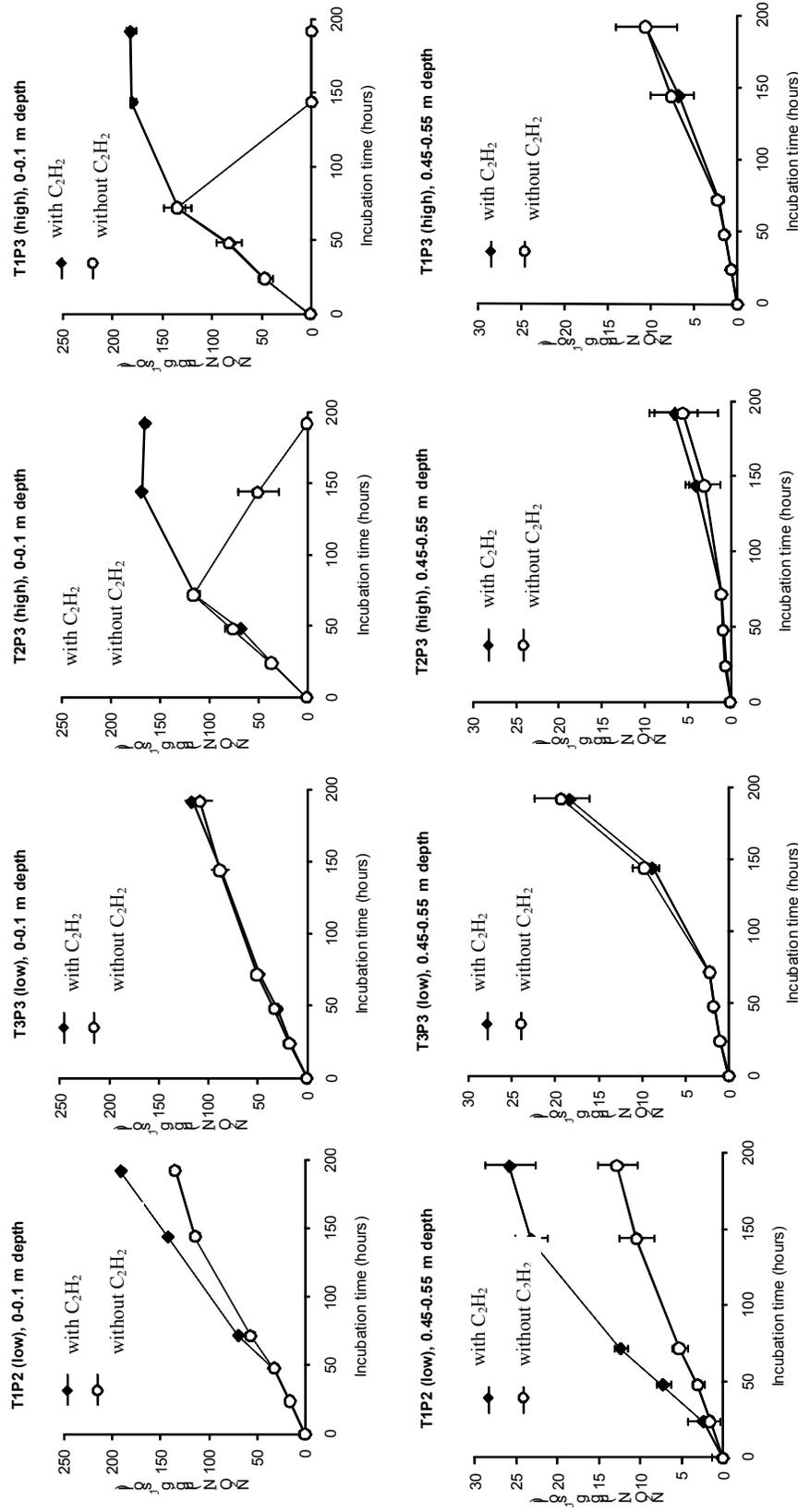
Figure 4.8. Production of N_2O in slurries of soil from four locations incubated under anaerobic conditions with added NO_3^- (potential denitrification). Points are the mean of 3 replicates and error bars show the standard deviation.

Sarah Connor

Movement of nitrogen through a riparian forest in a tropical, agricultural landscape.
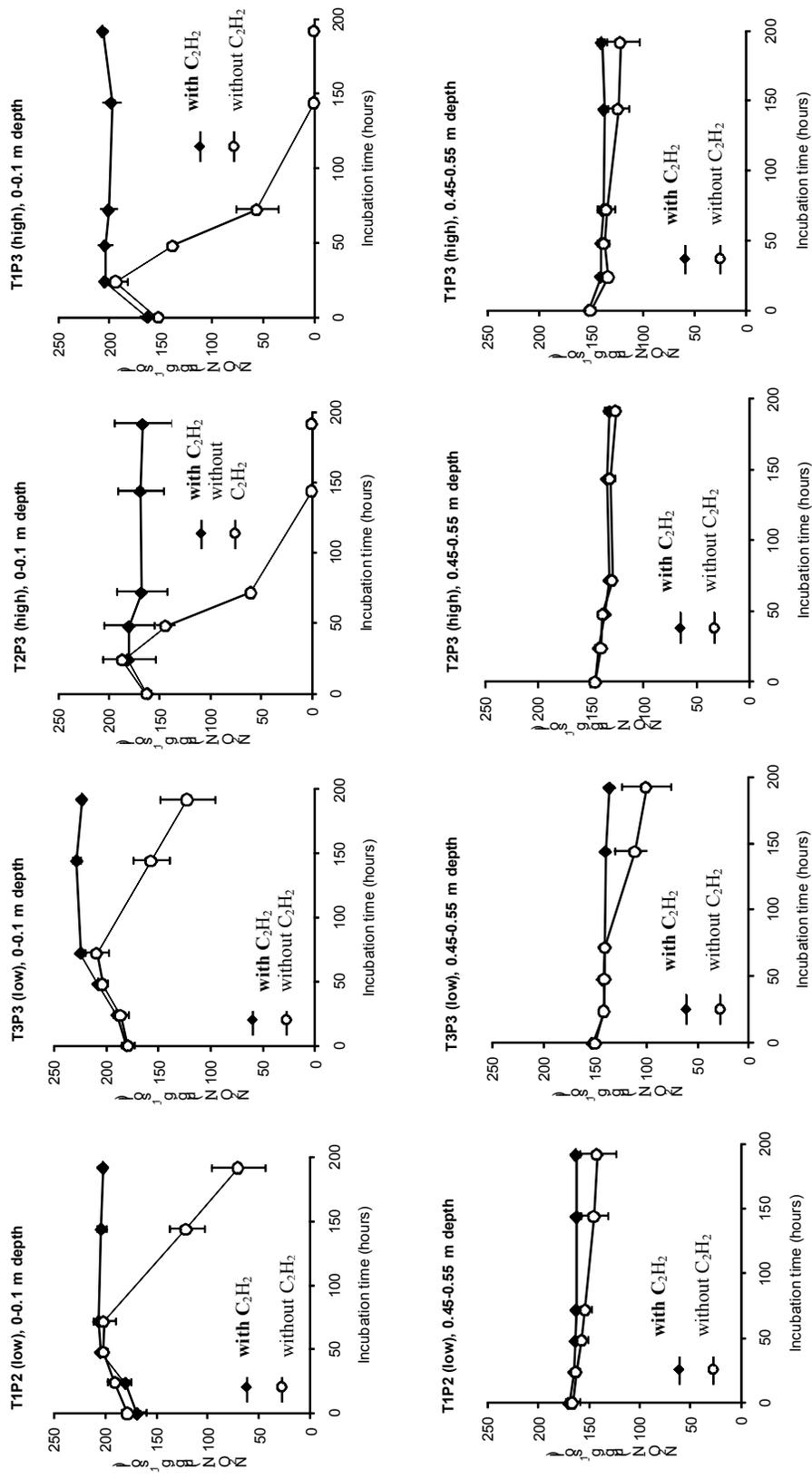
Figure 4.9. Reduction of N_2O in slurries of soil from four locations incubated under anaerobic conditions with added N_2O. Points are the mean of 3 replicates and error bars show the standard deviation.

4.4   Discussion

4.4.1 N_2O emissions from the soil surface

Nitrous oxide emissions from the study site were temporally and spatially variable, with a pronounced seasonal pattern. High variability in emissions is not uncommon in the tropics. For example, Vitousek *et al.* (1989) and Verchot *et al.* (1999) calculated coefficients of variation ranging between 94 and 195 % for N_2O emissions from tropical rainforest soils. Wet season N_2O emissions at Behana Creek were significantly higher than dry season emissions. This is consistent with other studies in tropical forests (Breuer *et al.*, 2000; García-Méndez *et al.*, 1991; Garcia-Montiel *et al.*, 2001; Keller and Reiners, 1994; Kiese and Butterbach-Bahl, 2002; Kiese *et al.*, 2003; Melillo *et al.*, 2001; Verchot *et al.*, 1999) where the magnitude of N_2O emissions was mainly associated with differences in rainfall and soil water content between the wet and dry seasons. Maximum wet season emission rates of up to 657 µg N_2O-N m^{-2} h^{-1} at Behana Creek were high, higher than the maximum wet season rates observed by Kiese and Butterbach-Bahl (2002) at the Pin Gin Hill site (571 µg N_2O-N m^{-2} h^{-1}), considered to be among the highest emission rates recorded for tropical forest soils. The Pin Gin Hill site is also located on coastal lowlands in the humid tropics of north east Queensland. The range of N_2O emission rates at Behana Creek, however, was much more variable that at the Pin Gin Hill site. During the wet season minimum and mean rates were lower at Behana Creek than at Pin Gin Hill (minimum 1 µg N_2O-N m^{-2} h^{-1} and mean 58 µg N_2O-N m^{-2} h^{-} at Behana Creek and minimum 106 µg N_2O-N m^{-2} h^{-1} and mean 141 µg N_2O-N m^{-2} h^{-1} at Pin Gin Hill). Dry season emissions, on the other hand, were similar at both sites (mean of 14 µg N_2O-N m^{-2} h^{-1} at Behana Creek and

17 µg N_2O-N m^{-2} h^{-1} at Pin Gin Hill). Subsequently, annual emissions were estimated to be 6.89 kg N ha^{-1} y^{-1} at Pin Gin Hill and 2.9 kg N ha^{-1} y^{-1} at Behana Creek. Both sites are composed of the same vegetation assemblage (complex mesophyll vine forest) and receive high annual rainfall (~3000 mm at Behana Creek and ~3600 at Pin Gin Hill), however, the Pin Gin Hill site is not a riparian site. Results from our riparian study, together with results from other lowland tropical forest sites comprising similar vegetation in north east Queensland (Butterbach-Bahl *et al.*, 2004; Kiese and Butterbach-Bahl, 2002; Kiese *et al.*, 2003), suggest that N_2O emissions from these forests are large. Inter-annual variability in emissions, however, may also be substantial, based on differences in annual rainfall as noted by Kiese *et al.* (2003). Climate change is likely to alter rainfall patterns, and subsequently soil water availability in tropical forests. This, in turn, may influence the magnitude and temporal patterns of N_2O and other trace gas emissions from the Australian humid tropics.

Maximum emissions measured at this site also exceeded those reported in other riparian studies. For example, in tropical riparian zones in Puerto Rico, Bowden *et al.* (1992) measured mean N_2O emissions of 40-300 µg N_2O-N m^2 h^{-1} at the Icacos site within the (upland) Luquillo experimental forest. Maximum emissions of 435 µg N_2O-N m^{-2} h^{-1} were reported. Emissions from that study were considered to be high compared to other riparian zone emission studies at the time. N_2O fluxes from the Icacos study were upscaled to losses of between 8.7 and 26.3 kg N ha^{-1} y^{-1}, based on the highest mean N_2O fluxes of between 100 and 300 µg N_2O-N m^{-2} h^{-1}. In this calculation it was assumed that such rates persisted over an entire year. Most riparian studies have reported N_2O emissions to fall within the range of 0.1 to 5.0 kg N_2O-N $ha^{-1}y^{-1}$ (e.g. Hernandez and Mitsch, 2006; Weller

et al., 1994). Mean annual emissions at Behana Creek (2.9 kg N_2O-N $ha^{-1}y^{-1}$) fell within this range. Some studies, however, reported much higher annual emissions from riparian zones of between 20 and 25 kg N_2O-N $ha^{-1}y^{-1}$ (e.g. Hefting *et al.*, 2003; Walker *et al.*, 2002). These high values were at sites with high N loads, principally from cropping or animal grazing activities. In contrast to most other riparian studies, results from Chapter 3 suggest that N emitted as N_2O from the Behana Creek site originates mostly from within the riparian zone, rather than N imported from agricultural areas upstream.

In the tropics, differences in the magnitude of N_2O emissions from the soil surface have been attributed to a wide range of environmental variables, many of which are interconnected. Variables include WFPS (Davidson *et al.*, 2004; Keller and Reiners, 1994), soil texture (Keller *et al.*, 2005), soil pH (Gharahi Ghehi *et al.*, 2012; Menyailo *et al.*, 2003) , concentrations of labile organic carbon in the soil (Garcia-Montiel *et al.*, 2003; Wieder *et al.*, 2011), production of CO_2 in the soil (Garcia-Montiel *et al.*, 2002), litterfall rates (Hergoualc'h *et al.*, 2008), litter decomposition rates (Kiese *et al.*, 2003), mineralisation rates (Hergoualc'h *et al.,* 2008), nitrification rates in shallow soils (Ishizuka *et al.*, 2005), soil C:N ratios (Kiese and Butterbach-Bahl, 2002), the influence of specific plant species (van Haren *et al.*, 2010) and the influence of leguminous species (Arai *et al.*, 2008; Hergoualc'h *et al.*, 2008). Results from the Behana Creek site revealed that, of the parameters measured, CO_2 emissions were the best predictor of N_2O emissions, explaining 73% of variability observed in N_2O emissions. Garcia Montiel *et al.* (2002) demonstrated an empirical relationship between N_2O and CO_2 production in Amazon soils with 69% of variability in N_2O emissions explained by CO_2. Keller *et al.* (2005), on the other hand, found a correlation between CO_2 and N_2O emissions only under dry season conditions.

Breuer *et al.* (2000), studying emissions from tropical forest sites in north east Queensland, found that different combinations of factors accounted for variability in N_2O emissions at each of the three sites studied. However, pooling the sites, >63% of variation in N_2O fluxes at all sites could be explained by a logarithmic regression model, driven by differences in WFPS, CO_2 emission rates and the C:N ratio in the soil.

With CO_2 data excluded, multiple regression analysis showed that N_2O fluxes from the soil surface were better predicted by surface soil parameters than by groundwater parameters. However, the overall R^2 value was low, so a large part of the variation in the magnitude of fluxes was not accounted for by measured parameters. It is likely that availability of organic C was important but that DOC was not the best estimate of available C (Nelson *et al.*, 1994).

The lack of predictive value from any of the measured groundwater parameters at the Behana Creek site, including depth to water table, suggests that N_2O emissions were principally driven from within the unsaturated zone. At the same time, the lack of predictive value of some soil parameters, such as soil NO_3^- concentration and pH, at our site suggests that these factors were not limiting N_2O production throughout the study period.

Generally, high ambient temperatures in the tropics favour the production of N_2O. As such, temperature is not generally considered an important factor in the variation of N_2O production in the tropics. Of the measured soil and groundwater parameters, however, correlation analysis identified soil temperature as being most closely correlated with N_2O

emissions at our site. Temperature was based on a single measurement from individual chambers taken at the time of gas sampling. Diurnal temperature fluctuations observed in near-surface soil at the soil pit, on the other hand, suggest that soil temperature could be expected to play an important role in the magnitude of N_2O emissions over the period of 24 hours. Blackmer *et al.* (1982) reported that up to 90% of diurnal N_2O variation could be attributed to changes in soil temperature in soils in a temperate region of the United States. The role of temperature would, however, be most notable at times when the effects of other soil parameters (e.g. WFPS) did not override the effect of temperature (e.g. Smith *et al.*, 1998). Temperature rise would increase biological activity and also cause soil air to expand, thereby promoting the expulsion of soil gases from the soil surface. At the same time, heightened biological activity would increase microbial respiration, reducing the availability of O_2 and increasing the amount of CO_2 produced in the soil. This would result in lower O_2 conditions, irrespective of the water content in the soil (WFPS). Subsequently, N_2O emissions from denitrification may be underestimated if estimates are made purely on the basis of WFPS. Assuming N_2O emissions increase with biological activity, daily N_2O emissions would be expected to reach maxima at around 15:00 hours AEST at Behana Creek and minima in the morning, at around 09.00 hours, coinciding with the maximum and minimum diurnal temperatures in near-surface soils. Nitrous oxide emissions were measured at the soil surface at between 13.00 and 15.00 hours throughout this study, likely capturing the highest emissions of the day.

Based on our litter manipulation experiments, the amount of recently fallen litter on the soil surface did not appear to influence the magnitude of N_2O emissions; neither did it influence soil N concentrations nor DOC concentrations in the top 0.10 m soil layer.

Wieder *et al.* (2011) noted a significant increase in soil DOC concentrations caused by the addition of litter to wet tropical forest soils over a 10 month manipulation experiment. As such, increased N_2O emissions from forest soils in their study were attributed, in part, to the increase in soil DOC.   Sayer and Tanner (2010) observed significant increases in soil NO_3^- concentrations in tropical, lowland forest sites when litter was added. This observation was made after 2 years of litter manipulation as part of a 5 year manipulation experiment. Nitrous oxide emissions were not measured as part of their study. Hergoualc'h *et al.* (2008) observed higher annual N_2O emissions (1.3 times) from soils in a coffee plantation that were shaded with leguminous trees, compared to soils without the presence of legumes (5.8 versus 4.3 kg N ha^{-1} y^{-1}). However, these researchers further attributed differences in N_2O emissions to the higher amounts of litter fall and mineral fertiliser application (1.2 times) associated with the soils from the plantation supporting leguminous shade trees.

The lack of significant change observed in soil N concentrations at our litter experimentation site in the Daintree forest is likely due to the relatively limited time that litterfall was manipulated (four months) prior to our soil and gas measurements. Nitrous oxide emissions did not differ significantly between treatments, nor did soil NO_3^- concentrations. However, the positive, albeit non-significant, correlation observed between soil NO_3^- concentration and N_2O emissions at the Daintree site suggests a positive tendency between soil NO_3^- concentrations and the magnitude of N_2O emissions. Continuation of the litter manipulation experiment over a period of at least two years would likely produce differences in soil NO_3^- concentrations between treatments, as demonstrated by Sayer and Tanner (2010). Similarly, measuring N_2O emissions and soil

NO_3^- concentrations at various distances from leguminous trees at the Behana Creek site may have improved knowledge of the influence of leguminous species on N_2O emissions.

Davidson *et al.* (2000) suggested that litterfall N could be used as a predictor of N_2O and NO emissions from forests. For example, high rates of litterfall N input from old-growth forests in Brazil and Costa Rica, and a legume-rich secondary forest in the Luquillo Forest in Puerto Rico, were associated with high surface N_2O emissions. Erickson, *et al.* (2001) proposed an exponential model for data collected from the afore-mentioned Puerto Rican study, in which the fraction of N lost as NO and N_2O increased with increasing litterfall N. The model was based on the assumptions of the CASA model (Carnegie Ames Stanford Approach) by Potter *et al.* (1996), whereby approximately 4% of the aboveground litterfall N would be lost as NO and N_2O. Applied to our site, with an estimated litterfall input of 169 kg N ha^{-1} y^{-1}, gaseous emissions of NO and N_2O of approximately 6.76 kg N ha^{-1} y^{-1} would be expected, considerably greater than the 2.9 kg N ha^{-1} y^{-1} that estimated from N_2O emission measurements at Behana Creek. At a lowland tropical forest site in north east Queensland (near the village of Bellenden Ker), Butterbach-Bahl *et al.* (2004) estimated NO emissions to be up to 8 times N_2O emissions, most notably at the beginning of the wet season after a long dry period. This suggests that NO emissions from the Behana Creek site could be substantial.

Although N_2O emissions from our humid tropical riparian forest site and other lowland rainforest sites are high, they are lower than those from sugarcane in similar areas. Recent studies of N_2O emissions in southern Queensland have shown N_2O emissions from sugarcane fields to be high, particularly in the wetter months: 350 μg – 17,000 μg N_2O-N

m^{-2} h^{-1} (November to February) and up to 350 µg N$_2$O-N m^{-2} h^{-1} (March to October) (Allen *et al.*, 2010). These results are in general agreement with previous studies carried out on sugarcane crops within Australia (Denmead *et al.*, 2007; Denmead *et al.*, 2008; Macdonald *et al.*, 2009; Wang *et al.*, 2009; Weier, 1999), suggesting that sugarcane crops are large emitters of N$_2$O.

4.4.2 Sources of N$_2$O

From our experiments, sources of N$_2$O were not identified. Based on differences in the water content of the soil over the study period, however, both nitrification and denitrification are likely to have produced N$_2$O emissions within the Behana Creek riparian zone. The balance of these sources of N$_2$O would change as soil water content fluctuated.

The relatively high soil temperatures (ranging between 21 and 38 $^{\circ}$C at 0.1 m depth), constant supply of DOC in near surface soil (mean 40.4 +/- 14.8 mg kg^{-1}) with soil DOC: NO$_3^-$N ratio consistently > 1.25, and a supply of soil NO$_3^-$ and NH$_4^+$ (0.6 to 50 mg NO$_3^-$N kg^{-1} and 0.5 to 36 mg NH$_4$-N kg^{-1}) (Chapter 3, Table 3.3), suggest that both nitrification and denitrification could be supported throughout the year. Which of the two processes dominate, and when and where within the riparian zone, would depend upon the relative proportions of the above in conjunction with the water content of the soil and its associated oxidation status at the time. Similarly, the occurrence of very low and very high emission rates, occurring within a short distance of each other, suggests that there is considerable small-scale below-ground spatial variability in factors affecting the rate N$_2$O production.

Soil water content varied spatially and temporally throughout the site. Based on soil water content at low site T3P3 (> 60% WFPS in surface soil throughout the study period), denitrification was the most likely source of N_2O emissions throughout the year in areas of < 4 m elevation within the riparian zone. Throughout the rest of the riparian site, however, WFPS only surpassed 60% during periods of heavy rainfall. Hence, nitrification is most likely to have been the principal contributor to N_2O emissions for most of the riparian site throughout most of the year. Nitrification rates were probably highest in soils between rain events in the wet season, when soils were close to 60% WFPS and partial pressures of O_2 were still relatively low. This would have resulted in a slowing of the nitrification rate yet an increase in the proportion of nitrified N emitted as N_2O (Khalil *et al.*, 2004).

In the areas of highest elevation (>5.4 m elevation) surface soil WFPS values were (<40%) at the height of the dry season, suggesting nitrification as the source of N_2O. At this time and at these locations, the water table was at ~4 m depth. Low N_2O emissions measured in June and July 2009 were likely due to water limitations hindering nitrification in the dry months (Davidson *et al.*, 1993; Singh and Kashyap, 2006). Sporadic dry season rainfall, however, may have temporarily raised the soil water content in the upper layers of the soil (< 0.1 m), producing short periods with conditions conducive to both denitrification and nitrification. The process most likely to prevail would depend upon the amount of O_2 available. This, in turn, would depend upon the soil moisture content, a function of the antecedent wetness of the soil and the intensity and duration of the rain event. Increased soil respiration at higher temperatures would also influence the availability of O_2, independently of soil moisture content. This could potentially limit conditions for nitrification and provide conditions more conducive to denitrification, despite low water

content in the soil. However, the accumulation of NO_3^- in riparian soils throughout the dry season provides clear evidence of nitrification occurring (Chapter 3), although the nitrification process was likely patchy in both time and space. Substantial, but short-lived, "pulses" of N_2O emission from nitrification are likely to have occurred with the arrival of dry season rainfall. Our experiments were not designed to capture these pulses, however, if patterns of N_2O emissions are to be identified at a finer temporal scale, more intensive sampling, or the use of automated sampling equipment, would be required. Ideally this would include in-situ measurements of temperature and soil water content.

4.4.3 *N_2O production at depth*

Laboratory experiments showed that riparian soil at depth had limited capacity to produce N_2O compared to surface soil. Seemingly in contradiction to this, in situ measurements of N_2O concentrations from within the soil profile revealed an increase in N_2O concentration with depth. The highest concentrations were located around 1.0 m below ground. This suggests that N_2O concentrations in near-surface soil remained low due to rapid diffusion to the atmosphere, despite N_2O production rates being greater near the surface. Yoh *et al.* (1997) reported that most N_2O produced in surface soils was rapidly emitted to the atmosphere and had a short residence time in the soil.

Nitrous oxide concentrations in soil air at depth and dissolved N_2O concentrations in groundwater at Behana Creek were at the higher end of the range of concentrations reported in other studies. However, N_2O produced at depth does not necessarily influence surface emissions of N_2O. Bowden *et al.* (1992) suggested that high concentrations of N_2O in the soil profile and groundwater could influence the magnitude of the flux of N_2O from

the soil surface. However, other researchers have suggested that this may not necessarily be the case (e.g. Ball *et al.*, 1997; DeSimone *et al.*, 2010; Van Groenigen *et al.*, 2005) with dissolved N_2O in groundwater reported to play an insignificant role in surface emissions (e.g. Hiscock *et al.*, 2003; Weymann *et al.*, 2009).

High soil water content throughout the unsaturated zone, particularly during the wet season, is likely to limit the surface emission of N_2O produced at depth due to inhibited diffusion (Ryden, 1981). Nitrous oxide produced at depth may become stored or "entrapped" within the unsaturated zone at this time or dissolved when incorporated into groundwater by a rising water table. The dissolution of gas from the unsaturated zone into rising groundwater may account for the higher concentrations of dissolved N_2O at 1.0 m depth observed on 17 March and at 0.5 m depth on 9 April at the soil pit. Both entrapment and dissolution of N_2O within the (quasi) saturated zone would extend the residence time of N_2O at depth. The transfer of N_2O between the saturated and unsaturated zones (Deurer *et al.*, 2008) is likely to occur continually throughout the wet season. This would be due to the constant water table fluctuation and limited N_2O diffusion to the soil surface at this time. Dissolved N_2O in groundwater can be transferred to the unsaturated zone through bubble-mediated mass transfer (Geistlinger *et al.*, 2010). With the rise and fall of the water table, N_2O trapped in bubbles closest to the water table surface will connect to the continuous soil gas phase and N_2O will transfer to the unsaturated zone. Chapter 2 showed that soil beneath the water table was only able to attain 74-79% saturation between 0.1 m and 1.0 m depth during periods of water table rise. This was attributed to trapped air, corresponding to a volume of 0.14 - 0.15 m^3 m^{-3}. These bubbles are likely to accumulate N_2O produced in the quasi-saturated zone, as N_2O is more soluble in air than in water.

Some of the N_2O produced and 'trapped' at depth within the riparian zone could potentially become consumed before reaching the soil surface, as discussed by Clough *et al.* (1999), Kellman and Kavanaugh (2008) and von der Heide *et al.* (2008). This would prevent the conservative transport of N_2O through the soil profile, and its ultimate emission to the atmosphere. The laboratory experiments indicated that riparian soils at depth had the capacity to reduce N_2O to N_2 albeit at a slower rate than in near surface soils and after a lag phase which, presumably, related to consuming NO_3^- in soils prior to initiating N_2O consumption. However, in contrast to the laboratory experiments, there is probably sufficient NO_3^- in riparian soil, resulting from in situ N cycling, to limit N_2O reduction for longer periods at the riparian site.

Nitrous oxide concentrations within the soil profile diminished over time in the absence of rainfall, yet this occurred whilst the soil water content within the profile was reasonably high (> 0.30 m^3 m^{-3}). High soil water content would hinder diffusion of N_2O to the surface. Nitrous oxide moving through surface soils may have become consumed under low O_2 conditions. Nitrous oxide in groundwater is likely to be transported away from the production zone, allowing it to be emitted elsewhere at a later time. Nitrous oxide may be delivered to the creek (Clough *et al.*, 2005), or to surface waters within the riparian zone (e.g. the gully) and/ or transported off site. The rapid sub-surface preferential flows occurring during large rain events in the wet season are likely to enhance the translocation of dissolved N_2O away from its production zone. Discharge of groundwater to the surface via exfiltration at times of high wet season rainfall will result in N_2O (and potentially N_2) becoming degassed and liberated into the atmosphere (Bowden and Bormann, 1986). Nitrous oxide produced at depth during the wet season, therefore, is likely to be either

stored (transferred between the unsaturated and the saturated zones), translocated or converted to N_2. Either way, limited diffusion of N_2O towards the soil surface in the wet season suggests that N_2O from depth may contribute little to N_2O emissions in situ.

Nitrous oxide produced at depth during the dry season, on the other hand, is more likely to contribute to surface N_2O emissions. Diffusion of N_2O through the top layers of soil would be less inhibited due to the greater proportion of air-filled pores over water-filled pores. However, at the same time, the lower rates of N_2O emission from the soil surface during the dry season were likely the result of low rates of nitrification due to low soil water contents. Although soil water content was not measured at depth at the gas sampling sites, soil was likely to have dried considerably in the top 0.5 m of the unsaturated zone at locations approximately > 4.5 m elevation (based on soil pit data). This would be conducive to the diffusion of N_2O from deeper within the profile, assuming N_2O is produced at depth at this time (ie. if there is sufficient substrate). Both surface soils and deeper soils are likely to produce N_2O in the lowest lying areas such as the gully, even in the dry season. These areas would constitute potential year round 'hotspots' for denitrification, subject to ongoing NO_3^- availability. During the dry season, however, even in topographic lows, soil water content is likely to be at the lowest end of the range to support denitrification.

4.4.4 N₂O consumption

Nitrous oxide consumption was inferred from the negative emissions observed from individual chambers during the dry season. Laboratory experiments demonstrated that riparian soils had a high capacity to reduce N_2O to N_2 under strictly anaerobic conditions,

yet only when something, most likely NO_3^-, became limiting. Negative N_2O emissions reported in the literature have often been neglected or dismissed as measurement error (Chapuis-Lardy *et al.*, 2007). Negative N_2O emissions have been reported in the tropics and sub-tropics during the dry season (Donoso *et al.*, 1993) and during both dry and wet seasons (Garcia-Montiel *et al.*, 2003; Verchot *et al.*, 1999). Verchot *et al.* (1999) reported negative N_2O fluxes in 30–40% of observations during the wet season and in 55–65% of measurements during the dry season but these values were not discussed. Negative emissions from Behana Creek soils were likely the result of consumption/reduction of N_2O in the surface soil. Since surface soils had < 60% WFPS during the dry season, aerobic processes such as aerobic denitrification (Bateman and Baggs, 2005; Garrido *et al.*, 2002; Morley *et al.*, 2008) or nitrifier denitrification (Poth, 1986; Wrage *et al.*, 2001) may have been responsible for N_2O consumption at this time. Alternatively, denitrification may have occurred at sites with <60% WFPS but where partial pressures of CO_2 were high (and O_2 lo) due to high microbial respiration rates. Negative emissions may also be attributed to atmospheric N_2O becoming trapped by soil, as suggested by Hénault *et al.* (1998).

Negative net emissions were not observed in the field during the wet season at our site. Under anaerobic conditions, the denitrification potential experiment in the laboratory showed that N_2O was produced in preference to N_2. However, the consumption experiment showed that, once NO_3^- that was naturally in the soil had been consumed, denitrifying bacteria in Behana Creek surface soils are capable of reducing N_2O to N_2.. This occurs since the reduction of NO_3^- is more energy efficient than the reduction of N_2O (Firestone *et al.*, 1980).

The range of environmental factors known to influence the ratio of N_2O: N_2 emissions is extensive. It includes organic C and NO_3^- availability, soil water content, partial pressure of O_2, soil pH, soil temperature, soil C:N ratio and texture and the size and genetic characteristics of the soil microbial community (e.g. Bandibas *et al.*, 1994; Blackmer and Bremner, 1978; Cuhel *et al.*, 2010; Firestone *et al.*, 1980; Keeney *et al.*, 1979; Knowles, 1982; Mosier *et al.*, 2002; Philippot *et al.*, 2011; Van Den Heuvel *et al.*, 2011; Weier *et al.*, 1993; Wood *et al.*, 2001). Since the range of factors is so broad, inter-relationships between these factors and microbial processes may be at play and the relationships become complicated. In general terms, it is believed that, the less conducive conditions are for denitrification, the higher the ratio of N_2O: N_2 (Granli and Bøckman, 1994). As such, the greater the availability of NO_3^- the lower the availability of C and the higher the partial pressure of O_2, the higher the proportion of N_2O over N_2 through denitrification. Our consumption experiment created saturated, completely anaerobic conditions, and only soil NO_3^- in the original soil sample was present. Under these conditions, insufficient C would have been the most likely factor limiting the reduction of N_2O to N_2 after the initial consumption of NO_3^-. However, it is unlikely that C was limiting, at least at the beginning of the experiment in surface soils, based on the relatively high soil total C contents measured. Other factors, therefore, must be limiting the reduction of N_2O under anaerobic conditions in these soils. It is also possible that N_2O reductase needs first to be induced (e.g. Cuypers *et al.,* 1995).

The work of Blackmer and Bremner (1978) and van den Heuvel *et al.,* (2011) found that low concentrations of NO_3^- delayed reduction of N_2O to N_2. However, where concentrations of NO_3^- were high, reduction of N_2O to N_2 was almost completely inhibited.

The reduction of N_2O to N_2 did not commence until NO_3^- had been completely depleted, corresponding to our findings. However, the above-named researchers found that the inhibitory effect of high NO_3^- concentrations on N_2O reduction increased with a decrease in soil pH. Bandibas *et al.* (1994), on the other hand, observed a positive correlation between mean N_2O emission and soil pH. Behana Creek soils were generally acidic, ranging from pH 4.9 through to 6.2 over the study period. Samples used in the N_2O production and consumption experiment all had pH <5.3, hence, the combination of the acidity of the soils, together with substantial concentrations of NO_3^-, may account for the dominance of N_2O over N_2 production from denitrification in Behana Creek soils under laboratory conditions .

Denitrification potential experiments were conducted at 20^oC, consistent with dry season temperatures in surface soils at Behana Creek ($20 - 23^oC$) experienced during the coolest months of the year. Temperature in the top 0-0.1 m of soil at the site generally ranged between 25 and $30^o\,C$ during the warmer months (and as high as 38^oC at one location) coincident with the wet season and when N_2O emissions measured in situ were highest. It is likely that, by conducting the laboratory experiment at the lowest temperature of the surface soil's in situ range, denitrification rates acquired from the denitrification potential experiment were lower than would have been acquired had the experiment been conducted at a higher temperature.

The composition of the denitrifier community may also influence the production and reduction of N_2O at the Behana Creek site, as other studies have found it to be important (Cavigelli and Robertson, 2000; Dannenmann *et al.*, 2008; Parkin *et al.*, 1985; Philippot *et*

al., 2009; Wakelin and Gregg, 2007; Wakelin *et al.*, 2008). Not all denitrifiers possess the *nosZ* gene required for encoding N_2O reductase (Ma *et al.*, 2011; Wood *et al.*, 2001). Denitrifiers lacking this gene are predisposed to the production of N_2O as a final product of denitrification and are unable to reduce N_2O to N_2. The proportion of denitrifiers capable of reducing N_2O within a community will therefore affect the proportions of the overall products of denitrification (Chèneby *et al.*, 1998; Ma *et al.*, 2011; Philippot *et al.*, 2011).

4.5   Conclusions

This study revealed that a forested riparian zone located in the humid tropics has the potential to sustain important gaseous loss of N in the form of N_2O, and those emissions vary considerably in time and space.   The highest hourly N_2O emission rates, during the wet season, were among the highest measured from tropical rainforests from around the world. In contrast, some very low emission rates were also observed in the wet season. N_2O production from the riparian forest followed a seasonal pattern, with the highest emissions observed in response to large wet season rainfall events and consistently lower emissions occurring throughout the dry season.

Nitrous oxide was probably the product of both nitrification and denitrification within the riparian zone. Spatial variability in N_2O emissions was related to riparian site topography and hydrology. The likely source of N_2O emitted to the atmosphere would have been related to soil water content which, in turn, would have related to topography. Low elevation sites, such as areas in and around the gully, were conducive to denitrification all year round due to prolonged soil wetness. In contrast, sites higher in the riparian landscape sustained conditions more conducive to nitrification for most of the year, except during

large wet season rain events. During such events denitrification was probably the sole source of N_2O.

Laboratory experiements under controlled anaerobic conditions demonstrated that denitrification from riparian soils produced high levels of N_2O, particularly in topsoils. However, once substrate became limiting, reduction of N_2O produced N_2. Differences were observed in N_2O reduction between topsoils from high and low locations with shorter lag times and faster reduction rates noted in soils from high sites. Nitrous oxide consumption processes were inferred at the site from occasional negative N_2O fluxes measured at the soil surface in the dry season under low soil moisture conditions. Aerobic denitrification or nitrifier denitrification may have been responsible for the reduction of N_2O at these times or by respiratory denitrification if anaerobic conditions had been induced by high levels of microbial respiration in the soil.

Manipulation of litterfall did not significantly influence the magnitude of N_2O emissions. However, longer term studies of over two years are recommended to further evaluate the role of litter on N_2O emissions from forested riparian zones.

Nitrous oxide was produced throughout the soil profile (sampled to 2.0 m depth), being present in soil air and dissolved in groundwater. Nitrous oxide produced at depth is unlikely to make a large contribution to surface N_2O emissions during the wet season due to high soil water content, which would inhibit the upward movement of N_2O through the soil profile.

Chapter 5.   Synthesis

The study was undertaken within a riparian zone on the coastal plain of the humid or 'wet' tropics of north east Queensland, Australia, in a landscape where agriculture (sugarcane) is the dominant land use. The principal aims of this study were to 1) assess the effectiveness of a forested riparian zone in this landscape at removing N from groundwater and 2) to assess the magnitude of N_2O emissions emitted from the riparian zone and 3) to infer the most significant biogeochemical processes that influence the movement of N through the riparian zone. Based on the scientific literature, there is a general expectation for riparian zones to improve water quality by removing NO_3^- from groundwater flowing through them. However, little research has been undertaken on this topic in ecosystems of the humid tropics. To my knowledge, at the time of writing, this is the first study to evaluate the movement of N through a forested riparian zone in an agricultural landscape of the humid tropics. By adopting a multi-dimensional approach, this work has advanced the understanding of tropical riparian zone hydrology and riparian N dynamics.

5.1   Summary of findings

Nitrate concentrations in groundwater entering the riparian zone from sugarcane fields were consistently low (<1 mg NO_3-N L^{-1}), and they did not decrease during passage through the forested riparian zone. Rather, the riparian forest itself was a source of NO_3^- to groundwater within the riparian zone and potentially a source of NO_3^- to the creek. Groundwater NO_3^- concentrations within the riparian zone were highest at the beginning of the wet season, coinciding with the first, large, in situ rainfall events. Measurements of soil and groundwater NO_3^- concentrations suggest that most groundwater NO_3^- derives from

within the riparian forest (ammonification and nitrification of N from abundant organic matter). Nitrate was leached from the riparian surface soils into groundwater by deep drainage or incorporated into groundwater with the rise and fall of the water table in the wet season. Subsequently, NO_3^- concentrations in groundwater at the creek bank were higher than concentrations in groundwater entering the riparian zone. Assuming groundwater is discharged into the creek and no further N transformations take place at the creek bank or in the hyporheic zone, a portion of N would be lost from the riparian zone and transferred to the creek through hydrological pathways.

Gaseous emissions were another key pathway for N loss from the riparian zone. The forested riparian zone was an important emitter of N_2O, with mean wet season N_2O emissions significantly higher than those of the dry season. Based on seasonally weighted means, it is estimated that the riparian zone loses approximately 2.9 kg N ha^{-1} y^{-1} to the atmosphere in the form of N_2O. This is above the median value for emissions from tropical forests and within the values reported for riparian zones around the world. However, in many cases, annual riparian N_2O emissions have been reported to be higher than those of this study. This is likely to be the case where N_2O emissions are associated with the denitrification of NO_3^- entering the system from agricultural runoff upslope with high inputs of NO_3^- from fertiliser. This was not found to be the case for the Behana Creek riparian zone, where N in groundwater appears to derive mostly from within the riparian zone itself. Laboratory experiments showed that, under controlled anaerobic conditions, riparian soils can emit large amounts of N_2O, however are also capable of producing N_2 which is also likely to be emitted from riparian soils.

Based on soil water content in surface soils, nitrification was likely to have been the most dominant source of N_2O within the riparian zone, with the exception of the lowest lying areas where soil water content was highest. In these areas denitrification was likely to have been the dominant source of N_2O throughout most of the year. Mean N_2O emissions across the site were considerably lower in the dry season than in the wet season (13 versus 59 μg N m^{-2} h^{-1}). In the dry season nitrification was likely low as a result of very low soil water content, particularly at the sites of highest elevation.

Riparian forest litterfall is abundant (12.19 Mt ha^{-1} y^{-1}). Experiments suggested that soil organic matter, rather than recent additions of litter, were the main source of N for nitrification within the riparian forest. Nitrate accumulated in surface soil throughout the dry season, but was rapidly leached to groundwater, or deeper within the unsaturated zone, with the event of wet season rainfall.

Laboratory experiments demonstrated that the riparian soils had great capacity to denitrify under anaerobic conditions and that N_2O was clearly emitted in preference to N_2. In the field, however, opportunities for denitrification were limited in time and space. 'Hot moments' for denitrification most likely existed at times of heavy, wet season rainfall, producing large 'pulses' of N_2O. However, these 'pulses' of denitrification would have been short-lived due to rapid drainage of riparian surface soils. The lowest lying areas (< 4 m elevation), on the other hand, were likely to constitute denitrification 'hotspots'. Denitrification in riparian surface soils would prevent a portion of soil NO_3^- from leaching into groundwater; however, it would also increase the emission of N_2O to the atmosphere from this site.

Nitrous oxide was produced throughout the soil profile within the riparian zone and was present in both the soil atmosphere and dissolved in groundwater. Low concentrations of O_2 in groundwater and high soil water contents in the unsaturated zone suggest that N_2O produced at depth was the product of denitrification. Nitrous oxide formed at depth, however, was unlikely to make a large contribution to surface N_2O emissions. Nitrous oxide produced at depth may become stored or 'entrapped' at depth or translocated off site by groundwater. Some of the N_2O produced at depth may be converted to N_2, which would experience a similar fate as that described for N_2O.

Aside removal by denitrification, nitrogen in soil water and groundwater is also presumably taken up by riparian vegetation during transpiration and may be assimilated by soil micro-organisms. However, these mechanisms were insufficient to prevent NO_3^- concentrations from increasing in groundwater as groundwater traversed the riparian zone towards the creek. The dynamic hydrology and variable discharge zones identified in this study during the wet season were likely to result in short residence time for groundwater within the riparian zone. This would limit the opportunity for NO_3^- removal to occur after wet season rainfall. Between rain events, both denitrification and nitrification are likely to occur simultaneously; soils in the low lying areas that retain high soil water content are likely to support denitrification and soils in the higher locations that drain rapidly are likely to support conditions for nitrification almost immediately in situ rainfall ceases. In the dry season the virtual cessation of groundwater flow suggested that any denitrification occurring in groundwater at this time would have little effect on the overall delivery of N to the creek. Sporadic dry season rainfall, on the other hand, would have stimulated

nitrification in dry surface soils. Nitrate accumulated in surface layers throughout the dry season, becoming mobilised at the onset of wet season rainfall.

5.2   Conclusions

The principal conclusions of this study are:

1) Overall, this riparian forest zone on a coastal plain of the humid tropics was ineffective at reducing NO_3^- concentrations in the groundwater moving through it.

2) The low-lying position of the riparian forest and its associated topography, are important factors controlling the transportation, transformations and fate of N within the riparian zone. The wetness of riparian forest soils is influenced by the proximity to the ground water table. Dynamic water table fluctuation in the wet season provided an efficient pathway for the transfer of NO_3^- from the unsaturated zone to the saturated zone. The direction and velocity of flow were influenced by riparian topography. Large, multidirectional wet season fluxes of groundwater and dissolved N were directed towards variable discharge zones.

3) Litterfall rates from the riparian forest were high. Forest-derived organic matter yields high concentrations of inorganic N which is nitrified and denitrified within the riparian zone. However, the cycling system is 'leaky', sustaining substantial losses of N through hydrologic and gaseous pathways.

4) Based on soil water content, gaseous losses of N in the form of N_2O are likely to derive predominantly from nitrification, although denitrification was the most

probable source of N_2O at times of heavy wet season rainfall and in topographic depressions throughout most of the year.

Chapter 6.   Implications and directions for future research

6.1   Implications of this research

Forested riparian zones have many valuable functions in human-impacted ecosystems. However, the results of this research suggest that the establishment or restoration of forested riparian zones in the Australian humid tropics may be of limited value for improving groundwater quality, particularly in the wet season. The forested riparian zone in this study was a net source of nitrate to groundwater, and potentially the creek and downstream environments. Similarly, other studies in this region have shown that riparian zones are limited in their capacity to trap sediments and nutrients from surface fluxes at times of intense rainfall (McKergow *et al.*, 2004a, 2004b). However, forested riparian zones in the humid tropics are known to provide other important services to the environment. They play an important role in preventing soil and stream bank erosion (McKergow *et al.*, 2004a) and in maintaining stream health (Arthington and Pearson, 2007). In general, forested riparian zones are important in the conservation of the biological diversity of rivers and the surrounding area (Decamps *et al.*, 2004). Despite occupying only a small proportion of the landscape, riparian zones can support a variety of wildlife in numbers that are significantly higher than in areas away from creeks and rivers (e.g. Gregory *et al.*, 1991). Riparian zones can link wildlife habitats providing connecting corridors for the movement of fauna. They provide food, standing water, shelter from predators, nesting and roosting sites, and a local microclimate with lower temperatures than in adjacent, unshaded, cropped land. The establishment of forested riparian zones also represents an opportunity for carbon sequestration, an initiative supported by the

Australian Federal Governments Clean Energy Future program under the newly established Biodiversity Fund. Forested riparian zones thus provide a range of environmental services that are far in excess of their surface area and are important features of the landscape. Total N_2O emissions from forested riparian zones in the humid tropics are likely to be small when compared to N_2O emissions from the surrounding agricultural land. Thus, land and water resource managers would be advised to take a holistic approach and consider the overall ecological and environmental services and benefits that riparian ecosystems provide, rather than focusing on the single function of water quality improvement.

Results from this study also suggested that riparian forest in the humid tropics constitutes a source of NO_3^- to groundwater, and potentially to downstream environments. There are two possible responses. One is that the N derived from forests is part of the natural cycling of this important nutrient and, considering the small areas of riparian forest in the coastal plain, the inputs of N from riparian forest must be insignificant compared to those from agricultural and urban activities. The other response is that, since it is known that N loads are elevated in these human-impacted regions, N inputs from all parts of the landscape should be considered. With this in mind, it would be important to take into account the composition of riparian vegetation when establishing or restoring riparian zones in the humid tropics. For example, it may be worthwhile to avoid planting N-fixing leguminous species in areas of high rainfall where the water table is shallow. Care might also be taken to prevent the proliferation of N_2-fixing invasive species within the riparian zone. Minimising the amount of N_2-fixing species might be expected to reduce the potential size of the N pool within the riparian zone, in turn reducing the amount of NO_3^- that could be

lost to groundwater and potentially to creeks. However, it should be kept in mind that N-fixing species are an integral part of naturally functioning forests, particularly in the tropics.

From a wider perspective, results from this study can contribute to more accurate riparian N budgets and denitrification models for humid, tropical regions around the world. A number of hydrological models have been developed to evaluate different aspects of the riparian zone. For example, the Ecosystem Management Model (REMM) (Inamdar, Lowrance *et al.*, 1999; Inamdar, Sheridan *et al.*, 1999) estimates riparian denitrification; the Riparian Nitrogen Model (RNM) (Rassam *et al.*, 2005) operates as a module within the model E2 (Argent *et al.*, 2005), recently renamed and incorporated into e Water Source integrated modelling system (e Water CRC, 2011). E2 is a node-link catchment-scale model designed to predict the hydrologic behaviour of catchments. The RNM estimates the removal of NO_3^- as a result of denitrification occurring when shallow groundwater interacts with riparian soils. The Riparian Mapping Tool (RMT) (Rassam and Pagendam, 2009), an extension of the RNM, is a GIS-based model designed to assist land managers in identifying riparian areas where rehabilitation is likely to be most effective in enhancing denitrification and reducing N loads. New findings from this study, such as the addition of N to groundwater resulting from N cycled within the riparian forest, and the lack of complete saturation of soils beneath the water table in the riparian zone, may enhance the performance of the afore-mentioned models when applied to sites in the humid tropics. Hydrologic data, groundwater and soil chemistry and riparian vegetation data collected throughout this study, could be used to calibrate such amendments to the models.

6.2 Direction for future research

As the first study of its kind in the humid tropics, this research has provided an overall picture of the movement of N through and within a riparian zone, over both wet and dry seasons. Since this study has touched on various aspects of the riparian zone (hydrology, soil and groundwater chemistry, riparian forest vegetation and N_2O emissions), further research could expand upon any one of these areas. For example, two areas within the realm of hydrology which merit further investigation are: 1) the delivery mechanisms of groundwater to the creek in the wet season, expanding the understanding of subsurface flowpaths in riparian zones of the humid tropics, and 2) the phenomenon of quasi saturation of riparian soils within the 'saturated' zone. The former would benefit from tracer techniques such as the isotopic composition of water (H and O) or [222] Radon concentrations, using recently developed, continuous, in-field measurement techniques (e.g. Burnett *et al.*, 2001; Munksgaard *et al.*, 2011). An in-depth study of the quasi-saturation of riparian soils should consider the relationship between entrapped air in the soil profile and the rapid rise and fall of the water table observed at the riparian site during times of high in situ rainfall. This may provide a link between air entrapment, groundwater ridging and the movement of gas.

More intensive measurement of N_2O emissions and near-surface soil parameters, such as DO and WFPS, using automated equipment, would help to quantify the factors affecting N_2O emissions from riparian zones on coastal plains in the humid tropics. The current study measured N_2O emissions once a day, always at approximately the same time, on selected dates. Measurement of soil and emission data on a finer scale at selected sites over

shorter periods would advance knowledge of temporal variation in soil parameters and the effects on N_2O emissions. Similarly, cataloguing riparian soil types would allow WFPS calculations to be made under different conditions, alerting researchers to the potential for the occurrence of either nitrification or denitrification.

The litterfall manipulation experiment done as part of this study did not evaluate the long-term effects of litterfall on soil and on gaseous emissions. Hence, the relationship between riparian forest litterfall, soil NO_3^- concentrations and N_2O emissions merits further investigation over a longer period, a minimum of two years. This could include close monitoring of litter quality, including C:N ratios. A study of tropical grass species suitable for NO_3^- uptake may also be beneficial, whereby suitable species could be introduced into newly established riparian zones.

Finally, an overall N balance for the riparian zone was not attempted in this study. To better understand the N cycle in a riparian zone in the humid tropics and the role of the gaseous and hydrologic vectors in the N balance, the following need to be quantified: 1) N inputs to the plant-soil-water system via N fixation, 2) losses of N to the atmosphere as N_2 and NO_x, 3) the movement of N into the creek as groundwater discharge. These were not quantified in this study but would further enhance our knowledge of riparian zones in agricultural landscapes on coastal plains of the humid tropics.

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