



## **The Storage, Mobilisation and Metabolism of Soil Nutrients and Carbon in an Australian Lowland River**

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# **The storage, mobilisation and metabolism of soil nutrients and carbon in an Australian lowland river**

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## **Abstract**

More than 45 000 dams, with the capacity to hold 15% of global river runoff, have been constructed on rivers around the world for diverse purposes including water supply, irrigation water and power. The effects of these dams on river flow are diverse and dependent upon the purpose of the dam; some dams stabilise flow to improve transportation, water access and agricultural productivity, while dams such as those for power generation create flow regimes that vary drastically over a period of hours. The benefits of regulating river flow for human needs comes with ecological costs to riverine ecosystems including local extinctions, depletion of ground water, declines in water quality and water availability. The specific ecological costs of flow regulation are dependent on how the new, regulated, flow regime differs from the natural flow regime of a river system.

Regulation of flow in Australia's lowland rivers has been undertaken to suppress the inherent flow variability and dampen flow extremes, largely to improve water access for floodplain based irrigated agriculture. Flow regulation in these systems captures moderate sized flows, releasing this stored water during periods of natural low flow. This stabilising of river flow has resulted in an increase in the abundance of introduced species and a decline in the diversity of native fish, macroinvertebrate, and littoral plant communities along with altering river channel geomorphology and decreasing water quality. These declines may be partly caused by the loss of moderate sized flows reducing lateral hydrological connectivity between terrestrial and aquatic ecosystems. In an attempt to reverse this effect, flow rules that are designed to increase the frequency of small to moderate sized flow pulses, which are mostly contained within the channel, have been introduced in many of Australian's lowland rivers.

This thesis investigated the role flow pulses and the associated inundation of in-channel features play in nutrient release and ecosystem processes in lowland rivers. Specifically, the exchanges between terrestrial and aquatic ecosystems mediated by the inundation of in-channel features and their short term effect on water chemistry and aquatic ecosystems were explored. Initially, a conceptual model was developed that divides these exchanges into two phases (i) an initial flush phase, where carbon and nutrients are flushed from soils and (ii) a soil processes phase, where soil microbial processes increase or reduce exchanges

of carbon and nutrients. Based on predictions of how these exchanges change with relative height within the channel of a lowland river the conceptual model then predicts the timing of peak solute concentrations during flow pulses of different stage heights.

The conceptual model predicted that stores of exchangeable inorganic nutrients and organic carbon, and its bioavailability, would increase with height in a lowland river channel. Nutrients and carbon were extracted from in-channel bench soils collected from varying heights in the Gwydir River with river water used as the extractant. The amount of exchangeable dissolved organic carbon (DOC) and dissolved reactive phosphorus (DRP) increased with height in the Gwydir River landscape, as predicted by the conceptual model. The exchangeable amount of  $\text{NH}_4^+$  decreased with height in the channel while exchangeable  $\text{NO}_3^-$  increased, suggesting that inundation frequency was effecting nitrogen transformations in these soils. The fraction of soil bioavailable carbon ( $\text{FBDOC}_{30}$ ) was not significantly related to any measured variable and seems to have been affected by inundation frequency low in the river channel and leaf litter quality higher in the channel. The distribution of  $\text{NO}_3^-$  and  $\text{FBDOC}_{30}$  across the levels in the landscape suggested that high rates of microbial activity may be occurring in the soils of the lowest bench in the Gwydir River landscape during inundation.

A rate of soil microbial activity associated with inundation of the lower bench levels of the Gwydir River channel was the opposite pattern to that predicted in the conceptual model and was further explored by monitoring rates of terminal electron accepting processes (TEAPs) in inundated soil cores. The amount of organic carbon mineralised by these processes increased with increasing inundation frequency, suggesting that the ability of the terrestrial soils microbial community to adapt to the conditions brought about by inundation increases with inundation frequency. This suggestion was further supported by the finding that the most frequently inundated soil was capable of both  $\text{Fe}^{3+}$  reduction and methanogenesis, processes that were not found in soils from higher in the landscape. The variation in the timing of the onset of the different TEAPs and the rate of metabolism occurring in the inundated soils of different levels in the Gwydir River channel along with their different stores of exchangeable carbon and nutrients suggest that flow pulses of different stage heights will facilitate different exchanges between the terrestrial and aquatic ecosystems.

Concentrations of organic carbon and nutrients were monitored during a flow pulse in the Namoi River to investigate their relationship to the flow pulse hydrograph. The Namoi River catchment, the adjacent catchment to the south of the Gwydir River, was used for this investigation due to a lack of similar flow pulses in the Gwydir River during the study period. The timing of peak concentrations of most solutes suggested they were flushed from in-channel features with the exception of DRP which, in addition to flushing, seems have been mobilised from these features by anaerobic soil processes. A diel pattern in DOC and  $\text{NH}_4^+$  concentrations was also identified during the flow pulse. The cause of this diel pattern in DOC is likely related to the photodegradation of DOM, producing highly bioavailable DOC that fuels increased metabolic rates of heterotrophic bacterio-plankton, reducing daytime DOC concentrations compared to those observed at night. Bioavailable DOC is produced in much greater quantities than  $\text{NH}_4^+$  during photodegradation of DOM and therefore enables the increased metabolic rates of heterotrophic bacterio-plankton to continue after photo-production of  $\text{NH}_4^+$  has ceased causing a rapid decline in  $\text{NH}_4^+$  concentration in the evening and resulting in night time concentrations of  $\text{NH}_4^+$  being lower than those found during the day.

To further investigate the cause of the diel pattern in DOC and  $\text{NH}_4^+$  concentrations, an experiment using pairs of mesocosms in which half were exposed to, and half excluded from, the natural sunlight light regime, was undertaken. Concentrations of DOC and  $\text{NH}_4^+$  and rates of community respiration (CR) and gross primary productivity (GPP) were monitored in the surface water above flooded soils contained in mesocosms. An increase in  $\text{NH}_4^+$  concentration was found in the light exposed treatment suggesting that photodegradation of DOM was occurring. However, photodegradation of DOM did not increase rates of respiration or affect DOC concentrations as no difference was found in these variables between the light and light excluded treatments. The static hydrology in the mesocosms may have reduced concentrations of suspended particles and the bacteria attached to these particles sufficiently to negate the effect of respiration on DOC concentrations in the mesocosms. If this is the case and, therefore, respiration is the cause of the diel pattern in DOC and  $\text{NH}_4^+$  concentrations observed in the Namoi River, then the loss of flow pulses due to flow regulation will result in both loss of exchanges between terrestrial and aquatic ecosystems as well as these increased rates of respiration that may

allow aquatic ecosystems to retain some the exchanged materials for longer than the duration of the flow pulse.

The effects of flow regulation and flow rules on exchanges between aquatic and terrestrial ecosystems facilitated by bench inundation in the Gwydir River were assessed by comparing three modelled flow scenarios; ‘with flow rules’, ‘without flow rules’ and a ‘natural’ flow regime scenario. Over a 29 year modelled period the frequency and duration of bench inundation events was very similar between the three modelled flow scenarios. The reason for the lack of effect of flow regulation or flow rules on the patterns of bench inundation is, perhaps, the loss of the benches closest to the channel bed. However, the introduction of flow rules did increase the duration of flow pulses below the level of the lowest bench, making it more similar to the ‘natural’ flow scenario, which in the longer term may facilitate the re-building of benches in this area of the channel.

The results from this thesis confirm some aspects of the original conceptual model while providing further information to allow modification of others. The importance of in-channel features such as anabranches and benches for facilitating exchanges between terrestrial and aquatic ecosystems has been confirmed using both laboratory methods and field observations. However, the stores of exchangeable carbon and nutrients varied with height in the river channel, as did the rates of soil metabolism; both of which will affect the exchanges facilitated by a flow pulse. The flow pulses themselves, may be more important to aquatic ecosystem health than originally proposed, if the observed diel pattern in DOC and  $\text{NH}_4^+$  concentrations are caused by increased rates respiration as was suggested. This respiration could provide the aquatic ecosystems with a mechanism to increase their retention of exchanged elements that limit respiration and production in the aquatic ecosystem allowing increased rates of these processes to continue after the passage of the flow pulse downstream.

## **Declaration**

This work has not been previously submitted for a degree or a diploma at any other university. To the best of my knowledge and belief, the thesis contains no material previously published or written by another person except where due reference is made in the text to all other materials used

Ben Woodward

August 2014

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## **Dedication**

This thesis is dedicated to the memory of

**Dr Christy Fellows**

You were my guide, mentor and friend. You saw in me an ability that I didn't know I had; you nurtured and grew my confidence, and I now, finally, I believe. Thank you Christy, you're sorely missed.

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# **Chapter 1. General introduction**

## **1.1 Australian lowland riverine landscapes – an introduction**

In Australia, lowland river reaches provide water for floodplain based irrigated agriculture that generates in excess of A\$10 billion annually (Thoms and Sheldon 2000a) and accounts for over half of the country's agricultural production (Driver et al. 2013). This makes these rivers vital water sources for human needs in all parts of Australia (Thoms and Sheldon 2000a). However, flow in these rivers is highly variable (Puckridge et al. 1998) due to (i) both seasonal and inter-annual variability in precipitation at large spatial scales (Murphy and Timbal 2008); (ii) the fact that most of these rivers are alloegenic with the bulk of their flow volume generated in comparatively small, usually upland areas, while the majority of river length is generally located in lowland areas (Thoms and Sheldon 2000a); and (iii) relatively high rates of evaporation, evapotranspiration and groundwater recharge in these lowland areas that reduces river flow through a low rainfall/runoff coefficient (Thoms and Sheldon 2000a). This high flow variability necessitates flow regulation, stabilising river flow and allowing these rivers to be reliable water sources for floodplain based agriculture (Thoms and Sheldon 2000a) but it has negatively impacted upon their ecological health (Bunn and Arthington 2002, Davies et al. 2010).

The endemic flora and fauna of Australian lowland rivers are adapted to, and potentially dependent on, the high flow variability of these rivers (Bunn and Arthington 2002) which creates 'boom' and 'bust' periods in their ecology (Kingsford et al. 1999, Bunn et al. 2006b). The 'boom' periods, of substantial and sometimes sustained floodplain inundation, provide a mechanism for the transportation of organisms, nutrients and organic carbon between lowland rivers and their floodplains (Boulton and Lloyd 1992, Baldwin and Mitchell 2000, Jenkins and Boulton 2003, Westhorpe et al. 2012) increasing primary production (Fellows et al. 2009), food availability (Bunn et al. 2006b, Balcombe et al. 2007) and generating a greater reproductive output from a range of taxa (Kingsford et al. 1999, Roshier et al. 2002, Jenkins and Boulton 2003). While the 'bust' periods, can reduce rivers to isolated waterholes, decreasing populations of water birds, fish and micro-invertebrates dramatically

compared to the ‘boom’ periods (Kingsford et al. 1999, Jenkins and Boulton 2003, Balcombe et al. 2005).

The ‘booms’ in Australian lowland river ecology are triggered by floodplain inundation events (Kingsford et al. 1999, Jenkins and Boulton 2003, Bunn et al. 2006a, Bunn et al. 2006b); however, these events are unpredictable due to the high flow variability inherent to these rivers and therefore are not ecologically reliable (Puckridge et al. 1998). Compared to these larger, floodplain inundating events, flow pulses, increases in flow that stay within channel, occur with greater frequency and have consequently been speculated as important for supplementing exchanges between terrestrial and aquatic ecosystems between floodplain inundation events (Sheldon and Thoms 2006, McGinness and Arthur 2011, Westhorpe and Mitrovic 2012). However, the frequency of flow pulses in many Australian lowland rivers has been reduced by flow regulation (Thoms and Sheldon 2000b, Page et al. 2005). The resulting reduction in connectivity caused by the loss of flow pulses has been postulated as one of the drivers behind declines in aquatic ecosystem health of some rivers in the Murray-Darling Basin (Davies et al. 2010).

Increasing the frequency of flow pulses has been mooted as a potential mechanism for improving the health of regulated lowland rivers (Thoms 2003, Sheldon and Thoms 2006, McGinness and Arthur 2011). Flow pulses inundate in-channel features that are common in Australian lowland rivers, such as anabranches, backwaters, cut-offs, shallow floodways and in-channel benches (Thoms and Sheldon 2000a, Vietz et al. 2004, Thoms et al. 2005). Many of these features accumulate terrestrially derived organic matter in a similar manner to the floodplain, thus when inundated these features may create similar exchanges to those that occur between the river and the floodplain during floodplain inundation events. However, exchanges of carbon, nitrogen and phosphorus between the river and in-channel features, which could lift nutrient limitation on primary production and carbon limitation on bacterial production in these rivers (Hadwen et al. 2010, Westhorpe et al. 2010), may be affected by the higher inundation frequency of these in-channel features (Baldwin and Mitchell 2000, Fierer and Schimel 2002, Heffernan and Sponseller 2004, Valett et al. 2005, Kerr et al. 2010).

Thus, whether similar exchanges occur during the inundation of in-channel features compared with those that occur during the inundation of the floodplain is not clear.

To gain an understanding of the importance of within-channel exchanges and their similarity to exchanges mediated during floodplain inundation events, this chapter will examine;

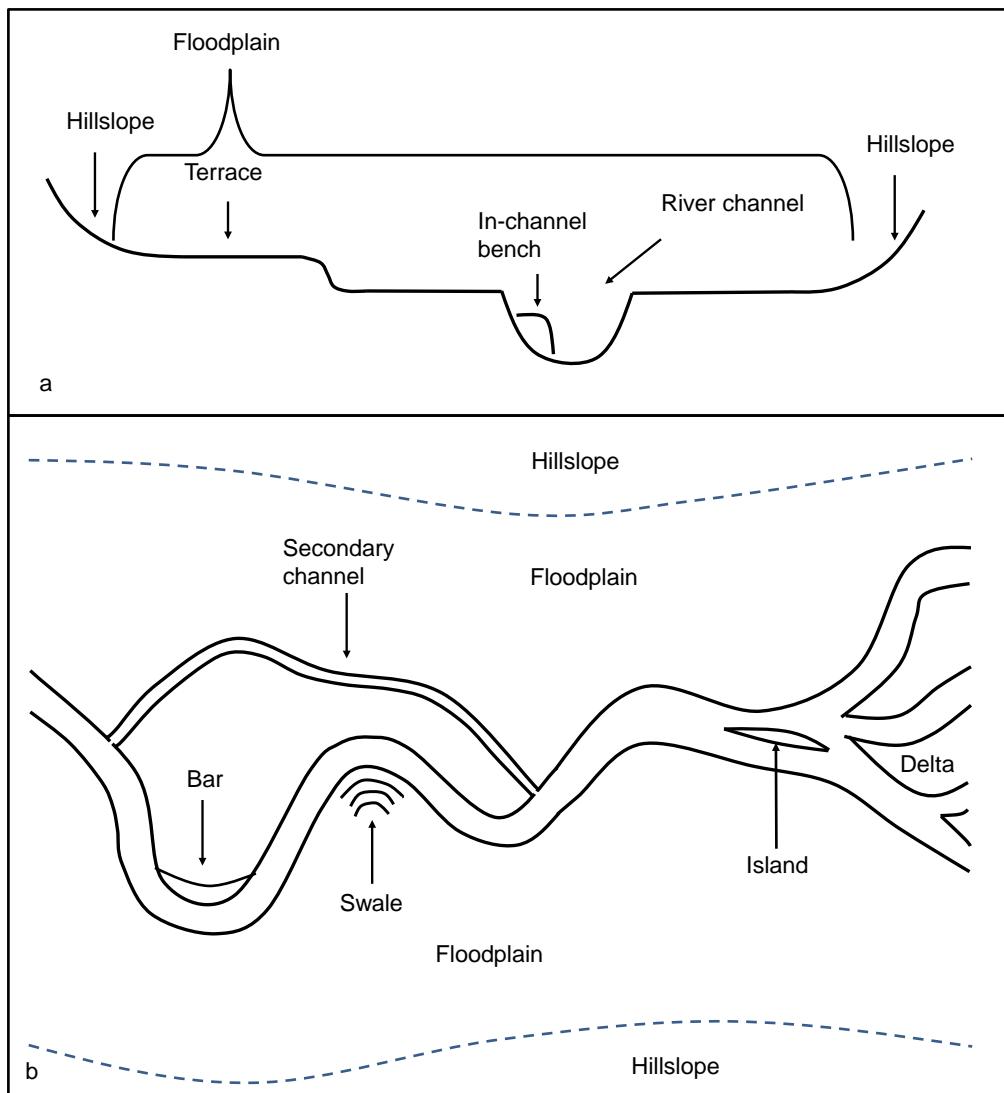
- The broad spatial patterns found in riverine landscapes in the context of hierarchical patch dynamics (Wu and Loucks 1995)
- Temporal patterns found in riverine landscapes and the role of river flow variability in creating these patterns
- The biogeochemistry of inundated soils
- In-channel benches; their formation, structure and potential for facilitating connectivity during flow pulses

Finally, using these investigations as a base, a conceptual model focused on how carbon and inorganic nutrients are exchanged between in-channel benches and inundating river water, and how these exchanges may differ with inundation frequency, is presented.

## 1.2 Spatial complexity in riverine landscapes

### 1.2.1 Broad spatial patterns in riverine landscapes

Riverine landscapes are complex ecological systems, subject to both temporal and spatial variability in physical and biological characteristics (Ward et al. 2002, Thorp et al. 2006). The physical components of riverine landscapes include the primary channel and its in-channel features such as bars, islands, and in-channel benches, as well as secondary channels such as anabranches, ox bows, and flood runners and wider floodplains including ridges, swales, levees, fans and deltas (Ward et al. 2002). At a broad spatial scale these landscape components can be defined as patches nested in a riverine landscape (Wiens 2002) (Figure 1-1).



**Figure 1-1:** A graphical representation of some of the different patches found in a riverine landscape at a large spatial scale (a) shows a cross section of riverine landscape and (b) an overview.

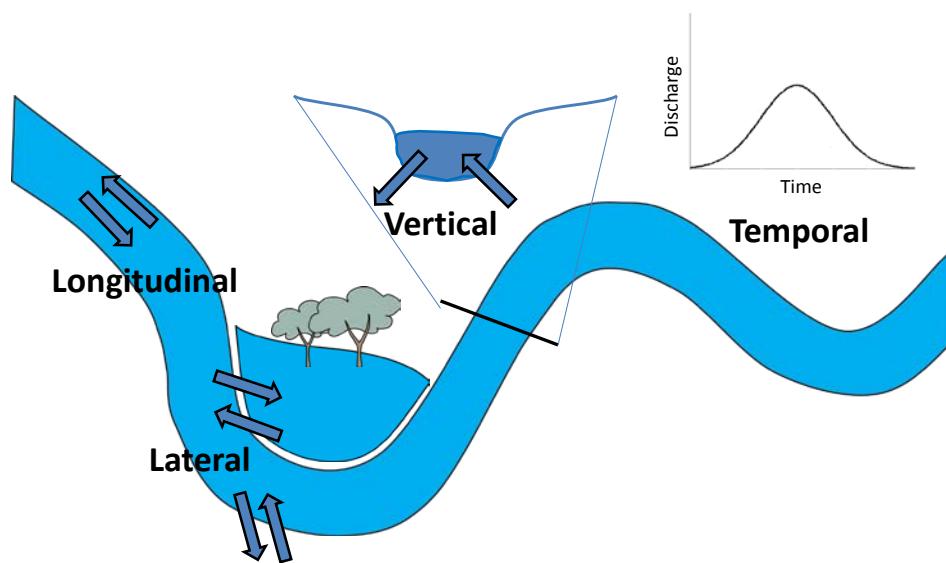
Patches have been identified in both terrestrial and aquatic ecosystems, Wu and Levin (1994), the authors of the hierarchical patch dynamics paradigm, define an ecological patch as being dependent on the system itself and the scale of investigation. For example, a patch may be an area of rocky well-draining soil, a geomorphological feature such as a secondary channel or a geographical region such as a coastal plain. Wu and Loucks (1995) illustrated that ecological systems are nested discontinuous hierarchies of patch mosaics where the dynamics of an ecological system are determined by a composite of patch dynamics across multiple scales. Within a patch, patterns and processes are linked, Wu and Loucks (1995) suggest an interplay where processes can maintain patterns and patterns constrain

processes. Finally, the hierarchical patch dynamics paradigm emphasises the importance of fine scale non-equilibrium states contributing to meta-stability at larger spatial scales (Wu and Loucks 1995). For example, patterns at the broad spatial scale of a floodplain may be maintained by variations or the ‘non-equilibrium’ state of flow in the river associated with this floodplain.

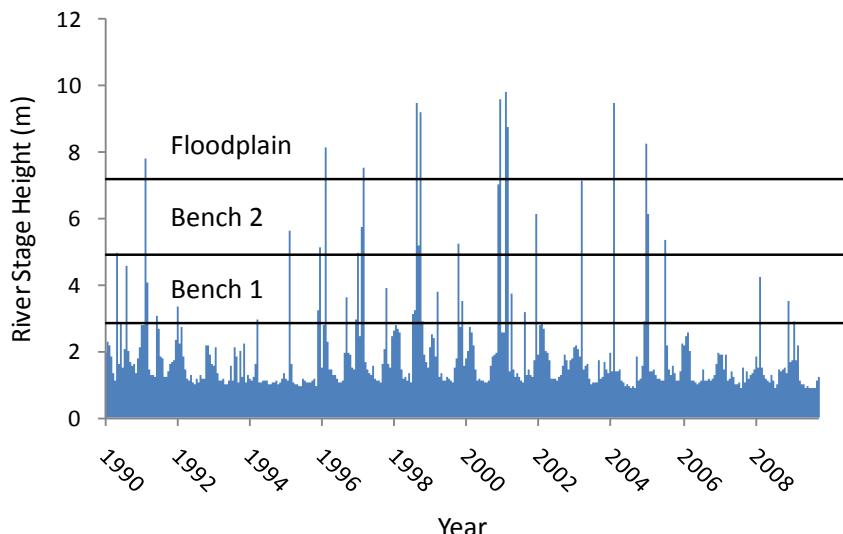
By definition, patches are unique from each other and therefore they have boundary areas between them; these areas are referred to as ecotones. Ecotones, are transitional areas between patches, that have a set of characteristics and interactions that are dependent on their position between distinct ecological systems (Naiman and Décamps 1990). For example, floodplains themselves on a broad scale, can be viewed as ecotones between river channels and upland regions while on a smaller spatial scale floodplains contain ecotones - between the land and water, between surface and ground waters and between in-stream habitat patches (Ward et al. 1999). Connectivity across ecotones connects adjacent ecological units, and is measured by the ease of which organisms, matter or energy can move between these units (Ward et al. 1999). However, floodplains in semi-arid areas, such as most of those in Australia’s Murray-Darling basin can also be viewed as ecosystems in their own right, due to the two alternating phases of “dry” and “inundated” that they experience too which the biota of these areas has adapted to (Colloff and Baldwin 2010).

Within riverine landscapes, connectivity between patches is often mediated by hydrological exchange. These exchanges occur across four dimensions; longitudinally - upstream to downstream, vertically - between the surface and subsurface, laterally - between a river and its floodplain and temporally through flow variability (Ward 1989) (Figure 1-2). The longitudinal movement of water from headwaters to lowland river reaches dominates in most river systems. Vertical hydrological connections within riverine landscapes link surface water to the hyporheic zone or sub-surface water bodies and stimulates productivity in both water bodies (Valett et al. 1994, Findlay 1995, Jones et al. 1995, Baker et al. 1999). Lateral connections within riverine landscapes are generally associated with floodplain inundation, and have been highlighted as significant in the ecology of riverine landscapes (Junk et al.

1989, Ward 1989). However, lateral hydrological connections can also occur ‘in-channel’, when increases in flow inundate in-channel features such as benches and anabranches but do not reach the floodplain. In large dryland rivers, within-channel connections are more common than those that connect a river and floodplain (Puckridge et al. 1998, Page et al. 2005) (Figure 1-3).



**Figure 1-2:** The four dimension of connections within a riverine landscape; longitudinal, vertical, lateral and temporal (Ward 1989).



**Figure 1-3:** The Gwydir River hydrograph at the Pallamallawa gauging station between 1990 and 2009. The horizontal lines show the average height above gauging level of the B1, B2 and FP levels at the study sites illustrating the more frequent inundation of the in-channel benches compared to the floodplain.

### 1.3 Temporal complexity in riverine landscapes

Flow is the ‘maestro’ variable in riverine ecology, it facilitates hydrological connectivity and affects patterns and processes occurring in riverine landscapes (Walker et al. 1995). The characteristics of flow; its magnitude, duration, frequency, timing and predictability, therefore have ecological relevance (Naiman et al. 2008) (Table 1-1). Thus, natural variability in flow is fundamental to production within, and sustainability of, riverine ecosystems (Poff et al. 1997, Bunn and Arthington 2002, Lytle and Poff 2004, Bunn et al. 2006b, Naiman et al. 2008).

**Table 1-1:** Common terms used to describe variability in river flows (adapted from Naiman et al. (2008))

Term	Definition
Magnitude	The amount of water moving past a fixed location per unit time. The larger (or smaller) the magnitude of a flood (or drought), the greater the expected physical impact.
Frequency	The number of events in a given period of time (e.g. per year). For a given river or stream, frequency is typically related inversely to magnitude.
Duration	The period of time associated with a particular flow event. Typically expressed in terms of the number of days a flood or drought lasts.
Timing	The date during the year that flood or drought occurs, often derived from long-term flow records
Predictability	The degree to which flood or drought events are temporally auto-correlated, typically on an annual cycle. Predictable events also might be correlated with other environmental signals (e.g., rainfall events, seasonal thermal extremes, photoperiod, sudden increase or decreases in flow)

Flow variability, particularly its timing, predictability and magnitude, shapes the biology of instream biota. Adaptations of in-stream biota to these aspects of flow follow similar patterns; timing affects life history adaptations, predictability alters behaviour, while magnitude and frequency require morphological adaptations (Lytle and Poff 2004). At a broader scale, Bunn and Arthington (2002) provide four principles that illustrate how riverine ecosystems are impacted by alterations to the natural flow regime; (i) physically changes to habitat can affect the distribution of aquatic plants, invertebrates and fish, (ii) altering the flow regime to which biota have adapted leading to recruitment failure and loss of biodiversity, (iii) altering the flow regime tends to increase the success of non-native species and (iv) changing the patterns of lateral and longitudinal connectivity restricts biota movements and leads to isolation of populations, failed recruitment and local extinctions.

Across a riverine landscape, flow variability creates a gradient of inundation frequencies that affects physical and chemical properties of soil and sediment as well as the biota they contain (Boulton and Lloyd 1992, Jenkins and Boulton 2003, Capon 2005, Valett et al. 2005). Floodplain soils have been referred to as a ‘seedbank’ for emerging invertebrates by Boulton and Lloyd (1992) who found that frequently inundated areas of the River Murray floodplain had a greater biomass and diversity of emerging invertebrates compared to less frequently inundated areas. In the Cooper Creek catchment of central Queensland, Australia, inundation frequency shaped the plant community structure and the abundance of seedlings emerging from floodplain soils (Capon 2005, Capon 2007). While in the Rio Grande River in New Mexico, USA, a frequently inundated floodplain was found by Valett et al. (2005) to have lower organic carbon stores than an infrequently inundated floodplain. This difference was believed to cause dissimilar biogeochemical responses to the inundation. Specifically, flood water over the less frequently inundated floodplain become anaerobic and ammonium was the dominant form of nitrogen while over the frequently inundated floodplain floodwater stayed aerobic and nitrate was the dominant form of nitrogen (Valett et al. 2005). Additionally, the infrequently flooded floodplain was believed to export a large amount of DOC while concentrations of DOC over the frequently flooded site were not different to those found in the main channel of the Rio Grande (Valett et al. 2005).

## **1.4 Spatial and temporal complexities in riverine landscapes and their effect on carbon and nutrient cycling**

### **1.4.1 The importance and variety of organic carbon**

Organic carbon is of fundamental importance to riverine landscapes; it is an energy source for invertebrates (Fischer et al. 2002) and fuels microbial communities that play a key role in the cycling of nutrients and are a potential food source for higher consumers (Dahm et al. 1998, Baker et al. 2000). Organic carbon is traditionally classified by its size fraction; particulate course organic carbon (PCOC; >1 mm), fine particulate organic carbon FPOC (<1 mm) and dissolved organic carbon DOC (<0.45 µm). DOC is the dominant form of organic

carbon found in freshwater environments, making up between 50% and 80% of organic matter transported in rivers (Spitz and Leenheer 1991), however, particulate forms of organic carbon are thought to be of greater importance to riverine foodwebs (Thorp et al. 1998).

Not all of the DOC transported in freshwater environments, is labile, available for immediate consumption, due to its low food ‘quality’ (Findlay and Sinsabaugh 1999, Docherty et al. 2006). The food ‘quality’ or bioavailability of DOC is defined either by the ability of a specific consumer group to utilise a particular carbon source or more generally by the ability of ultraviolet light to breakdown the DOC molecules (Moss 1998). Generally speaking, labile carbon sources in freshwater ecosystems include leachate from fresh leaves (O'Connell et al. 2000) and exudates from algae (Kaplan and Bott 1989) while refractory, low ‘quality’ organic carbon sources include leachate from aged leaf litter, bark and soil (O'Connell et al. 2000, Francis and Sheldon 2002). It is possible for low ‘quality’, high molecular weight carbon to be transformed to more bioavailable forms in the environment by photodegradation breaking down large DOM molecules increasing its bioavailability (Moran and Zepp 1997).

Regardless of its bioavailability, organic carbon in freshwater environments, can be broadly defined as being either autochthonous, originating from within the freshwater environment, or allochthonous, sourced externally from the freshwater environment. There has been much debate as to whether lowland rivers are predominantly dependent on autochthonous or allochthonous carbon sources (Thorp and Delong 2002). However, searching for a single answer ignores the variability in riverine systems, which may not be permanently dependent on either carbon source but fluctuate between sources depending on conditions such as hydrology, temperature and turbidity (Thorp and Delong 2002).

Hydrology plays a key role in determining the importance of autochthonous or allochthonous carbon sources in river ecosystems. During periods of intermediate and low

connectivity (low flow) between floodplain water bodies and the main river channel in the Danube River, autochthonous carbon was found to be the dominant form of aquatic carbon, while allochthonous carbon was dominant during periods of high connectivity (increased flow) (Hein et al. 1999, Hein et al. 2003). Gawne et al. (2007) found similar variation in the carbon source fuelling aquatic production in the River Murray of south eastern Australia, where increased flow suppressed phytoplankton production and increased allochthonous inputs. Similar findings of the effects of flow on autochthonous production and allochthonous carbon have been found in many rivers around the world (Boyer et al. 1997, Bernal et al. 2002, Petry et al. 2002, Valett et al. 2005, Gawne et al. 2007, Fellows et al. 2009, Westhorpe et al. 2012).

Periods of increased flow that mobilise allochthonous carbon from terrestrial sources can be considered as ‘hot moments’ of biogeochemical activity in riverine landscapes (McClain et al. 2003, Harms and Grimm 2008). These ‘hot moments’ can influence nutrient concentrations within the river and in inundated soils (Heffernan and Sponseller 2004, Valett et al. 2005, Noe and Hupp 2007). Increased rates of microbial metabolism in inundated soils, due to increased connectivity within the landscape improving microbial access to organic carbon, can quickly render soils anaerobic starting a sequence of terminal electron accepting processes which affect the exchanges of nutrients between inundated soils and the inundating water (Hedin et al. 1998, Baker et al. 1999, Baldwin and Mitchell 2000). This sequence starts on inundation with oxygen reduction consuming oxygen within the soil profile (Hamilton et al. 1997, Baldwin and Mitchell 2000, Liesack et al. 2000). Following the loss of oxygen, denitrification consumes nitrate present in surface and soil water (Heffernan and Sponseller 2004, Banach et al. 2009b) after which phosphate may be released from inundated soils due to the reduction of iron and sulfate (Baldwin et al. 1997, Roden and Edmonds 1997). Thus, the consumption of organic carbon during inundation events has direct consequences for the mobilisation or retention of nutrients from inundated soils.

### **1.4.2 The release of phosphorus from inundated soils**

Phosphorus is an important element in freshwater ecosystems as it is commonly found to be limiting primary productivity (Elser et al. 2007). Phosphorus is found in either inorganic form as phosphate or orthophosphate or in organic molecules. Inorganic phosphorus is preferentially used by both bacteria and phytoplankton (Cotner and Wetzel 1992) and often limits primary productivity in Australian lowland rivers (Hadwen et al. 2010, Westhorpe et al. 2010), therefore, its release from floodplains and in-channel features during periods of increased flow is of importance to the ecology of these rivers.

A soil's ability to sorb phosphates largely depends on its anion exchange capacity, which is determined by the amount of aluminium and iron oxides, weathered kaolin clays (under acidic conditions) and amorphous material present in a soil (Schaetzl and Anderson 2005). In saturated soils and sediments the biogeochemical cycling of phosphorus is influenced by many factors including dissolved oxygen concentrations, pH and the activity of microbes (Reddy et al. 1999).

The activity of anaerobic microbes is thought to play the largest role in the release of bound phosphorus from inundated soils and sediments (Baldwin et al. 1997, Roden and Edmonds 1997).  $\text{Fe}^{3+}$  reducing bacteria liberate phosphorus from Fe oxides and oxyhydroxides during  $\text{Fe}^{3+}$  reduction (Roden and Edmonds 1997); while sulfate reducing bacteria produce  $\text{H}_2\text{S}$  which releases phosphate from solid ferric minerals (Bostrom et al. 1988). The development of anoxia, however, is not a requirement for phosphorous release from inundated soils and sediments (Qiu and McComb 1994, 1995, Reddy et al. 1999). Qiu and McComb (1995) found significant releases of phosphate from lake sediments that were kept aerobic on re-wetting, however, these releases were smaller than when sediments were anaerobic.

### **1.4.3 Forms and the release of nitrogen from saturated soils**

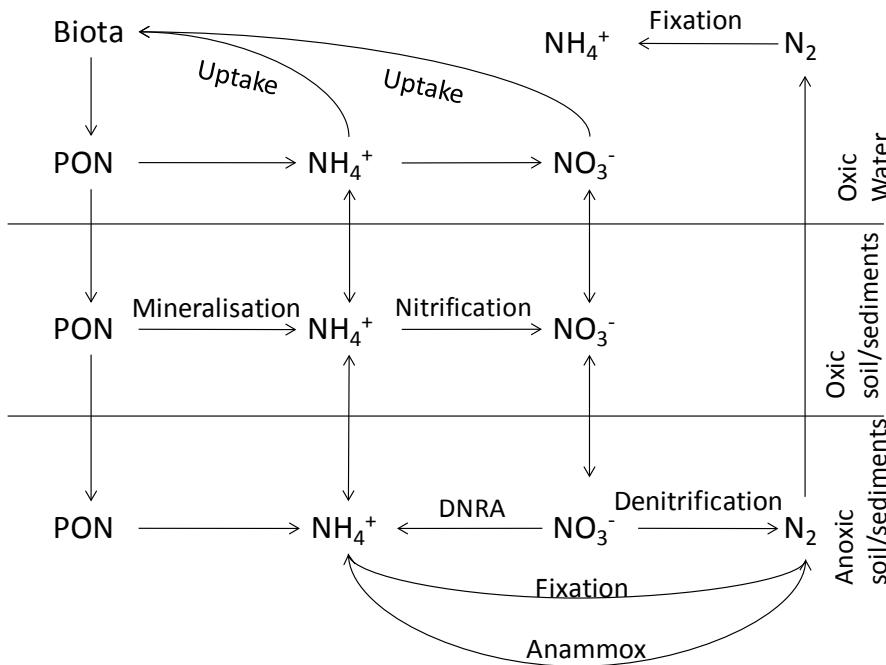
Nitrogen in freshwater ecosystems is found in many forms including in molecular form ( $\text{N}_2$ ), in reduced forms as ammonium and amine groups (- $\text{NH}_2$ ), in organic matter and as oxides including nitrate and nitrite and nitrous oxide (Duff and Triska 2000). Nitrogen availability often limits primary productivity in aquatic ecosystems (Elser et al. 1990) with dissolved inorganic forms of nitrogen used preferentially by phytoplankton and bacteria (Duff and Triska 2000). Nitrogen has been found to be limiting primary production in Australian lowland rivers (Hadwen et al. 2010, Westhorpe et al. 2010), therefore, the dynamics of nitrogen release or retention between inundated soil and river water can have consequences for the ecology of Australian lowland rivers.

Large flushes of nitrate and ammonium are often observed on the wetting of dry soils (Birch 1960, Sparling and Ross 1988, West et al. 1988, Qiu and McComb 1996, Valett et al. 2005, Kobayashi et al. 2009). Following mobilisation nitrogen can be transformed between nitrate and ammonium and other forms of nitrogen with the dominant process dependent on environmental conditions such as the presence or absence of oxygen, the functional abilities of the microbial population and the amount of nitrogen and carbon present (Baldwin and Mitchell 2000, Burgin and Hamilton 2007) (Figure 1-4).

Ammonium is produced by the mineralisation of organic matter and can subsequently be biologically assimilated or converted, by nitrification, to nitrate (Patrick and Reddy 1976). Both mineralisation and nitrification are microbially mediated, with nitrification only occurring under aerobic conditions. In anaerobic soils or sediments, ammonium may still be produced via organic matter mineralisation and assimilated into biomass; however, other microbially mediated processes can affect its fate. In anaerobic environments microbes are able to produce ammonium via dissimilatory nitrate reduction to ammonium (DNRA). This may occur via one of two pathways, either coupled to sulfur oxidation or via fermentation (Burgin and Hamilton 2007). DNRA is believed to be a dominant process where carbon concentrations are high and nitrate concentrations low (Burgin and Hamilton 2007). A

stylised representation of the nitrogen cycle in aquatic and soil systems is provided in Figure 1-4.

Nitrate is also affected by microbial processes whose occurrence is dependent on the presence or absence of oxygen (Firestone et al. 1980, Firestone and Davidson 1989). Under aerobic conditions, nitrate can be produced by nitrification. Under anaerobic conditions nitrate can be lost via DNRA, as discussed above (see Figure 1-4) or via denitrification. Denitrification is a microbial process that couples the oxidation of nitrate with the reduction of organic carbon (Ponnamperuma 1972, Baker et al. 1999, Morrice et al. 2000, Whitmire and Hamilton 2005) producing either nitrous oxide or di-nitrogen gas, both of which have a low solubility in water and are prone to diffuse from the aquatic environment (Hill 1996). The conversion of nitrate to nitrous oxide or di-nitrogen gas can also be coupled to the oxidation of iron and mediated either abiotically or by microbes (Burgin and Hamilton 2007). Nitrate may also be assimilated into biomass under either aerobic or anaerobic conditions. Lastly, nitrate may be lost via anaerobic ammonium oxidation (anammox), which is a chemolithotrophic process that combines nitrite with ammonium producing di-nitrogen gas (Burgin and Hamilton 2007).



**Figure 1-4:** The nitrogen cycle in aquatic systems (modified from Baldwin and Mitchell 2000) (PON - particulate organic nitrogen) (DNRA - dissimilatory nitrate reduction to ammonium).

#### 1.4.4 The effects of repeated cycles of wetting and drying on nutrient cycling

It is largely unknown how repeated sequences of inundation and drying effect nutrient and carbon cycling in soils (Baldwin and Mitchell 2000, Baldwin et al. 2000, Fierer and Schimel 2002, Fierer et al. 2003, Wilson et al. 2011). Inundation isolates a soil from the atmosphere and often results in anaerobic conditions in the soil profile and potentially in the water column above the inundated soil (Smith 1985, Valett et al. 2005, Hladz et al. 2011). The reasons for the development of anaerobic conditions are twofold; (i) oxygen diffuses 10000 times slower in water than in air, limiting rates of oxygen supply to inundated soils (Gottschal 1985) and (ii) rates of soil metabolism increase during inundation, increasing rates of oxygen consumption (Valett et al. 2005, Sánchez-Andrés et al. 2010, Wilson et al. 2011). If a soil is frequently rendered anaerobic it may alter its microbial community by selecting for facultative bacteria that can survive and grow under either aerobic and anaerobic conditions, rather than an obligate bacteria which require either aerobic or anaerobic conditions (Baldwin and Mitchell 2000). This change in microbial community structure may affect how nutrients are cycled during periods of inundation. The

mobilisation of phosphorus, for example, could be reduced if sulfate reducing bacteria, obligate anaerobes (Gibson 1990), are lost from soil microbial communities. Additionally, rates of denitrification, a process carried out by facultative anaerobic bacteria, may increase due to reduced competition for organic carbon. Little research has been completed on the effects of wetting and drying cycles on soil microbial communities, either those driven by rainfall or irrigation mediated increasing soil moisture (Fierer et al. 2003) or by increases in river flow inundating floodplain soils (Baldwin and Mitchell 2000). However, Fierer et al. (2003) illustrated that the microbial community of soils that do not naturally experience frequent wetting and drying may be altered if the frequency of these events increase. Moreover, evidence of wetting and drying cycles affecting soil microbial functional abilities was provided by Franzluebbers et al. (1994) who observed that repeated wetting and drying cycles decreased the activity and growth of facultative aerobic nitrifying bacteria. Course taxonomic changes in soil bacterial community structure have also been observed as a consequence of soil rewetting (Aanderud and Lennon 2011).

Changes to the microbial community are not the only changes that may affect how nutrients are cycled in frequently inundated soils. The amount of crystalline  $\text{Fe}^{3+}$  reduces after repeated wetting and drying events (Darke et al. 1996), increasing the availability of  $\text{Fe}^{3+}$  to bacterial reduction (Munch and Ottow 1980, Lovley 1991, Roden 2003) which is likely to lead to more phosphorus bound to Fe oxides and oxyhydroxides being released. Nitrogen cycling may also be affected, with predictions of increased coupling of nitrification and denitrification resulting in greater losses of soil nitrogen (Baldwin and Mitchell 2000). However, repeated cycles of wetting and drying may increase soil nitrogen stores, if it increases the resistance of some plant nitrogen compounds to microbial attack (Franzluebbers et al. 1994).

Soil carbon and the fraction of bioavailable soil carbon are affected by wetting and drying cycles in largely unknown ways. The effects of inundation on the bioavailable fraction of soil DOC is unclear as it is both consumed and produced during inundation. During inundation rates of soil metabolism increase, consuming bioavailable soil carbon (Valett et al. 2005,

Wilson et al. 2011), however, this may be off-set, in the short term, by the liberation of DOC from bulk soil carbon stores (Lundquist et al. 1999, Wilson et al. 2011). In the longer term, repeated wetting and drying cycles and the associated production and consumption of bioavailable soil carbon may deplete the fraction of bulk soil carbon that is converted into DOC during inundation, reducing the supply of both DOC and bioavailable DOC (Fierer and Schimel 2002).

It is not clear how these physical, chemical and biological changes that occur in frequently inundated soils will affect the exchanges of organic carbon and inorganic nutrients between the more frequently inundated in-channel features compared to those of the less frequently inundated floodplain. In addition to the changes mediated by inundation frequency, levels of different heights in the landscape have been shown to differ in aspects such as soil texture and organic content (Sheldon and Thoms 2006, Southwell and Thoms 2011) that will also affect exchanges of organic carbon and inorganic nutrients mediated by inundation. Therefore, gaining an understanding of how these soil properties vary with height in the landscape will improve our understanding of the exchanges likely to occur during inundation.

## **1.5 In-channel benches – special geomorphic features**

The potential role of in-channel features, such as benches, in facilitating exchanges between the terrestrial and aquatic environments has been highlighted by many authors (Thoms and Olley 2004, Sheldon and Thoms 2006, Southwell and Thoms 2011). But given the uncertainty, highlighted above, surrounding how inundation frequency affects the mobilisation and cycling of organic carbon and inorganic forms of nitrogen and phosphorus, it is unclear if the inundation of in-channel benches will create exchanges that are similar to those that occur during floodplain inundation events. This section of the thesis will focus on in-channel benches; investigating what they are, how they are formed and the stores of carbon and nutrients found in their soils.

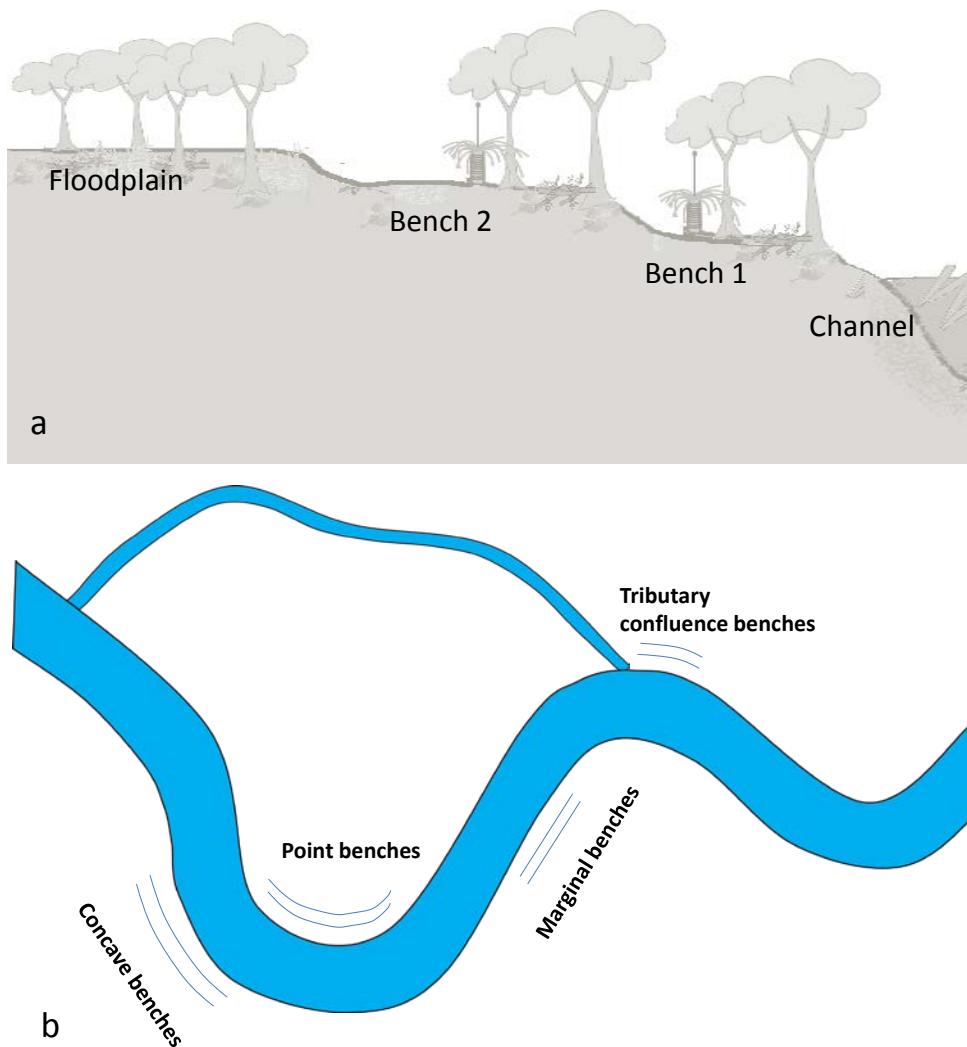
### **1.5.1 Defining and classifying in-channel benches**

The common definition of an ‘in-channel bench’ is a horizontal surface within a river channel, although there is no universally accepted definition of an in-channel bench in the literature (Vietz 2008). It is generally accepted that in-channel benches are depositional features that accumulate large quantities of organic matter in their soils and as leaf litter on their surfaces (Woodyer et al. 1979, Page and Nanson 1982, Changxing et al. 1999, Sheldon and Thoms 2006, Vietz 2008). In-channel benches can occur singly or in groups at different heights in a river channel and are found at multiple longitudinal locations along a river channel (Figure 1-5). This variety has led to some confusion in in-channel bench classification. For example, Vietz et al. (2008) found 33 qualifiers proceeding the term “bench” in a review of the English-language literature relating to fluvial benches. Four broad in-channel bench classifications based on location in the river channel were outlined by Changxing et al. (1999) from work in the Dee River in the UK. This classification system has gained wider acceptance including use in an Australian context by Vietz (2008) in his PhD. thesis concerning the formation and destruction of concave benches in the Ovens River and his previous publication (Vietz et al. 2004).

1. **Concave (counterpoint) benches** as suggested by their name are located on the concave bank of tight river bends. They are largely constructed from sandy silts with a mean soil particle size of 0.02 mm and an organic content of 5.8% (Changxing et al. 1999). The organic content of concave benches increases from their base to their surface while soil particle size decreases (Woodyer et al. 1979, Nanson and Page 1983, Changxing et al. 1999).
2. **Point benches** are located near the apex point of convex river bends (Woodyer et al. 1979, Changxing et al. 1999, Thoms and Olley 2004). They are dominated by silty sands with a mean soil particle size of 0.06 mm (Changxing et al. 1999). They have a distinct basal discontinuity which is marked by a decreased soil particle grain size overlying a coarser basal layer, however, their organic matter content is relatively uniform throughout the bench at approximately 4% (Changxing et al. 1999).

3. **Marginal benches** are somewhat of an intermediate between concave and point benches in terms of sediment grain size and organic content. Only a limited number of marginal benches were found by Changxing et al. (1999), these were described as having a mean soil particle size of 0.058 mm with an organic content of 5.3%, they were lower in elevation in the river channel than either point or concave benches.
4. **Tributary confluence benches** are common along upland areas of regulated streams (Petts 1984) but were not found on the Dee River by Changxing et al. (1999). Consequently they were not described in any detail apart from a brief note that they were the most coarse grained of any in-channel bench type.

In-channel benches are particularly abundant in the meandering lowland rivers of inland Australia (Woodyer 1968, Nanson 1980, Page and Nanson 1982, Sheldon and Thoms 2006, Southwell and Thoms 2011). For example, concave in-channel benches were found, on average, every 0.5 and 1 km in the midland and lowland Ovens River, respectively, and although not specifically detailed the density of all in-channel bench types has been reported to be much higher (Vietz et al. 2004).



**Figure 1-5:** Conceptual representation of (a) multiple in-channel benches occurring at one location along a river and (b) the positions of each of the different in-channel bench types outlined by Changxing et al. (1999).

### 1.5.2 Concave bench formation and destruction

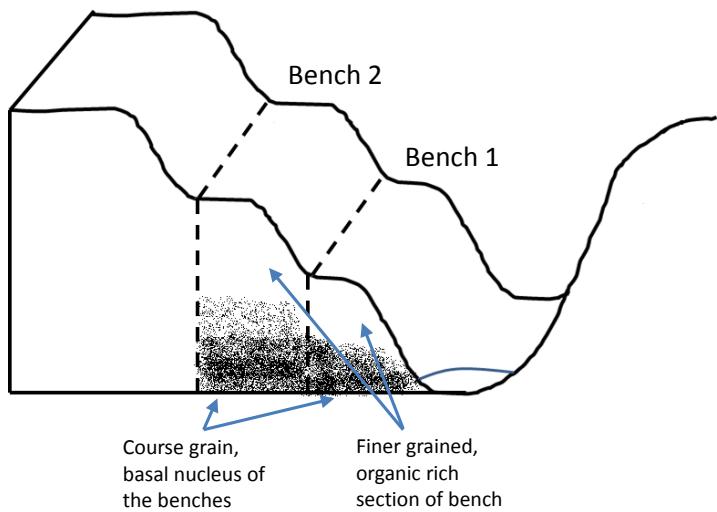
There are two widely cited conceptual models of concave bench formation: (i) the aggradation phase model of Erskine and Livingstone (1999) and (ii) the channel migration model of Page and Nanson (1983). The aggradation model suggests that erosion during catastrophic floods destroys in-channel benches while medium sized floods re-deposit sediments, re-building in-channel benches (Erskine and Livingstone 1999). The channel migration model of Page and Nanson (1983) suggests that channel widening at tight river

bends, causing flow separation and back flow, resulting in sedimentation and the development of an in-channel bench on the concave bank. Specifically, a longitudinal shaped bar is formed at the point of flow separation due to a reduction in flow velocities (flow expansion phase), this bar forms a platform for sedimentation and in-channel bench formation (nucleus phase). Aggradation of fine sands, due to the reduction in flow velocities associated with flow separation continues until the in-channel bench reaches about 2/3 bankfull stage height when vegetation becomes established further increasing sedimentation rates (mature bench phase). At this point, Nanson and Page (1983) found that River Red gums became established causing rapid sedimentation. Finally, lateral extension of the concave bench develops at the upstream end due to further point bar development as the convex bank expands further (bench extension phase) (Nanson and Page 1983).

Work by Vietz et al. (2012) found the channel migration model best explained the formation of concave benches in the Ovens River of Victoria, south eastern Australia. The conditions created by the expansion of the river channel at abrupt river bends reduced flow velocities causing the deposition of suspended sediment. Using flow models Vietz et al. (2012) illustrated that the deposition of sediment at this location was persistent during all flow heights from bench full to bankfull and beyond. Destruction of in-channel benches was not directly investigated by Vietz et al. (2012) but they speculated that prolonged periods of low flow are likely to be destructive to in-channel benches. This idea is backed by evidence that flow regulation, which produces prolonged periods of low flow, decreased the frequency of in-channel benches in a regulated reach of the Barwon-Darling River compared to a similar but unregulated reach (Sheldon and Thoms 2006).

The process of concave bench formation as outlined by Page and Nanson (1983) provides an insight into the structure of in-channel benches commonly cited in the literature. Concave benches have been found to have two parts; an underlying basal nucleus consisting of coarse grained sediments, formed in the nucleus stage, which is overlain by fine sediments, rich in organic matter, deposited during later stages of formation (Woodyer et al. 1979,

Nanson and Page 1983, Erskine and Livingstone 1999) (Figure 1-6). It is the storage of organic carbon and nutrients in the organic matter rich, upper bench soil that may allow for ecologically important exchanges of organic carbon and inorganic nutrients between terrestrial and aquatic ecosystems during flow pulses.



**Figure 1-6:** A conceptual model in-channel bench cross section illustrating the course base layer and a fining of soil texture with height within the bench.

### 1.5.3 Nitrogen, phosphorus and carbon in in-channel bench soils

Little is known about the dynamics of carbon and nutrients in in-channel bench soils either during inundation or between inundation events. In the only study so far published on carbon and nutrients in these soils, Southwell and Thoms (2011) found that in-channel benches in the Darling River had increasing total phosphorus and total carbon contents with greater height in the river channel and that total nitrogen content was not related to in-channel bench height. Less is known about the cycling of in-channel benches during inundation events. Vietz et al. (2012) showed that benches retain sediments and particulate organic matter via sedimentation. Denitrification rates were found to increase during with the length of inundated period in artificial floodplains built in an agricultural stream suggesting that benches soils may work in a similar manner (Roley et al. 2012). However, they may release smaller sized fractions of organic matter (Sheldon and Thoms 2006) as well

as inorganic nutrients. In-channel benches, therefore, can be viewed as areas of storage for organic carbon and nutrients within the river channel that when inundated create exchanges between the terrestrial aquatic ecosystems; it is the nature of these exchanges that are the subject of this thesis.

## **1.6 The storage and release of carbon and nutrients from in-channel benches; a conceptual model**

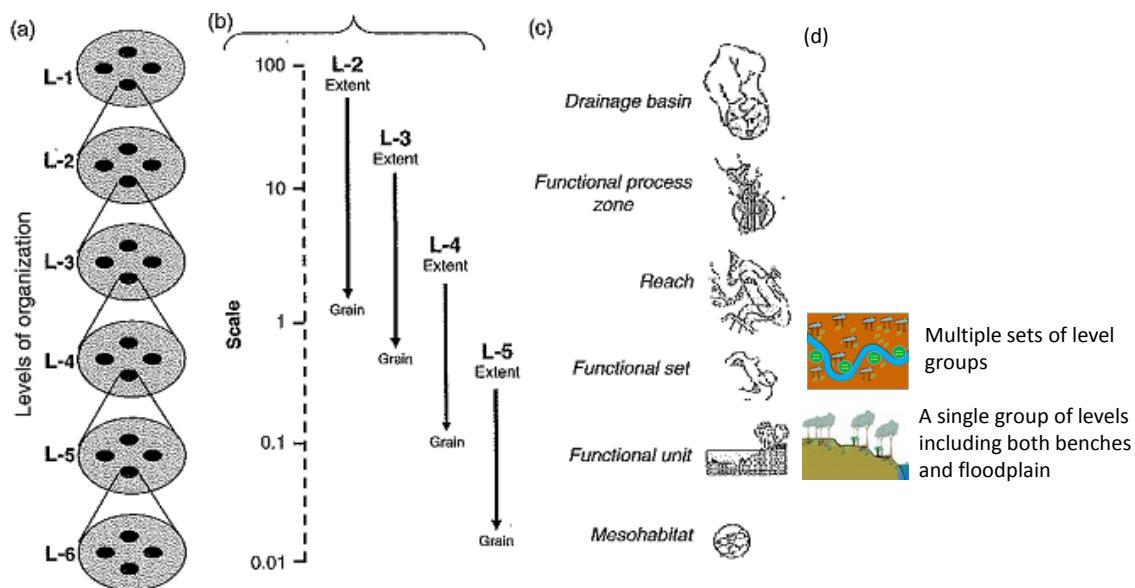
### **1.6.1 The role of in-channel benches in facilitating terrestrial/aquatic exchanges**

In-channel benches have large stores of carbon and nutrients and are ideally located, within river channels, for facilitating exchanges between terrestrial and aquatic environments in regulated rivers (Sheldon and Thoms 2006; Southwell and Thoms 2011). However, little is known about the biogeochemical response of in-channel benches to inundation or how this varies across in-channel benches of different heights. Based on a review of the scientific literature regarding the effects of inundation frequency on carbon and nutrient cycling in soils and what is known about the stores of nutrients and carbon in in-channel bench soils a conceptual model suggesting; (i) what is stored in in-channel bench soils of different heights, (ii) how these benches will respond to inundation and (iii) the timing of peaks in solute concentrations resulting from these stores and processes during a flow pulse has been outlined below (Figure 1-9).

### **1.6.2 Spatial scale of the model**

This thesis investigates in-channel benches in the lowland Gwydir River, located in the northern Murray-Darling Basin, Australia. Each in-channel bench set investigated consisted of four horizontal levels; channel bed (CH), bench 1 (B1), bench 2 (B2) and floodplain (FP) levels (Figure 1-5a). Taking a landscape ecological perspective; each level is nested in a bench set, which is nested in the study reach of the lower Gwydir River, which is nested in

the Gwydir River Valley. As per Thorp et al. (2008) “hierarchical organisation of patches with a riverine landscape” each in-channel bench set investigated would fall into the category of a functional unit and the multiple in-channel sets as a functional set nested in a river reach (Figure 1-7).



**Figure 1-7:** Hierarchical organisation of patches within a riverine landscape. (a) A conceptual diagram of hierarchical patches where patches at one scale are nested within a level of organisation above; (b) the scale associated with a hierarchically organised system and the implication of grain and extent based on hierarchical theory; (c) physical patches of the riverine landscape that can be recognised at various levels of organisation and scale (Thorp et al. 2008); and (d) where both a single level set and multiple level sets in a river reach would sit in this hierarchical organisation.

### 1.6.3 Temporal component

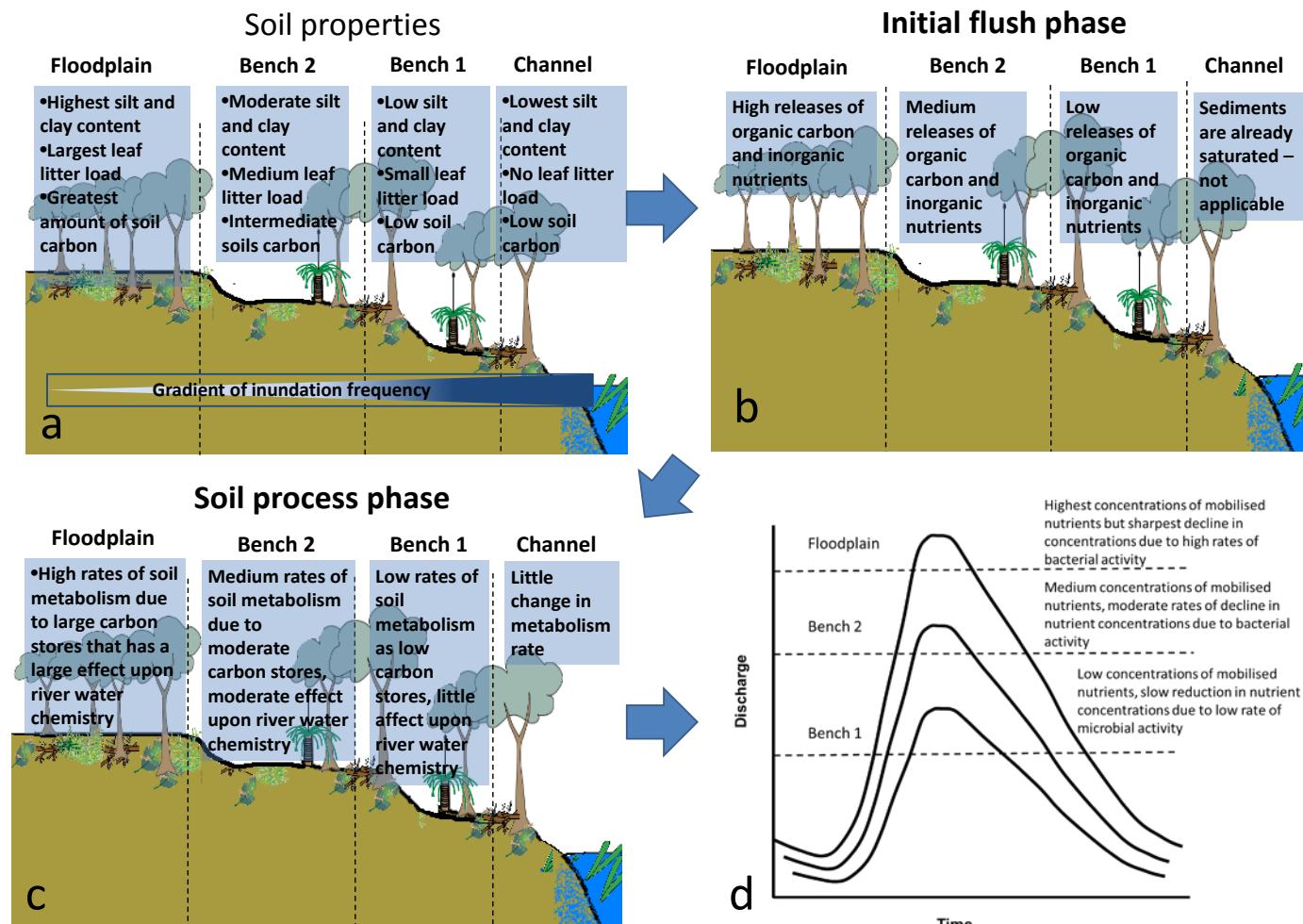
Temporally, levels in a riverine landscape experience alternating conditions of wetting and drying which need to be incorporated in this conceptual model. The first temporal component of this model is the ‘dry period’ in-between inundation events, when a level in the landscape is above river stage height. These periods can extend for months or years depending in-channel height and the prevailing climatic conditions. However, the main focus of this thesis is on the processes that occur during inundation. On wetting, soils

release an ‘initial flush’ of carbon and nutrients to the inundating water, this release has been defined as the second temporal component in the model. After the ‘initial flush’, exchanges of carbon and nutrients occurring between the inundated level and the inundating water are largely determined by metabolic processes occurring within the soil, termed here the ‘soil process’ phase. It should be noted that there is no clear temporal boundary between the ‘initial flush’ and ‘soil process’ phases; in fact it is likely that soil processes are beginning while solutes are still being flushed from a soil. A conceptual representation of these processes is presented in (Figure 1-8).

It is also important to note that during a flow event the temporal phases outlined above may occur simultaneously across different heights within a riverine landscape. River stage height can take hours or days to rise to its maximum level during a flood or flow event. Therefore, the lower levels may have been inundated for hours, while levels in the middle of the channel are only just being inundated and levels still higher in the channel such as high benches or the floodplain may not yet be inundated. Thus, during a flow event it is possible for all three temporal components of this model to be occurring at the same time. The exchanges that occur during a flow pulse are the sum of all the different processes that are occurring at different levels in the landscape.

Dry period	<ul style="list-style-type: none"> <li>Accumulation of organic carbon via terrestrial primary production and the integration of leaf litter into the soil profile</li> <li>Soil processes limited by soil moisture content</li> <li>Mineralisation and nitrification are the dominant process affecting the fate of nitrogen</li> <li>Wind erosion and deposition</li> </ul>
Initial flush	<ul style="list-style-type: none"> <li>Large initial flush of organic carbon and inorganic nutrients from the inundated soils</li> <li>This release has been shown to be related to microbial biomass, however the specific processes are still unknown</li> <li>Aerobic respiration, including nitrification will be occurring during this phase.</li> <li>Erosion or deposition</li> </ul>
Soil processes	<ul style="list-style-type: none"> <li>Increased rates of soil respiration result in the loss of oxygen from soils and the commencement of anaerobic respiration</li> <li>Denitrification will result in the loss of nitrate</li> <li>Sulfate and iron reduction will increase the mobility of phosphate</li> <li>Continued erosion and deposition</li> </ul>

**Figure 1-8:** Temporal components of this conceptual model and the processes that affect stores of soil nutrients and potential exchanges between the terrestrial environments.



**Figure 1-9:** The effects of inundation frequency on (a) soil resources at different heights in a dryland river channel , (b) release of carbon and nutrients on inundation, (c) rates of soil metabolism during inundation, and (d) concentrations of carbon and nutrients during flow events.

## **1.7 Thesis Overview, Aims and structure**

As yet there is no clear understanding of the role that flow pulses and inundated in-channel features play in supplementing lowland river ecosystems with accumulated allochthonous carbon and inorganic nutrients. Previous studies of in-channel benches have either focused on their mode of formation and destruction (Woodyer et al. 1979, Nanson 1980, Page and Nanson 1982, Nanson and Page 1983, Changxing et al. 1999, Erskine and Livingstone 1999, Thoms and Olley 2004, Southwell and Thoms 2006, Vietz et al. 2012) or on their storage of organic carbon and nutrients (Sheldon and Thoms 2006, Southwell and Thoms 2011). The release or retention of nutrients and carbon from inundated in-channel benches has not previously been quantified thus we cannot be sure of their ability to supplement aquatic ecosystems with terrestrially derived carbon or if they are sources or sinks for inorganic nutrients that could fuel local in-stream productivity. There has, however, been a recognition that we need a greater understanding of flow pulses and what is mobilised during these events from the inundation of in-channel features (Davies et al. 1994, Puckridge et al. 1998, Sheldon 2005, Bunn et al. 2006b).

Given this knowledge gap, the broad aim of this thesis is to improve our understanding of the role that in-channel benches play in providing organic carbon and inorganic nutrients to aquatic ecosystems during periods of increased flow. This thesis is set out in the following manner;

Chapter 1 - Investigates spatial and temporal variability in riverine landscapes and the effects of this variability on nutrient and carbon cycling. The focus then shifts to in-channel benches; defining an in-channel bench then reviewing what is known about their formation, structure and stores of carbon, nitrogen and phosphorus. Based on these reviews, a conceptual model is presented that formulates the hypotheses that drives the investigations in the following chapters.

Chapter 2 - Gives details of the study sites; the Gwydir and Namoi River catchments.

Chapter 3 - Investigates the distribution of inorganic nutrients, DOC and its bioavailability found within the Gwydir River channel. These distributions are investigated across in-channel and floodplain levels in order to determine the effects of inundation frequency across a gradient of soil properties.

Chapter 4 - Examines and compares the terminal electron accepting processes occurring in inundated soil sampled from different levels in the Gwydir River landscape.

Chapter 5 - Investigates nutrients and DOC dynamics that occurred during a flow event in the lower Namoi River (the Namoi River was used due to a lack of flow pulses in the Gwydir River during the study period for this thesis).

Chapter 6 – Investigates the diel patterns in  $\text{NH}_4^+$  and DOC concentrations found during the flow pulse in the Namoi River (chapter 5) using mesocosms in a laboratory based experiment.

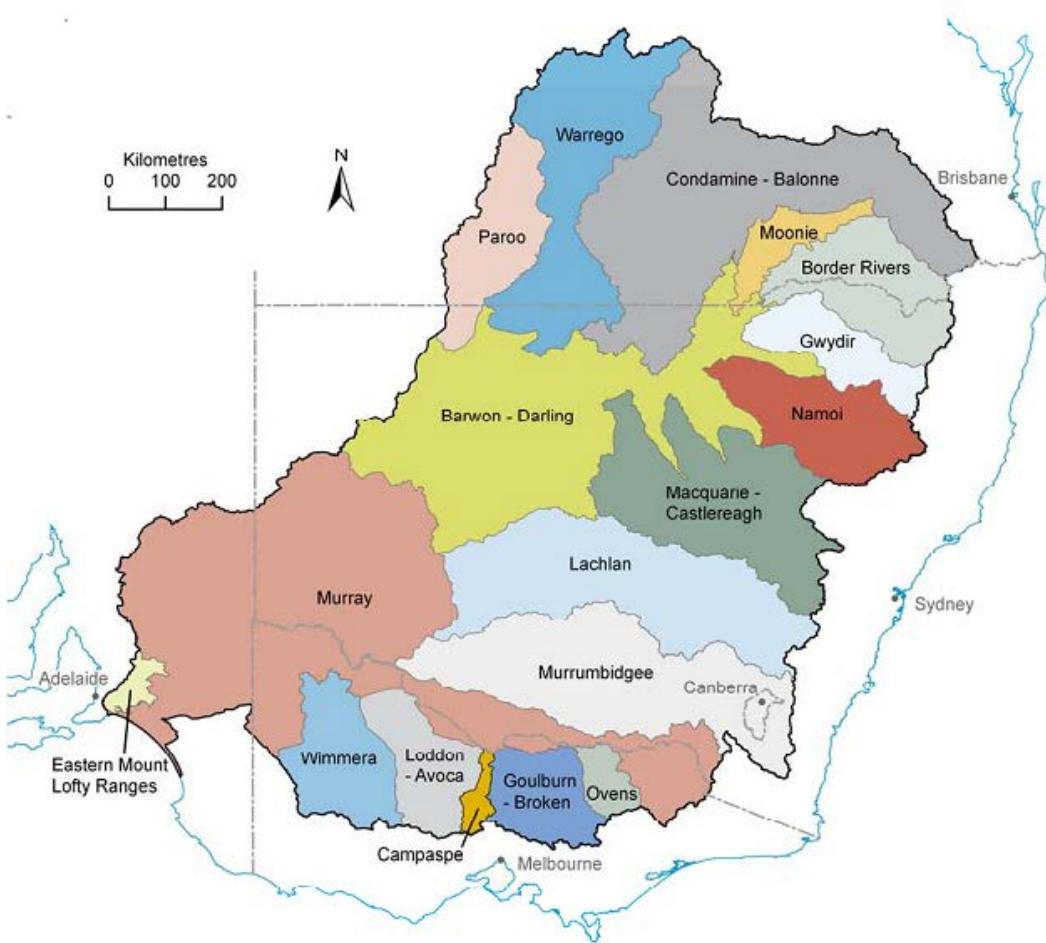
Chapter 7 – Uses modelled river flows to investigate the frequency that in-channel benches in the Gwydir River are inundated under three flow scenarios; with flow rules, without flow rules and under a natural flow regime.

Chapter 8 - Provides of a summary of the finding of the thesis. The findings of each chapter are summarised and used to update the conceptual model presented in Chapter 1, highlighting the implications of this research for river management and the areas where further research is warranted.

## **Chapter 2. Site Descriptions**

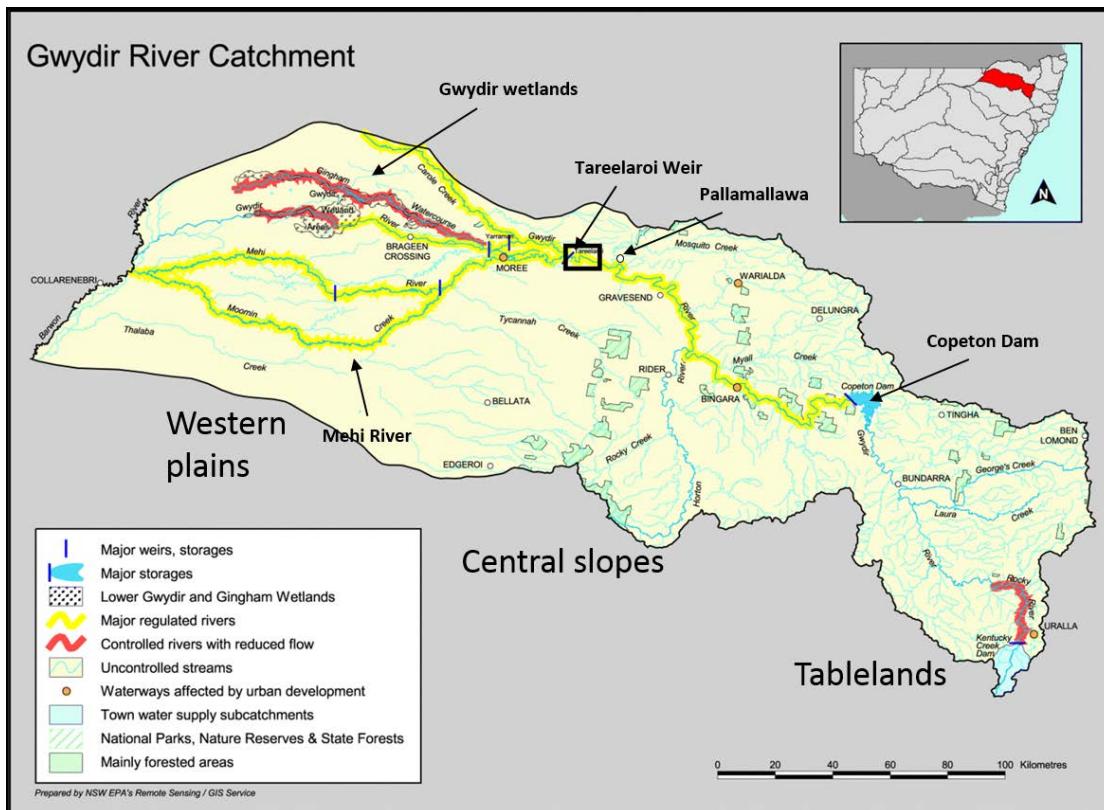
### **2.1 The Gwydir River Catchment**

The Gwydir River catchment is located within the northern region of the Murray Darling Basin, Australia, between the Border Rivers catchment to the north and the Namoi River catchment to the south (Figure 2-1). Its eastern boundary is formed by the Great Dividing Range and it extends west to the town of Collarenebri (Figure 2-2). The River rises in the southern part of the New England Plateau, near Uralla at an elevation of 1050 m above sea level from where it flows into the Barwon River in the western plains country. The Tareelaroi Weir splits the river in two; the southern branch becomes the Mehi River and the northern branch continues as the Gwydir River terminating in the Gwydir Wetlands, which are a Ramsar listed, wetland delta complex. Overall the topography of the Gwydir region includes three distinct areas; the plateau area in the east, the slopes area in the central catchment and the plains area in the west of the catchment (Figure 2-2).



**Figure 2-1:** Map of the Catchments in the Murray-Darling Basin (CSIRO 2007a); the neighbouring Gwydir and Namoi catchment are located in the northern part of the MDB between the Border Rivers catchment and the Macquarie-Castlereagh catchment.

The major tributaries of the Gwydir River are the Copes, Moredun, Georges and Laura Creeks as well as the Horton River. These tributaries all join the river at the base of slopes area, above Gravesend, in the eastern part of the catchment (Figure 2-2). In this part of the catchment the streams have sandy or stony beds with moderate to high flow rates and are formed upon granodiorite and granite (Thoms et al. 1998). In contrast, the lower catchment below Gravesend has flows that are generally slower and the river bed is comprised of sand and silt (Thoms et al. 1998). This western plains area encompasses a large fertile lowland river floodplain, a result of the weathering of basalts (Thoms et al. 1998). Overall, the catchment covers a total area of approximately 26500 km<sup>2</sup>.



**Figure 2-2:** Map of the Gwydir River, including tributaries, major water storages and weirs.

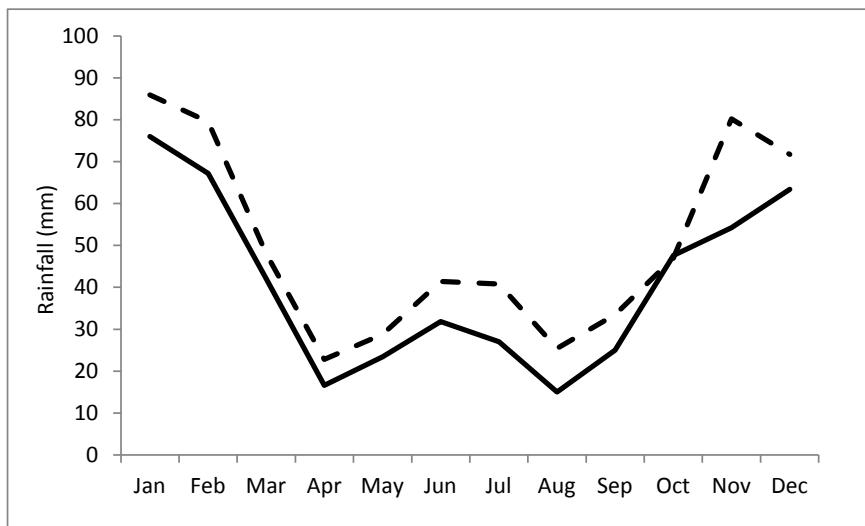
The black square indicates the study area, which is presented in more detail in Figure 2-5 (sourced from: <http://www.environment.nsw.gov.au/ieo/Gwydir/maplg.htm>).

### 2.1.1 Climate

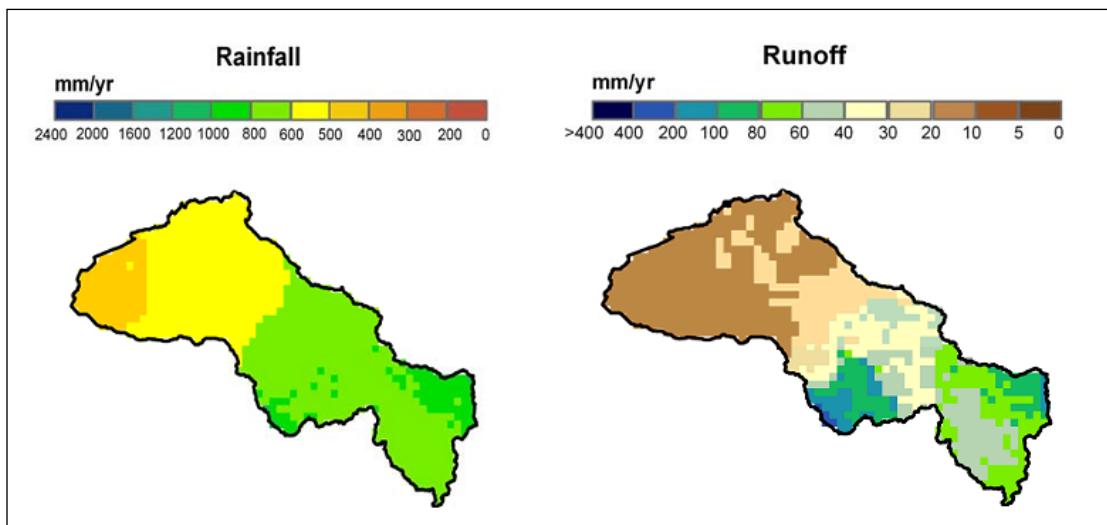
Rainfall in the Gwydir catchment is dominated by summer storms that form as a result of tropical low pressure systems and monsoonal troughs decaying into rain depressions moving inland from the north-east (Thoms et al. 1998). Winter rainfall, though not as common as summer rainfall, is caused by cold fronts moving up from the south or south-west lifting warmer moister air from the north-east (Thoms et al. 1998).

There is a distinct temperature and rainfall gradient between the east and west of the catchment; the east is cooler and wetter while the west is drier and hotter.

Mean annual rainfall in the headwaters of the catchment is in excess of 750 mm while at the junction of the Mehi and Barwon Rivers it is less than 450 mm (Thoms et al. 1998). Rainfall is highly variable between years across the entire catchment as illustrated by the difference in mean and median monthly rainfall (Figure 2-3). Mean monthly rainfall and runoff also vary spatially in the catchment with the greater amounts of runoff produced in the east of the catchment (Figure 2-4).



**Figure 2-3:** Median (solid line) and mean (dashed line) monthly rainfall from Moree aero weather station from between 1995 and 2014 (data sourced from Australian Bureau of meteorology web site).



**Figure 2-4:** Spatial distribution of annual rainfall and modelled runoff averaged for the Gwydir catchment from 1895 – 2006 (CSIRO 2007a)

### 2.1.2 Land use and water extraction

Land use in the Gwydir Catchment is dominated by agriculture. The largest land users are dryland pasture followed by dryland cropping (Table 2-1). Irrigated agriculture only accounts for 3.6% of the land area of the catchment (Table 2-1) but is the largest water user in the catchment.

The Gwydir River is highly regulated with over 44% of the long term average stream flow extracted from the river each year (CSIRO 2007a). The amount of water extracted from year to year varies from less than 100 GL to greater 500 GL with more water extracted during years of increased river flow (CSIRO 2007a). The largest flow regulator on the Gwydir River is Copeton Dam, with a storage capacity of over a million mega litres (ML). Construction of the dam, near the lower end of the New England Plateau (Figure 2-2), was completed in 1976. Another major flow regulator on the Gwydir River is Tareelaroi Weir, constructed at the junction between the Mehi and Gwydir Rivers (Figure 2-2) it regulates the flow between these river systems and is capable of holding 2500 ML.

**Table 2-1:** Summary of land use in the year 2000 in the Gwydir Catchment (CSIRO 2007a)

Land use Area	percentage	Ha
Dryland pasture	58.60%	1 462 400
Dryland crops	22.40%	559 000
Native vegetation	15.00%	372 900
Irrigated crops	3.60%	90 500
Water	0.20%	4 900
Plantation forests	0.10%	1 500
Urban	0.10%	2 700
Total	100.00%	2 493 900

### **2.1.3 Zones of the Gwydir River**

Thoms et al. (1998) identified 5 distinct river zones in the Gwydir River; the pool, constrained, armoured, mobile and meander zones. Each of these river zones reflects variation in stream gradient, power, valley dimensions and boundary material that affect its ability to adjust to changes in flow and sediment regimes (Thoms et al. 1998). Within both the mobile and meandering zones Thoms et al. (1998) describe in-channel depositional features, such as in-channel benches and bars, as common features.

### **2.1.4 Study sites**

The sites used during this study are within the meandering zone of the Gwydir River, as defined by Thoms et al. (1998). The study area was located approximately 30 km upstream of Moree and comprised of five individual sites (Figure 2-5). Each site had four level heights; CH, B1, B2 and FP which are referred to as levels in this thesis, as they represented horizontal plains found in the Gwydir River landscape (Figure 1-5a).

These sites have been described below based on their soil particle size distributions of their soils, the amount of leaf litter found on in-channel bench surfaces, the calculated return intervals for flow that would inundate each level at each site and estimated date of last inundation event of each level at each site have also been presented. Photos of the sites have been provided in Figure 2-8.

### **2.1.5 Methods**

Quadruplicate samples of both soil and leaf litter were randomly collected from all levels (CH, B1, B2 and FP) at all sites. The collection was completed by placing a 0.25 m<sup>2</sup> metal quadrat randomly on the surface of each level then collecting all litter (excluding large logs and branches) within this area by hand, then using a shovel, a volume of soil (10 cm x 10 cm x 10 cm) was collected. All samples were transported back to Griffith University for analysis.

At Griffith University, litter samples were dried overnight at 40 °C then sorted into categories of ‘sticks’, ‘leaves’, ‘grasses’ and ‘coarse particulate organic matter’ (CPOM), with the category of ‘sticks’ including bark and seeds. CPOM was defined as anything that passed through a 2 mm sieve or was not recognisable. The dry weight of each litter category recorded. Soil particle size distribution were determined from each soil sample using the methods of Day (1965). Briefly, soils were broken up using a rubber mortar and pestle and passed through a 2mm sieve. The soils were then shaken overnight on an end on end shaker with a chemical dispersant to break up soil aggregates. This mixture was then poured into volumetric flasks and made up to 1000 mL with the addition of deionised water. This mixture was then mixed from one minute with a plunger and a hydrometer used to measure the specific gravity of the solution measured after 5 minutes, when all the sand was assumed to have dropped out of solution and after 5 hours, when the silt was assumed to have dropped out of solution (see Chapter 3 for detailed descriptions of both of these methods).

The return interval for flow volumes which would inundate each level at each site was calculated using the River Analysis Package (RAP) (Marsh et al. 2003). The input data for RAP was produced by the IQQM flow model for the Gwydir River at the Pallamallawa gauging station (Figure 2-2), spanning from 1/01/1930 to 30/06/2009 (DIPNR, 2005), this gauge was the closest available to the study region. Partial series analysis was used to calculate the return intervals of different flow volumes which were converted to river stage height using data from the Pallamallawa gauging station operated by the New South Wales Office of Water (NOW) from volume and stage data spanning 28/10/1980 to 20/11/2000. When analysed across all stage heights the relationship between flow volume and stage height was not linear. To overcome this lack of linearity four relationships between flow volume and stage height were derived for different stage heights (0.82 m - 1 m, 1 m - 2m, 2 m - 7.20 m, 7.21 m - 9.59 m) with boundaries of the different stage heights chosen to maximise model fit ( $r^2$ ). The height of each level above river flow height was measured using a dumpy level. The calculate the height of each level about the river gauging height at the Pallamallawa gauging station the river level river on the day of measurement was added to their measured height. The date that each level was also calculated from this data by comparing the level height at each site with the generated river stage heights.



**Figure 2-5:** Study area in the Gwydir River catchment, with each of the study sites shown.

## 2.1.6 Results

### Site 1

Site 1 was the most upstream of all the sites. Clear in-channel bench levels were present at this site but the slope of the channel was relatively shallow. Soils at this site were coarse, dominated by sand (Figure 2-6). Ground cover was minimal but where it was present it consisted of small tufts of grass. Canopy cover was absent on all but the floodplain level which is reflected in the small amounts of leaf litter found at this site (Figure 2-7). The flood return intervals for the different levels at this site were greater than those of the other sites with the exception of Site 2 (Table 2-2).

### Site 2

Site 2 is the next site downstream from Site 1. This site was vegetated which generated a larger standing stock of litter and it had finer textured soil compared to Site 1 (Figure 2-6). River red gums (*Eucalyptus camaldulensis* Dehnh.) were the

dominant vegetation type. The flood return intervals at this site were higher than at the other sites with the exception of the B1 levels which whose flood return interval was similar to the same level at Site 1 (Table 2-2).

### **Site 3**

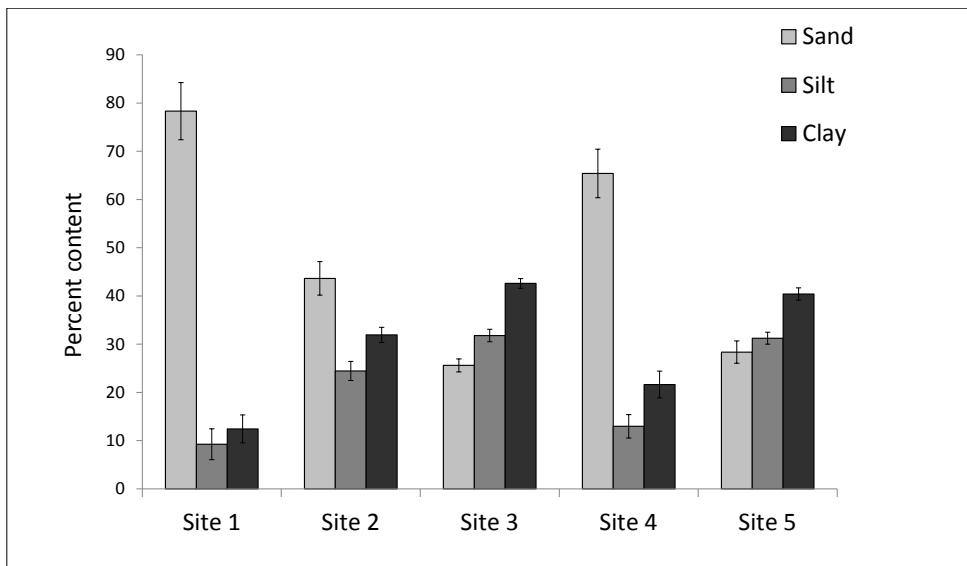
Site 3 comprises a set of benches located downstream of Site 2. The soil of this site had the lowest sand content of any of the study sites (Figure 2-6). The site was moderately vegetated compared with the other sites as illustrated by its standing stock of leaf litter (Figure 2-7). The levels at this site were inundated with similar frequency as Sited 4 and 5 (Table 2-2).

### **Site 4**

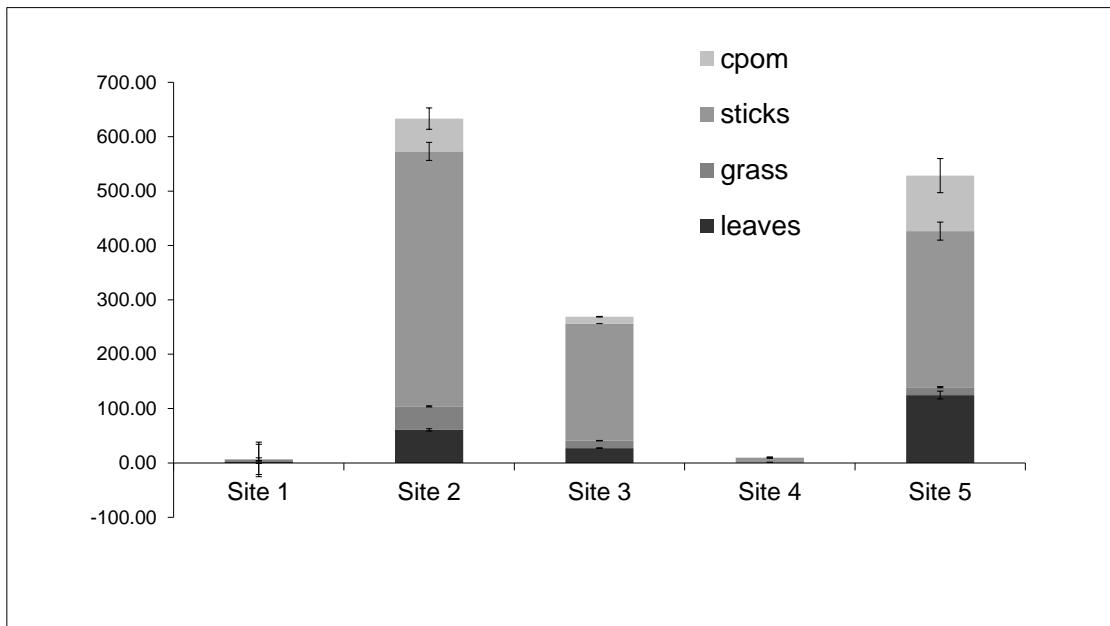
This site is a point bar with coarse soils that were dominated by sand (Figure 2-6). The inundation frequency of these levels being similar to Sites 3 and 4 (Table 2-2). Ground and canopy cover were both sparse, except on the B2 and FP levels which both had a heavy covering of grasses.

### **Site 5**

Site 5 was the most downstream of all sites, it has fine textured soil (Figure 2-6) and a high standing stock of leaf litter on each level (Figure 2-7). All bench levels at this site except for the CH level had heavy ground and canopy cover. The inundation frequencies of each level were lower than most other sites (Table 2-2).



**Figure 2-6:** Sand, silt and clay content averaged across the levels of each site  $\pm$  one standard error of the mean.



**Figure 2-7:** Standing stock of total litter and its composition from each of the sites in the Gwydir River. Standing stocks of total litter were broken into CPOM, sticks, grasses and leaves.

**Table 2-2:** The calculated flood-return intervals (years) for each of the levels at each of the sites.

	Site 1	Site 2	Site 3	Site 4	Site 5
CH	PS	PS	PS	PS	PS
B1	0.75	0.75	0.25	0.25	0.25
B2	1	3	0.5	0.25	0.25
FP	4	12	1	1	2

PS = permanently saturated

**Table 2-3:** The calculated most recent inundation event for each of the levels at each of the sites.

	Site 1	Site 2	Site 3	Site 4	Site 5	Average level height
CH	PS	PS	PS	PS	PS	PS
B1	13/02/08	13/02/08	24/01/09	24/01/09	21/11/08	24/01/09
B2	28/12/04	11/12/04	21/11/08	13/02/08	13/02/08	21/11/08
FP	11/12/04	NA	11/12/04	11/12/04	11/12/04	28/12/04

PS = permanently saturated



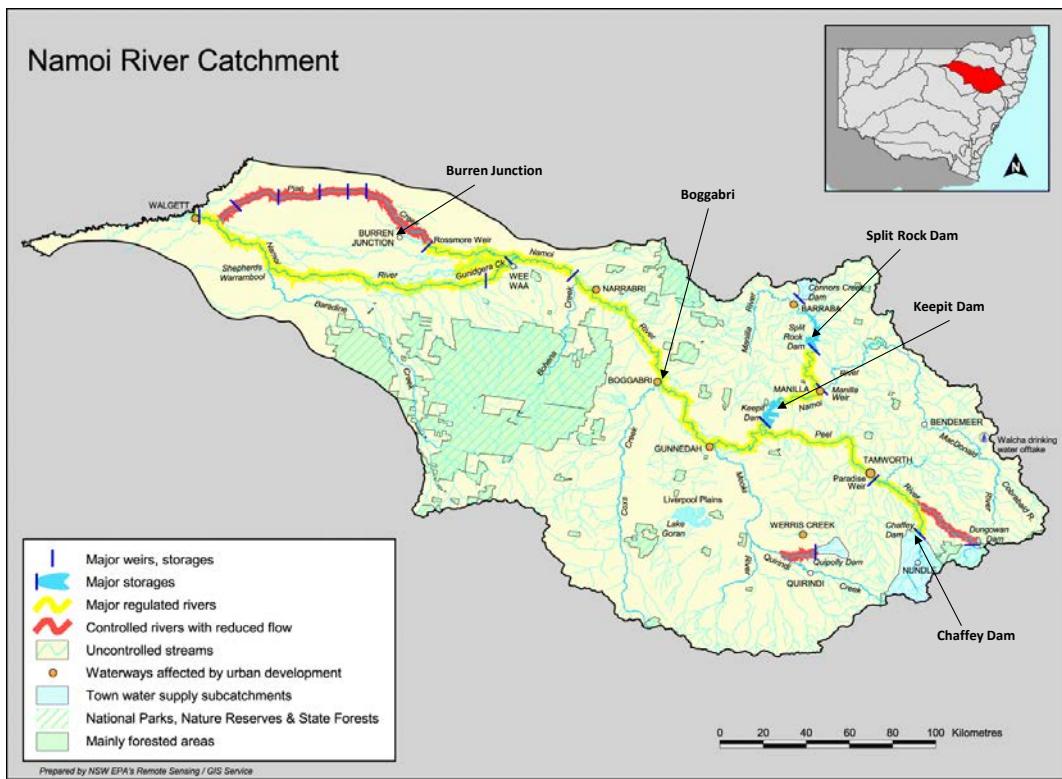
**Figure 2-8:** Photos of field sites. a) Site 1 showing B1; b) Site 2 showing B1 and B2; c) Site 3 showing B1; d) Site 5 showing B2; e) Site 4 showing B2.

## 2.2 The Namoi Catchment

It was hoped that a flood or flow event in the Gwydir Catchment would be sampled during the candidature period for this thesis, however, this did not happen. In light of this a flow event was sampled in the Namoi River which is similar in many characteristics to the Gwydir River.

Like the Gwydir catchment, the Namoi catchment is located within the northern part of the Murray-Darling Basin (Figure 2-1) it is bordered by the Macquarie-Castlereagh, Barwon to the southwest and Gwydir regions to the north (Figure 2-1). The catchment covers an area of approximately 42 000 km<sup>2</sup> (CSIRO 2007b). The river rises out of the Great Dividing Range and travels in a westerly direction for approximately 850 km until it reaches the Barwon River at Walgett. During this journey it passes through two distinct regions; the mountainous New England Plateau and the low angle plains of the west (Thoms et al. 1999).

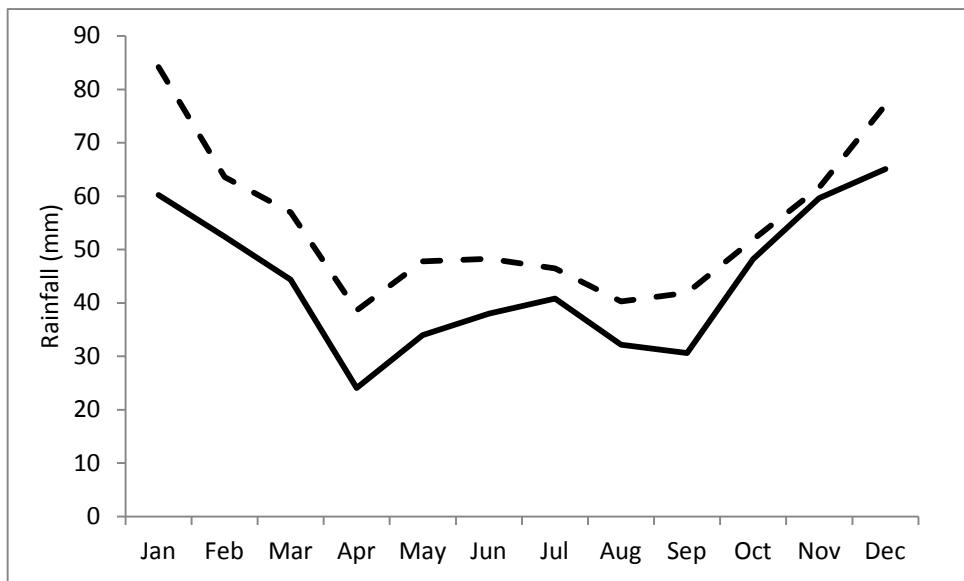
The New England Plateau, is located in the east of the catchment and most of the tributaries that the Namoi River rise on this Plateau and join the river upstream of Boggabri (Figure 2-9). The major tributaries of the Namoi River include Coxs Creek and the Mooki, Peel, Cockburn, Manilla, and McDonald Rivers. Downstream of Boggabri, the flatter western plains area of the catchment makes up approximately two thirds of the catchment area (CSIRO 2007b) and contains many anabranches, tributaries and distributary channels (Thoms et al. 1999).



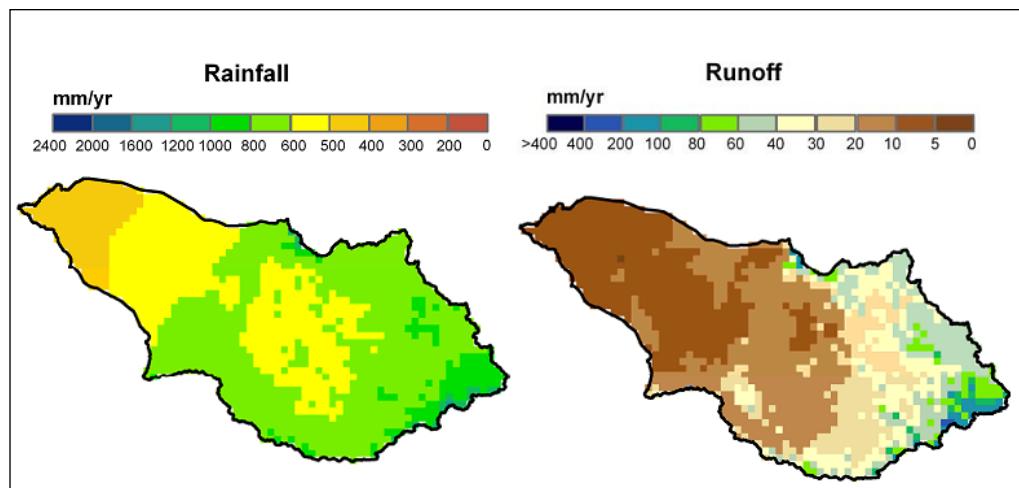
**Figure 2-9:** Map of the Namoi River, including tributaries, major water storages and weirs.  
(sourced from: <http://www.environment.nsw.gov.au/ieo/Namoi/maplg.htm>).

### 2.2.1 Climate

Over the entire catchment mean annual rainfall is 633 mm per year and mainly occurring in the summer months but monthly rainfall is highly variable (Figure 2-10). However, the mountainous eastern region is wetter and cooler than the western plains region. There is a distinct divide in the rainfall in the catchment (Figure 2-11) the east of the catchment receives an annual mean of approximately 1000 mm per year while the west only receives 450 mm (CSIRO 2007b).



**Figure 2-10:** Median (solid line) and mean (dashed line) monthly rainfall from Narrabri West Post Office weather station from between 1891 and 2013 (data sourced from Australian Bureau of meteorology web site).



**Figure 2-11:** Spatial distribution of annual rainfall and modelled runoff averaged for the Namoi catchment from 1895 – 2006 (CSIRO 2007b).

### 2.2.2 Land use and water extraction

Like the Gwydir River, the Namoi River is highly regulated. The two major water storages are Keepit Dam on the Namoi River itself and Split Rock Dam on the Manilla River (Figure 2-9). The smaller Chaffy Dam is also located on the Peel River (Figure 2-9). Farm dams within the catchment are another major water storage (CSIRO

2007b). Agriculture is the major land use within the Namoi Valley with the dominant forms including grazing, wheat and cotton cropping on the alluvial floodplains. Cotton is the main irrigated crop in the catchment, accounting for three-quarters of water use (CSIRO 2007b).

### **2.2.3 Study site**

The flow event was monitored at Buglibone which is located within the lowland area of the Namoi River catchment, approximately 75 km from the confluence with the Darling River, near Burren Junction (Figure 2-9). The dominant tree species is the native River Red Gum (*Eucalyptus camaldulensis*) and the non-native Weeping Willow (*Salix babylonica*).

# **Chapter 3 Patterns of soil nutrients, carbon and soil carbon bioavailability across a gradient of inundation frequencies and soil properties in a dryland river landscape**

## **3.1 Introduction**

Riverine landscapes are spatially complex ecosystems that include a broad range of habitats that only become hydrologically connected to the river under specific flow conditions (Ward et al. 2002). These hydraulic connections have previously been described as a four dimensional matrix – longitudinal connections between headwaters and lowlands, lateral connections between rivers and floodplains, vertical connections between surface and hyporheic waters and temporal connections through different flow events (Ward 1989). The lateral connections between rivers and floodplains, facilitated by flooding events, provide a mechanism for two-way exchange that is important for the productivity of both systems (Junk et al. 1989, Spink et al. 1998). However, in Australian lowland rivers these flood driven lateral connections are sporadic due to highly variable flow regimes (Puckridge et al. 1998). In these systems, smaller more frequent flow pulses, that inundate in-channel features, are thought to create similar exchanges to those that occur during floodplain inundation, providing a nutrient pulse and carbon subsidy to the aquatic ecosystem between floodplain inundation events (Thoms 2003, Sheldon and Thoms 2006, McGinness and Arthur 2011, Westhorpe and Mitrovic 2012).

Flow regulation in many of Australia's lowland rivers has reduced the frequency of flow pulses (Page et al. 2005) contributing to declines in river ecosystem health in many of these systems (Davies et al. 2010). Increasing the frequency and size of flow pulses by limiting the availability of water for irrigation extraction during reservoir spills or when high flows enter rivers from unregulated tributaries, has been mooted as a method to improve the ecosystem health in Australian, flow regulated, lowland rivers (McGinness and Arthur 2011, Westhorpe and Mitrovic 2012). However, the

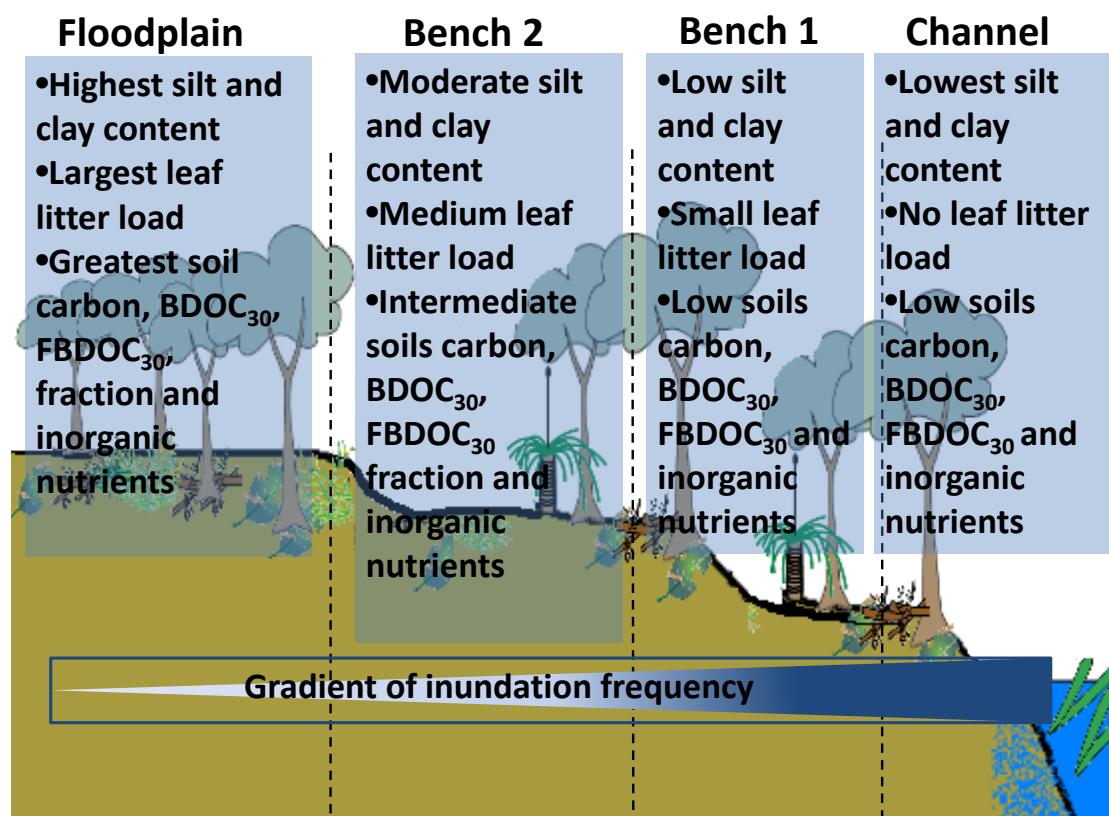
effects of flow pulses on riverine ecosystems are unclear (Davies et al. 1994, Puckridge et al. 1998, Sheldon 2005, Bunn et al. 2006b).

The ecological benefits of these flow pulses depend on the assumption, that similar to floodplain inundation events, flow pulses increase primary productivity (Bunn et al. 2003, Fellows et al. 2007) and microbial activity (Burns and Ryder 2001) in aquatic ecosystems, stimulating aquatic food webs (Boulton and Lloyd 1992, Bunn et al. 2003). However, increases in primary productivity and microbial activity in these systems depend on the exchanges that are facilitated during flow pulses; specifically, if they increase concentrations of organic carbon and inorganic nutrients sufficiently to remove limitation on rates of primary and microbial productivity (Hadwen et al. 2010, Westhorpe et al. 2010).

In-channel benches are horizontal in-channel features that accumulate terrestrially derived organic matter and are believed to play a significant role in facilitating exchanges during flow pulses (Sheldon and Thoms 2006, Southwell and Thoms 2011). Southwell and Thoms (2011) showed that the soils of in-channel benches contain carbon, nitrogen and phosphorus but these stores varied with bench height in the Barwon-Darling River. However, it is inorganic nutrients and organic carbon concentrations in Australian lowland rivers that, respectively, limit primary and bacterial productivity (Hadwen et al. 2010, Westhorpe et al. 2010). The distribution of these elements in riverine soils is more variable than that of total carbon and total nutrients (Gallardo 2003) being influenced by soil characteristics such as texture, organic content and inundation frequency (Jenny 1980, Baldwin and Mitchell 2000); that change with height in riverine landscapes (Woodyer et al. 1979, Page and Nanson 1982, Vietz 2008).

The objective of this chapter is to examine the distribution of exchangeable inorganic nitrogen and phosphorus, DOC and the amount ( $BDOC_{30}$ ) and ( $FBDOC_{30}$ ) fraction of

DOC that is bioavailable in the soils of the Gwydir River landscape. In this landscape four heights were investigated; spanning the channel (CH), two levels of in-channel benches, B1 and B2 and the floodplain (FP) which are referred to as levels, as they represented horizontal plains found in the Gwydir River landscape (Figure 1-5a). These levels had different soil properties and inundation frequencies (Chapter 2), therefore, exploring the effects of these varying factors on the distribution of organic carbon and inorganic nutrients will improve our understanding on how these resources are stored in riverine landscapes. The conceptual model presented as Figure 3-1 predicts that as distance from the channel bed increases, soil texture will decrease while standing stocks of leaf litter increase as will stores of soil inorganic nutrients, DOC,  $BDOC_{30}$  and  $FBDOC_{30}$ .



**Figure 3-1:** A conceptual diagram illustrating the predicted changes in soil properties and stores of mobile soil nutrients across the different levels in Gwydir River.

The specific questions being asked in this chapter are;

1. Do levels higher in the Gwydir River landscape have larger stores of water extractable nitrate ( $\text{NO}_3^-$ -N), ammonium ( $\text{NH}_4^+$ ), dissolved reactive phosphate (DRP), DOC, finer soil texture, larger stores of leaf litter and total carbon and higher C:N ratio compared to those closer to the channel bed?
2. What amount ( $\text{BDOC}_{30}$ ) and fraction ( $\text{FBDOC}_{30}$ ) of the DOC extracted from soils of the different levels in the Gwydir River landscape is bioavailable under aerobic and anaerobic conditions and does this vary across levels in the landscape?
3. What are the relationships between soil total carbon, silt and clay content with mobile  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ , DRP, DOC and  $\text{FBDOC}_{30}$  and do they differ across the levels in the Gwydir River landscape?

## 3.2 Methods

### 3.2.1 Soil and litter collections

Quadruplicate soil and leaf litter samples were randomly collected from sites 1, 2, 3, 4 and 5 (see Chapter 2 for site descriptions) from the CH, B1, B2 and FP levels in the Gwydir River landscape in June of 2009. Samples were collected by randomly placing a  $0.25 \text{ m}^2$  quadrat on the surface of each level and collecting all leaf litter within this area. The resulting litter samples were stored in sealed zip-lock plastic bags with the air expelled. Any large logs or branches contained within the quadrat were excluded from the analysis as they are not large sources of DOC to the river (O'Connell et al. 2000). After litter collection, a shovel was used to extract a volume of approximately  $10 \text{ cm} \times 10 \text{ cm} \times 10 \text{ cm}$  of soil, which was stored in re-sealable bags with all air expelled. Finally, 30 L of water from the Gwydir River was collected. All samples were transported back to Griffith University where the soil and water samples were stored overnight at  $4^\circ\text{C}$  before processing and the litter sample prepared for oven drying.

### **3.2.2 Litter**

In the laboratory, litter samples were dried overnight at 40 °C then sorted into categories of ‘sticks’, ‘leaves’, ‘grasses’ and ‘coarse particulate organic matter’ (CPOM) then weighed. CPOM was defined as anything that passed through a 2 mm sieve or was not recognisable. Bark and seeds were included in the ‘sticks’ category.

### **3.2.3 Nutrient and DOC extractions**

Each soil sample was homogenized and approximately 140 g sub-sampled for use in extractions. The remaining soil was dried and stored for analysis of particle size distribution and total C and N content. The sub-samples used for extractions were mixed with river water in a 1:1 ratio in acid washed plastic centrifuge bottles to create a slurry. River water was used as the extractant to provide more realistic information about the amount of soil carbon and nutrients able to be mobilised during inundation (Heffernan and Sponseller 2004). Bottles containing river water and soil slurries were placed on a shaker table for one hour to ensure equilibrium, after shaking the slurries were centrifuged for 15 minutes at 3000 rpm to aid filtration. To ensure no residue from the filter could contaminate the samples, all filter papers were rinsed with 200 mL of milli-Q water prior to use. The supernatant from the centrifuged slurries was filtered; first using an Advantec GF-75 glass fibre filter paper to remove larger particles then using a 0.2 µm (Whatman Ref – 7182-004) membrane filter paper. The resulting filtrate was separated into 4 portions; 15 mL for analyses of  $\text{NH}_4^+$ -N,  $\text{NO}_3^-$ -N, and DRP concentrations, 30 mL for an initial DOC concentration, both these proportions were immediately frozen, from the remaining filtrate, two 30 mL samples were used for aerobic and anaerobic DOC bioavailability incubations.

### **3.2.4 DOC bioavailability incubations**

To estimate the amount of bioavailable DOC ( $\text{BDOC}_{30}$ ) and the bioavailable fraction of mobile DOC ( $\text{FBDOC}_{30}$ ) two separate 30 mL samples of filtrate (described above)

were incubated under aerobic and anaerobic conditions. These filtrates were poured into 250 mL glass screw top Schott bottles with lids modified to take a rubber septa. Incubations were conducted using a method adapted from Marmonier et al. (1995) where a microbial inoculum is incubated in a solution of known DOC concentration for a period of time and the decline in DOC concentration after incubation is assumed to the bioavailable fraction of DOC. The microbial inoculum was created by shaking a 0.2 µm filter paper, used in the extraction process (detailed above) with 10 mL of milli-Q water for 30 minutes. An inoculum was made for each level of each site and incubated with a DOC sample extracted from the same site and level, ensuring an appropriate microbial community was incubated with each extracted DOC sample. To account for the DOC added in the inoculum, blanks from each level at each site were created using milli-Q water and 2 mL of the appropriate inoculum solution.

After the addition of the DOC solution and the microbial inoculum to the Schott bottles the availability of oxygen was manipulated as below, and then the bottle were incubated. Bottles for anaerobic incubations were sealed and anaerobic conditions created by purging the headspace with high purity N<sub>2</sub> gas for 4 minutes while agitating bottle contents. For the aerobic treatment, bottle lids were screwed on half a turn only. All bottles were incubated in a dark constant temperature room at 26 °C for 30 days. The incubation temperature of 26 °C was chosen as it is approximately the average summer temperature (averaged across day and night) in the lowland Gwydir River catchment). After incubation, samples were re-filtered using rinsed 0.2 µm (Whatman 7182-004) membrane filters. The resulting filtrate was frozen until analysis of DOC as described below. BDOC<sub>30</sub>, the amount of extracted DOC that was bioavailable, was calculated as the difference between the pre and, blank corrected, post incubation DOC concentrations. While, FBDOC<sub>30</sub>, the fraction of bioavailable DOC extracted, was calculated as the difference between pre and, blank corrected, post incubation DOC concentrations and expressed as a percentage of the pre-incubation DOC concentrations.

### **3.2.5 Soil particle size distribution and soil total C and N**

In preparation for particle size distribution and total C and N content analysis, soils were air dried at 70°C for 4 days. Sub-samples of approximately 50-100 g were then taken from the bulk samples, soil lumps were broken-up using a mortar and rubber pestle until the soil passed through a 2 mm sieve. Approximately 5 g of this sieved soil had all visual roots removed and was ground to <150 µm in preparation for total C and N analysis. The remaining soil was used for particle size analysis.

Soil particle size distribution was determined using the methods of Day (1965). To each sub-sample, 10 mL of Calgon® and 10 mL of 1 M sodium hydroxide were added as chemical dispersants before the addition of 400 mL of deionised water. This mixture was placed in an ‘end-over-end’ shaker overnight to aid the dispersion process. After shaking, the soil mixtures were transferred to 1000 mL measuring cylinders and deionised water added to fill each container to the 1000 mL mark. A blank ‘control’, generated using 10 mL of Calgon®, 10 mL of 1 M sodium hydroxide in a 1000 mL measuring cylinder, made up to 1000 mL with deionised water, was used for temperature corrections. Each mixture was hand stirred for 1 minute using a plunger. 5 minutes after mixing, when all the sand was assumed to have fallen out of suspension, a hydrometer was used to measure the specific density of the solution. This measurement was repeated 5 hours after mixing when all silt was assumed to have dropped out of suspension.

### **3.2.6 Analytical procedures**

Oxidised nitrogen ( $\text{NO}_2^- + \text{NO}_3^-$ ; here reported as  $\text{NO}_3^-$ ) was analysed using the cadmium reduction method with a segmented flow analyser (OI Analytical, FS3100). The cadmium reduction method uses a cadmium column to reduce nitrate to nitrite. The amount of nitrite produced is then determined by diazotizing with sulphanilamide and coupling with N-(1-naphthyl)-ethylenedia-mine dihydrochloride forming a highly coloured azo dye that is measured colourmetrically (APHA 1998).

$\text{NH}_4^+$ -N was analysed using a Bran and Luebbe, AA3, nitroprusside and salicylate method for water and sea water (Bran and Luebbe, AA3 method number G-171-96).  $\text{NH}_4^+$  reacts with salicylate and hypochlorite ions in the presence of ferricyanide ions to form the salicylic acid analog of indophenol blue. Nitroprusside was the catalyst for this reaction.

Dissolved reactive phosphorus (DRP) was analysed using the ascorbic acid reduction method with a segmented flow analyser (OI Analytical, FS3100). In this method orthophosphate reacts, in an acid medium, with ammonium molybdate and antimony potassium tartrate to form a heteropoly acid – phosphomolybdic acid, which is reduced to a intensely coloured molybdenum blue by ascorbic acid (APHA 1998).

DOC was measured on a Shimadzu TOC-VCPh/CPN analyser using a high temperature catalytic oxidation method. In this method, the sample is injected into a 680 °C, oxygen rich atmosphere, oxidising the DOC to carbon dioxide ( $\text{CO}_2$ ) which is measured on a non-dispersive infrared detector. Soil total C and N content was measured using an isotope ratio mass spectrometer with a Eurovector Elemental Analyser (Isoprome-EuroEA 3000, Milan, Italy).

### **3.2.7 Statistical analysis**

#### **Differences in soil properties and mobile soil nutrients between the different level heights in the Gwydir River landscape**

A randomised block design, with level as the fixed factor, was used to determine differences between the levels in the Gwydir River landscape. This design was used to test for differences in total and categorised amounts of leaf litter, soil fractions of sand, silt and clay, soil C:N ratios, mobile soil nutrients and DOC between levels in the landscape. None of the data generated were normally distributed and it was

unable to be rendered normal using transformation. Therefore, PERMANOVA, permutational multivariate analysis of variance, which does not assume a normal distribution in the data was used (Anderson 2001). The resemblance matrix was based on Euclidian distances between samples after the differences between variables had been normalised. PERMANOVA was run using the PERMANOVA add-on in Primer V6 6.1.0.1 (Clarke and Gorley 2007) with a minimum of 9000 permutations. The pair-wise function within the PERMANOVA add-on was used post-hoc to extract differences between the levels and was completed with a separate run of the permutation routine. In this case, as the analysis is based on a single factor and the resemblance matrix was generated using Euclidian distance, the pair-wise testing corresponds to the original  $t$  statistic (Anderson et al. 2008).

### **The BDOC<sub>30</sub> and FBDOC<sub>30</sub> from different bench heights.**

Differences in BDOC<sub>30</sub> and FBDOC<sub>30</sub> were tested both across levels in the landscape under aerobic and anaerobic conditions and for differences within a level under aerobic and anaerobic conditions. To test for differences in BDOC<sub>30</sub> and FBDOC<sub>30</sub> across levels in the Gwydir River landscape under both aerobic and anaerobic conditions PERMANOVA was used with the same design and parameters as detailed above. To investigate if aerobic or anaerobic conditions affected either FBDOC<sub>30</sub> or BDOC<sub>30</sub> within a level, the pairwise comparison function in PERMANOVA was used, with a separate run of the permutation routine. The resemblance matrix was calculated by Euclidian distance and the pair-wise testing carried out corresponds to the original  $t$  statistic (Anderson et al. 2008). As multiple  $t$ -tests were being used the probability value used to decide significance was Bonferroni adjusted resulting in a new critical  $p$ ,  $p = 0.01$  reducing the chance of type I errors.

## **Relationships between soil properties and concentrations of mobile nutrient in each of the different levels**

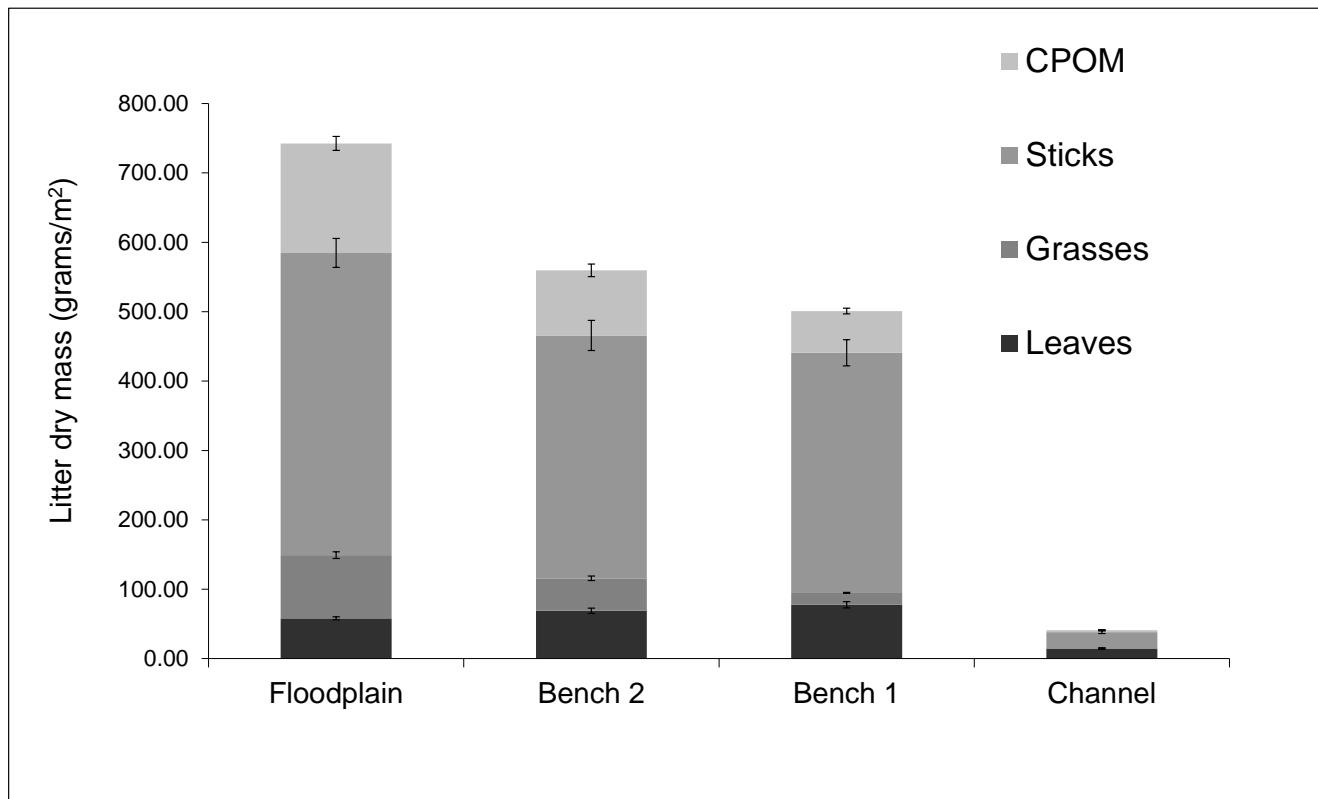
To explore relationships between soil silt and clay content and total soil carbon content to the concentrations of mobile  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ , DRP, DOC and FBDOC<sub>30</sub>, distance based linear modelling was used (Anderson et al. 2008). Distance based linear modelling is founded on a resemblance matrix and uses permutations rather than the normality assumption that underlies linear modelling, therefore, it is more robust to data that does not conform to a normal distribution (Anderson et al. 2008). The PERMANOVA add-on in Primer V6 6.1.0.1 (Clarke and Gorley 2007) was used for this analysis and significant relationships were defined as those with a  $p$ -value < 0.05.

## **3.3 Results**

### **3.3.1 Do levels higher in the Gwydir River landscape have larger stores of water extractable $\text{NO}_3^-$ -N, $\text{NH}_4^+$ , DRP, DOC, finer soil texture, larger stores of leaf litter and total carbon and higher C:N ratio compared to those closer to the channel bed?**

#### **Litter**

The mass of the standing stocks of total litter increased with increasing level height in the Gwydir River landscape. Level in the landscape had a significant effect on the standing stocks of sticks, with the CH level having significantly lower stick standing stock than all other levels (Pseudo F = 5.337, df = 3,  $p$  < 0.002). Mean standing stocks of CPOM on each level were found to increase significantly with increasing height in the landscape (Pseudo F = 4.2403, df = 3,  $p$  < 0.005) and pair-wise testing found that standing stocks of CPOM on the CH level was significantly lower than all other levels (Table 3-1). Height in the landscape also had a significant effect on the quantity of leaves found on each level (Pseudo F = 3.940, df = 3,  $p$  < 0.013) but unlike other litter components, it did not increase with height in the landscape rather peaked on the B1 level and declined with greater height in the landscape (Figure 3-2).



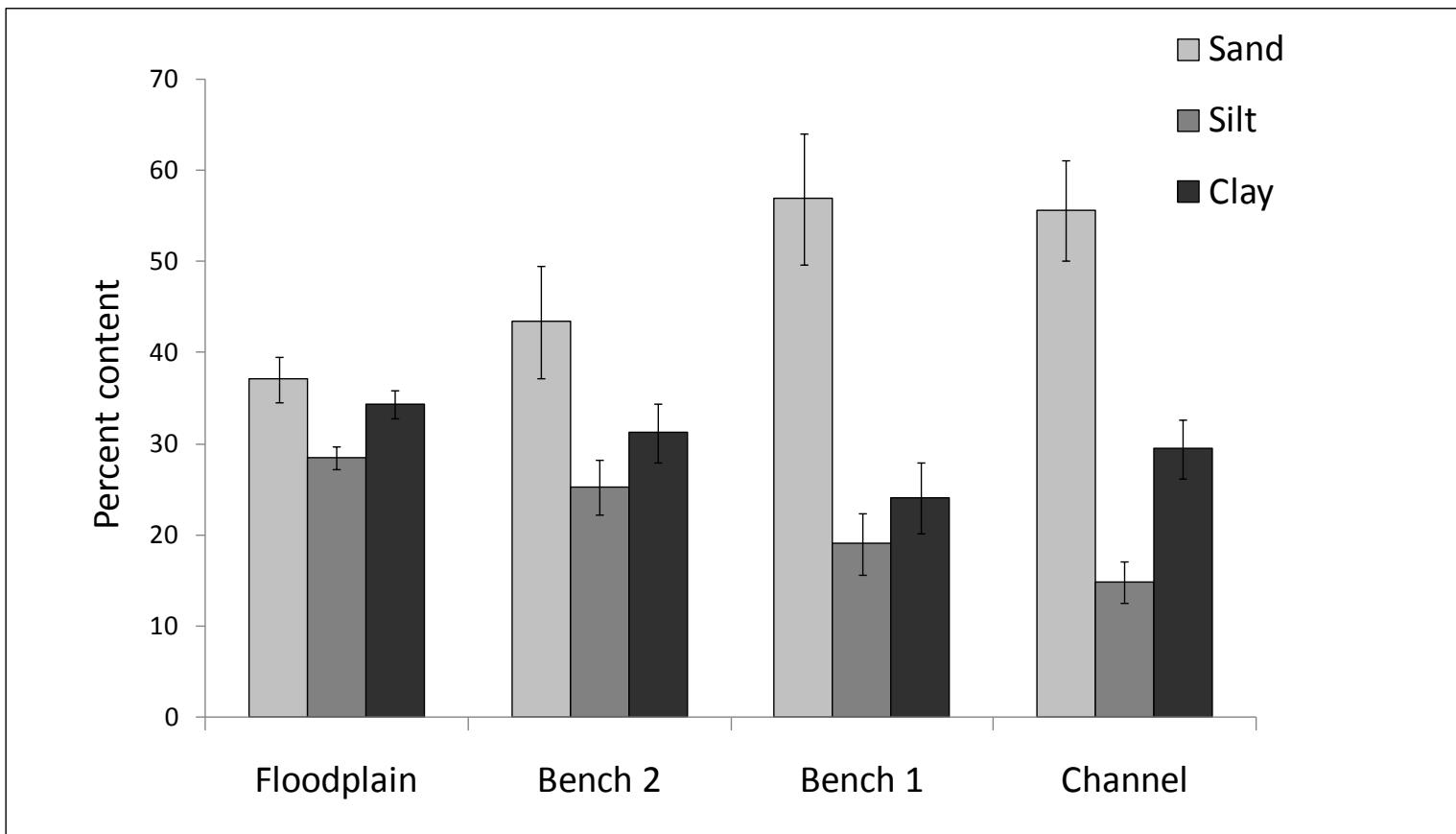
**Figure 3-2:** Standing stocks of total litter and its composition from the CH, B1, B2 and FP levels in the Gwydir River landscape. Standing stocks of total litter were broken into CPOM, sticks, grasses and leaves

**Table 3-1:** Summary of results for analysis of variance (PERMANOVA) and LSD pair-wise tests for the effect of level on standing stocks of CPOM, grasses, leaves and sticks. Pseudo F = the f-value, t = the t-statistic, df = degrees of freedom, p = the probability of the null hypothesis being true. Significant differences were defined as  $p < 0.05$  and are denoted with \* and significance levels of  $p < 0.01$  are denoted with \*\*

		CPOM			Grasses			Leaves			Sticks		
		Pseudo		Pseudo		Pseudo		Pseudo		Pseudo			
	df	F	p	F	p	F	p	F	p	F	p		
Level	3	4.240	0.005**	8.958	0.000**	3.940	0.013*	5.337	0.002**				
<b>Pair-wise testing</b>													
		t	p	t	p	t	p	t	p	t	p		
CH, B1		3.081	0.000**	5.068	0.000**	2.989	0.004**	3.817	0.000**				
CH, B2		2.285	0.000**	3.095	0.000**	3.142	0.003**	3.508	0.000**				
CH, FP		3.497	0.000**	4.166	0.000**	4.081	0.001**	4.399	0.000**				
B1, B2		0.833	0.459	1.889	0.022*	0.182	0.853	0.163	0.872				
B1,FP		2.041	0.035*	3.342	0.000**	0.876	0.3997	0.711	0.486				
B2,FP		0.970	0.344	1.677	0.102	0.731	0.469	0.498	0.631				

### Soil particle size distribution

The clay content of the soil of the different levels stay relatively consistent across the levels in the landscape but the sand content decreased and the silt content increased with greater height in the landscape. A significant difference was found in the sand and silt content, but not the clay content, of the soil from the different levels in the Gwydir River landscape (Table 3-2). Sand and clay made up the majority of the soil across all the levels (Figure 3-3). Pair-wise testing showed the mean silt content of the FP level was significantly higher than that of CH and B1 levels (Table 3-2). The B1 and CH levels had sand contents that were not significantly different from each other but were greater than that of the FP level (Table 3-2).



**Figure 3-3:** Percentage of sand, silt and clay of soil from the CH, B1, B2 and FP levels in the Gwydir River landscape. Error bars represent one standard error of the mean.

**Table 3-2:** Summary of results for analysis of variance (PERMANOVA) and LSD pair-wise tests for the effect of level in the Gwydir River landscape on soil sand, silt and clay content.

Pseudo F = the f-value, t = the t-statistic, df = degrees of freedom, p = the probability of the null hypothesis being true. Significant differences were defined as  $p < 0.05$  and are denoted with \* and significance levels of  $p < 0.01$  are denoted with \*\*

	Sand			Silt			Clay	
	df	Pseudo F	p	Pseudo F	p	Pseudo F	p	
Level	3	2.910	0.043*	5.602	0.002**	1.928	0.132	
<b>Pair-wise testing</b>								
		t	p	t	p	t	p	
CH, B1		0.135	0.893	1.027	0.304	NA	NA	
CH, B2		1.471	0.150	2.773	0.008**	NA	NA	
CH, FP		3.089	0.004*	5.125	0.000**	NA	NA	
B1, B2		1.406	0.165	1.433	0.161	NA	NA	
B1, FP		2.604	0.012*	2.661	0.012*	NA	NA	
B2, FP		0.897	0.387	0.892	0.381	NA	NA	

## Soil Properties

Level in the Gwydir River landscape had a significant effect on soil moisture (Pseudo F = 5.845, df = 3,  $p < 0.000$ ). At the time of sampling soil moisture increased through B1, B2, FP and CH levels. The moisture content of the CH level was highest (Table 3-3) and significantly different from all the other levels (Table 3-4). The FP level had significantly higher moisture content than both the B1 and B2 levels (Table 3-4).

The total carbon and nitrogen content of soil varied across the levels in the Gwydir River landscape (Table 3-3). Total soil carbon was significantly lower in the CH level compared to B2 and FP levels, while the FP level had significantly higher soil carbon than either the B1 or B2 levels (Table 3-4). Soil total nitrogen was significantly greater in the FP level compared to all other levels (Table 3-4).

**Table 3-3:** The means ( $\pm$  one standard error) of various soil properties for each of the levels investigated within the dryland Gwydir River.

	Floodplain	bench 2	bench 1	Channel bed
Moisture content (%)	14.80 $\pm$ 0.14	14.48 $\pm$ 0.38	11.74 $\pm$ 0.43	19.81 $\pm$ 0.56
Total carbon (%)	3.2 $\pm$ 0.1	1.8 $\pm$ 0.05	1.4 $\pm$ 0.06	1.1 $\pm$ 0.03
Total nitrogen (%)	0.3 $\pm$ 0.06	0.2 $\pm$ 0.00	0.1 $\pm$ 0.15	0.1 $\pm$ 0.00
C/N ratio (mass)	14.3 $\pm$ 0.12	13.2 $\pm$ 0.08	12.9 $\pm$ 0.07	12.7 $\pm$ 0.07

**Table 3-4:** Summary of results for analysis of variance (PERMANOVA) and LSD pair-wise tests for the effect of level on soil total carbon and nitrogen percentages, C/N ratio and percent moisture. Pseudo F = the f-value, t = the t-statistic, df = degrees of freedom, p = the probability of the null hypothesis being true. Significant differences were defined as  $p < 0.05$  and are denoted with \* and significance levels of  $p < 0.01$  are denoted with \*\*

	Moisture			Total Carbon			Total Nitrogen			C/N ratio		
	Pseudo			Pseudo			Pseudo			Pseudo		
	df	F	p	F	p	F	p	F	p	F	p	
Level	3	5.845	0.000**	13.750	0.000**	14.920	0.000**	3.233	0.026*			
<b>Pair-wise testing</b>												
		t	p	t	p	t	p	t	p	t	p	
CH,B1		2.021	0.016*	1.006	0.316	1.271	0.211	1.731	0.094			
CH,B2		2.577	0.002**	2.514	0.018*	2.915	0.007**	2.138	0.038*			
CH,FP		4.008	0.000**	7.023	0.000**	8.409	0.000**	2.590	0.015*			
B1,B2		1.193	0.208	1.183	0.241	1.352	0.180	0.582	0.573			
B1,FP		2.641	0.001**	4.624	0.000**	4.940	0.000**	1.122	0.270			
B2,FP		1.598	0.037*	3.388	0.001**	3.243	0.003**	0.518	0.613			

## Dissolved Organic Carbon

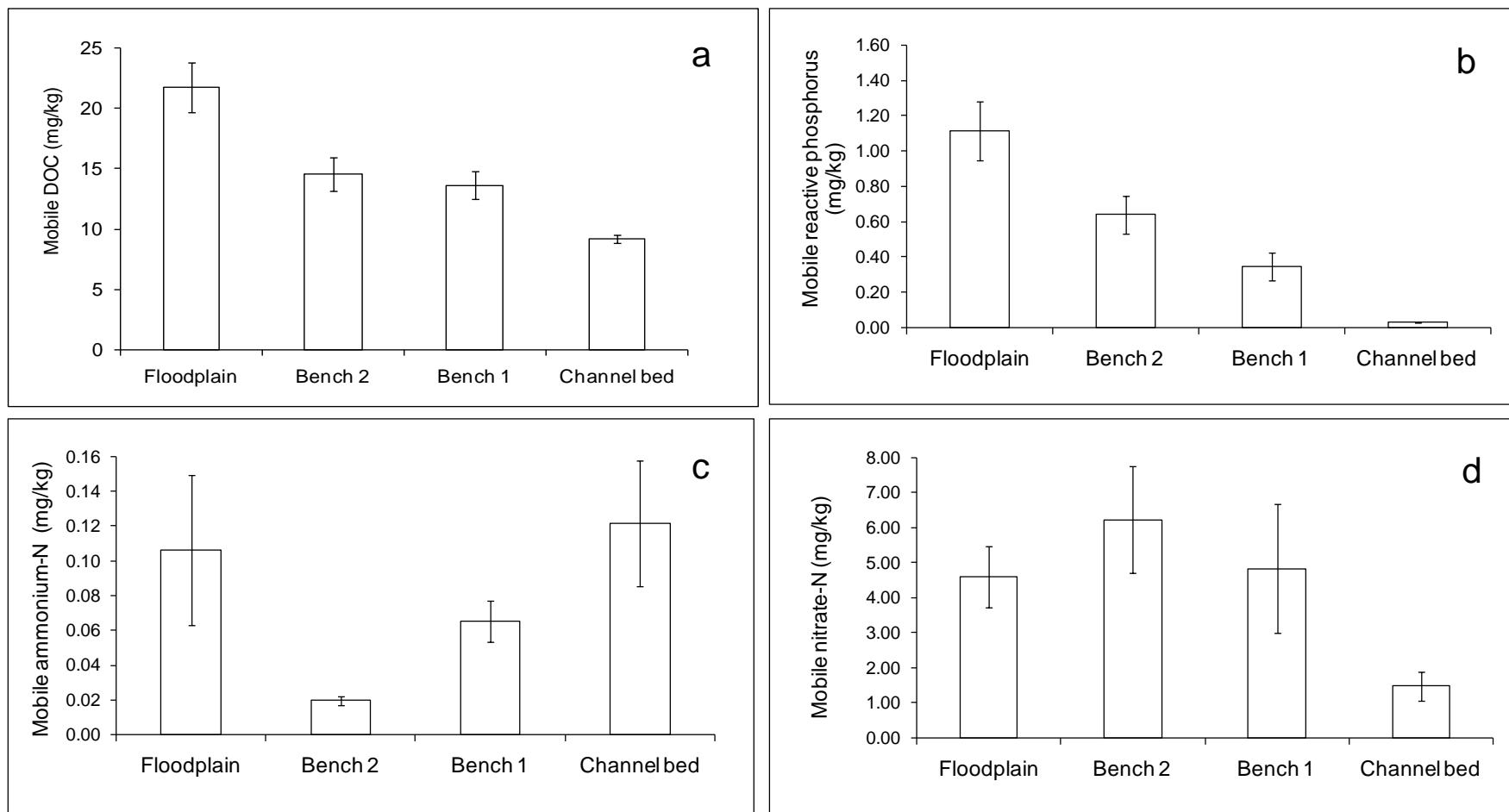
The concentration of mobile DOC increased with increasing level height in the Gwydir River landscape (Figure 3-4a). These increases in DOC across the levels were statistically significant and all levels were found to be significantly different from each other with the exception of B1 from B2 level and B2 from FP level (Table 3-5).

## Nutrients

The soils of each level in the Gwydir River landscape had different concentrations of water soluble nutrients. The amount of DRP significantly increased (Pseudo F = 19.517, df = 3,  $p < 0.000$ ) with increasing level height in the landscape (Figure 3-4b) and all levels were found to be significantly different from each other (Table 3-5).

Likewise, the amount of  $\text{NH}_4^+$ -N varied significantly (Pseudo F = 3.059, df = 3,  $p < 0.022$ ) across levels. The B2 level had the smallest amount of mobile  $\text{NH}_4^+$  with higher concentrations in both B1 and CH levels (Figure 3-4c) while the FP had the highest mobile concentrations of  $\text{NH}_4^+$ -N. Significant increases in mobile soil  $\text{NH}_4^+$ -N were found between the CH level and both B1 and B2 levels, as well as between the B2 and FP levels (Table 3-5).

Level in the Gwydir River landscape had a significant effect on the concentration of mobile  $\text{NO}_3^-$ -N in the soils (Pseudo F = 3.195, df = 3,  $p < 0.023$ ). The CH level had the lowest concentration of  $\text{NO}_3^-$ -N, with higher concentrations being found in both B1 and B2 levels and  $\text{NO}_3^-$ -N in FP level soil was lower than in the B2 level soil (Figure 3-4d). Significant increases were found between B2 level and the CH and B1 levels (Table 3-5).



**Figure 3-4:** The concentrations of (a) DOC, (b) DRP, (c)  $\text{NH}_4^+$  and (d)  $\text{NO}_3^-$ -N in the soils of each of the different levels in the Gwydir River landscape. Error bars represent one standard error of the mean.

**Table 3-5:** Summary of results for analysis of variance (PERMANOVA) and LSD pair-wise tests for the effect of level on the soil concentrations of DOC,  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$  and DRP. Pseudo F = the f-value, t = the t-statistic, df = degrees of freedom, p = the probability of the null hypothesis being true. Significant differences were defined as  $p < 0.05$  and are denoted with \* and significance levels of  $p < 0.01$  are denoted with \*\*

		DRP		DOC		$\text{NH}_4^+$		$\text{NO}_3^-$ -N	
		Pseudo		Pseudo		Pseudo		Pseudo	
	df	F	p	F	p	F	p	F	p
Level	3	14.171	0.000**	19.517	0.000**	3.059	0.022	3.195	0.024

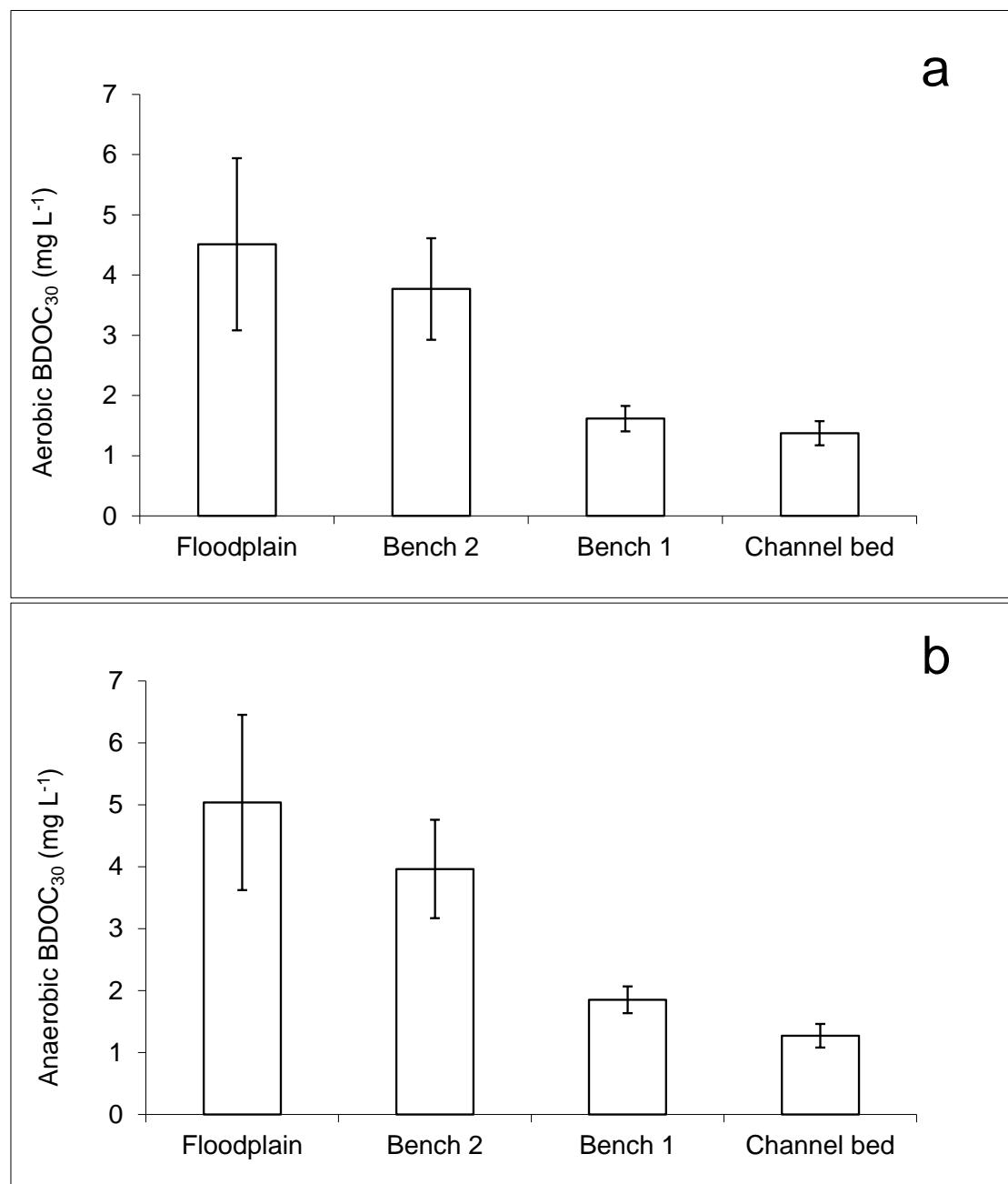
  

Pair-wise testing									
		t	p	t	p	t	p	t	p
CH, B1		4.819	0.000**	3.296	0.000**	2.316	0.020*	1.812	0.065
CH, B2		6.717	0.000**	5.640	0.000**	2.7450	0.003*	3.026	0.001**
CH, FP		5.539	0.000**	6.534	0.000**	0.275	0.795	1.102	0.284
B1, B2		1.806	0.083	2.651	0.011*	1.138	0.285	3.214	0.000**
B1,FP		2.991	0.005*	4.530	0.000**	1.618	0.064	0.131	0.906
B2 FP		1.619	0.122	2.344	0.022*	1.949	0.000**	1.471	0.152

### 3.3.2 What amount ( $\text{BDOC}_{30}$ ) and fraction ( $\text{FBDOC}_{30}$ ) of the DOC extracted from soils of the different levels in the Gwydir River landscape is bioavailable under aerobic and anaerobic conditions and does this vary across levels in the landscape?

$\text{BDOC}_{30}$  varied significantly across the levels in the Gwydir River Landscape (Table 3-6) under both aerobic (Pseudo F = 4.017, df = 3,  $p < 0.006$ ) and anaerobic conditions (Pseudo F = 5.109, df = 3,  $p < 0.003$ ).  $\text{BDOC}_{30}$  was largest in the FP soil and decreased on each level down to the CH level where the lowest amount of  $\text{BDOC}_{30}$  was found. Under both aerobic and anaerobic conditions the B1 level had significantly less  $\text{BDOC}_{30}$  than either the FP level while under anaerobic conditions the CH level had significantly less  $\text{BDOC}_{30}$  than the B2 level. The presence or absence of oxygen had no effect on  $\text{BDOC}_{30}$  either across all levels (Pseudo F = 0.084, df = 1,  $p$

< 0.785) or within an individual level (Table 3-7). Mean  $\text{BDOC}_{30}$  across all levels under aerobic and anaerobic conditions, respectively, was  $2.77 \pm 0.46 \text{ mg L}^{-1}$  and  $2.93 \pm 0.46 \text{ mg L}^{-1}$ .



**Figure 3-5:** BDOC<sub>30</sub> under (a) aerobic and (b) anaerobic conditions, expressed as a percentage of the total DOC extracted. Error bars represent one standard error of the mean.

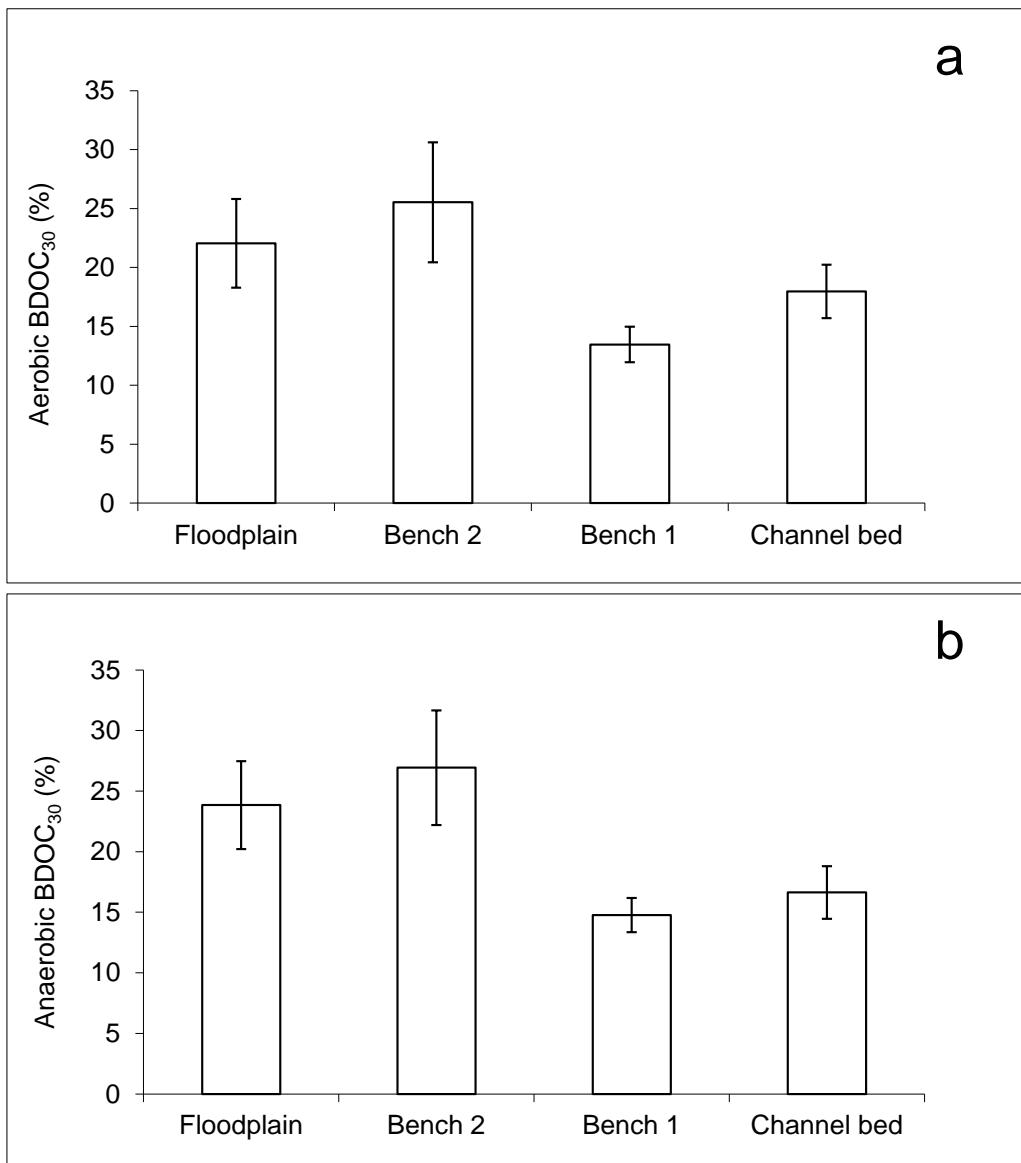
**Table 3-6:** Summary of results for analysis of variance (PERMANOVA) and LSD pair-wise tests for the effects of level on  $\text{BDOC}_{30}$  under both aerobic and anaerobic conditions. Pseudo F = the f-value, t = the t-statistic, df = degrees of freedom, p = the probability of the null hypothesis being true. Significant differences were defined as  $p < 0.05$  and are denoted with \* and significance levels of  $p < 0.01$  are denoted with \*\* for the main test and at  $p < 0.01$  for the LSD tests and denoted with \*.

		Aerobic BDOC availability		Anaerobic BDOC availability	
	df	Pseudo F	p	Pseudo F	p
Level	3	4.017	0.006*	5.109	0.003**
<b>Pair-wise testing</b>					
		t	p	t	p
C, B1		0.753	0.487	1.736	0.094
C, B2		2.753	0.005*	3.291	0.001*
C, FP		2.496	0.001*	2.782	0.001*
B1, B2		2.363	0.025	2.518	0.01*
B1, FP		2.3215	0.002*	2.381	0.002*
B2, FP		0.641	0.538	0.786	0.502

**Table 3-7:** The effect of aerobic and anaerobic conditions on  $\text{BDOC}_{30}$  across all levels in the landscape and within each level, results from factorial PERMANOVA and LSD pair-wise testing. Pseudo F = the f-value, t = the t-statistic, df = degrees of freedom, p = the probability of the null hypothesis being true. Significant differences were defined as  $p < 0.05$  and are denoted with \* and significance levels of  $p < 0.01$  are denoted with \*\* for the main test and at  $p < 0.01$  for the LSD testing and denoted with \*.

$\text{BDOC}_{30}$			
	df	Pseudo F	p
Level	3	9.079	0.001**
$\text{O}_2$ availability	1	0.084	0.785
<b>Pair-wise testing within levels</b>			
	df	t	p
C	1	0.379	0.722
B1	1	0.562	0.568
B2	1	0.149	0.886
FP	1	0.211	0.829

$\text{FBDOC}_{30}$  varied significantly across levels in the Gwydir River landscape (Table 3-6) under both aerobic (Pseudo  $F = 2.990$ ,  $df = 3$ ,  $p < 0.033$ ) and anaerobic (Pseudo  $F = 3.704$ ,  $df = 3$ ,  $p < 0.014$ ) conditions. Under both conditions the B2 level had the largest fraction of  $\text{FBDOC}_{30}$  while the B1 level had the smallest (Figure 3-5). Under both aerobic and anaerobic conditions the B1 level had significantly less  $\text{BDOC}_{30}$  than either the B2 or FP levels while under anaerobic conditions the CH level had significantly less  $\text{FBDOC}_{30}$  than the B2 level. The presence or absence of oxygen had no effect on  $\text{FBDOC}_{30}$  either across all levels (Pseudo  $F = 0.107$ ,  $df = 1$ ,  $p < 0.745$ ) or within an individual level (Table 3-7). Mean  $\text{FBDOC}_{30}$  across all levels under aerobic and anaerobic conditions, respectively, was  $19.48 \pm 0.21\%$  and  $20.10 \pm 0.20\%$ .



**Figure 3-6:** FBDOC<sub>30</sub> under (a) aerobic and (b) anaerobic conditions, expressed as a percentage of the total DOC extracted. Error bars represent one standard error of the mean.

**Table 3-8:** Summary of results for analysis of variance (PERMANOVA) and LSD pair-wise tests for the effects of level on FBDOC<sub>30</sub> under both aerobic and anaerobic conditions. Pseudo F = the f-value, t = the t-statistic, df = degrees of freedom, p = the probability of the null hypothesis being true. Significant differences were defined as p < 0.05 and are denoted with \* and significance levels of p < 0.01 are denoted with \*\* for the main test and at p < 0.01 for the LSD testing and denoted with \*.

		Aerobic FBDOC availability		Anaerobic FBDOC availability	
	df	Pseudo F	p	Pseudo F	p
Level	3	2.990	0.033*	3.704	0.014*
<b>Pair-wise testing</b>					
		t	p	t	p
C, B1		1.875	0.064	0.863	0.396
C, B2		1.663	0.106	2.252	0.030
C, FP		1.015	0.334	1.673	0.106
B1, B2		2.579	0.011*	2.721	0.008**
B1, FP		2.323	0.015*	2.318	0.013*
B2, FP		0.786	0.436	0.827	0.412

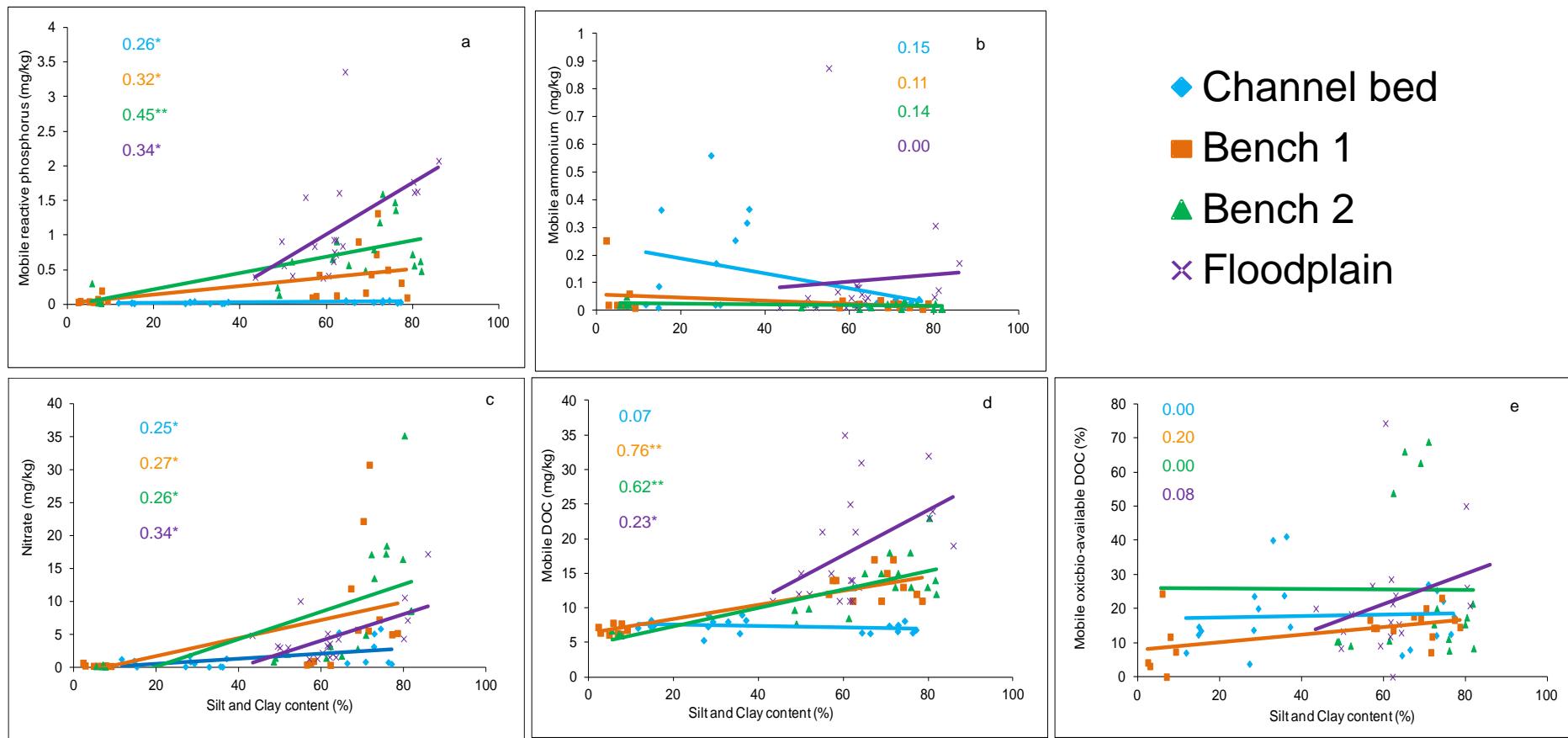
**Table 3-9:** The effect of aerobic and anaerobic conditions on FBDOC<sub>30</sub> across all levels in the landscape and within each level, results from factorial PERMANOVA and pair-wise testing. Pseudo F = the f-value, t = the t-statistic, df = degrees of freedom, p = the probability of the null hypothesis being true. Significant differences were defined as p < 0.05 and are denoted with \* and significance levels of p < 0.01 are denoted with \*\* for the main test and at p < 0.01 for the LSD testing and denoted with \*.

FBDOC <sub>30</sub>			
	df	Pseudo F	p
Level	3	5.094	0.002
O <sub>2</sub> availability	1	0.107	0.745
<b>Pair-wise testing within levels</b>			
	df	t	p
C	1	0.422	0.676
B1	1	0.612	0.543
B2	1	0.180	0.823
FP	1	0.327	0.752

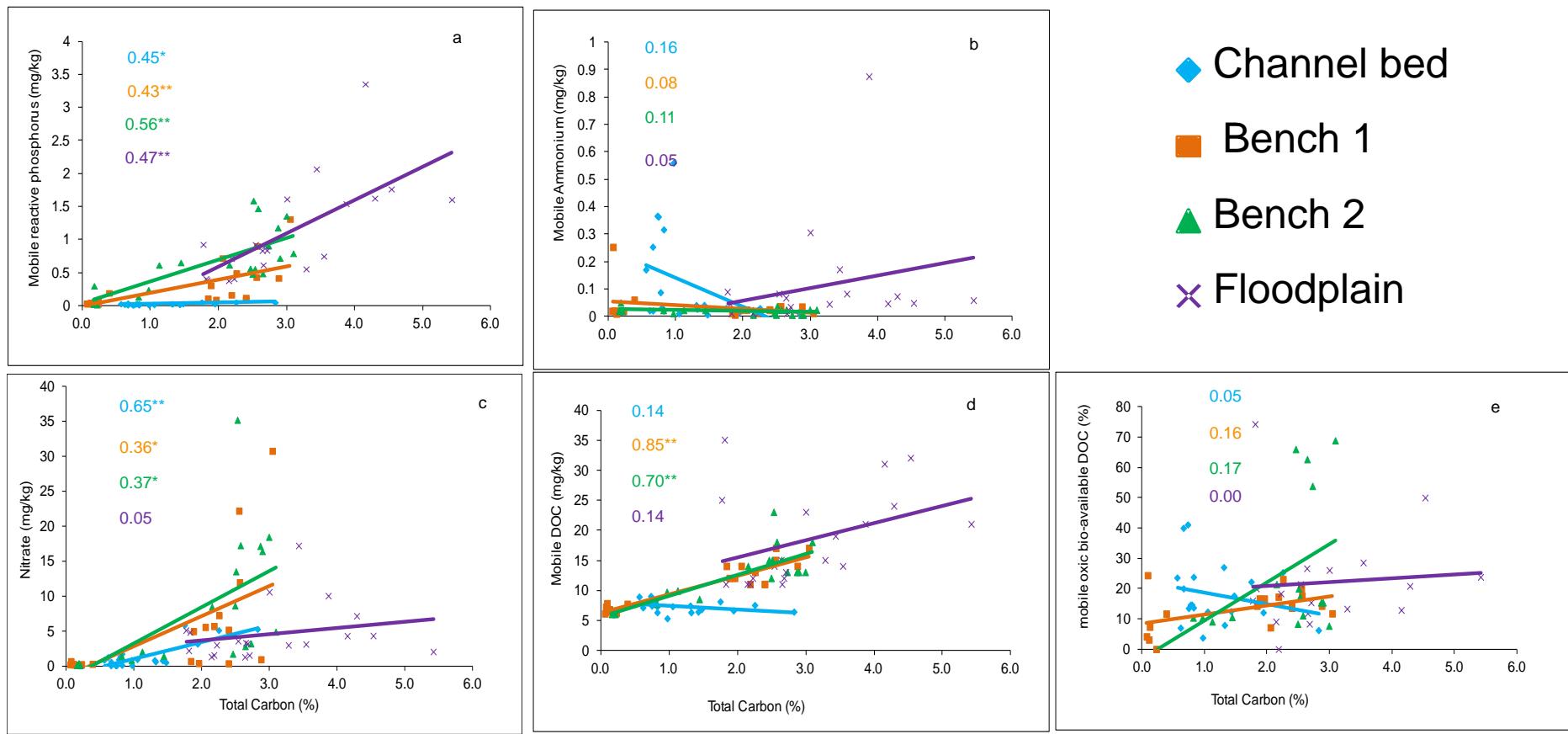
### **3.3.3 What are the relationships between total soil carbon and soil silt and clay content with extractable $\text{NO}_3^-$ -N, $\text{NH}_4^+$ , DRP, DOC and $\text{BDOC}_{30}$ and do they differ at different heights in the Gwydir River landscape?**

The percentage content of silt and clay found in soils from the Gwydir River landscape was positively correlated with the amount of mobile DRP,  $\text{NO}_3^-$ -N and DOC on all levels in the landscape with the exception of DOC in CH level (Figure 3-6). The FP soil, when compared to other levels, showed stronger relationships between silt and clay content and concentrations of DOC and DRP. No relationship was evident between mobile concentrations of  $\text{NH}_4^+$  or the  $\text{BDOC}_{30}$  with soil silt and clay content on any level.

Significant relationships were found between extractable soil nutrients and total soil C, although they were not as strong as those found with soil silt and clay content. However, significant positive relationships were found between DRP and total soil C for all levels in the landscape and for  $\text{NO}_3^-$ -N on all levels excluding the FP (Figure 3-7). The high total soil C content of the FP soil increased the quantities of mobile inorganic nutrients, with the exception of  $\text{NO}_3^-$ , making it distinct from the other soils investigated in the Gwydir River landscape.



**Figure 3-7:** The relationships between soil silt and clay content of each level with mobile concentrations of a) DRP, b)  $\text{NH}_4^+$ , c)  $\text{NO}_3^-$ -N, d) DOC and e)  $\text{BDOC}_{30}$ . Reported in the same colour of the regression line is the  $r^2$  value for this relationship with \* denoting a significant relationship at  $p < 0.05$  and \*\* at  $p < 0.001$ .



**Figure 3-8:** The relationships between the amount of total soil carbon and concentrations of a) DRP, b)  $\text{NH}_4^+$ , c)  $\text{NO}_3^-$ -N, d) DOC and e) bio-available DOC.

Reported in the same colour as the regression line is the  $r^2$  value for this relationship with \* denoting a significant relationship at  $p < 0.05$  and \*\* at  $p < 0.001$ .

## **3.4 Discussion**

### **3.4.1 Do levels higher in the Gwydir River landscape have larger stores of water extractable $\text{NO}_3^-$ -N, $\text{NH}_4^+$ , DRP, DOC, finer soil texture, larger stores of leaf litter and total carbon and higher C:N ratio compared to those closer to the channel bed?**

As predicted by the conceptual model (Figure 3-1), the size of standing stocks of total litter increased with level height in the Gwydir River landscape but not all of the components of litter followed this pattern. This relationship between standing stock of total litter load and height in the landscape is similar to the distribution of litter found on benches in the Barwon-Darling River in south eastern Australia (Sheldon and Thoms 2006). On the levels in the Gwydir River landscape the standing stock of leaves peaked on the B1 level, the lowest in-channel bench level. In contrast, Sheldon and Thoms (2006) found the greatest standing stocks of leaves on the floodplain level in the Barwon-Darling River landscape. However, it should be noted that litter fall in Australian floodplains forests is highly seasonal, with peak rates occurring in late spring and summer (Robertson et al. 1999) and the timing of sampling may have affected litter distributions. Thus any temporal variation in the amounts and distribution of the standing stocks of litter that was not captured by this study. The distribution of leaves in the landscape is important when trying to understand distributions of nutrient and carbon resources, as on a weight to weight basis leaves release more DOC that is bioavailable when inundated than other litter components or soil (O'Connell et al. 2000, Francis and Sheldon 2002).

The results for soil texture followed the predictions made in the conceptual model (Figure 3-1) as the benches higher in the Gwydir River landscape had proportionally greater contents of silt and lower contents of sand compared with lower levels. The fining of soil texture with bench height has been repeatedly found in other rivers throughout the Murray-Darling Basin (Woodyer et al. 1979, Nanson and Page 1983, Thoms and Olley 2004). While outside Australia, Asselman and Middelkoop (1995) found a fining of sediments with increased distance from the river in European floodplains.

The soil silt content in the Gwydir River landscape was correlated with mobile DRP; both increased with height in the channel as predicted in the conceptual model (Figure 3-1). A similar finding between total phosphorus and sediment texture was presented by Southwell and Thoms (2011) in benches of the Barwon-Darling river. Within a river landscape wetting and drying cycles are known to affect soil phosphorus, particularly phosphate (Baldwin and Mitchell 2000, Kerr et al. 2010). Phosphate is released from soil on inundation (Wilson and Baldwin 2008) and repeated wetting and drying cycles reduce a soils ability to retain phosphate (Kerr et al. 2010). Therefore, the greater inundation frequency of the levels lower in the Gwydir River landscape may have caused their soils to store less mobile DRP compared to higher levels. It is likely that both soil texture and inundation frequency influenced extractable soil DRP in the Gwydir River, however, the methodology employed in this study does not allow these effects to be separated.

The complex gradients in soil properties and inundation frequency across the levels in the Gwydir landscape affected the form of soil inorganic nitrogen but had little effect on the total amount of inorganic nitrogen found in the soil of each level. This finding contradicts the suggestions made in the conceptual model (Figure 3-1) that the amount of mobile soil  $\text{NO}_3^-$  and  $\text{NH}_4^+$  would increase with height in the channel. Below the FP level in the Gwydir River landscape there was a pattern of mobile soil  $\text{NH}_4^+$  increasing and mobile soil  $\text{NO}_3^-$ -N decreasing as levels got progressively closer to the channel bed. This pattern may be caused by the reduced inundation frequency at higher levels in the landscape, increasing the periods of aerobic conditions, allowing more  $\text{NH}_4^+$  to be converted to  $\text{NO}_3^-$  via nitrification. Decreasing concentrations of  $\text{NH}_4^+$  with greater distance from the river has been noted by Heffernan and Sponseller (2004) who compared riparian soils to bank soils in Sycamore Creek, Phoenix USA and by Wassen et al. (2003) across a gradient of floodplain vegetation types in a Polish floodplain, neither of these studies offered explanations for their observations.

The decreasing amount of mobile  $\text{NO}_3^-$ -N found lower in the Gwydir River landscape is likely the result of the increased inundation frequency of these soils. Inundation can flush  $\text{NO}_3^-$  from soil (Qiu and McComb 1996, Wilson and Baldwin 2008) and create conditions conducive to denitrification (Fellows et al. 2011) resulting in  $\text{NO}_3^-$  losses. It is likely that the lower stores of soil total carbon, DOC and  $\text{FBDOC}_{30}$  of soil lower in the landscape limit rates of denitrification suggesting that flushing of  $\text{NO}_3^-$  from soils may be the dominant mechanism of  $\text{NO}_3^-$  loss in these lower levels.

The amount of mobile DOC found in the soil of the Gwydir River landscape was lowest in the CH level and increased with greater height in the landscape. Leaf litter is a known source of soil DOC (Kalbitz et al. 2000) therefore, the greater amounts of leaf litter and older age of levels higher in the landscape (Thoms and Olley 2004) are likely the source of the higher concentrations of mobile DOC found in these levels. Moreover, the lower levels in the landscape are inundated more frequently which may reduce soil stores of mobile DOC due to flushing and respiration losses (Valett et al. 2005, Kobayashi et al. 2009, Wilson et al. 2011). However, these losses may be replenished by the sedimentation of silts and clay, and their associated organic matter (Woodyer et al. 1979, Nanson and Page 1983, Vietz et al. 2012). Therefore, the amount of DOC found in the soil of the different levels in the Gwydir River landscape is likely to be the result of the changing importance of these mechanisms of DOC import and export.

### **3.4.2 What fraction of the DOC extracted from soils of the different levels in the Gwydir River landscape is bioavailable ( $\text{BDOC}_{30}$ ) under aerobic and anaerobic conditions and does this change across levels in the landscape?**

Approximately 20% of the DOC extracted from soil in the Gwydir River landscape was bioavailable which is comparable to the 10-44% found in other laboratory incubation studies (Jandl and Sletten 1999, Kalbitz et al. 2000, Yano et al. 2000, Sachse et al. 2001) but this fraction varied across different levels in the Gwydir River landscape. Other studies have

shown that the fraction of bioavailable soil DOC varies with soil depth, land use, soil contamination and litter quality (Boyer and Groffman 1996, Lundquist et al. 1999, Merckx et al. 2001) however, only litter quality is likely to have varied in the Gwydir River landscape. Litter quality decreases with age (Baldwin 1999) and the age of litter is likely to increase with height in the landscape, given that higher levels have been shown to be older than lower levels (Thoms and Olley 2004). These changes should decrease soil FBDOC<sub>30</sub> on levels higher in the landscape. This may explain why the B2 level had greater FBDOC<sub>30</sub> than the FP level but it can not explain the low FBDOC<sub>30</sub> found in the B1 soil, which had the largest stores of leaves and the lowest amount of CPOM in its leaf litter stores. The higher inundation frequency of the B1 level compared to the B2 and FP levels may have affected the FBDOC<sub>30</sub> found in it soils while the permanent inundation of the CH level is likely to have affected the FBDOC<sub>30</sub> found in its soils.

Soil respiration consumes BDOC and rates of soil respiration increase during and following inundation of previously dry soil (Sánchez-Andrés et al. 2010, Wilson et al. 2011) but are reduced under permanent inundation (Küsel and Drake 1998). Therefore, the permanent inundation of the CH level should increase its FBDOC<sub>30</sub> while the high inundation frequency of the B1 level should decrease its FBDOC<sub>30</sub>, which fits the patterns observed in the lower levels of the Gwydir River landscape. Therefore, it seems likely that respiration is affecting FBDOC<sub>30</sub> in the lower levels in the Gwydir River landscape. A similar effect of wetting and drying cycles was shown by Fierer and Schimel (2002) who observed that repeated wetting and drying cycles reduced soil respiration in forest soil implying that stores of BDOC had been reduced.

### **3.4.3 What are the relationships between soil total carbon, silt and clay content with nutrients, DOC and DOC bioavailability and do they differ at different heights in the Gwydir River landscape?**

### **3.4.3.1 Ammonium and nitrate**

In the Gwydir River landscape there was a positive relationship between total soil C and  $\text{NO}_3^-$ . This positive correlation may have resulted from mineralisation of organic matter producing  $\text{NH}_4^+$  and its subsequent nitrification to  $\text{NO}_3^-$ . Supporting this suggestion is the opposing pattern found in  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations on the CH, B1 and B2 levels which suggests nitrification is converting  $\text{NH}_4^+$  to  $\text{NO}_3^-$  in these soils. Interestingly, the FP level exhibited neither a correlation between  $\text{NO}_3^-$ -N and total soil C nor the opposing concentrations of  $\text{NO}_3^-$ -N and  $\text{NH}_4^+$  that was found in soils lower in the landscape. This implies that inorganic N dynamics in the FP soil is influenced by some other factor that does not affect the other levels in the landscape as strongly, possibly its significantly higher soil moisture.

Unfortunately, there is little information about the spatial distribution of inorganic nitrogen in floodplain soils or the soil properties that may influence its distribution in this environment (Bai et al. 2007). However, an investigation into the distribution of inorganic nitrogen species across multiple flood frequency zones in a semi-arid Chinese floodplain revealed  $\text{NH}_4^+$  to be positively correlated with soil pH and  $\text{NO}_3^-$  to be negatively correlated to total soil C (Bai et al. 2007). Bai et al. (2007) suggested that volatilisation of  $\text{NH}_3^+$  increasing with soil pH caused the positive relationship between these variable and noted that soil high in total C were also coarse grained and  $\text{NO}_3^-$  would have been easily leached from these soils.

### **3.4.3.2 DRP, DOC and FBDOC<sub>30</sub>**

The amount of DRP and DOC were both positively correlated with soil texture on all levels of the Gwydir River channel, with the exception of DOC in the CH level. The steepness of the regression line between these variables increased with height in the landscape (Figure 3-7) illustrating that soils higher in the landscape, when compared to soils closer to the river bed, have greater concentrations of DRP and DOC at the same soil silt and clay content.

Inundation of soils, which is more frequent in the lower levels, releases both DOC (Kobayashi et al. 2009, Wilson et al. 2011) and phosphate (Qiu and McComb 1994, Wilson

and Baldwin 2008). Thus, this weaker relationship between soil silt:clay content with soil phosphate and DOC in the lower levels of the Gwydir River channel may have been caused by their greater inundation frequency compared to levels higher in the landscape. Alternatively, total soil carbon was greater in the soil of higher levels and it was significantly correlated to both phosphate and DOC, allowing these higher levels to store more phosphate and DOC at similar silt and clay contents.

### 3.1 Conclusions

The various levels within the lowland Gwydir River landscape were found to have different quantities of mobile soil nutrients, DOC, BDOC<sub>30</sub> and FBDOC<sub>30</sub>. However, temporal variation was not assessed in this chapter and it is possible that seasonal factors such as rates of litter fall and time since last inundation, rather than inundation frequency may affect the amounts and distribution of these properties. At the time of sampling, concentrations of mobile DRP and DOC increased with level height as did the amount of total soil carbon and the soil silt content. Significant correlations were found between both soil silt and clay content and soil total C with mobile stores of DOC and DRP. A significant correlation was also found between the amount of mobile soil NO<sub>3</sub><sup>-</sup>-N and soil silt and clay content as well as with total soil C. The dominant form of inorganic N found across all levels was NO<sub>3</sub><sup>-</sup>-N with the fraction of NH<sub>4</sub><sup>+</sup> increasing in the more frequently inundated soils lower in the landscape. This pattern suggests that inundation results in the loss of NO<sub>3</sub><sup>-</sup> from inundated soils, likely from either mobilisation and/or denitrification and in the higher, less frequently inundated soils NH<sub>4</sub><sup>+</sup> is being nitrified to NO<sub>3</sub><sup>-</sup> which was more stable in these soils due to their lower inundation frequency. The amount, and form, of inorganic nitrogen found in FP level soil level did not fit the pattern of altering NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>-N concentrations found with changing level height lower in the landscape suggesting that other factor(s) are influencing soil NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> dynamics on this level.

The release of carbon and nutrients from inundated levels, whether they be in-channel benches or on the floodplain, during flow pulses and flooding events is thought to supplement the overall productivity of aquatic ecosystems (Junk et al. 1989, Sheldon and

Thoms 2006, Westhorpe et al. 2008). The volume and form of carbon and nutrients released from soils on inundation will depend on what is stored both on their surface as leaf litter and the contents of the soil itself. This chapter illustrated that the stores of nutrients and carbon within the soils of the Gwydir River landscape varied with height. This implies that the amount and type of nutrients and the amount and bioavailability of DOC mobilised into the aquatic ecosystem will be affected by the stage height of a flow pulse. Therefore, aquatic ecosystems in these rivers may respond differently to flow pulses that reach different stage heights due to different ratios of carbon and nutrients being mobilised.

# **Chapter 4. Inundation frequency and terminal electron accepting processes occurring in inundated bench and floodplain soils**

## **4.1 Introduction**

Inundation of terrestrial soil can provide an important connection between the terrestrial and aquatic environments and has been attributed as the ‘life-line’ of large river productivity, providing subsidies of organic carbon and nutrients to the main channel (Junk et al. 1989, Bunn et al. 2006b). Although the overall role of flooding in riverine productivity is well recognised (Junk et al. 1989, Bunn et al. 2006a) the spatial and temporal variability of the soil processes that facilitate these exchanges are less well understood (Ward et al. 2002, Banach et al. 2009a, Banach et al. 2009b). Carbon and nutrients are initially mobilised from soil by a flush upon inundation, however, stores of soil carbon and nutrients which can be flushed on inundation are not evenly distributed in riverine landscapes (Chapter 3, Bai et al. 2007, Ogden et al. 2007). Soil that has dried between inundation events has larger flushes of carbon and nutrients due to the greater osmotic stresses causing the lysing of bacterial cells and the release of nutrients contained within them (Qiu and McComb 1994, Fierer et al. 2003, Wilson and Baldwin 2008). After these flushing events soil bacteria can make soils a source or sink of nutrients through different forms of anaerobic respiration that consume organic carbon (Hamilton and Lewis 1987, Baldwin and Mitchell 2000, Baldwin et al. 2000, Noe and Hupp 2007). However, little is known about the distribution of these anaerobic processes in riverine soils (Baldwin and Mitchell 2000).

Soil respiration is stimulated on inundation due to the increased availability of carbon and nutrients (Valett et al. 2005, Kobayashi et al. 2009). Heterotrophic organisms use these resources by oxidizing organic carbon in a variety of terminal electron accepting processes (TEAPs) to gain energy for metabolism and growth (Vroblesky and Chapelle 1994). These processes include the reduction of oxygen, nitrogen (denitrification), iron and sulfate and the production of methane (methanogenesis) (Chapelle et al. 1995, Baker et al. 1999, Morrice et al. 2000). Each of these processes has its own environmental significance;

denitrification removes  $\text{NO}_3^-$ , a potential aquatic pollutant (Hill 1996), from the water and soil but may produce  $\text{N}_2\text{O}$  a powerful greenhouse gas (Mosier et al. 1998); sulfate reduction produces sulfide which can be toxic at high concentrations (Wang et al. 2003), methanogenesis produces  $\text{CH}_4$ , another greenhouse gas (Segers 1998), while  $\text{SO}_4^{2-}$  and  $\text{Fe}^{3+}$  reduction may increase the mobility of phosphate (Bostrom et al. 1988, Roden and Edmonds 1997) which is commonly found to limit primary productivity in freshwater ecosystems.

It is possible to predict the spatial and temporal distribution of these processes based upon their ‘free energy yields’, the thermodynamic estimates of the amount of energy generated by a given chemical process under standard conditions (Stumm and Morgan 1995). Free energy yields (Table 4-1) have been used to predict the spatial distributions of these processes in a range of different environments (e.g. Carlton et al. 1989, Chapelle et al. 1995, Hedin et al. 1998). To use free energy yields to predict the environmental distribution of TEAPs it must be assumed that, in a given environment, the metabolic reaction that yields the most free energy will be dominant (Zehnder and Strumm 1988). This assumption may not always hold depending on environmental conditions such as the presence or absence of electron donors and acceptors and the presence or absence of microbial groups able to carry out each reaction (Baker et al. 1999) and the rate at which each reaction is carried out (kinetics) (Heimann et al. 2009).

**Table 4-1:** Thermodynamics of heterotrophic redox reactions (most negative value for Kcal/Equiv equals the highest free energy yield for microbes) (Modified from Baker (2000)).

Stoichiometry for different microbial terminal electron accepting processes with acetate as the electron donor	Free energy $\Delta G$ (w) (kcal)
Aerobic Respiration $\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$	-120.0
Denitrification $\text{CH}_2\text{O} + (4/5)\text{NO}_3^- + (4/5)1.6\text{H}^+ = (7/5)\text{H}_2\text{O} + (2/5)\text{N}_2 + \text{CO}_2$	-113.9
Mn (IV) Reduction $\text{CH}_2\text{O} + 2\text{MnO}_2 + 4\text{H}^+ = 2\text{Mn}^{2+} + 3\text{H}_2\text{O} + \text{CO}_2$	-81.3
Fe (III) Reduction $\text{CH}_2\text{O} + 8\text{H}^+ + 4\text{Fe(OH)}_3 = 4\text{Fe}^{2+} + 11\text{H}_2\text{O} + \text{CO}_2$	-27.7
Sulfate Reduction $\text{CH}_2\text{O} + (1/2)\text{SO}_4^{2-} + (1/2)\text{H}^+ = (1/2)\text{HS}^- + \text{CO}_2 + \text{H}_2\text{O}$	-25.0
Methanogenesis $\text{CH}_2\text{O} + (1/2)\text{CO}_2 = (1/2)\text{CH}_4 + \text{CO}_2$	-19.2
Fermentation $\text{CH}_2\text{O} + (1/3)\text{H}_2\text{O} = (2/3)\text{CH}_3\text{OH} + (1/3)\text{CO}_2$	-8.6

Note.  $\Delta G^\circ(w)$  is the change in Gibbs free energy calculated as  $\Delta G^\circ(w) = \Delta G^\circ - RT \ln [H^+]^p$ , where  $[H^+] = 1 \times 10^{-7}$  M and p is the stoichiometric coefficient for  $H^+$  in a given reaction. For reductive reactions it is important to note that the actual  $\Delta G^\circ$  (w) for a given system will depend on the type of organic matter being oxidised, and that alternative terminal electron accepting processes often involve oxidation of low molecular weight fermentation products

In saturated environments the distribution of these metabolic processes is dependent upon hydraulic flow rate (Chapelle et al. 1995, Morrice et al. 2000), the amount of labile organic carbon (electron donors) (Baker et al. 1999, Alewell et al. 2008) and the supply of electron acceptors (Baker et al. 1999, Liesack et al. 2000). In lake and ocean sediments, and deep aquifers, the vertical distribution of TEAPs has been shown to follow thermodynamic predictions, with the dominant TEAP changing over very fine scales, millimetres to

centimetres, due to low rates of solute transportation and high amounts of available organic carbon (Carlton et al. 1989). In deep and riparian aquifers TEAPs also followed thermodynamic predictions with the spatial distributions being determined by flow rate and direction as well as the availability of organic carbon (Champ et al. 1979, Vroblesky and Chapelle 1994, Hedin et al. 1998, Vidon and Hill 2005). However, within the hyporheic zone closer to the stream, greater hydrologic variability in flow paths and velocities is thought to disrupt supplies of electron donors and acceptors resulting in a distribution of TEAPs that does not follow thermodynamic predictions (Baker et al. 1999, Morrice et al. 2000). So, the distribution of TEAPs seems to follow thermodynamic predictions unless variability in flow paths disrupts supplies of electron donors and acceptors while the distance between TEAPs is determined by the availability of organic carbon and flow rate. These findings relate to areas that are permanently saturated, the constraints may be different in freshly inundated soils.

The presence of oxygen ( $O_2$ ) is a fundamental difference between the saturated environments discussed above, and floodplain or in-channel bench soils, which experience saturated conditions relatively infrequently.  $O_2$  will be present in these soils both prior to inundation and during the early stage of inundation. The presence of  $O_2$  in aerated, non-inundated soils may affect the assumption that all functional microbial groups are present (Baldwin and Mitchell 2000). The tolerance of soil bacteria to  $O_2$  varies between groups, with some groups able to survive both with and without  $O_2$ , while others require  $O_2$  and other groups find  $O_2$  toxic (Tiedje et al. 1984, Cypionka et al. 1985, Nealson and Saffarini 1994, Baldwin and Mitchell 2000). Organisms that carry out  $Fe^{3+}$  and  $Mn^{4+}$  reduction, denitrification and fermentation are believed to be facultative anaerobes so they can survive with or without  $O_2$  (Smith 1985). Thus,  $Fe^{3+}$  and  $Mn^{4+}$  reduction, denitrification and fermentation could be expected to occur in most soils. In contrast, organisms capable of dissimilatory  $NO_3^-$  reduction to  $NH_4^+$ ,  $SO_4^{2-}$  reduction and methanogenesis are thought to be obligate anaerobes and are therefore not expected to be prevalent in well aerated soils (Gottschal 1985).

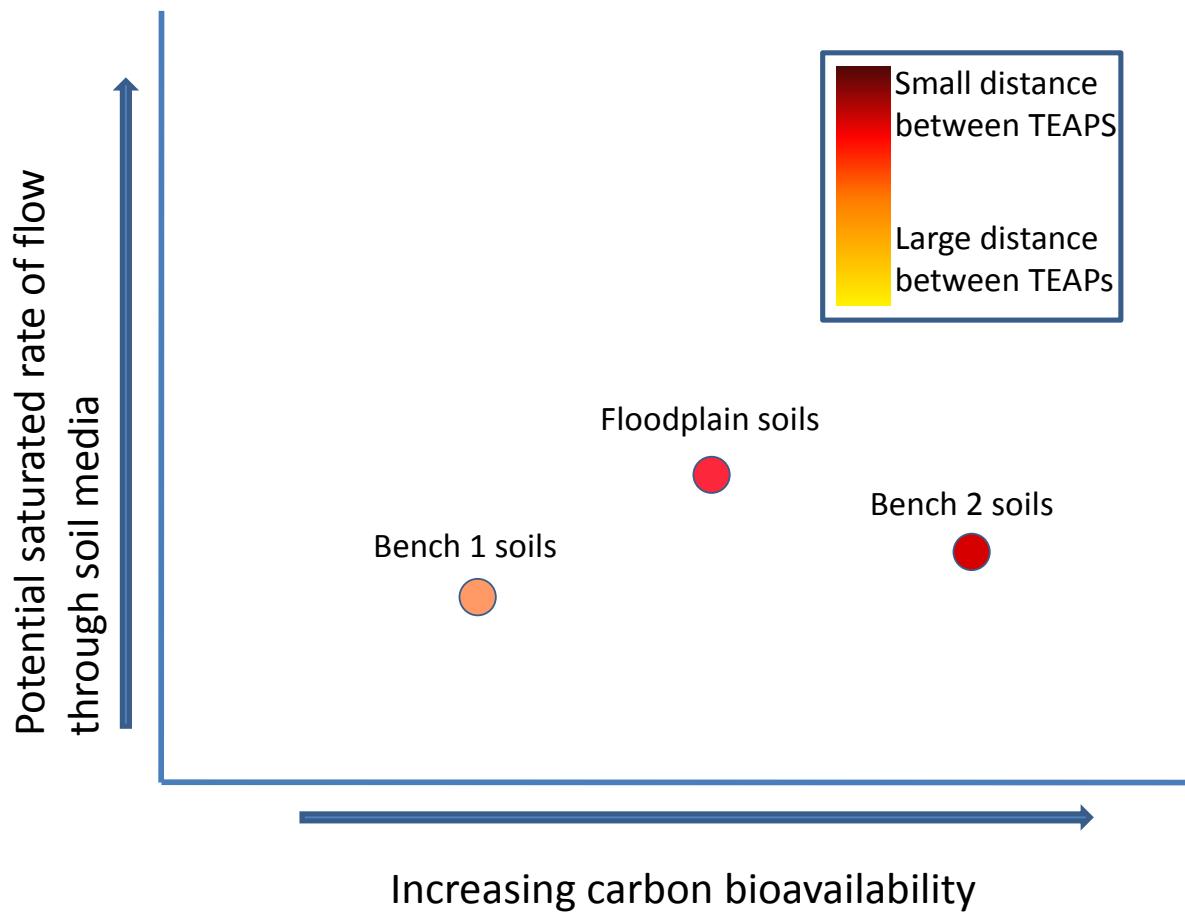
The O<sub>2</sub> content of soil is variable and dependent on soil structure, water content and the availability of carbon. Water content affects soil O<sub>2</sub> content for two reasons; (a) that water is only slightly soluble in water and, depending on temperature water can only hold approximately 10 mg L<sup>-1</sup> and (b) that O<sub>2</sub> diffuses 10000 times slower in water than in air (Gottschal 1985). Therefore, the long-term water content of a soil may affect the structure of its microbial community and therefore, its ability to perform functions predominantly carried out by obligate anaerobes, such as sulfate reduction or methanogenesis (Tiedje et al. 1984, Gottschal 1985, Smith 1985). In addition to soil water content, soil structure affects soil O<sub>2</sub> content by changing soil porosity, while the availability of carbon also influence the amount and distribution of O<sub>2</sub> within an aerated soil by affecting rates of soil metabolism (Tiedje et al. 1984, Gottschal 1985, Smith 1985). Variance in these factors can create O<sub>2</sub> gradients reaching from a few millimetres to over a metre into a soil profile (Gottschal 1985). However, in oxygenated soil zones there are anaerobic microsites where obligate anaerobic bacteria may survive (Tiedje et al. 1984, Gottschal 1985, Smith 1985). In riverine soils it has been suggested that inundation history may shape the microbial community present in that soil (Baldwin and Mitchell 2000, Fierer et al. 2003, Wilson and Baldwin 2008).

In-channel benches, are common geomorphological feature in Australian lowland rivers (Vietz et al. 2004) that possess a range of qualities that suggest that periods of inundation may be “hot moments” when benches become “hot spots” of biogeochemical activity (McClain et al. 2003). These potential “hot moments” are likely to occur due to the variable hydrological conditions, periodic inundation and drying, that allows a build-up of reactants in the soils when not inundated, with the “hot moments” occurring during periods of increased flow. However, benches occur at different heights in river channels and each level has different properties that suggest that the dynamics of TEAPs during periods of inundation may vary on benches of different heights. Benches lower in the river channel are inundated with greater frequency and have smaller stores of organic carbon than benches higher in the river channel (Chapter 2, Chapter 3). The greater inundation frequency of lower benches may shape the soil microbial community to be more adaptable to the conditions brought about by inundation, allowing these communities to progress through the sequence of TEAPs faster than benches higher in the river channel. However, the

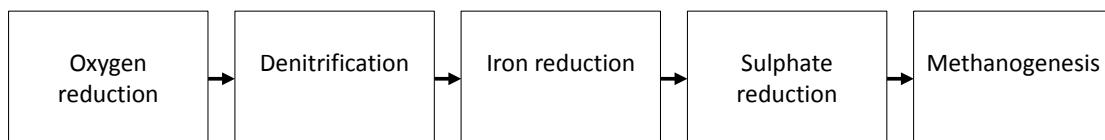
greater stores of organic carbon found in benches higher in the channel (Chapter 3) provides a greater source of energy for the different TEAPs which may allow thermodynamic constraints on the sequential nature of TEAPs to be lifted causing less energetically beneficial TEAPs to occur in association with, or even before, more energetically favourable TEAPs.

Using an estimated hydraulic flow rate and the fraction of bioavailable DOC measured in Chapter 3, it is possible to predict the ‘distance’ in time between the commencement of different TEAPs across the levels in the Gwydir Landscape (Figure 4-1) based on studies of TEAPs in saturated environments (see above). These estimates of hydraulic flow through the soil were based upon the ease or difficulty experienced when extracting a pore water samples from the soil of each level (see methods this Chapter). The difficulty in extracting pore water samples from the soil of each level decreased with increasing level height and likely reflects soil structural formation, with increasing soil hydraulic conductivity due to the formation of macro-pores in the more developed soil higher in the landscape. These predictions, presented in Figure 4-1, assume that the full suite of electron acceptors and biota capable of each process are present in each level in the Gwydir River channel.

The sequence in which a bench or floodplain soil passes though these TEAPs will affect the timing of when they becomes sinks for  $\text{NO}_3^-$  and sources of DRP,  $\text{N}_2\text{O}$  and  $\text{CH}_4$  affecting the biogeochemistry of flow pulses. It is even possible that some TEAPs may not occur in bench soil due to prolonged periods between inundation events making them harsh environment for facultative anaerobic bacteria (Baldwin and Mitchell 2000).



**Figure 4-1:** A conceptual model predicting the effects of water flow rate and the bioavailability of soil DOC ( $BDOC_{30}$ ) (chapter 3) on this distance in time between the TEAPS on each level in the Gwydir River landscape. This model assumes that all of the electron acceptors and biota capable of reducing them are present in each of the soils.



**Figure 4-2:** The expected sequence of TEAPs based on thermodynamically predicted energy yields that will occur after the inundation of the Gwydir River soils.

This chapter explores the occurrence and sequence of terminal electron accepting processes during experimental inundation of bench and floodplain soils from the lowland Gwydir River. The specific research questions being asked are;

1. Was the inundated soil from different levels in the Gwydir River channel equally capable of all of the different TEAPs?
2. When inundated do the different levels in the Gwydir River channel progress through the sequence of TEAPs as predicted by thermodynamics?
3. How much carbon was consumed by each of the different TEAPs
4. How much carbon did the TEAPs consume on each of the levels and did the fraction of carbon consumed by each of different TEAPs vary on the different levels?

## 4.1 Methods

### 4.1.1 Study area

This experiment was conducted on the bench set from Site 2 (see Chapter 2 for site description). The data presented in this description of the study area was extracted from the data presented in Chapter 3. This site was chosen as it had the largest range of inundation frequencies (see Chapter 2) and the greatest amounts of BDOC<sub>30</sub>. On average this site had less silt and clay compared to other bench sets but had a higher percentage of total soil carbon (Chapter 2). Extractable amounts of DOC were comparable to other bench sites but it had high concentrations of extractable NH<sub>4</sub><sup>+</sup> and moderate amounts of extractable NO<sub>3</sub><sup>-</sup>-N and SRP in comparison to the other sites investigated this thesis. The physical and chemical properties of the soils on each level at Site 2 are presented in Table 4-2.

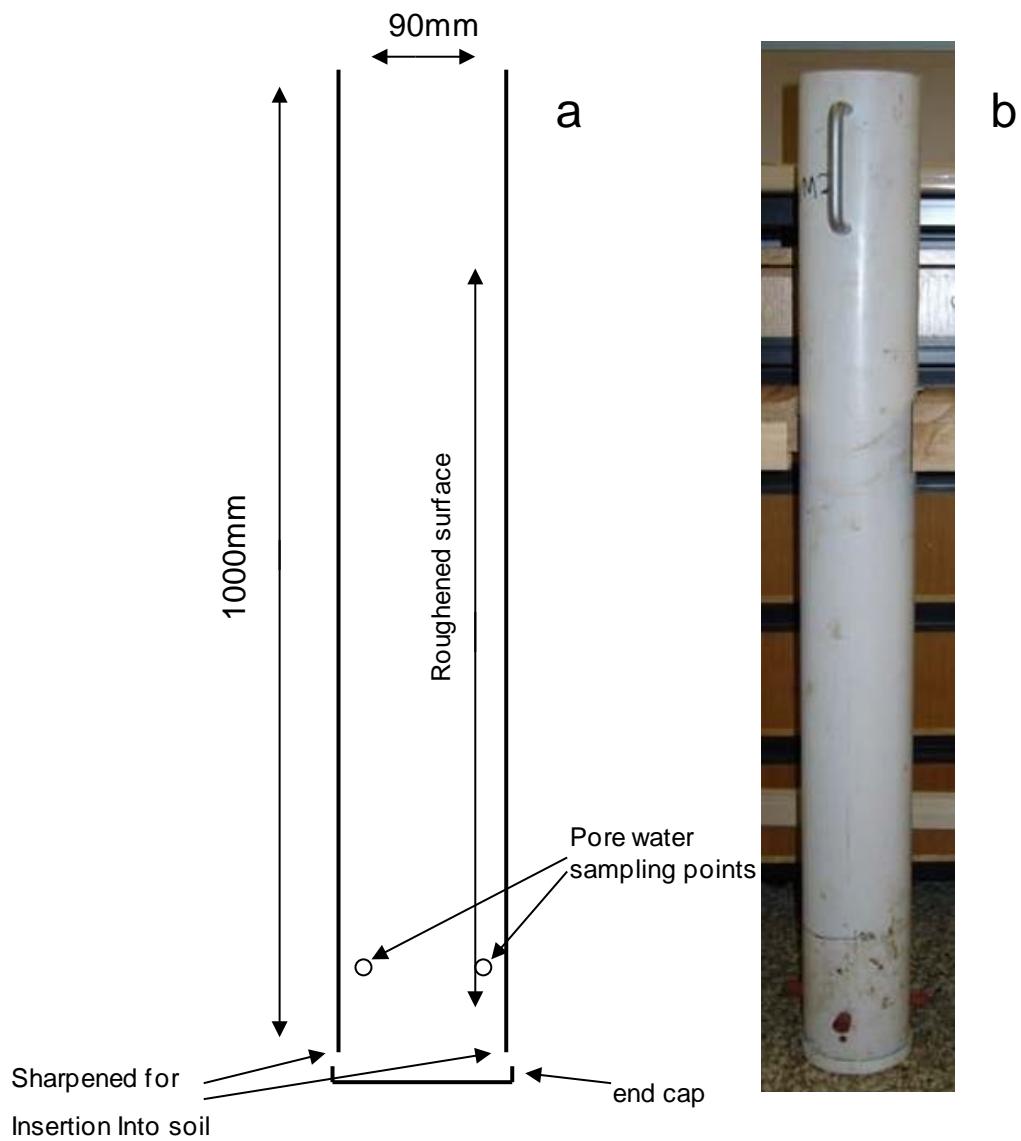
**Table 4-2:** Summary of the soil characteristics of each of the B1, B2 and FP levels at site 2 (this data was extracted from the data presented in chapter 3 that was used to characterise the different levels in the Gwydir River landscape)

	B1	B2	FP
Total soil Carbon (%)	2.3 ± 0.24	2.7 ± 0.24	3.9 ± 0.6
Water extractable DOC (mg/kg)	15.10 ± 2.09	18.52 ± 1.56	23.71 ± 0.89
Bioavailable DOC <sub>30</sub> (mg/kg)	2.22 ± 0.07	11.75 ± 0.67	4.74 ± 0.24
NO <sub>3</sub> <sup>-</sup> -N (mg/kg)	0.56 ± 0.1	3.13 ± 0.33	3.23 ± 0.24
NH <sub>4</sub> <sup>+</sup> -N (mg/kg)	0.02 ± 0.06	0.02 ± 0.00	0.07 ± 0.00
SRP (mg/kg)	0.19 ± 0.04	0.69 ± 0.04	1.66 ± 0.3
Soil silt and clay content (%)	59.72 ± 1.25	67.86 ± 1.93	63.83 ± 0.54
Flood return interval (years)	0.75	3	12

#### 4.1.2 Mesocosms and soil collection

Plastic (PVC) mesocosms, 1000 mm in length and 90 mm in diameter (Figure 4-3) were used to extract intact soil cores and conduct the incubations. The bottom end of each mesocosm was sharpened and handles installed approximately 150 mm from the top to aid insertion into the soil. To prevent preferential flow of surface water down the internal wall of the PVC pipe during pore water sampling, this area was roughened using heavy sand-paper. The mesocosms were inserted in the soil and four replicate, intact, soil cores extracted from CH, B1, B2 and FP levels. The CH level was initially included, however, the extraction of pore water samples from this level was not possible due to a low saturated hydraulic conductivity, precluding its inclusion in the final experiment. After collection, the bottom of each mesocosm was closed with a PVC cap and sealed using PVC cement. The cement was allowed to dry before inundation and the commencement of the incubation period. Samples of soil pore water were collected from four 5 mm diameter holes located 50 mm from the bottom of the mesocosm and at a soil depth of approximately 100 mm; these

holes were separated by approximately 90 degrees (Figure 4-3). Four holes were used to ensure that enough pore water could be extracted for analysis.



**Figure 4-3:** Illustrates the mesocosm used during the inundation the soils from each level of the site 2 as a) a schematic b) photo of the mesocosm in use.

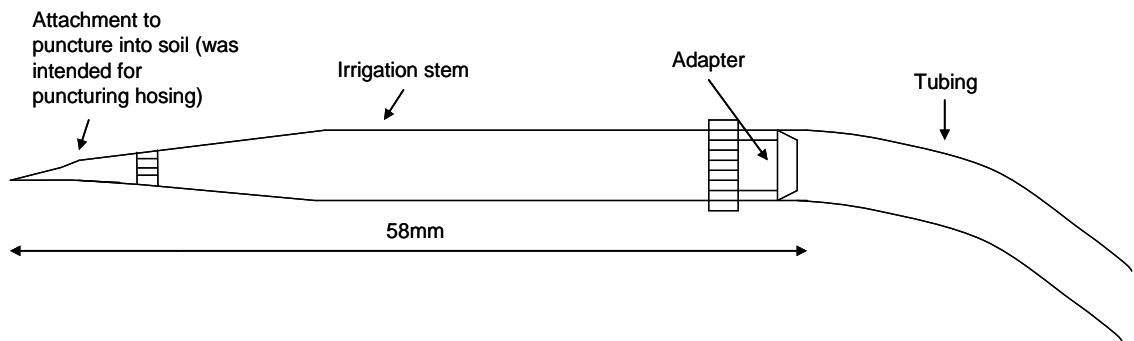
#### **4.1.3 Inundation and sampling**

To inundate the soil cores 40 L of water from the Gwydir River was collected. From this water concentrations of N<sub>2</sub>O, CH<sub>4</sub> and Fe<sup>2+</sup> were measured, however NO<sub>3</sub><sup>-</sup>-N and SO<sub>4</sub><sup>2-</sup> concentrations used as time zero measurements in this chapter were taken from the Gwydir River on a subsequent trip and therefore changes their concentration between time zero and the first sampling point, 2 hours following inundation, have not been considered.

The soil in each mesocosm was inundated with 2.5 L of river water approximately 30 hours after soil and water collection. Throughout the incubation period, surface water was measured for NO<sub>3</sub><sup>-</sup>-N, SO<sub>4</sub><sup>2-</sup> and dissolved oxygen (DO) concentrations and pore water for concentrations of Fe<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>-N, NH<sub>4</sub><sup>+</sup>-N, SO<sub>4</sub><sup>2-</sup>, N<sub>2</sub>O and CH<sub>4</sub>. The mesocosms were incubated in a dark constant temperature room to avoid potential algal growth that could provide an additional carbon source. The temperature in this room was set at 26°C for the duration of the experiment, minimising the effects that temperature fluctuations may have on dissolved gas concentrations. To measure concentrations of TEAP-sensitive solutes, 25 ml samples of surface water were taken from approximately 100 mm above the soil surface, this was done using a gas tight syringe after lowering a known length of plastic tubing into the surface water. Pore water was also extracted using a gas tight syringe and tubing, but a hard plastic irrigation attachment was used on the inserted end to penetrate into the soil core (Figure 4-4). Penetrating the soil core with the sampling device ensured that pore water samples were collected away from the PVC piping/soil boundary diminishing the likelihood of surface water drawdown. Furthermore, pore water was extracted slowly, further reducing the potential for surface water drawdown. A sample of 30 ml of pore water was collected at each sampling time.

Pore and surface water sampling was carried out together throughout the experimental inundation with an initial sample taken 2 hours following inundation after which sampling was conducted approximately 4 hourly for the first 48 hours of inundation. For the remainder of the experimental period sampling was carried out approximately every 10 hours. Mesocosms were sampled 21 times, however due to leaks developing during

sampling one B2 mesocosm was only sampled 18 times and two of the FP mesocosms 19 and 20 times, respectively. This high frequency sampling regime was undertaken to enable characterisation of processes which occur during short periods of inundation, like those experienced during the passage of a flow pulse.



**Figure 4-4:** A schematic of the device used to sample the pore water from inside the PVC piping.

For each pore water sample, dissolved  $\text{N}_2\text{O}$  and  $\text{CH}_4$  were extracted, using the headspace equilibrium method of Kling et al. (1992) then the sample was filtered for dissolved solutes. Dissolved gasses were extracted by shaking a syringe with high purity nitrogen gas in a 1:1 ratio of water to gas for two minutes to equilibrate the dissolved gases within the headspace. The headspace gasses from the syringe were then extracted into pre-evacuated vials and stored until analysis. Following gas extractions a minimum of 13 ml of sample was filtered at 0.45  $\mu\text{m}$  using polyethersulfone (PES) syringe filters (Sartorius) for analysis of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N,  $\text{SO}_4^{2-}$  and subsequently frozen at -20°C until analysis. An additional 5 ml of each pore water sample was filtered at 0.2  $\mu\text{m}$  using a polytetrafluoroethylene syringe filter (Whatman) into a centrifuge tube containing 4 ml of Ferrozine® for  $\text{Fe}^{2+}$  analysis (Stookey 1970). These samples were stored at room temperature until analysis.

#### 4.1.4 Analytical methods

The concentration of  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N and  $\text{SO}_4^{2-}$  were measured colorimetrically on a Westco Smartchem SC 200 Discrete Wet Chemistry Analyser at Griffith University.  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N was analysed using the SmartChem method 376N-0405C (equivalent of the USEPA 353.2)

and are reported here as  $\text{NO}_3^-$ -N. This method reduced  $\text{NO}_3^-$  to  $\text{NO}_2^-$  using a cadmium column, a coloured azo dye was then formed by reacting  $\text{NO}_2^-$  with sulfanilamide and N-(naphthyl)-ethylenediamine dihydrochloride, the colour intensity of this dye was read at 550nm. The  $\text{NO}_3^-$ -N detection limit was 0.43 millimol of  $\text{NO}_3^-$ -N  $\text{L}^{-1}$ .  $\text{NH}_4^+$ -N was analysed using SmartChem Method 213N-0405C (equivalent to USEPA 350.1), where sample is buffered at pH 9.5, then distilled into a boric acid solution. Ammonia then reacts with alkaline phenol and hypochlorite to form idenophenol blue, which is measured for absorbance at 630 nm. Ammonium detection limit is 0.05 mg  $\text{NH}_4$ -N  $\text{L}^{-1}$ . The SmartChem method 471N-0405C (equivalent to USEPA 375.4) was used to measure the concentration of  $\text{SO}_4^{2-}$ . In this method sulfate is converted into a barium sulfate suspension and the turbidity measured at 420 nm. The detection limit for sulfate was 0.99 millimol of  $\text{SO}_4^{2-}$   $\text{L}^{-1}$ . Results that were equal to or less to these limits were assigned a value of half of the detection limit.  $\text{N}_2\text{O}$  was analysed on a gas chromatograph (GC) (Agilent 6890 series) with a micro Electron Capture Detector (ECD) using methane/argon as the carrier gas.  $\text{CH}_4$  was analysed using a flame ionizing detector (FID) on the same GC using helium as the carrier gas.  $\text{Fe}^{2+}$  iron concentrations were determined colorimetrically using a Shimadzu UV160A photospectrometer after reaction with ferrozine (Stookey 1970). Dissolved oxygen was measured using a TPS Model WP-82Y.

#### 4.1.5 Data analysis

The process of sampling each mesocosm resulted in a reduction in the volume of water which was not subsequently replaced. Therefore, all variables are expressed in terms of area of soil inundated. This was calculated by dividing the amount of water left in the mesocosm at the time of sampling by the concentration of the solute of interest at that time point, providing a solute mass. This mass was then divided by the area of each mesocosm, providing a mass per area unit. To calculate peak rates of solute consumption or production, the difference in the masses of a solute between each sampling point were calculated and this was divided by the time elapsed between the sampling points. The difference in the mass of a solute over the entire experimental period was used to calculate its overall rate of consumption or production.

To calculate the amount of carbon mineralised by each TEAP, an assumption was made that any decrease in the concentration of  $O_2$ ,  $NO_3^-$ -N,  $NH_4^+$ -N and  $SO_4^{2-}$  or increase in  $Fe^{2+}$  and  $CH_4$  concentrations were microbially driven and thus a predictable (from stoichiometry presented in Table 4-1) amount of organic carbon mineralised (Baker et al. 1999).  $CH_2O$  was used as an average organic substance (after Stumm and Morgan 1995) and is herein referred to as organic carbon. On each level in the landscape the total amount of organic carbon mineralised was calculated by adding up that mineralised by each individual TEAPs occurring in that soil through the duration of experimental inundation. The contribution of each TEAP to this total has been expressed as a percentage. Similarly, the overall sum of organic carbon mineralisation across all levels was calculated and the contribution of each TEAP expressed as a percentage.

In calculating the amount of organic carbon consumed by each TEAP it was assumed that the soil within each mesocosm was a closed system, however, two exceptions were made. The first exception was made for  $NO_3^-$ -N due to the large flushes and rapid decreases in  $NO_3^-$ -N concentration found in the surface water above the B1 soil, while pore water concentrations remained near detection limit suggesting that denitrification was occurring in the inundated soil consuming  $NO_3^-$ -N from the surface water. The second exception was made for  $O_2$  where the closed system was, again, extended to include the surface water.

In the case of  $O_2$  reduction this assumption of a closed system is likely to have resulted in an underestimation of the actual amount of  $O_2$  reduction occurring. The surface water masses of  $O_2$  used to calculate  $O_2$  reduction represent a balance between atmospheric  $O_2$  supply and its reduction in the soil. Therefore, once equilibrium was reached between supply and subsequent reduction, any ongoing  $O_2$  reduction was no longer detectable.  $SO_4^{2-}$  reduction is also likely to have been underestimated, if rates of increase in the mass of  $SO_4^{2-}$  in the pore and surface water were greater than the rate of  $SO_4^{2-}$  reduction, then  $SO_4^{2-}$  reduction would not be detected. Denitrification may also have been underestimated if  $NO_3^-$ -N was being supplied by nitrification or overestimated if  $NO_3^-$ -N was being biologically assimilated.

#### **4.1.6 Statistical analysis**

To test for differences in masses of DO,  $\text{NO}_3^-$ -N,  $\text{NH}_4^+$ -N,  $\text{Fe}^{2+}$ ,  $\text{SO}_4^{2-}$  and  $\text{CH}_4$  across both time and level, a repeated measure PERMANOVA was used. PERMANOVA creates a permutation based, non-parametric analogue to ANOVA (Anderson 2001) and was carried out using PERMANOVA+ for Primer (Clarke and Gorley 2007). A minimum of 999 permutations is recommended by Anderson et al. (2008) to be able to determine difference at a significance level of 0.05. In all cases greater than 9000 permutations were performed including during pair-wise testing. Pair-wise testing in PERMANOVA is carried out using *t*-tests based on permuted distributions (Anderson et al. 2008).

## **4.2 Results**

### **4.2.1 Dissolved Oxygen**

Bench level did not have a significant effect on the mass of DO found in the surface water above the inundated soil (Pseudo  $F = 1.641$ ,  $df = 2$ ,  $p < 0.195$ ) but time did (Pseudo  $F = 20.95$ ,  $df = 20$ ,  $p < 0.001$ ) and there was no interaction between level and time (Pseudo  $F = 0.4306$ ,  $df = 40$ ,  $p < 0.999$ ). Although not significant, there were different patterns in the mass of DO through time in surface water above each of the soils. These differences are likely caused by different rates of  $\text{O}_2$  consumption between the levels (Figure 4-5a). The mass of DO in the water overlying the B1 soil decreased from  $14.43 \pm 0.23$  millimol  $\text{m}^{-2}$  to  $5.20 \pm 0.35$  millimol  $\text{m}^{-2}$  soon after inundation. The maximum rate of  $\text{O}_2$  consumption found over the B1 soil was  $1.37 \pm 0.52$  millimol of  $\text{O}_2 \text{ m}^{-2} \text{ h}^{-1}$  and over the entire inundation period B1 soil consumed DO at a rate of  $0.05 \pm 0.00$  millimol of  $\text{O}_2 \text{ m}^{-2} \text{ h}^{-1}$ . In comparison, B2 soil reached a minimum DO mass of  $4.27 \pm 1.04$  millimol of  $\text{O}_2 \text{ m}^{-2}$ , which was lower than that found in B1 soil. This lower mass of  $\text{O}_2$  was not driven by a greater maximum DO consumption rate of (which was  $0.46 \pm 0.14$  millimol of  $\text{O}_2 \text{ m}^{-2} \text{ h}^{-1}$  over the B2 soil) rather by B2 soil maintaining the rate of  $\text{O}_2$  reduction for a longer period than B1 soil. There was less of a decrease in the mass of DO in the surface water over the FP soil, where a minimum of  $5.59 \pm 0.84$  millimol of  $\text{O}_2 \text{ m}^{-2}$  was reached with a maximum consumption rate of  $0.82 \pm 0.26$

millimol of  $O_2$   $m^{-2} h^{-1}$  and an overall rate of  $0.04 \pm 0.010$  millimol of  $O_2$   $m^{-2} h^{-1}$ . The minimum mass of dissolved DO occurred 41.5 hours after inundation in B1 and FP soils and 79 hours after inundation in B2 soils.

## 4.2.2 Nitrate

### *Surface water*

Both level (Pseudo F = 10.10, df = 2,  $p < 0.001$ ) and time (Pseudo F = 7.52, df = 20  $p < 0.001$ ) were found to have a significant effect upon the amount of  $NO_3^-$ -N in the surface water during the experimental period. However, a significant interaction between level in the landscape and time was also found (Pseudo F = 3.61, df = 40,  $p < 0.001$ ).  $NO_3^-$ -N was released from the inundated soil of the B1 and B2 levels but no release was found from the FP level (Figure 4-5b). After two hours of inundation the mass of  $NO_3^-$ -N above the B1 soil peaked at  $55.46 \pm 12.34$  millimol of  $NO_3^-$ -N  $m^{-2}$  but was quickly consumed with maximum rates of consumption reaching  $8.57 \pm 2.48$  millimol of  $NO_3^-$ -N  $m^{-2} h^{-1}$ . Above the B2 soil a lower peak of  $13.73 \pm 3.00$  millimol of  $NO_3^-$ -N  $m^{-2}$  was reached in the surface water two hours after inundation. The rate of  $NO_3^-$ -N consumption was also lower in the B2 compared to the B1 soil, at  $2.36 \pm 0.33$  millimol of  $NO_3^-$ -N  $m^{-2} h^{-1}$ . Above the FP soil the mass of  $NO_3^-$ -N  $m^{-2}$  did not increase following inundation.

### *Pore water*

A significant difference in the mass of pore water  $NO_3^-$ -N was found between the levels (Pseudo F = 29.884, df = 2,  $p < 0.001$ ) but time did not have a significant affect (Pseudo F = 1.607, df = 20,  $p < 0.054$ ) and there was no interaction between time and level (Pseudo F = 0.7627, df = 40,  $p < 0.846$ ). Across the levels, the B1 soil had significantly less  $NO_3^-$ -N than B2 ( $t = 5.969$ ,  $p < 0.001$ ) and FP soils ( $t = 8.540$ ,  $p < 0.001$ ) with no difference being found between B2 and FP ( $t = 1.550$ ,  $p < 0.127$ ). After inundation  $NO_3^-$ -N concentrations in both B2 and FP soils increased, reaching a peak about 12 hour later, and declined until 46 hours after inundation; while the concentrations of  $NO_3^-$ -N in pore waters of the B1 soil did not increase during this period (Figure 4-5c). Maximum rates of  $NO_3^-$ -N consumption were 0.01

$\pm 0.01$ ,  $0.31 \pm 0.11$  and  $0.11 \pm 0.00$  millimol of  $\text{NO}_3^-$ -N  $\text{m}^{-2} \text{ h}^{-1}$ , respectively, in B1, B2 and FP soils. The mass of  $\text{NO}_3^-$ -N increased in all soil after approximately 100 hours of inundation as surface water levels became close to the soil surface.

#### 4.2.3 Ferrous iron

Both level and time were found to have a significant effect on the mass of  $\text{Fe}^{2+}$  in the pore water of the inundated soils (Pseudo F = 19.026, df = 2,  $p < 0.001$ ; Pseudo F=2.784, df=20,  $p < 0.003$ ) a significant interaction between time and level was also found (Pseudo F = 2.374, df = 40,  $p < 0.002$ ). The mass of  $\text{Fe}^{2+}$  in the pore water of flooded soil remained low in all soils until approximately 40 hours after inundation. After this point production of  $\text{Fe}^{2+}$  began in B1 soil and continued for the remainder of the experimental period. No change was observed in  $\text{Fe}^{2+}$  concentration in either B2 or FP soils (Figure 4-5d).

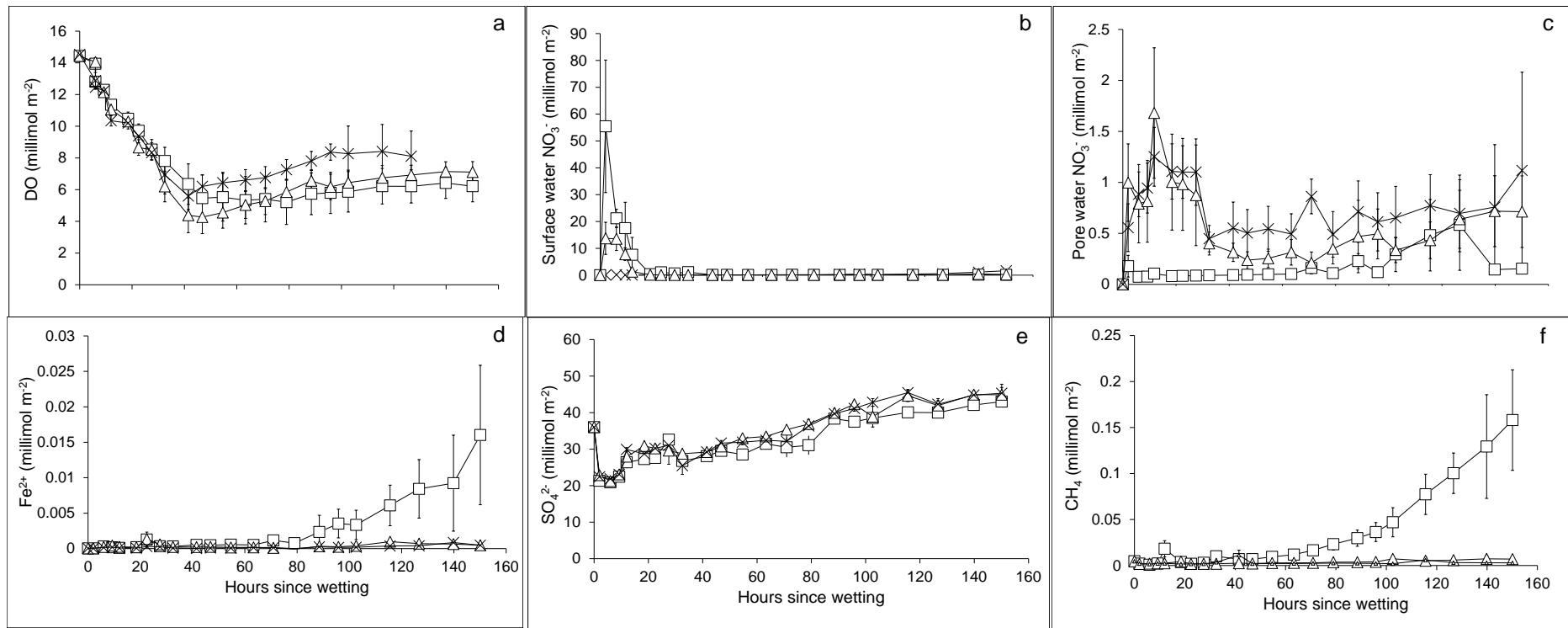
#### 4.2.4 Sulfate

Bench level was found to have a significant effect on the mass of  $\text{SO}_4^{2-}$  in the pore water of each soil (Pseudo F = 20.087, df = 2,  $p < 0.001$ ). There was also a significant effect of time on the mass of  $\text{SO}_4^{2-}$  (Pseudo F = 92.581, df = 20,  $p < 0.001$ ) likely due to increases in concentrations during the experimental period (Figure 4-5e). No significant interaction was found between time and level (Pseudo F = 1.0539, df = 40,  $p < 0.396$ ). The B1 soil had significantly lower in  $\text{SO}_4^{2-}$  concentrations than both B2 ( $t = 5.591$ ,  $p < 0.001$ ) and FP level soils ( $t = 5.586$ ,  $p < 0.001$ ), with no difference between FP and B2 soils. Overall  $\text{SO}_4^{2-}$  was produced at a rate of  $0.68 \pm 0.01$ ,  $0.56 \pm 0.02$ ,  $0.56 \pm 0.00$  millimol of  $\text{SO}_4^{2-}$   $\text{m}^{-2} \text{ h}^{-1}$ , respectively, in B1, B2 and FP soils.

#### 4.2.5 Methane

Both level and time were found to have a significant effect on the mass of  $\text{CH}_4$  in the pore water of the inundated soils (Pseudo F = 66.27, df = 2,  $p < 0.001$ ; Pseudo F = 8.139, df = 20,  $p < 0.001$ ) and a significant interaction between level and time was found (Pseudo F = 7.176,

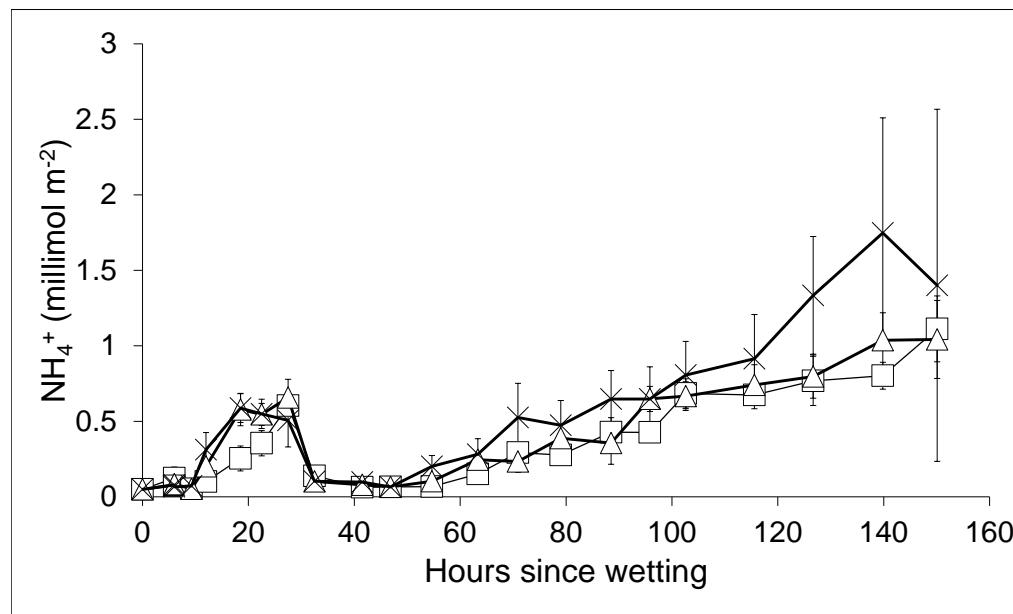
$df = 40$ ,  $p < 0.001$ ).  $\text{CH}_4$  concentrations in the pore water of B2 and FP soils remained relatively constant during the experimental inundation while those in B1 soil began to increase after 40 hours after inundation (Figure 4-5f). A maximum rate of production of 0.002 millimol of  $\text{CH}_4 \text{ m}^{-2} \text{ h}^{-1}$  was found in the B1 soil producing a maximum mass of  $0.158 \pm 0.00$  millimol  $\text{m}^{-2}$  in this soil.



**Figure 4-5:** The mass of solutes affected by TEAPs during the experimental period. (a) Surface water DO (b) Surface water NO<sub>3</sub><sup>-</sup>-N (c) Pore water NO<sub>3</sub><sup>-</sup>-N (d) pore water Fe<sup>2+</sup> (e) pore water SO<sub>4</sub><sup>2-</sup> (f) pore water CH<sub>4</sub>. White boxes represent B1, white triangles B2 and crosses FP soils. Error bars represent one standard error of the mean.

#### 4.2.6 Ammonium

Both level and time were found to have a significant effect on the mass of  $\text{NH}_4^+$ -N in the pore water of the inundated soils (Pseudo  $F = 8.141$ ,  $df = 2$ ,  $p < 0.001$ ; Pseudo  $F = 15.542$ ,  $df = 20$ ,  $p < 0.001$ ) but no significant interaction between level and time was found.  $\text{NH}_4^+$ -N concentrations in the pore water of all levels began to increase approximately 10 hours following inundation but decreased again after 30 hours of inundation. After this initial period, the mass of  $\text{NH}_4^+$ -N in the pore water of all soils steadily increased for the remainder of the experimental period with the exception of the floodplain level where the mass of  $\text{NH}_4^+$ -N decreased at the final sampling point.

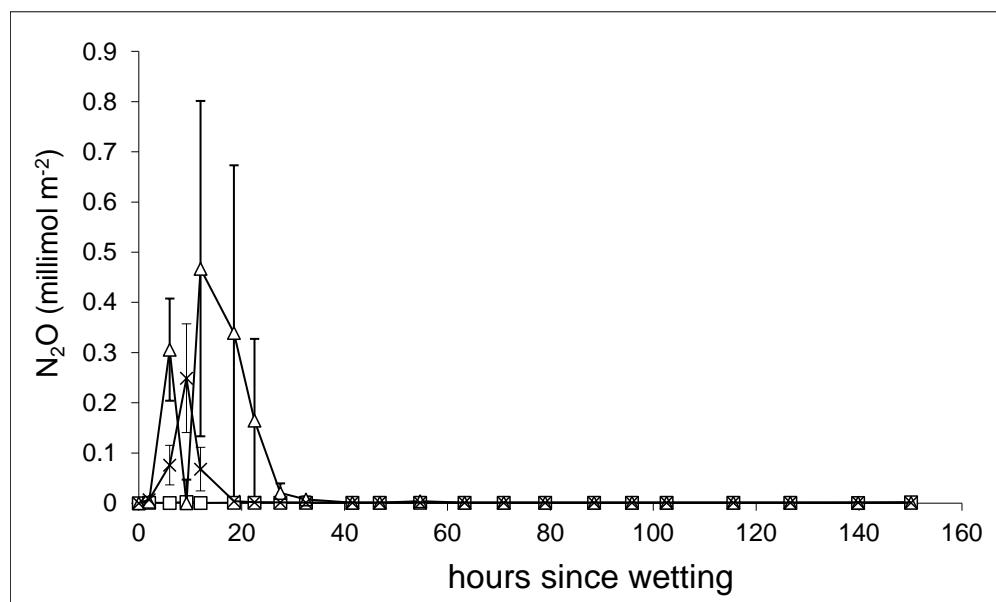


**Figure 4-6:** Shows the mass of ammonium found in the pore water of each of the levels. White squares are B1 pore water, white triangles B2 and crosses are FP pore waters. Error bars represent one standard error of the mean.

#### 4.2.7 Nitrous oxide

There was a significant effect of level on the mass of pore water nitrous oxide (Pseudo  $F = 4.516$ ,  $df = 2$ ,  $p < 0.005$ ), with B1 significantly different from both B2 ( $t = 2.453$ ,  $p < 0.004$ ) and FP ( $t = 3.317$ ,  $p < 0.001$ ). There was also a significant effect of time on the mass of

nitrous oxide (Pseudo F = 1.801, df = 20,  $p < 0.031$ ), however no interaction between time and level was found (Pseudo F = 1.347, df = 40,  $p < 0.0821$ ). Nitrous oxide production commenced 9 hours after inundation in B2 and FP soils. Both soils reached peak production 12 hours after inundation;  $0.093 \pm 0.015$  millimoles of  $\text{N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  in B2 soil and  $0.062 \pm 0.021$  millimoles of  $\text{N}_2\text{O-N m}^{-2} \text{ h}^{-1}$  in FP soil (Figure 4-6). The production of  $\text{N}_2\text{O-N}$  ceased at different times in each of the soils, producing different timed maximum  $\text{N}_2\text{O-N}$  concentrations. Concentrations in both B2 and FP soils dropped below detection limit approximately 20 and 40 hours after inundation, respectively. B1 pore water showed little change in  $\text{N}_2\text{O-N}$  concentrations during the experimental wetting.

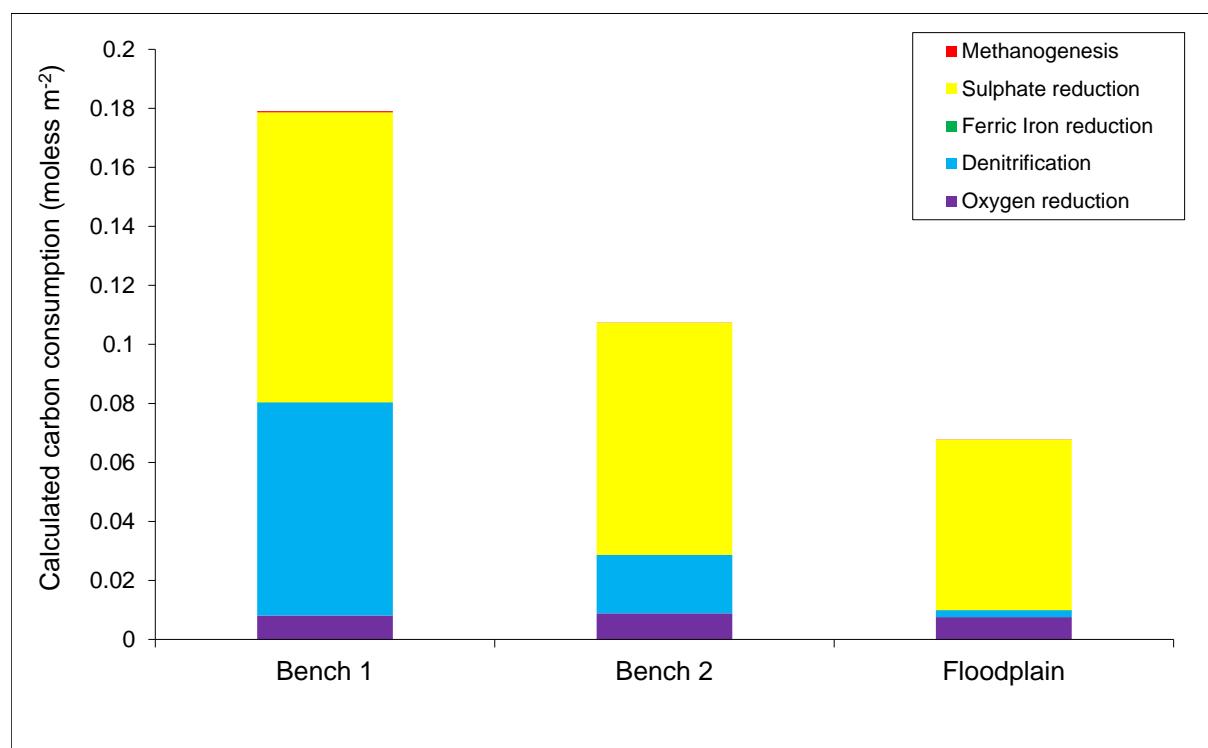


**Figure 4-7:** Shows the mass of nitrous oxide found in the pore water of each of the levels. White squares are B1 pore water, white triangles B2 and crosses are FP pore waters. Error bars represent one standard error of the mean.

#### 4.2.8 The mineralization of organic carbon

The amount organic carbon needed to be mineralised to account for the changes in solutes sensitive to TEAPs varied between the levels in the Gwydir River and between the different electron accepting processes (Figure 4-7). The greatest amount of organic carbon mineralised during the experimental period occurred in B1 soil, where the changes in

electron acceptor concentrations over the entire experimental period required 0.18 moles of organic carbon  $\text{m}^{-2}$ . The changes in the mass of electron acceptors in B2 and FP soils required 0.10 and 0.07 moles  $\text{m}^{-2}$  of organic carbon to be mineralised, respectively. Across all levels,  $\text{SO}_4^{2-}$  reduction was responsible for 64.02% of the carbon mineralised, while denitrification and  $\text{O}_2$  reduction accounted for 25.72% and 10.11%, respectively. The amount of iron reduction accounted for less than 0.01% of carbon mineralisation while methanogenesis was responsible for 0.14%.



**Figure 4-8:** Shows the amount of carbon mineralised on each level in the landscape and the TEAP that contributed to this mineralisation.

## **4.3 Discussion**

### **4.3.1 When inundated, do the different levels in the Gwydir River channel progress through the sequence of TEAPs as predicted by thermodynamics?**

In the presence of all electron acceptors, thermodynamics predicts that oxygen reduction will be the first dominant TEAP, due to it having the highest free energy yield. In the inundated Gwydir River soils, O<sub>2</sub> consumption began upon inundation and continued for at least the next 40 hours of inundation, as illustrated by the decreasing surface water DO masses during this period. However, O<sub>2</sub> reduction may not have been the only active TEAP during this period. NO<sub>3</sub><sup>-</sup>-N concentration in the surface water above the inundated B1 soil decreased during this period. Similar decreases were observed in the pore water of the B2 and FP soils within 4 and 12 hours of inundation, respectively. These declines suggest denitrification (Corstanje and Reddy 2004, Banach et al. 2009b), the next thermodynamically predicted TEAP, was also occurring within the soil profile at the same time as O<sub>2</sub> reduction, although other mechanisms may also have been responsible. The observed reductions in the mass of nitrate may also have been caused by assimilation or dissimilatory nitrate reduction to ammonium (DNRA). However, the lack of an increase in NH<sub>4</sub><sup>+</sup>-N masses of sufficient magnitude to match the decreases in NO<sub>3</sub><sup>-</sup>-N masses during this period implies that if DNRA was not a major contributor to the loss of NO<sub>3</sub><sup>-</sup>-N. Biological assimilation of NO<sub>3</sub><sup>-</sup>-N may also have contributed to NO<sub>3</sub><sup>-</sup>-N losses during this period, however, rates of NO<sub>3</sub><sup>-</sup>-N assimilation are generally lower than the observed losses of NO<sub>3</sub><sup>-</sup>-N. It therefore seems most likely that denitrification was dominant mechanism of NO<sub>3</sub><sup>-</sup>-N during this experiment.

Denitrification is commonly found to occur in the presence of O<sub>2</sub> but at reduced rates compared to those that occur under anaerobic conditions (Parkin and Tiedje 1984, Burgin and Groffman 2012). Further evidence of the presence of O<sub>2</sub> in the soil during this period was found in B2 and FP soils, with nitrification (discussed further below), an autotrophic process which requires O<sub>2</sub>, suspected to be occurring in the first 12 hours of inundation in

these soils. The rate of denitrification was smaller in B2 and FP soils compared to B1 soils, with this variation potentially caused by the presence of O<sub>2</sub> within the soil profile of B2 and FP soils.

After the loss of O<sub>2</sub> and NO<sub>3</sub><sup>-</sup>-N from the pore waters of the inundated soils thermodynamics predicts that Fe<sup>3+</sup> reduction, SO<sub>4</sub><sup>2-</sup> reduction and methanogenesis, respectively, will be the next dominant TEAPs. However, in all soils there was evidence of SO<sub>4</sub><sup>2-</sup> reduction occurring before Fe<sup>3+</sup> reduction. Approximately 30 hours after inundation when soil NO<sub>3</sub><sup>-</sup>-N became close to the minimum detection limit, the mass of SO<sub>4</sub><sup>2-</sup> decreased in all soils suggesting SO<sub>4</sub><sup>2-</sup> reduction. These decreases in SO<sub>4</sub><sup>2-</sup> concentration lasted for approximately 10 hours, after which concentrations begin to increase again (this increase in SO<sub>4</sub><sup>2-</sup> concentrations was unexpected and is discussed below). Sulfate reducers, although generally believed to be obligate anaerobes (Smith 1985), can survive short periods of aerobic conditions (Cypionka et al. 1985) and some species are capable of aerobic respiration (Dannenberg et al. 1992). Therefore, it is possible that viable populations of sulfate reducers are able to survive in the aerated bench and floodplain soils and can respond quickly to inundation.

Sulfate reduction occurring in the inundated soil may have masked Fe<sup>3+</sup> reduction if sulfides and Fe<sup>2+</sup> were precipitating out of solutions as ferrous sulfides (Stumm and Morgan 1995). If this were the case, Fe<sup>3+</sup> reduction would not have been detected as the amount of Fe<sup>2+</sup> would not increase, while SO<sub>4</sub><sup>2-</sup> reduction as indicated by the loss of SO<sub>4</sub><sup>2-</sup> would still have been detected. This would make SO<sub>4</sub><sup>2-</sup> reduction appear to be outcompeting Fe<sup>3+</sup> reduction, as was observed prior to 40 hour of indention in B1 soil and for the duration of the experiment in B2 and FP soils. The observed reductions in SO<sub>4</sub><sup>2-</sup> may also have been caused by biological assimilation, however, the methodology used during this experiment does not allow the contribution of biological assimilation to be assessed.

Methanogens are generally believed to be out-competed for organic carbon by both Fe<sup>3+</sup> reducers and SO<sub>4</sub><sup>2-</sup> reducers (Segers 1998) creating either a temporal or spatial divide between methanogenesis and other forms of anaerobic respiration. Specifically, this has

been shown for  $\text{SO}_4^{2-}$  reducers in lakes and estuarine sediments and in swampy soils (Lovley et al. 1982, Orem and Polcin 1982, Westermann and Ahring 1987); with  $\text{Fe}^{3+}$  reducers it has been shown in wetlands (Roden and Wetzel 1996) and in a rice paddy soil fertilized with  $\text{Fe}^{3+}$  (Jäckel and Schnell 2000). In the B1 soil  $\text{Fe}^{3+}$  reduction and methanogenesis were not temporally separated, with both processes starting at approximately the same time after inundation and continuing for the remainder of the experiment. The co-occurrence of  $\text{Fe}^{3+}$  reduction and  $\text{CH}_4$  production has previously been observed in a bottle incubated soil slurry experiment, where various electron donors were added (Metje and Frenzel 2005). Moreover, additions of highly available electron donors to a rice paddy soil by Achtnich et al. (1995) illustrated that when sufficient electron donors are present thermodynamic restrictions regarding the dominance of different TEAPs are lifted. Thus, it is likely that the B1 soil had viable microbial populations that are capable of performing these different functional processes and a large enough supply of electron donors to reduce the competition between different TEAPs allowing  $\text{Fe}^{3+}$  reduction and methanogenesis to co-occur.

#### **4.3.2 Were the inundated soils from different levels in the Gwydir River channel equally capable of all of the different TEAPs?**

Bench level did not affect the concentration of DO found in the surface water of the inundated soils despite differences in the amount of soil carbon and bioavailable soil carbon (Table 4-2) and the different amounts of organic carbon mineralised in each soil during this experiment. Valett et al. (2005) suggested that a greater build-up of carbon, in the form of soil carbon and leaf litter, in a disconnected and irregularly inundated floodplain was responsible for greater decreases in DO concentrations during its inundation when compared to that over a regularly inundated floodplain. A similar finding was also presented by Hladyz et al. (2011) who, in freshly inundated dry stream beds in south eastern Australian, found that increased leaf litter loads caused greater decreases in surface water DO concentrations. This suggests that rates of  $\text{O}_2$  reduction, even in the FP where the lowest rates of metabolism were found, were sufficient to overcome re-aeration rates and drive down the surface water DO concentrations. It also suggests that rates of  $\text{O}_2$  reduction

between the three soils were not sufficiently different to overcome the equalising effects of re-aeration from the atmosphere and create significantly different DO concentration during the inundated period.

Despite these initial decreases in surface water DO concentration it is likely that DO was still present in the B2 and FP soils during the first 12 hours of inundation and again in all soils after approximately 110 hours of inundation when surface water levels were approaching the soil surface. The presence of O<sub>2</sub> is suggested by increases in NO<sub>3</sub><sup>-</sup>-N concentration during these periods, implying that nitrification, an autotrophic aerobic microbial process, was occurring. During the first 12 hours of inundation no increase in the mass of NO<sub>3</sub><sup>-</sup>-N occurred in B1 soil, suggesting that no O<sub>2</sub> was present in this soil during this time. Moreover, the rapid decrease in the mass of surface water NO<sub>3</sub><sup>-</sup>-N over the B1 soil implies that rates of denitrification were not inhibited by the presence of O<sub>2</sub> during these first hours of inundation. Decreases in NO<sub>3</sub><sup>-</sup>-N concentration in the pore water of the B2 and FP levels began 12 hours after inundation, indicating that at this time denitrification rates exceeded rates of nitrification. In the last 30 hours of inundation the water level over the soil was very low and O<sub>2</sub> may have been diffusing into the soil profile from the atmosphere. This diffusion would allow nitrification to occur accounting for the increases in NO<sub>3</sub><sup>-</sup>-N found in all soils at this time.

While the process of denitrification is likely the mechanism responsible for the loss of NO<sub>3</sub><sup>-</sup>-N from all soils, N<sub>2</sub>O, a by-product of denitrification was only produced in B2 and FP soils. During the first 12 hours of inundation both B2 and FP soils produced N<sub>2</sub>O while none was produced by the B1 soil, despite it having the greatest rates of denitrification. The production of N<sub>2</sub>O during denitrification is influenced by many factors including; the presence of NO<sub>3</sub><sup>-</sup>-N, degree of anoxia, pH, temperature, organic matter availability and microbial populations (Blackmer and Bremner 1978, Firestone et al. 1980, Firestone and Davidson 1989, Weier et al. 1993, van Cleemput 1998). The presence of DO in the pore water of B2 and FP soils was suggested by the increase in mass of NO<sub>3</sub><sup>-</sup>-N, indicating that nitrification was occurring in these soils during the first 10 hours of inundation. This initial

10 hour period was also when N<sub>2</sub>O was being produced by B2 and FP soils suggesting that the presence of DO and NO<sub>3</sub><sup>-</sup>-N in these soils increased the production of N<sub>2</sub>O (Blackmer and Bremner 1978, Firestone et al. 1980).

NO<sub>3</sub><sup>-</sup>-N was absent from all soils after 27 hours of inundation creating conditions conducive for Fe<sup>3+</sup> reduction (Nealson and Saffarini 1994, Stumm and Morgan 1995), however, only in B1 soil, the most frequently inundated, did Fe<sup>3+</sup> reduction occur. It is likely that the higher inundation frequency of B1 soil compared to either B2 or FP soils influenced rates of Fe<sup>3+</sup> reduction during the experimental period by altering chemical conditions in the soil and shaping its microbial community. Soil inundation reduces the amount of crystalline Fe<sup>3+</sup> (Darke et al. 1996) increasing its availability for bacterial mediated reduction (Munch and Ottow 1980, Lovley 1991, Roden 2003). Thus, conditions for Fe<sup>3+</sup> reduction are more favourable in B1 soil than in either B2 or FP soils. Additionally, the higher inundation frequency of B1 soil may have shaped its microbial community to one that can respond faster to the changing conditions brought about by inundation. For example, Banach et al. (2009b), in a Polish floodplain noted that two weeks of inundation was required before any evidence of Fe<sup>3+</sup> reduction was found. Moreover, Peters and Conrad (1996) incubated aerobic soils from 6 different environments under anoxic conditions and found that all soils were able to reduce Fe<sup>3+</sup> but it took 10 days of anoxic incubation for this process to begin. Given this context, the shorter period of inundation of the Gwydir River soils during this experiment suggests that a Fe<sup>3+</sup> reducing community did not have sufficient time to develop in B2 and FP soils while the greater inundation frequency of B1 soil allows its microbial community to adapt faster to the conditions brought about by inundation.

In contrast to Fe<sup>3+</sup> reduction, SO<sub>4</sub><sup>2-</sup> reduction appears to have occurred in all soils despite the mass of SO<sub>4</sub><sup>2-</sup> increasing in the pore waters of these soils throughout the experimental period. Increasing SO<sub>4</sub><sup>2-</sup> mass was unexpected given that inundated soils have previously been shown to consume SO<sub>4</sub><sup>2-</sup> (Achtnich et al. 1995, Peters and Conrad 1996). SO<sub>4</sub><sup>2-</sup> can be produced by oxidation of H<sub>2</sub>S or S<sup>2-</sup> (Stumm and Morgan 1995) in the presence of O<sub>2</sub>, by the mineralisation of organic SO<sub>4</sub><sup>2-</sup> (Probert 1983), by microbially mediated disproportion of

elemental sulfur (Thamdrup et al. 1993) or by  $\text{NO}_3^-$  reduction being coupled with  $\text{S}^{2-}$  oxidation (Burgin and Hamilton 2008). Given that for most of the experimental period soil conditions were likely to be anaerobic, the oxidation of  $\text{H}_2\text{S}$  or  $\text{S}^{2-}$  is unlikely. It is difficult to assess the likelihood of the other sulfate production mechanisms, particularly, that of microbially mediated disproportion as it leave no other indicators of its occurrence.  $\text{NO}_3^-$  driven  $\text{SO}_4^{2-}$  production may have occurred early in the experimental period when  $\text{NO}_3^-$  masses were rapidly declining. But given the high organic contents of the bench soils mineralisation of organic  $\text{SO}_4^{2-}$  is a likely source  $\text{SO}_4^{2-}$  to the pore water of the inundated soils. Large increases in  $\text{SO}_4^{2-}$  concentrations were observed by Du Laing et al. (2008) during the inundation of a regularly inundated European floodplain soil. This soil had been treated with the addition of ground willow leaves at a rate of 7% of soil dry weight to increase its organic content. This treatment significantly increased the amount of  $\text{SO}_4^{2-}$  found in the pore water of this soil. Given the high organic content of bench soils in Australian dryland rivers (Sheldon and Thoms 2006), the mineralisation of the organic  $\text{SO}_4^{2-}$  from this organic matter is the likely source of the increasing  $\text{SO}_4^{2-}$  concentrations observed during the period of inundation.

The mass of  $\text{SO}_4^{2-}$  was significantly lower in the pore water of B1 soil than in either B2 or FP soils. If, as suggested above, the increases in the mass of  $\text{SO}_4^{2-}$  during the incubation period were caused by the mineralisation of organic  $\text{SO}_4^{2-}$  then perhaps the rate of organic  $\text{SO}_4^{2-}$  mineralisation were lower in B1 soil which, in turn, would reduce the mass of  $\text{SO}_4^{2-}$  in the pore water of B1 compared to B2 and FP soils. Alternatively, the higher amount of organic material found in B2 and FP soils may have given these soils a greater source of  $\text{SO}_4^{2-}$  compared to the B1 level. However, despite its proportionally lower percent of soil carbon and lower amounts of bioavailable soil DOC, B1 soil mineralised more organic carbon than either B2 or FP soils (Figure 4-7), so it is perhaps more likely that B1 soils had greater rates of  $\text{SO}_4^{2-}$  reduction decreasing  $\text{SO}_4^{2-}$  concentrations compared to B2 and FP soils. The higher inundation frequency of the B1 soil may mean it supports a greater population of sulfate reducing bacteria compared to either B2 or FP soils, which enabled this greater rate of sulfate reduction.

As well as the lowest concentrations of  $\text{SO}_4^{2-}$  the B1 soil was the only soil to produce  $\text{CH}_4$ . Permanently inundated soils with high organic matter contents, such as wetlands soils are known to produce large amounts of methane (Boon and Sorrell 1995, Segers 1998), however the high organic content of the B2 and FP soils did not influence the production of  $\text{CH}_4$  during the experimental period. It is possible that the low inundation frequency of B2 and FP soils makes them harsh environments for methanogens. However, methane production has been found in a range of aerobic soils that have no history of anoxic conditions after they had been incubated in anaerobic conditions for 15 days (Peters and Conrad 1995). In a similar experiment, using aerobic soils from different environments, Peters and Conrad (1996) found that 15-20 days of anoxic incubation were needed before the onset of  $\text{CH}_4$  production. Both of these periods are significantly longer than the 6 days of inundation used during the incubation of the Gwydir River soils, so it is possible that given a longer period of inundation with its associated anaerobic conditions, both B2 and FP soils may have produced  $\text{CH}_4$ .

#### **4.3.3 Was there variation in the amount of carbon consumed on each of the levels, by the different TEAPs?**

Rates of organic carbon mineralisation in saturated environments are dependent upon the supplies of carbon and electron acceptors, their contact time with biologically and chemically active soils and sediments, and the ability of the microbial community present in the soil to utilise these resources (Hedin et al. 1998, Baker et al. 2000, Morrice et al. 2000). The mesocosms used in this experiment eliminated any differences in the contact time between pore water and the soil particles between soils from the different levels in the Gwydir River landscape. Therefore, the supply of electron donors and acceptors present in each soil and the functional ability of the microbial community within the soil were considered to be the main determinants of the rate of organic carbon mineralisation. Both of these factors seem to have influenced the amount of carbon mineralised in the soils from the different levels in the Gwydir River landscape.

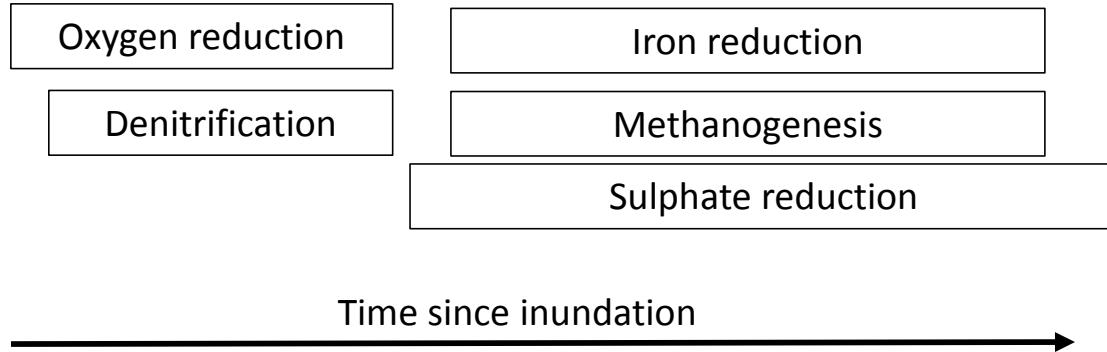
The B1 soil had microbial community that was more quickly able to adapt to the conditions brought about by inundation and the largest supply of  $\text{NO}_3^-$ . Together these factors allowing it to mineralise more organic carbon than either the B2 or FP soils. The supply of  $\text{SO}_4^{2-}$  was not limiting  $\text{SO}_4^{2-}$  reduction in any soil, however, the B1 reduced greater amounts of  $\text{SO}_4^{2-}$  than either the B2 or FP soils suggesting that its microbial community was better able to make use of this resource than the microbial community found in either the B2 or FP soils. Unlike supplies of  $\text{SO}_4^{2-}$  which were large and relatively equal across the different soils the supply of  $\text{NO}_3^-$  was greater in the B1 soil than in either the B2 or FP soils. This greater supply allowed for greater amounts of denitrification in the B1 soil that mineralised more organic carbon than compared to the B2 and FP soils.  $\text{O}_2$  reduction mineralised the next most organic carbon behind  $\text{SO}_4^{2-}$  reduction and denitrification. However, about equal amounts of  $\text{O}_2$  were reduced in the soils of each level indicating their microbial communities were equally capable of reducing the  $\text{O}_2$  supplied by re-aeration.

The high organic carbon content of bench soils means they are a potential carbon source to carbon limited lowland Australian river ecosystems (Westhorpe et al. 2010). Inundation of bench soils can mobilise organic carbon during periods of increased flow (Sheldon and Thoms 2006). However, part of this organic carbon is respired in the soil before it can be released into the surface water of the river thus reducing the amount of organic carbon entering the river. Therefore, the amount of organic carbon respired during the inundation of these floodplain and channel soils may affect the amount of DOC that is released to the river during periods of increased flow.

## 4.4 Conclusions

The two most energetically favourable TEAPs,  $\text{O}_2$  reduction and denitrification, were temporally separated from the other TEAPs in the inundated soils of the Gwydir River (Figure 4-8) After the loss of  $\text{O}_2$  and  $\text{NO}_3^-$ -N from the soils,  $\text{SO}_4^{2-}$  reduction was the next TEAP to commence, which is contrary to thermodynamic predictions (see Figure 4-2). In the Gwydir River soils  $\text{SO}_4^{2-}$  reduction was the most dominant TEAP in terms of the amount of

organic carbon mineralised. The importance of  $\text{SO}_4^{2-}$  reduction in this system is likely related to the soils large stores of  $\text{SO}_4^{2-}$  that were released upon inundation.



**Figure 4-9:** A conceptual diagram of the actual sequence of TEAPs that occur after the inundation of the Gwydir River soils.

Within two hours of inundation,  $\text{O}_2$  reduction was occurring in all soils, whether denitrification was occurring during this initial period of inundation is unclear. However, it was occurring after the soils had been inundated for two hours in the B1 soil. In contrast, denitrification did not commence until 12 hours after inundation in either B2 or FP soils. B1 soils were also able to support both  $\text{Fe}^{3+}$  reduction and methanogenesis, albeit at low rates, neither of which occurred in B2 or FP soils. Taken together, these results suggest that the microbial community within B1 soil was able to switch to alternative forms of respiration faster, during periods of inundation, when compared with the soil microbial communities found in soils higher in the landscape. The greater adaptability of the B1 microbial community contributed to it mineralising more organic carbon than either the B2 or FP levels. However, this was also influenced by the greater releases of  $\text{NO}_3^-$ -N from the B1 level, allowing denitrification to consume more organic carbon than it did on either the B2 or FP levels.

These results suggest that the inundation of different levels in the Gwydir River landscape will have different environmental consequences. Frequently inundated levels will consume more organic carbon,  $\text{NO}_3^-$ -N and  $\text{SO}_4^{2-}$  through soil respiration and may become sources of

the greenhouse gas CH<sub>4</sub> faster than less frequently inundated soils. In comparison, less frequently inundated benches are likely to release a greater proportion of stored carbon into the water column, have less of an effect upon NO<sub>3</sub><sup>-</sup>-N and SO<sub>4</sub><sup>2-</sup> concentrations in the stream but emit greater amounts of N<sub>2</sub>O, another greenhouse gas. Suggestions have been made for river managers to target the inundation of benches with environmental flows to increase the amount of DOC in the river stimulating in-stream heterotrophic production (Westhorpe et al. 2008). However, if such flows increase the inundation frequency of benches it is likely to affect the exchanges of organic carbon and nutrients that these flow are intended to facilitate.

# **Chapter 5. Hydrologically driven and diel patterns of nutrients during a flow pulse in an Australian lowland river**

## **Disclaimer**

The DOC data presented in this chapter is also presented by Westhorpe et al. (2012) a paper that I am a co-author on (see appendix). In 2008 I sampled a flow pulse in the Namoi River, a river which has previously been sampled during flooding events by Doug Westhrope and Simon Mitrovic who identified a diel pattern in DOC concentration during 2004 flooding event and are the other authors on the 2012 paper. Westhorpe et al. (2012) used the DOC data from the 2008 flow pulse to illustrate that in the Namoi River a diel pattern in DOC concentration occurred during a large flood event in 2004 and the 2008 flow pulse. In this chapter, the DOC data from the 2008 flow pulse is used to complement a diel pattern in  $\text{NH}_4^+$  concentration that was also found during this event.

## **5.1 Introduction**

The importance of natural flow variability to the ecology of rivers has been widely recognised (Tockner et al. 1999, Tockner et al. 2000) particularly in arid and semi-arid rivers (Molles et al. 1998, Puckridge et al. 1998, Valett et al. 2005). This natural flow variability, however, has led to flow regulation in many rivers around the world in order to secure water resources for human needs (Vörösmarty et al. 2004, Nilsson et al. 2005). Australian lowland rivers are no exception; weirs and dams have been constructed to supply water for irrigated agriculture, in many Australian lowland rivers including, in its largest river system, the Murray-Darling Basin (Thoms and Sheldon 2000a). The effect of flow regulation on Australian lowland rivers is large as regulation creates stable flow conditions in these rivers that naturally have some of the most variable flow regimes of any of the world's rivers (Puckridge et al. 1998). This loss of flow variability is thought to have contributed to declines of river health in many lowland rivers in the Murray-Darling Basin (Davies et al. 2010).

Flow regulation in Australian lowland rivers most dramatically affects flow pulses (Page et al. 2005); moderate increases in discharge that stay within the river channel. The moderate magnitude of flow pulses means they occur more frequently than floodplain inundation events (Thoms 2003, Page et al. 2005) potentially giving them an ecological significance in these river systems where floodplain inundation events are sporadic (Puckridge et al. 1998). Similar to floodplain inundation events, flow pulses can create carbon, nutrient and sediment exchanges between terrestrial and aquatic environments by inundating of in-channel features, such as benches and anabranches (Sheldon and Thoms 2006, McGinness and Arthur 2011, Vietz et al. 2012). However, there is a lack of empirical data concerning flow pulses in lowland rivers that hampers our understanding of the impacts of flow regulation on these systems. Furthermore, the need for a greater understanding of the ecological role of flow pulses has been noted by many authors (Davies et al. 1994, Puckridge et al. 1998, Sheldon 2005, Bunn et al. 2006b).

There is a greater understanding of the role that increased flow plays in mobilising organic carbon and inorganic nutrients in small, high order streams (e.g. McHale et al. 2002, Inamdar and Mitchell 2007, Vidon and Cuadra 2011). During these increases in flow, higher order streams have greater volumes of water moving through their catchments altering the normal flow path of water moving to the stream, resulting in the mobilisation of carbon and nutrients from the surrounding landscape (Buffam et al. 2001, Inamdar and Mitchell 2007, Vidon and Cuadra 2011). The flow path taken by the solutes and the mechanisms by which the solutes are mobilised from the surrounding landscape control the expression of solutes in stream water during flow events (Inamdar et al. 2004). Therefore, the timing in peak concentration of each solute can be used to provide information about carbon and nutrient sources within the catchment (eg. Hornberger et al. 1994, Inamdar 2007). These principles have been used to investigate flow pulses in high order streams but have not been used to investigate the sources of carbon and nutrients to lowland rivers during flow pulses.

Hydrological and geomorphological differences exist between small, headwater catchments and lowland rivers that are likely to affect the sources of carbon and nutrients to the river and in-stream ecological and biogeochemical responses to flow pulses. Lowland rivers have larger catchments and Australian lowland rivers are allogenic, that is, the area that generates the majority of their flow is small in comparison to the overall distance the river flows (Thoms and Sheldon 2000a). In comparison, headwater streams have smaller catchments, where the generation of runoff feeding stream flow is more evenly distributed in the catchment. Therefore, there is comparatively more opportunity for the mobilisation of materials ‘in-stream’ in a lowland river compared with a high order stream. Furthermore, the allogenic nature of Australian lowland rivers means that the time and distance that a flow pulse travels downstream is likely greater than the time it takes for the water to move along flow paths to the river. Thus, in Australian lowland rivers the opportunity for the mobilisation of carbon and nutrients from in-channel sources is likely to be higher than from the water moving through the catchment to the river.

Benches and anabranches are in-channel features of Australian lowland rivers that store carbon and nutrients in their soil and large amounts of leaf litter on their surfaces (Chapter 3, McGinness and Arthur 2011, Southwell and Thoms 2011). The in-channel location of these features means they are inundated during flow pulses potentially mobilising the resources stored in and on their soils. In-channel features are common in Australian lowland rivers; for example, 3.7 benches were found every kilometre in an incised, clay bed reach of the Ovens River (Vietz et al. 2004), while in a 380 km reach of the Macintyre River Thoms et al. (2005) identified a total of 69 anabranches with a total length of 236 km or 62% of the total river length in the study area. Given this density and the large distances that flow pulses travel ‘in-channel’ there are numerous interactions between the water of a flow pulse and nutrient and carbon rich in-channel features. Therefore, it is likely that these features significantly contribute to the increases in carbon and nutrient concentrations observed during flow pulses in these rivers (McGinness and Arthur 2011, Westhorpe et al. 2012).

Despite their conceptual importance to Australian lowland rivers, studies focusing on the chemical and ecological responses to flow pulses in lowland rivers are rare; most studies investigating flow pulses are limited to either temperate rivers such as the Rhine or Danube Rivers (Van den Brink et al. 1992, Heiler et al. 1995, Hein et al. 1999) or tropical rivers such as the Orinoco or Paraguay River (Hamilton and Lewis 1987, Hamilton et al. 1995, Hamilton et al. 1997). In the Australian context, McGinness and Arthur (2011) investigated DOC concentrations in flood and flow events in the lower Macintyre River, focusing on spatial coverage to explore the role of anabanches; which were found to be significantly contributing to the DOC mobilised in the river during these events. High frequency temporal coverage was provided by Westhorpe et al. (2012) who describe a diel pattern in DOC concentrations during a flood and a flow pulse in the lower Namoi River. To explain this pattern they suggested that photodegradation of terrestrially derived dissolved organic matter (DOM) created a source of labile DOC that fuelled rates of bacterio-plankton metabolism causing daytime DOC concentrations to be lower than night time concentrations. If this suggestion is correct then other solutes such as  $\text{NH}_4^+$  (Bushaw et al. 1996, Fellman et al. 2013) and  $\text{PO}_4^{3-}$  (Francko and Heath 1979) that have been shown to be affected by photodegradation of DOM may also exhibit diel patterns in concentrations during these events. To assess the short-term response of water chemistry in an Australian lowland river a flow pulse in the lower Namoi River was monitored for changes in water chemistry every 4 hours for approximately 6 days.

The previous chapters of this thesis have focused on in-channel features in the Gwydir River, whereas here the focus shifts to the Namoi River, which lies adjacent to the Gwydir River. This change of study site was necessary due to a lack of flow pulses and flooding events in the Gwydir River during the study period. This change allowed in-situ, real time measurements rather than just mesocosm based estimates to provide information about the short-term changes in water chemistry that occur during flow pulses in an Australian lowland river. The two catchments are similar in many of their physical, hydrological and climatic characteristics (see Chapter 2); both are allochthonous, rising in the eastern upland area of their catchments, where most of their river flow is generated and then both travel in a generally westward direction into riverine plains country. The riverine plains country in

both catchments is characterised by complex patterns of tributaries and anabranches, and is subject to extensive flooding. In fact, the flooding in these catchments can be so extensive that during large floods water may be exchanged between the Namoi and Gwydir Rivers (Pietsch 2006). Furthermore, the soils on the riverine plains of both the Gwydir and Namoi Catchments has been shown to be similar in many key physical and chemical properties including saturated conductivity, field bulk density, macroporosity, sand and clay content, pH, exchangeable Ca, Mg, Na and cation exchange capacity (Vervoort et al. 2003).

The specific questions being asked in the chapter are:

1. What are the relationships between the concentration of the different solutes and flow during the flow event in the lower Namoi River and does this provide information about their sources?
2. Was there evidence that the concentration of nutrients followed a diel pattern during the flow pulse?

## 5.2 Methods

A flow pulse in the Namoi River was sampled approximately every 4 hours for total nitrogen (TN), total organic nitrogen (TON), ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), total phosphorous (TP), particulate phosphorus (PP), dissolved reactive phosphorus (DRP), dissolved organic carbon (DOC) and turbidity. During the study 36 samples were taken between 11:30 am on the 6<sup>th</sup> of December and 07:00 am on the 12<sup>th</sup> of December 2008. This period encompassed the later stages of the rising limb and the entire falling limb of the flow pulse (Figure 5-2). Most samples were taken in duplicate, however due to auto-sampler malfunction only a single sample was taken on two occasions. Previous sampling of flow and flood events in the Namoi River have shown minimal variation between replicate samples justifying the low replication taken during this event (Westhorpe and Mitrovic 2012, Westhorpe et al. 2012). During daylight hours samples were collected from the river using two 10 L buckets, with each bucket used as a replicate, while night samples were taken using a programmable Manning auto-sampler (model 4901). Ice was kept in the auto-sampler overnight, which kept the temperature below 10°C until sample collection in the next morning. During

daylight hours when water samples were collected by hand a YSI model 610 DM sonde was used to measure dissolved oxygen (DO) and specific conductivity.

### **5.2.1 Analytical procedures**

After collection, river water was filtered using 0.45 µm cellulose acetate syringe filters (Sartorius Stadim) or left unfiltered. The filtered samples were analysed for DOC, NO<sub>3</sub><sup>-</sup>-N (NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup>), NH<sub>4</sub><sup>+</sup>, TDN, TDP and DRP. Unfiltered samples were analysed for TN, TP and turbidity. PP was calculated as the difference between TP and TDP. TON was estimated as the difference between dissolved inorganic nitrogen (NO<sub>3</sub><sup>-</sup> + NH<sub>4</sub><sup>+</sup>) and total nitrogen. This estimation likely results in an over-estimation of the concentrations of TON due to estimate including concentrations of dissolved gasses. Total nitrogen and phosphorus were digested with a simultaneous persulfate digestion at 120°C (Hosomi and Sudo 1986) and then analysed as NO<sub>3</sub><sup>-</sup>-N and DRP, respectively. NO<sub>3</sub><sup>-</sup>-N was measured using the cadmium reduction method. DRP was analysed with the ascorbic acid reduction method. Both NO<sub>3</sub><sup>-</sup> and DRP were measured on a segmented flow analysis instrument (OI Analytical FS3100). NH<sub>4</sub><sup>+</sup> was measured using the catalysis with nitroprusside and salicylate method on a Bran and Luebbe, AA3. DOC was measured on a Shimadzu TOC-VCPh/CPN analyser using a high temperature catalytic oxidation method. Turbidity was analysed on a Hach 2100AN turbidimeter. Hydrographic information for the event was obtained from a gauging station at Buglibone, operated by the New South Wales Office of Water (NOW), located upstream of the sampling location.

### **5.2.2 Data analysis**

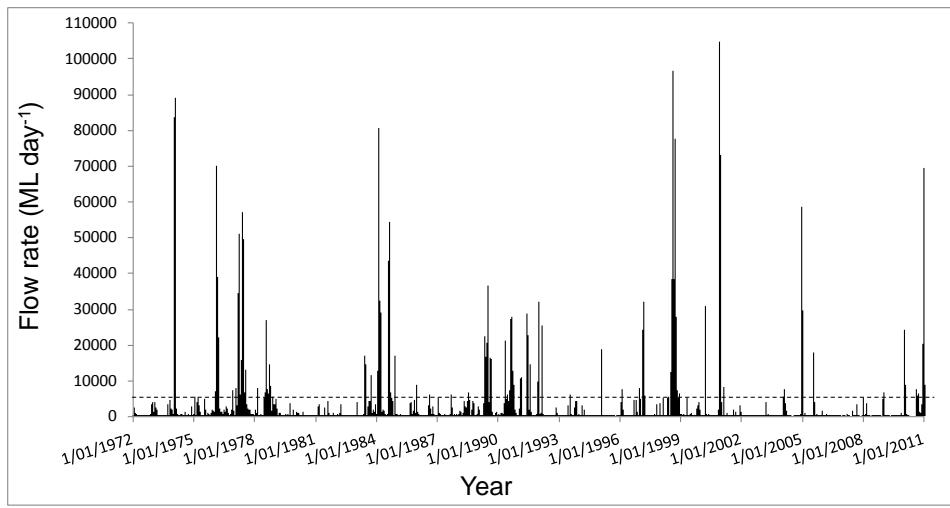
The concentrations of nutrients and DOC observed during the flow event were either hydrologically driven, occurred in a diel pattern or were affected by both hydrology while exhibiting some diel pattern in their concentration. Solute concentrations during the flow pulse were visually inspected in relation to the flow hydrograph and to identify possible diel patterns in their concentrations. If a diel pattern in concentration was suspected, *t*-tests were performed to identify whether a significant difference existed between day and night

concentrations. A ‘day’ sample was defined as occurring when the majority of the time between sampling points fell between 7:00 am and 7:00 pm and ‘night’ between 7:00 pm and 7:00 am. Linear regression was used to investigate the relationship between  $\text{NO}_3^-$ -N and DOC with  $\text{NH}_4^+$  to assess potential mechanisms that may have been effecting  $\text{NH}_4^+$  concentrations. All statistical analysis was undertaken using SPSS version 19.0 (IBM 2010).

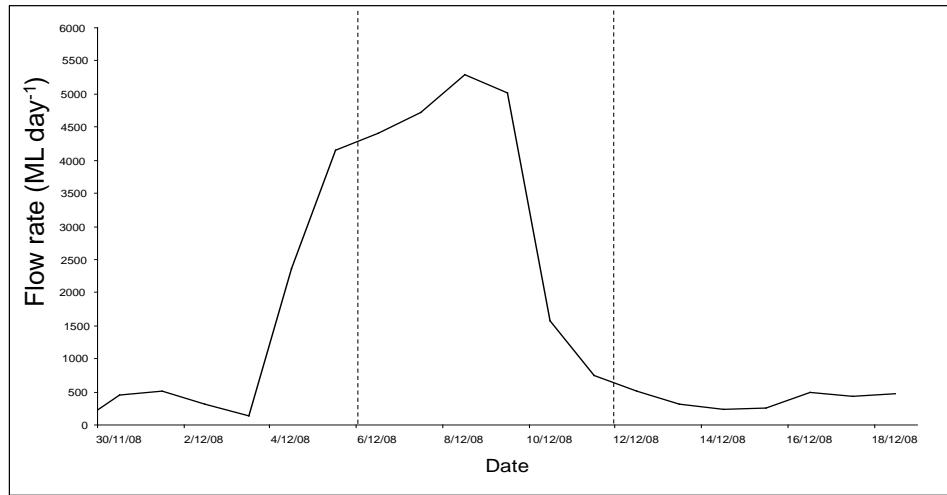
## 5.3 Results

### 5.3.1 Flow hydrology

This flow event is typical of those experienced in the Namoi River, with the rainfall that generated the event falling in the Peel River sub-catchment, located in the eastern, mountainous part of the Namoi catchment. The flow pulse travelled downstream for approximately 6 days before it was sampled near the Buglibone gauging station. At this gauging station the Australian Bureau of Meteorology defines a minor flood to occur at a river stage height of 4.9 metres. The maximum stage height reached in this event was 3.4 metres, therefore, it is unlikely that this flow reached the floodplain. The long term hydrograph for this gauging station is presented in Figure 5-1 and the hydrograph from this flow pulse as Figure 5-2.



**Figure 5-1:** The long term hydrograph for the Bugibone gauging station on the lower Namoi River. The dashed line shows a flow rate of  $5000 \text{ ML day}^{-1}$  the approximate flow rate reached during this flow event.

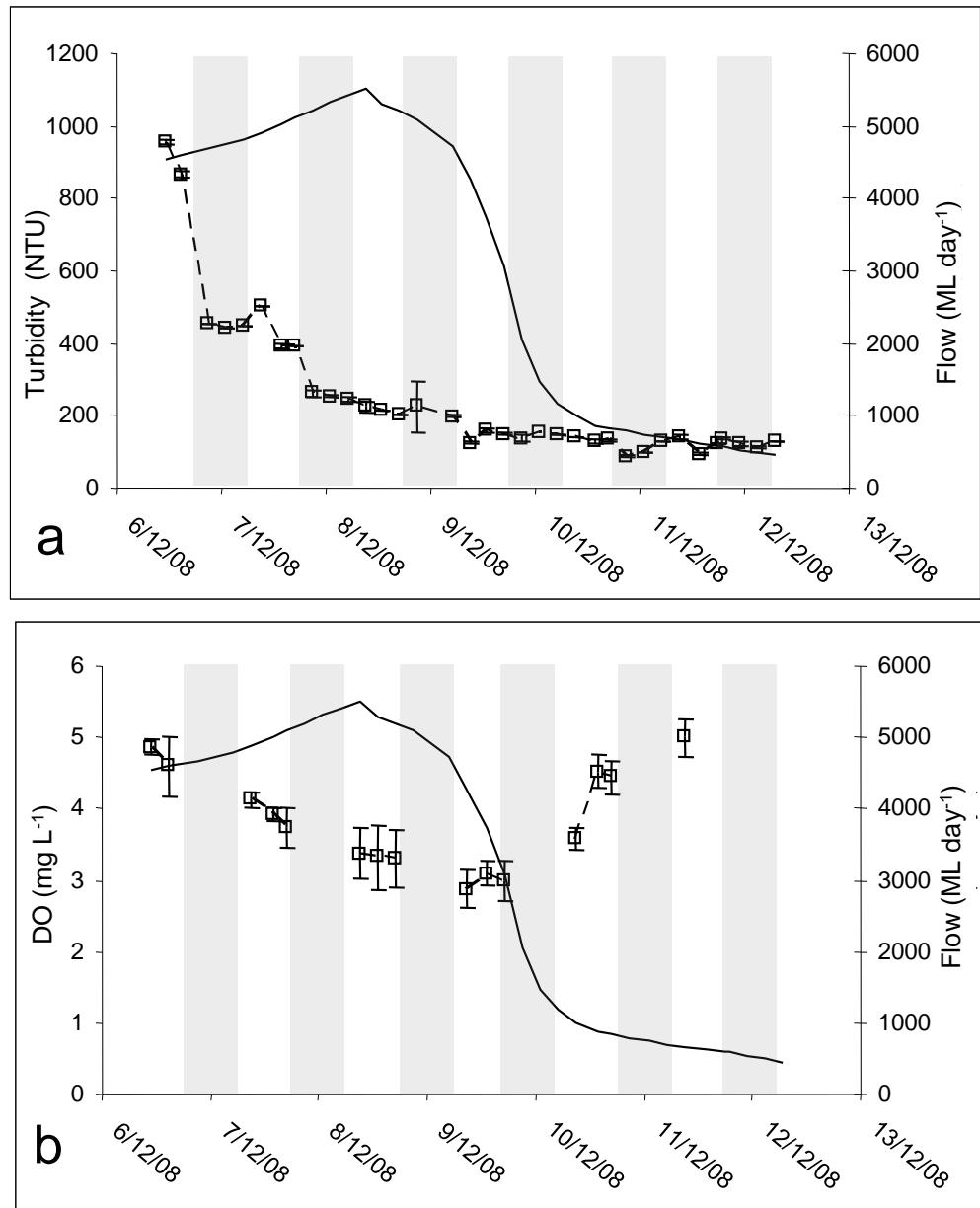


**Figure 5-2:** Hydrograph of mean flow pulse in the Namoi River ( $\text{ML day}^{-1}$ ). The dashed lines signify the start and end of the sampling period.

### 5.3.2 Physio-chemical patterns during the flow pulse

Turbidity was highest at the initial sampling of the river and declined for the remainder of the flow pulse (Figure 5-3a). DO concentrations decreased steadily on the rising limb reaching its lowest concentration of  $2.88 \pm 0.26 \text{ mg L}^{-1}$  early on the falling limb, from where

it increased to a maximum of  $4.99 \pm 0.25 \text{ mg L}^{-1}$  on the final sample taken from the flow pulse (Figure 5-3b).



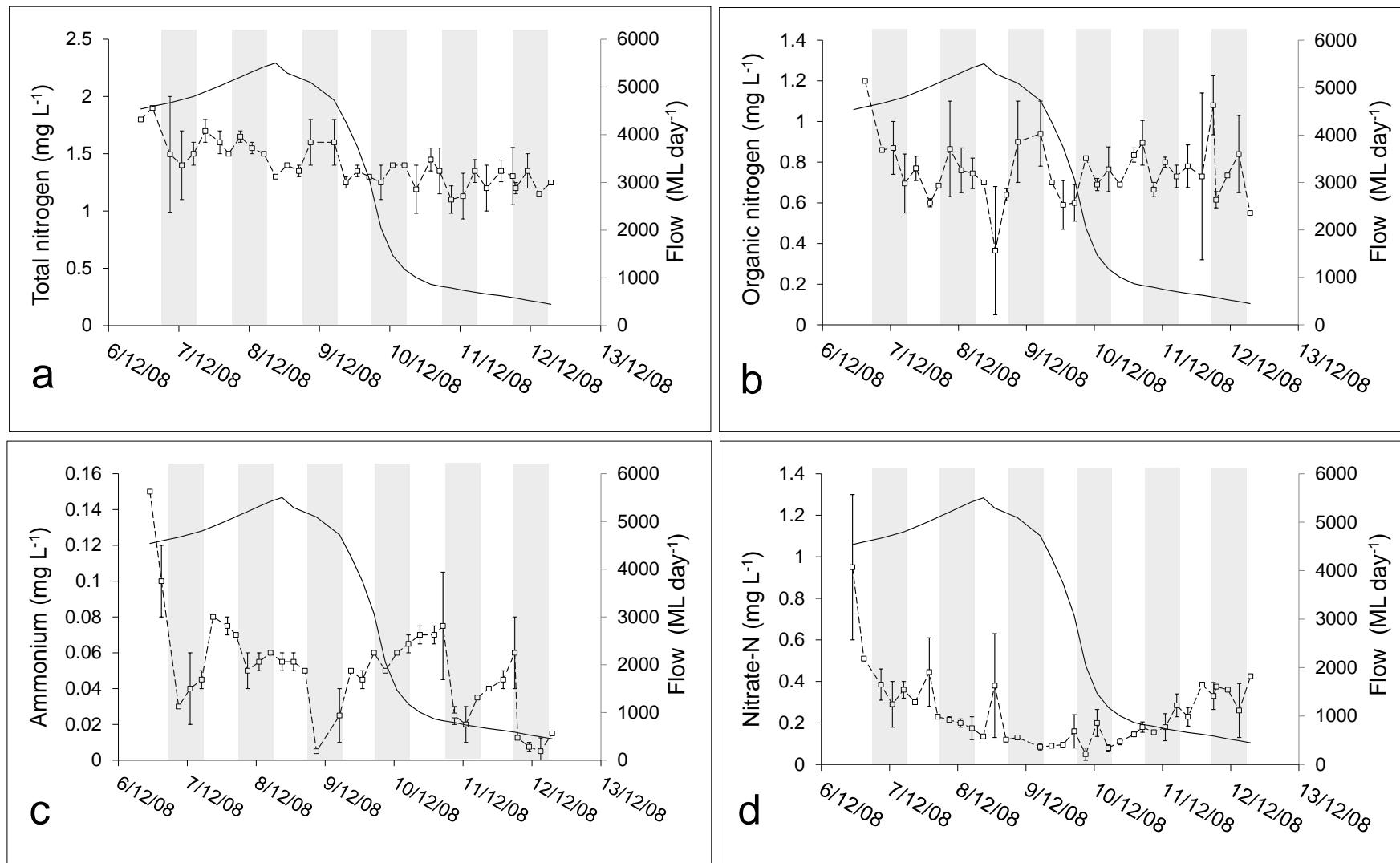
**Figure 5-3:** Mean river flow and (a) turbidity and (b) dissolved oxygen (dissolved oxygen measurements were only taken in daylight hours). The dark bands represent night time and the error bars one standard error of the mean.

### 5.3.2.1 Nitrogen Species

TN concentration peaked at  $1.9 \text{ mg L}^{-1}$  (single sample) on the rising limb of the flow pulse from where it declined for the remainder of the event, reaching its lowest concentration of  $1.25 \pm 0.05 \text{ mg L}^{-1}$  at the final sampling of the flow pulse (Figure 5-4). Over the entire flow pulse the concentration of TN averaged  $1.39 \pm 0.03 \text{ mg L}^{-1}$ . The contribution of organic and inorganic nitrogen to TN varied throughout the flow pulse. Organic nitrogen accounted for 63% of TN and inorganic nitrogen 37% at the first sampling point of the flow event while later on the rising limb the contribution of inorganic nitrogen had increased 61% of TN and organic nitrogen had decreased to 39% of TN.

Organic nitrogen concentrations were variable between sampling times and showed some evidence of a diel pattern during the first three days of sampling (Figure 5-4b). Over the entire event average daytime organic nitrogen concentration was  $0.66 \pm 0.04 \text{ mg L}^{-1}$  and night time  $0.78 \pm 0.04 \text{ mg L}^{-1}$  but this difference was not significant ( $t = 0.811, p > 0.420$ ). Organic nitrogen concentration peaked at  $1.2 \text{ mg L}^{-1}$  (single sample) at the first sampling point and generally declined for the duration of the flow event (Figure 5-4b) with a mean of  $1.08 \pm 0.03 \text{ mg L}^{-1}$  over the entire event.

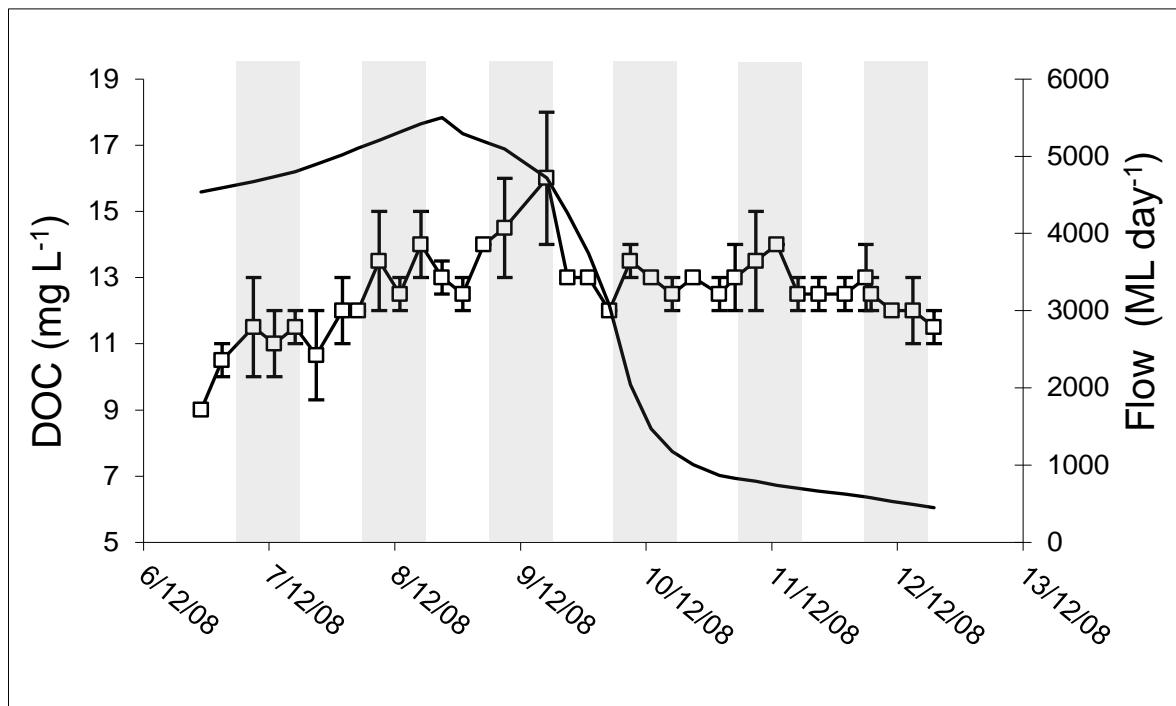
$\text{NO}_3^-$ -N and  $\text{NH}_4^+$  behaved differently during the passage of the flow pulse.  $\text{NO}_3^-$ -N concentration peaked on the rising limb of the hydrograph and declined until the final stages of the falling limb when they began to increase (Figure 5-4d). The greatest concentration of  $\text{NO}_3^-$ -N was  $0.95 \pm 0.35 \text{ mg L}^{-1}$ , the smallest  $0.05 \pm 0.03 \text{ mg L}^{-1}$ , with the mean concentration being  $0.26 \pm 0.02 \text{ mg L}^{-1}$ . No diel pattern was evident in the  $\text{NO}_3^-$ -N concentrations (Figure 5-4d); therefore testing for a difference in day and night concentration was not carried out. Over the entire sampling period  $\text{NH}_4^+$  concentrations averaged  $0.06 \pm 0.005 \text{ mg L}^{-1}$  but unlike  $\text{NO}_3^-$ -N, which was influenced by flow,  $\text{NH}_4^+$  showed strong evidence of a diel pattern in its concentration (Figure 5-4c). Mean day time  $\text{NH}_4^+$  concentration was  $0.062 \pm 0.007 \text{ mg L}^{-1}$  and night time concentration nearly half this at  $0.033 \pm 0.004 \text{ mg L}^{-1}$ . A *t*-test revealed this to be a significantly difference ( $t = 5.056, p > 0.000$ ).



**Figure 5-4:** Mean river flow and concentrations of nitrogen species; (a) total nitrogen, (b) dissolved organic nitrogen, (c)  $\text{NH}_4^+$ , (d)  $\text{NO}_3^-$ -N. The dark bands represent night time and the error bars one standard error of the mean.

### 5.3.2.2 Dissolved organic carbon

DOC concentrations also exhibited behaviour suggesting that it was varying on diel basis (Figure 5-5). Mean day time concentration of DOC was  $12.15 \pm 0.35 \text{ mg L}^{-1}$  and night time  $13.05 \pm 0.43 \text{ mg L}^{-1}$ ; a difference that was found to be significant ( $t = -2.155, p < 0.035$ ). DOC concentration also appear to be affected by flow, with concentrations increasing on the rising limb and reaching a peak early on the falling limb (Figure 5-5). Over there entire event the mean DOC concentration was  $12.54 \pm 0.29 \text{ mg L}^{-1}$ .

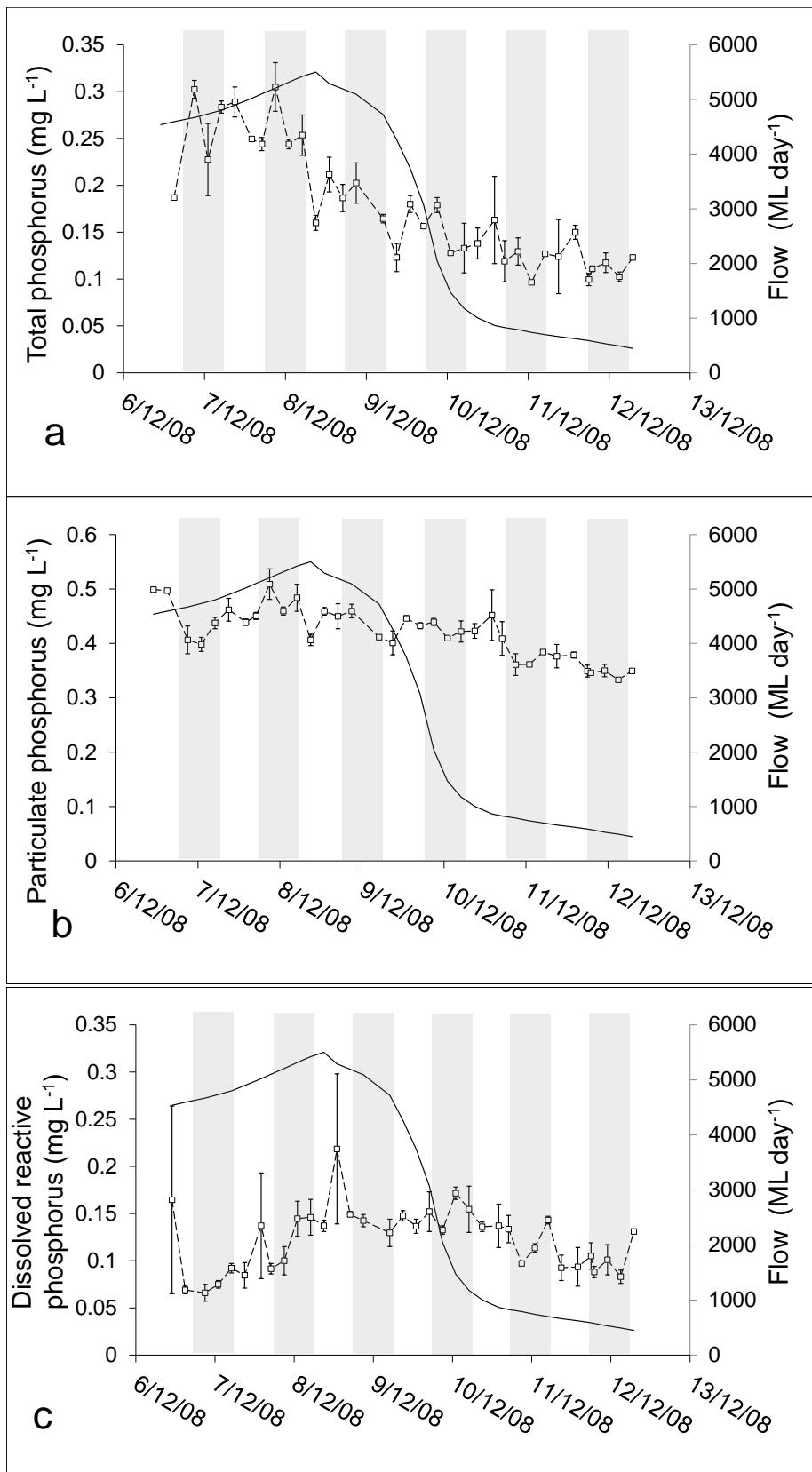


**Figure 5-5:** Mean river flow and DOC concentrations during the flow pulse. The dark bands represent night time and the error bars one standard error of the mean.

### 5.3.2.3 Phosphorus species

TP concentration peaked at  $0.50 \pm 0.01 \text{ mg L}^{-1}$  12 hours before the highest stage height then declined to  $0.33 \pm 0.00 \text{ mg L}^{-1}$  on the tail of the falling limb (Figure 5-6a). There was no evidence of a diel pattern in TP concentrations (Figure 5-6a) and further testing was not carried out. PP contributed strongly to TP on the rising limb of the flow pulse were it made up 75% of TP, while on the tail of the falling limb its contribution declined to 28%. The decrease in the contribution of PP to TP was driven by both a decrease in PP concentration

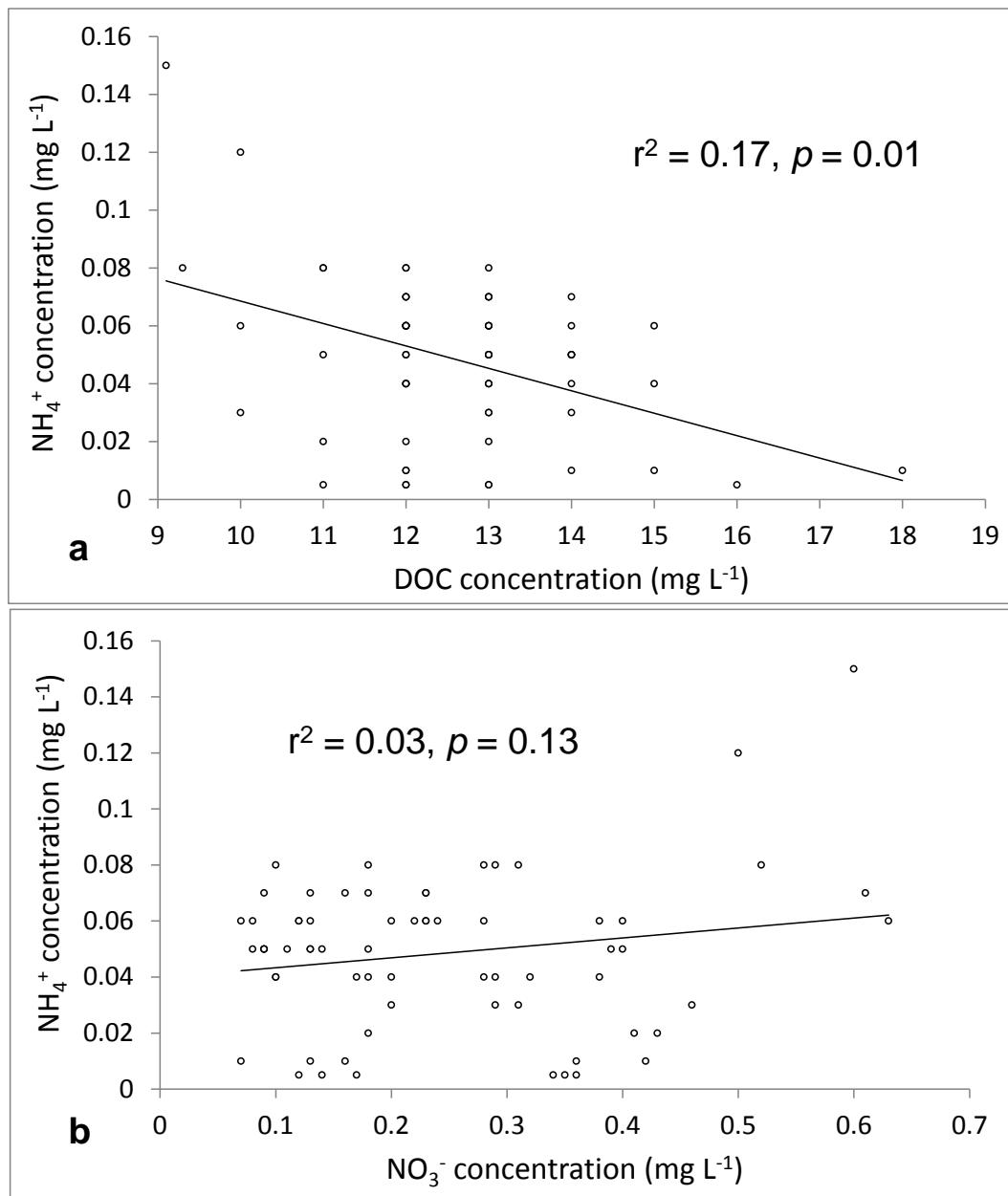
and an increase in DRP concentration during the course of the flow pulse (Figure 5-6b). DRP concentrations were low on the rising limb of the flow pulse but increased during the falling limb, reaching a peak of  $0.21 \pm 0.07 \text{ mg L}^{-1}$  late on the falling limb of the flow pulse. Mean DRP concentration was  $0.12 \pm 0.01 \text{ mg L}^{-1}$  and mean PP concentration  $0.42 \pm 0.01 \text{ mg L}^{-1}$ . PP did not show any evidence of diel variation (Figure 5-6b, c) in its concentration and no testing for a difference in day and night concentration was carried out. There was some evidence of a diel pattern in the concentration of DRP on the rising limb of the flow hydrograph where daytime concentrations were higher than those found at night, however, this difference was not significant ( $t = 1.448$ ,  $p = 0.153$ ).



**Figure 5-6:** Mean river flow and concentrations of phosphorus species; (a) total phosphorus, (b) particulate phosphorous, (c) dissolved reactive phosphorus. The dark bands represent night time and the error bars one standard error of the mean.

### 5.3.3 Relationships between $\text{NH}_4^+$ with DOC and $\text{NO}_3^-$

Concentrations of  $\text{NH}_4^+$  during the passage of the flow event were found to be significantly negatively related to DOC concentration ( $F$  statistic = 13.42,  $r^2 = 0.17$ ,  $p = 0.01$ ) but no relationship was found with  $\text{NO}_3^-$  concentration (Figure 5-7a, b).



**Figure 5-7:** Relationships of  $\text{NH}_4^+$  concentrations DOC (a) and  $\text{NO}_3^-$  (b) during the flow pulse in the Namoi River.

## **5.4 Discussion**

### **5.4.1 What are the relationships between the concentration of the different solutes and flow during the flow event in the lower Namoi River and does this provide information about their sources?**

#### **5.4.1.1 Phosphorus species and flow**

During the flow pulse in the Namoi River concentrations of PP peaked on the rising limb of the hydrograph with erosion from in-channel features the likely source of PP to the river. Evidence of erosion and deposition of in-channel bench soils during periods of increased flow have been found during investigations into bench stratigraphy in the Barwon-Darling River (Woodyer et al. 1979, Nanson and Page 1983, Thoms and Olley 2004). Moreover, in-channel benches soils have high concentrations of total phosphorus (Southwell and Thoms 2011). It therefore seems probable that erosion from these features is the source of PP during the Namoi River flow pulse.

During the flow pulse peak, DRP concentration lagged behind peak PP concentration, suggesting that DRP was mobilised by a different mechanism than PP. A similar suggestion was made by Pacini and Gächter (1999) who also observed a lag in peak DRP concentration behind PP concentration during flow events in a first order stream in central Switzerland. Unlike PP which is eroded from in-channel soils (McDowell et al. 2001, McDowell and Wilcock 2004, Vidon and Cuadra 2011), DRP is released from soils via two main pathways; an initial flush, known as the birch effect (Wilson and Baldwin 2008) or by a microbially driven processes occurring under anaerobic conditions (Qiu and McComb 1994, Baldwin 1996). If a flush from inundated in-channel features was the main source of DRP during this flow pulse then concentrations should peak prior to or with peak stage height when the largest land areas is inundated, providing the largest source of DRP. This suggestion is backed by data presented in Chapter 3 where concentrations of mobile DRP increased with height in the Gwydir River channel, implying that as river stage height increases a larger area with greater stores of DRP would be inundated and therefore greater flushes expected.

However, maximum DRP concentration occurred after peak flow and coincided with the lowest concentration of DO suggesting DRP was released from anaerobic soils. Similar findings were presented by Van den Brink et al. (1992) who found that anaerobic soils caused the release of  $\text{PO}_4^{3-}$  during periods of increased flow, increasing  $\text{PO}_4^{3-}$  concentrations in floodplain lakes along the lower Rhine and Meuse Rivers.

#### 5.4.1.2 Nitrogen species and flow

During the Namoi River flow pulse, peak  $\text{NO}_3^-$ -N concentration occurred on the rising limb of the hydrograph suggesting it was flushed from soils. The flushing of surface soils as water moves to the stream has been identified as a major source of  $\text{NO}_3^-$  to high order streams during storm events (Buffam et al. 2001, Inamdar 2007). Depending upon the timing of water moving through a catchment, peak  $\text{NO}_3^-$  concentrations have been observed on both rising (McHale et al. 2002, Inamdar et al. 2004, Inamdar 2007) and falling limbs (Buffam et al. 2001, Petry et al. 2002). The hypothesis that most of the solutes mobilised during the flow pulse in the Namoi River came from in-channel sources fits with the observed timing of peak  $\text{NO}_3^-$  concentration as no lag would be expected from in-channel sources.

Furthermore, the rapid decrease in  $\text{NO}_3^-$ -N concentrations found after its peak concentration is likely due to high rates of denitrification similar to those found in the lower bench levels of the Gwydir River (Chapter 4).

Assessing the relationship between flow and  $\text{NH}_4^+$  or DON during the flow pulse in the Namoi River is difficult as they both exhibited a diel pattern in their concentration, which uncoupled relationships with flow. During flow events in headwater streams sources of  $\text{NH}_4^+$  and organic nitrogen to streams include throughfall and leaf litter leaching that occurs along flow paths to the stream (Hagedorn et al. 2000, Buffam et al. 2001, Inamdar and Mitchell 2007). In lowland rivers in-channel features, such as in-channel benches and anabranches, stores large amounts of leaf litter (Sheldon and Thoms 2006, McGinness and Arthur 2011) and are a likely source of organic nitrogen and  $\text{NH}_4^+$  during periods of increased flow. The diel patterns found in both  $\text{NH}_4^+$  and DON suggest that their

concentrations were being affected by processes other than flow during the passage of the flow pulse down the Namoi River, these patterns are discussed further below.

#### **5.4.1.3 Dissolved organic carbon and flow**

In the Namoi flow pulse, DOC concentrations were influenced by river stage height but also varied on a diel basis. During flow events in high order streams peaks in DOC concentration are commonly found on the rising limb of the hydrograph suggesting it is flushed from soils (Boyer et al. 1997, Buffam et al. 2001). Similarly, in a Paraguayan lowland river peak DOC concentration were found on the rising limb of flow pulses and flooding events (Hamilton et al. 1997). However, Australian lowland rivers it seems that the length of a flow event affects the timing of peak DOC concentration. During larger flooding events in Namoi and Macintyre Rivers, peak DOC concentration occurred on the rising limb but in shorter flow pulses in these rivers, including the one described here, peak DOC concentration occurred on the falling limb.

The cause of peak DOC concentrations occurring on the falling limb during flow pulses may be the diel pattern in DOC concentrations observed in the Namoi River or the limited time that in-channel features are inundated for during these events. The shorter duration of inundation of in-channel features could affect DOC concentrations. The leaf litter of common Australian riparian tree species has been shown to release most of their DOC over 10 days of inundation (O'Connell et al. 2000, Francis and Sheldon 2002, Sheldon and Thoms 2006). As the flow pulse only lasted 8 days, the continuing release of DOC from leaf litter may have caused DOC concentrations to remain elevated into the falling limb of the flow pulse. Alternatively, the diel pattern in DOC concentration found during flow events in the Namoi River showed larger oscillations on the rising limb compared to the falling limb which may affect the timing of peak DOC concentration during flow pulses (Westhorpe et al. 2012). If, as suggested by Westhorpe et al. (2012) these patterns are caused by the photo-production of bioavailable DOC then the larger oscillations suggest that more DOC is being metabolised on the rising limb compared to the falling limb which may decrease DOC concentrations in comparison to the falling limb.

### **5.4.2 What is the cause of the diel pattern in the concentration of $\text{NH}_4^+$ and DOC during the flow pulse?**

Significant differences in day and night concentrations of DOC and  $\text{NH}_4^+$  were found during the flow pulse in the Namoi River. Mean day time concentration of DOC were lower, and mean  $\text{NH}_4^+$  concentration higher, compared to those found at night. Other studies have independently documented diel patterns in DOC and  $\text{NH}_4^+$  (Kaplan and Bott 1982, Warwick 1986, Kaplan and Bott 1989, Harrison et al. 2005), however, to the authors' knowledge diel patterns in these solutes have not previously been simultaneously observed. Furthermore, when diel differences in DOC concentration have previously been observed they are generally higher during the day and lower at night (Kaplan and Bott 1982, 1989), the opposite pattern to that found during the flow pulse in the Namoi River. Similarly, when diel patterns in  $\text{NH}_4^+$  have previously been observed they are higher at night compared to during the day (Warwick 1986, Harrison et al. 2005), again, the opposite pattern to that observed during the flow pulse in the Namoi River.

The mechanism behind the diel patterns in  $\text{NH}_4^+$  concentration, observed in other systems, was higher day time nitrification rates (Warwick 1986, Harrison et al. 2005). It is unlikely that higher day time nitrification rates were the cause of the diel pattern in  $\text{NH}_4^+$  concentration observed during the flow pulse in the Namoi River as an opposing pattern in  $\text{NO}_3^-$  concentration was not found. During the day, downstream of a wastewater treatment plant, Warwick (1986) found that steam temperature, DO and pH were higher than at night, increasing daytime rates of nitrification and  $\text{NO}_3^-$  concentrations while decreasing daytime  $\text{NH}_4^+$  concentrations. Likewise, Harrison et al. (2005) illustrated that a subtropical Mexican stream, affected by agricultural runoff, became anaerobic at night causing nitrification to cease increasing night time  $\text{NH}_4^+$  concentration and decreasing  $\text{NO}_3^-$  concentration. Unlike these two studies a relationship between  $\text{NO}_3^-$  and  $\text{NH}_4^+$  was not found during the flow pulse in the Namoi River inferring that nitrification was not strongly affecting the concentrations of either  $\text{NH}_4^+$  or  $\text{NO}_3^-$  during the passage of the flow pulse and suggesting that another mechanism was affecting  $\text{NH}_4^+$  concentrations.

DOC concentrations also occurred in a diel pattern during the flow pulse in the Namoi River, but similar to the  $\text{NH}_4^+$  concentrations, this pattern occurred in the opposite direction to most other observations of diel differences in DOC concentration. In other studies that have observed diel differences in DOC concentrations, increased day time DOC concentrations have been attributed to the release of photosynthates during algal production (Kaplan and Bott 1982, 1989, Parker et al. 2010). An exception to this pattern was presented by Parker et al. (2010) who reported day time DOC concentrations that were lower than those found at night in the Clark Fork River, Montana, USA, attributing this pattern to increased flow and pH at night. A diel pattern in flow were not observed during the passage of the Namoi River flow pulse (Figure 5-2) and therefore it is unlikely to have influenced DOC concentrations during this event. Westhorpe et al. (2012) suggest that the diel pattern in DOC concentration during this flow pulse and another larger flooding event in the Namoi River were linked to the photodegradation of terrestrial organic matter, producing labile DOC which stimulated bacterio-plankton metabolism decreasing DOC concentrations during the day. This explanation may tie the diel pattern in DOC to the diel pattern in  $\text{NH}_4^+$  concentrations that occurred during the 2008 flow pulse.

During laboratory studies the release of  $\text{NH}_4^+$  and bioavailable DOC have been observed during the photodegradation of humic substances and leaf leachates (Mopper and Stahovec 1986, Bushaw et al. 1996, Bushaw-Newton and Moran 1999, Wetzel 2006, Fellman et al. 2013). Photodegradation of terrestrially derived organic matter into  $\text{NH}_4^+$  and bioavailable DOC molecules increasing metabolic rates of bacterio-plankton increases demand for C and N (Bushaw et al. 1996, Dahlén et al. 1996, Moran and Zepp 1997, Waisser and Robarts 2004). In the Namoi River, this is suggested to drive down DOC concentrations during the daylight hours, which provides a mechanism explaining the lower daytime DOC concentrations but not the higher  $\text{NH}_4^+$  concentrations found during the day. Photodegradation of DOM producing greater amounts of DOC than  $\text{NH}_4^+$  which may have allowed a high demand for  $\text{NH}_4^+$  to continue into the evening, perhaps, causing the rapid decreases in  $\text{NH}_4^+$  concentrations observed during the flow pulse in the Namoi River.

Bioavailable DOC is produced at a rate close to an order of magnitude greater than  $\text{NH}_4^+$  during photodegradation of leaf leachates of common Australian riparian tree species (pers comm. JB Fellman). The greater supply of bioavailable DOC allows elevated baterio-plankton metabolic rates to continue into the evening when  $\text{NH}_4^+$  photo-production has ceased, causing declines in  $\text{NH}_4^+$  concentration observed in the evenings of the flow pulse. Although rates of metabolism are likely to have remained high in the evening, decreasing  $\text{NH}_4^+$  concentrations, bulk DOC concentrations would increase due to photo-production of bioavailable DOC ceasing and DOC being supplied from inundated soil and leaf litter (Chapter 3, O'Connell et al. 2000, Francis and Sheldon 2002). This is the likely mechanism behind the negative relationship found between DOC and  $\text{NH}_4^+$  concentrations during the passage of the flow pulse. Once the bioavailable DOC had been consumed in the evening demand for  $\text{NH}_4^+$  decreases and its concentrations increase again due to the inundated soils and leaf litter becoming a source of  $\text{NH}_4^+$  (Chapter 3). In the morning, photodegradation of DOM and the production  $\text{NH}_4^+$  recommences.

Summer flow events in Australian lowland rivers provide conditions conducive to the photodegradation of DOM; a supply of DOM and a strong source of UV light (Moran and Zepp 1997). During a summer flow pulse in an Australian lowland river, DOM is supplied from the inundated land areas surrounding the river (Westhorpe and Mitrovic 2012) and UV light is in the extreme range as defined by the Australian Bureau of Meteorology (Australian Bureau of Meteorology: <http://www.bom.gov.au/climate/data/>). Additionally, Waiser and Robarts (2004) illustrated that a well-mixed environment facilitates higher rates of photodegradation. It is likely that the increases in turbulence found during periods of increased flow provide high mixing rates, facilitating DOM photodegradation during the Namoi River flow pulse.

The frequency of flow pulses, such as the one studied in the Namoi River, has declined due to flow regulation in many Australian lowland rivers (Page et al. 2005). Therefore, the inputs of DOM available for photodegradation and photo-transformation into bioavailable forms of DOC has also reduced, potentially impacting river health. The addition of a

bioavailable source of DOC to a headwater stream in North Carolina, USA increased the abundance and biomass of microbes and invertebrates (Wilcox et al. 2005). Therefore, the loss of bioavailable DOC supplied by the photodegradation of mobilised terrestrial organic matter during flow pulses may have contributed to poor ecosystem health in some Australian lowland river systems (Davies et al. 2010).

## 5.5 Conclusions

This flow event was generated by rainfall in the upper catchment of the Namoi River, from where it moved downstream for approximately 6 days before sampling. During this passage downstream, the water pulse mobilised both dissolved and particulate carbon and nutrients. The timing of peaks in concentrations of most solutes suggested that they were mobilised from in-channel sources, indicating the potential role that in-channel features such as benches and anabranches play in subsidising lowland rivers between the more sporadic floodplain inundation events.

Diel patterns in DOC and  $\text{NH}_4^+$  concentration were found during this flow event. It seems likely that these patterns were caused by the photodegradation of DOM driving in-stream bacterio-plankton heterotrophic production by increasing the bioavailability of both carbon and nitrogen during the day. Photodegradation of DOM may provide a source of bioavailable carbon and nitrogen to the aquatic ecosystem while the increased rates of bacterio-plankton heterotrophic production may allow the retention of organic carbon and nutrients in the aquatic ecosystem. If so, then these flow pulses could affect aquatic ecosystems for a period of time following their passage downstream. Further investigation into the ecological effects of flow pulses and the possible role of photodegradation of DOM is needed to clarify their potential effects on aquatic ecosystem health.

# **Chapter 6. Diel patterns in DOC and NH<sub>4</sub><sup>+</sup> during flow events; the roles of gross primary productivity, community respiration and photodegradation of dissolved organic matter**

## **6.1 Introduction**

Diel cycles in biogeochemical processes cause diel patterns in various attributes of aquatic ecosystems including pH and concentrations of dissolved gases, trace elements, nutrients, stable isotopes, and suspended particles (Grimm 1987, Bäckström et al. 2002, Drysdale et al. 2003, Gammons et al. 2007, Parker et al. 2007, Parker et al. 2010). These cycles usually only evident under stable hydrological conditions (Nimick et al. 2011). However, during a large flooding event in the Namoi River, New South Wales, Australia, a diel pattern in DOC concentrations was observed (Westhorpe et al. 2012). This pattern was again observed during flow pulse in the same river system but this time in conjunction with a diel pattern in NH<sub>4</sub><sup>+</sup> concentration (Chapter 5, Westhorpe et al. 2012). The occurrence of diel patterns in DOC and NH<sub>4</sub><sup>+</sup> concentrations has previously been observed, however, in these cases DOC concentrations are generally higher, and NH<sub>4</sub><sup>+</sup> concentrations lower, during the day (Kaplan and Bott 1982, Warwick 1986, Harrison et al. 2005, Parker et al. 2010). This is the opposite pattern to that observed during the flow events in the Namoi River (Chapter 5, Westhorpe et al. 2012). Moreover, to the authors' knowledge, never have diel cycles in the concentrations of DOC and NH<sub>4</sub><sup>+</sup> been observed concurrently. It seems likely, therefore, that the diel pattern in DOC and NH<sub>4</sub><sup>+</sup> concentrations observed during the flow pulse in the Namoi River are not caused by those mechanisms that have previously been identified to cause diel patterns in DOC and NH<sub>4</sub><sup>+</sup>.

Diel patterns in DOC concentrations have been observed in both marine (Gasol et al. 1998) and freshwater systems including lakes (Geller 1986, Lindell et al. 1996), wetlands (Ziegler and Fogel 2003) and in rivers and streams (Walsh 1965, Kaplan and Bott 1982, 1989, Parker et al. 2010). These patterns are caused by metabolic processes; algal production during the

day increasing DOC concentrations which is consumed by heterotrophic metabolism while at night the absence of photosynthesis causes night time concentrations to be lower than during the day due to continued heterotrophic metabolism (Kuserk 1984). There was evidence of algal production influencing DOC concentrations during the 2004 flooding event in the Namoi River, with daytime DOC maxima occurring in the afternoon (Westhorpe et al. 2012), which is characteristic algal productivity (Nimick et al. 2011). Algal production is unlikely, however, to be the cause of the diel pattern in DOC concentration observed during the flow events in the Namoi River as it would create higher daytime DOC concentrations, as has previously been observed (Kaplan and Bott 1982, Kuserk 1984). However, higher rates of algal productivity in the afternoon that increase DOC into the night can not be completely ruled out as the cause of the observed diel pattern in DOC concentration.

Where previously observed diel patterns in  $\text{NH}_4^+$  have been accompanied by an opposing pattern in  $\text{NO}_3^-$  concentration indicating diel variation in rates of nitrification were the cause (Warwick 1986, Harrison et al. 2005). Such an opposing pattern in  $\text{NO}_3^-$  concentrations was not found during the Namoi River flow pulse implying that varying rates of nitrification were not strongly affected  $\text{NH}_4^+$  or  $\text{NO}_3^-$  concentrations. Westhorpe et al. (2012) suggested that the mechanism behind the diel patterns in DOC found in the Namoi River was the photodegradation of DOM producing bioavailable DOC that increases rates of heterotrophic metabolism, driving down DOC concentrations during the day. Photodegradation of DOM provides a possible link between the diel pattern in DOC and  $\text{NH}_4^+$  observed during the Namoi River flow pulse.

Photodegradation of DOM generates bioavailable DOC and  $\text{NH}_4^+$  (Mopper et al. 1991, Wetzel et al. 1995, Bushaw et al. 1996, Bushaw-Newton and Moran 1999). The influence on photodegradation on DOC concentrations has been observed in laboratory studies (Mopper and Stahovec 1986), in sea water (Kieber et al. 1990, Mopper et al. 1991) and in fresh water (Kieber et al. 1990, Wetzel et al. 1995, Dahlén et al. 1996). In freshwaters, the photodegradation of DOC was linked to seasonal changes in DOC concentration in Canadian wetlands (Waiser and Robarts 2004) and shown as the mechanism for decreasing DOC concentration along a flow path in the Everglades of southern Florida (Wetzel 2006). In

Australia, Howitt et al. (2008) used direct sunlight to illustrate that DOM found in billabong water was more susceptible to photodegradation than leaf leachate from river red gum (*E. camaldulensis*) and Fellman et al. (2013) used laboratory incubations to show that leachate from common Australian riparian tree species release bioavailable DOC and NH<sub>4</sub><sup>+</sup> during photodegradation.

Photodegradation of DOM produces greater amounts of bioavailable DOC than NH<sub>4</sub><sup>+</sup> (pers comm J.B. Fellman), chapter 5 suggests that this difference plays a role in creating the diel patterns in NH<sub>4</sub><sup>+</sup> concentration observed during the flow pulse in the Namoi River. The greater production of bioavailable DOC allows increased rates of in-stream heterotrophic metabolism to continue after the photo-production of NH<sub>4</sub><sup>+</sup> has ceased. These high rates of metabolism consume any available NH<sub>4</sub><sup>+</sup> causing the rapid decline in NH<sub>4</sub><sup>+</sup> concentrations observed in the evening of the 2008 Namoi River flow pulse (Chapter 5). NH<sub>4</sub><sup>+</sup> is a highly bioavailable form of dissolved nitrogen, which is used in preference to NO<sub>3</sub><sup>-</sup> by bacteria (Kirchman 1994). Its rapid utilisation in the environment could explain why photo-production of NH<sub>4</sub><sup>+</sup> has not previously been observed outside of the laboratory (Bushaw et al. 1996, Bushaw-Newton and Moran 1999, Fellman et al. 2013). But this rapid utilisation, after photo-production has ceased, may be the mechanism behind the sharp declines in NH<sub>4</sub><sup>+</sup> concentration observed during the 2008 flow pulse in the Namoi River.

This chapter investigates the cause of the diel pattern in DOC and NH<sub>4</sub><sup>+</sup> concentrations found during the flow pulse in the Namoi River focusing on the roles of gross primary productivity and the photodegradation of DOM increases rates of community respiration. This investigation was carried out using mesocosms, where a treatment of shading was used to exclude the natural light regime from half the mesocosms and the effects on NH<sub>4</sub><sup>+</sup> and DOC concentration and rates of community respiration (CR) and gross primary productivity (GPP) monitored. Four specific research questions have been proposed:

1. Can the diel pattern in NH<sub>4</sub><sup>+</sup> and DOC concentrations observed during the flow pulse in the Namoi River be replicated in the laboratory under a natural light regime?

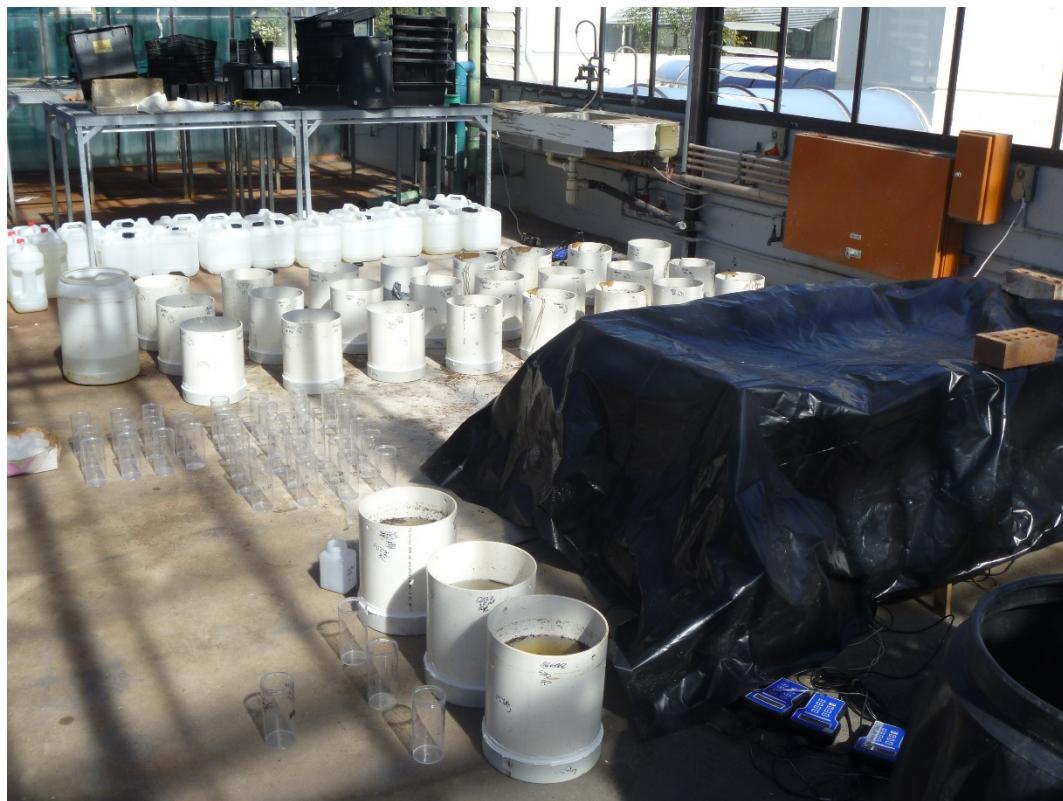
2. Does the complete exclusion of the natural light regime from inundated riverine soils affect the concentrations of  $\text{NH}_4^+$  or DOC compared to those under a natural light regime?
3. Does the level in the landscape inundated affect any diel differences in DOC and  $\text{NH}_4^+$  concentrations in under a natural light regime or between natural light and light exclusion treatments?
4. Do daily rates of GPP and CR occurring in the flooded mesocosms affect the concentrations of  $\text{NH}_4^+$  and DOC found in the surface water?

## 6.2 Methods

The response of DOC and  $\text{NH}_4^+$  concentrations to the exclusion or inclusion of the natural light regime was monitored in surface water above inundated soil cores contained in mesocosms. Intact soil cores were collected from B1, B2 and FP levels at sites 1, 2, 3 and 4 in the Gwydir River channel. The mesocosms were constructed from PVC piping 300 mm high and with a diameter of 300 mm. Before the mesocosms were inserted into the ground they were washed with river water and allowed to air dry. Each soil core was isolated from the surrounding soil matrix by inserting the PVC piping 10 cm into the ground and removing the soil surrounding the mesocosm, the core was then cut from the soil at the bottom of the core using a shovel. Two cores were taken from each level at each site, these cores were paired during the incubation period; one being exposed to the natural light regime and the other shaded, to exclude the natural light regime. The collection of river water, used to inundate the soils, was undertaken by submerging acid-washed 20 litre containers into the river, care was taken not to collect any disturbed sediments during this process. The river water was collected immediately before transportation of the soil cores back to Griffith University. During transportation the river water was kept shaded and upon arrival at Griffith University stored overnight at 4 °C before being used to inundate the soil cores.

Those mesocosms to be excluded from the natural light regime were placed under an A-frame and covered with two layers of tarpaulin (Figure 6-1). An area of the tarpaulin was partially lifted (to a level lower than the top of the mesocosms) to reduce any affect that

covering had on temperature. The soils were inundated with 7 litres of river water and concentrations of dissolved oxygen (DO),  $\text{NH}_4^+$ , and DOC monitored for 5 days. Samples for  $\text{NH}_4^+$  and DOC were taken 15 times during this period and DO concentration logged every hour. For each DOC and  $\text{NH}_4^+$  sample 300 ml of surface water was removed, filtered at 0.45  $\mu\text{m}$  using PES syringe filters (Sartorius) and immediately frozen. DO probes were deployed on 4 randomly chosen natural light/light exclusion paired soil cores ( $n = 8$  deployed DO probes). The aim of monitoring DO concentration during the incubation was to investigate the possible role of primary production and/or community respiration in creating a diel pattern in  $\text{NH}_4^+$  and DOC concentrations.



**Figure 6-1:** The experimental set up illustrating the natural light treatment mesocosms in the open and the light exclusion treatment mesocosm under the tarpaulin.

### 6.2.1 Analytical procedures

Dissolved oxygen concentration and water temperature were measured using DO sensors (YSI 5739; YSI Incorporated, Yellow Springs, Ohio, U.S.A.) attached to data-loggers (TPS 601;

TPS Pty Ltd., Queensland, Australia), which recorded DO and temperature at 1 hour intervals for the duration of the incubation period. A small pump was placed in front of the DO sensors to ensure flow saturation across the sensor membrane (Figure 6-2). The concentration of  $\text{NH}_4^+$  was measured colorimetrically on a Westco Smartchem SC 200 Discrete Wet Chemistry Analyser at Griffith University using SmartChem Method 213N-0405C (equivalent to USEPA 350.1). In this method the sample is buffered at pH 9.5, then distilled into a boric acid solution.  $\text{NH}_4^+$  then reacts with alkaline phenol and hypochlorite to form idenophenol blue, which is measured for absorbance at 630 nm.  $\text{NH}_4^+$  detection limit is 0.05 mg  $\text{NH}_4^+ \text{-N L}^{-1}$ . DOC was measured on a Shimadzu TOC-VCPh/CPN analyser using a high temperature catalytic oxidation method. The sample is injected in an oxygen rich atmosphere at 680 °C and  $\text{CO}_2$  is produced by the oxidation of DOC and measured on a non-dispersive infrared detector. This method has a detection limit of 0.05 mg of C  $\text{L}^{-1}$ .



**Figure 6-2:** View into a mesocosm fitted with DO probe; illustrating the position of the pump ensuring flow saturation over the DO sensor and the clear surface water within the mesocosm. The photo was taken on the morning of the second day of the experiment at approximately 10:30 am.

### 6.2.2 Data analysis

From the mesocosms fitted with DO probes, night time changes in DO concentration in the natural light and light exclusion treatments were used to estimate community respiration and reaeration rates using the night time regression model of Young et al. (2004). The oxygen deficit (actual DO concentration minus 100% saturation oxygen concentration) was plotted against the change in DO concentration between each sampling time. Linear models between these variables were then constructed for each night during the incubation period. These models were based on a minimum of 6 hours of data (Fellows et al. 2006, Fellows et al. 2007), with the specific 6 hour period of the model chosen to maximise the model fit ( $r^2$  value) (Young et al. 2004). Night time was defined as 18:00 to 06:00. In this model, the slope of the resulting linear regression is the reaeration rate and the y-intercept the rate of community respiration. Rates of GPP were calculated at hourly intervals as per Young et al. (2004);

$$GPP = \frac{dO}{dt} + R - kD$$

Where:      GPP = Gross primary productivity

$\frac{dO}{dt}$  = the rate of change in oxygen concentration

R = respiration rate

k = reaeration rate

D = oxygen deficiency (saturation DO concentration – actual DO concentration)

Changes in DO concentration over time ( $\text{mg O}_2 \text{ L}^{-1} \text{ hr}^{-1}$ ) were converted to an aerial unit ( $\text{mg O}_2 \text{ m}^{-2} \text{ hr}^{-1}$ ) by multiplying by the volume of soil and water in the mesocosms (14.13 L) then dividing by the surface area of the soil in the mesocosm ( $0.07 \text{ m}^2$ ) (Fellows et al. 2009).

These rates were converted to units of carbon assuming that 1 mole of carbon is equivalent

to 1 mole of O<sub>2</sub> for both respiration and photosynthesis (Lampert 1984, Bender et al. 1987). Concentrations of NH<sub>4</sub><sup>+</sup> and DOC were converted from mg L<sup>-1</sup> to an aerial basis by multiplying the concentration at the time of sampling by the volume of water in the mesocosm at the time of sampling and then dividing this by the surface area of soil in the mesocosm (0.07 m<sup>2</sup>).

### 6.2.3 Statistical analysis

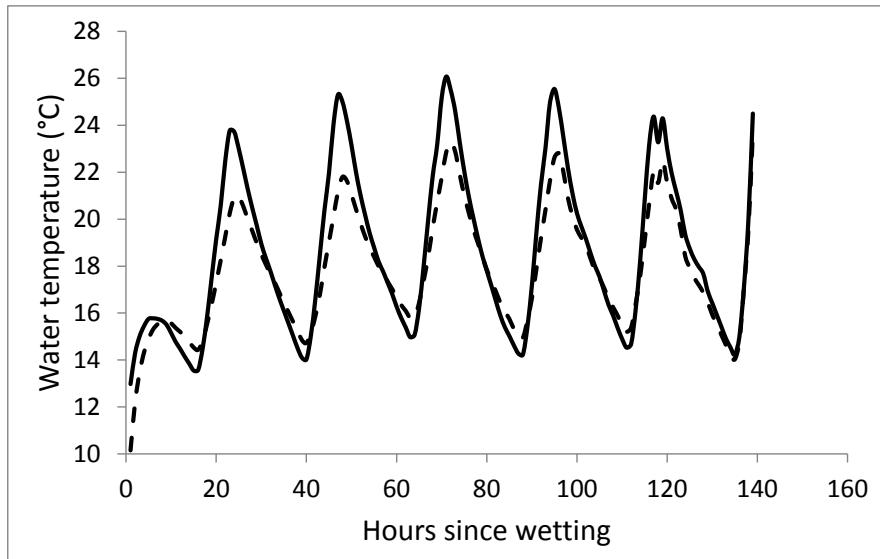
Initial investigations of diel differences in DOC and NH<sub>4</sub><sup>+</sup> concentration in the natural light treatment mesocosms (Question 1) involved visually exploring that data to identify evidence of diel changes in concentrations. If a diel pattern was suspected, further testing between night and day DOC and NH<sub>4</sub><sup>+</sup> concentrations was carried out using PERMANOVA. To explore the differences in DOC and NH<sub>4</sub><sup>+</sup> concentrations between the light and light exclusion treatments (Question 2) PERMANOVA analysis was run comparing concentrations between these treatments across all sites and levels. Finally, to explore differences in DOC and NH<sub>4</sub><sup>+</sup> concentrations between the different positions in the landscape (Question 3) PERMANOVA analysis was run within levels regardless of site. All PERMANOVA analysis carried out using one way PERMANOVAs which were completed using the PERMANOVA add-on in Primer V6 6.1.0.1 (Clarke and Gorley 2007). Resemblance matrices were constructed using Euclidian distances between samples with data where the difference between the variables had been normalised. A minimum of 999 permutations were used in each test as recommended by Anderson et al. (2008). A significant effect was defined as those with a *p*-value < 0.05.

The relationship between concentrations of DOC and NH<sub>4</sub><sup>+</sup> in the water column and rates of GPP and CR in the mesocosms (Question 4) were investigated using distance based linear modelling. Distance based linear modelling is based upon a resemblance matrix and uses permutations rather than the normality assumptions that underlie linear modelling (Anderson et al. 2008). Therefore, it is more robust to data that does not conform to a normal distribution. PERMANOVA add-on in Primer V6 6.1.0.1 (Clarke and Gorley 2007) was used for this analysis and significant relationships were defined as those with a *p*-value < 0.05.

## 6.3 Results

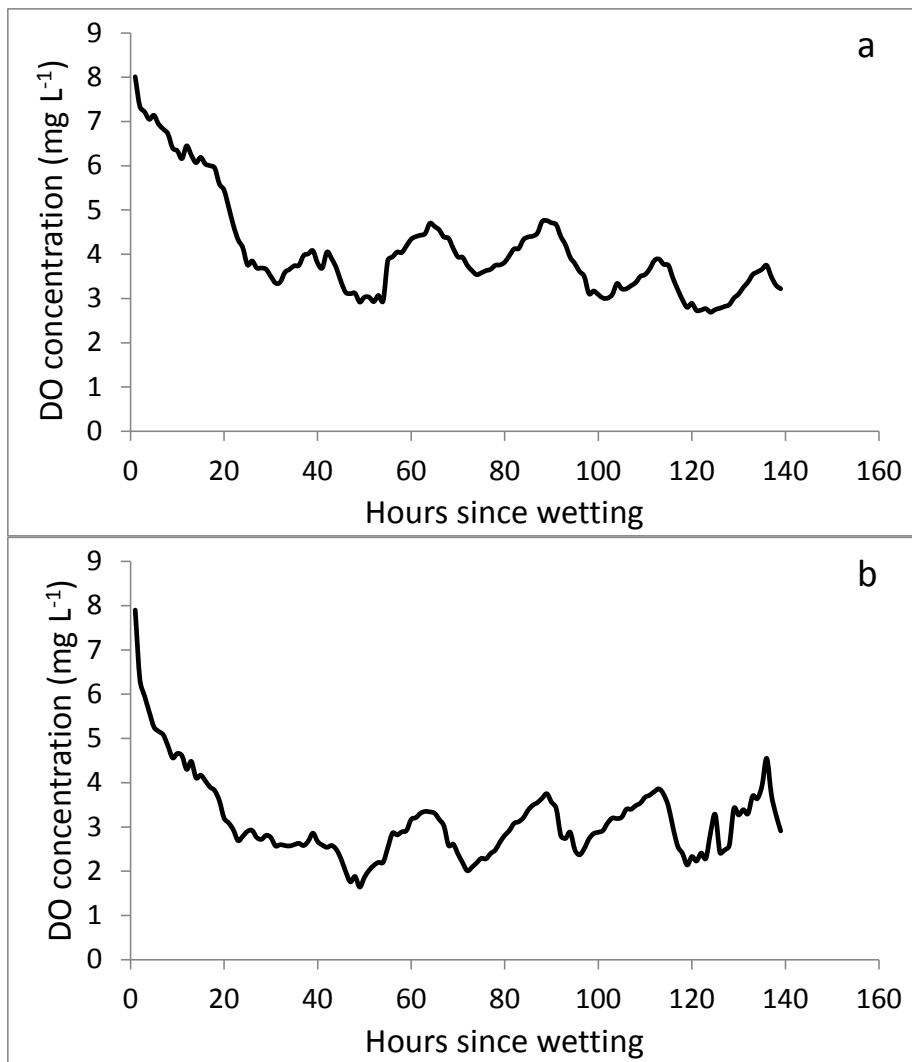
### 6.3.1 Temperature and dissolved oxygen

The mean water temperature in the light exclusion treatment was  $17.88 \pm 0.11$  °C while in the natural light treatment it was  $18.56 \pm 0.15$  °C; a difference that was statistically significant (Pseudo F = 4.056, df = 1, p = 0.046) (Figure 6-3). Day time temperatures in the light and light exclusion treatments were  $19.92 \pm 0.25$  °C and  $18.61 \pm 0.19$  °C and night time temperatures  $17.30 \pm 0.13$  °C and  $17.17 \pm 0.10$  °C, respectively.



**Figure 6-3:** Average diel temperature fluctuations in the natural light and exclusion treatment mesocosms. Natural Light mesocosms are shown in the full line and the light exclusion mesocosms in the dashed line.

After inundation concentrations of DO decreased in all mesocosms. These decreases masked the diel changes in dissolved oxygen concentrations that occurred in the initial 40 hours of inundation. After this initial period, most mesocosms fitted with data loggers exhibited diel patterns in the concentration of DO in the surface water. Though, some mesocosms had clear diel differences than other. Figure 6-4 illiterates examples of clearly diel DO concentration patterns from natural light and exclusion treatments.



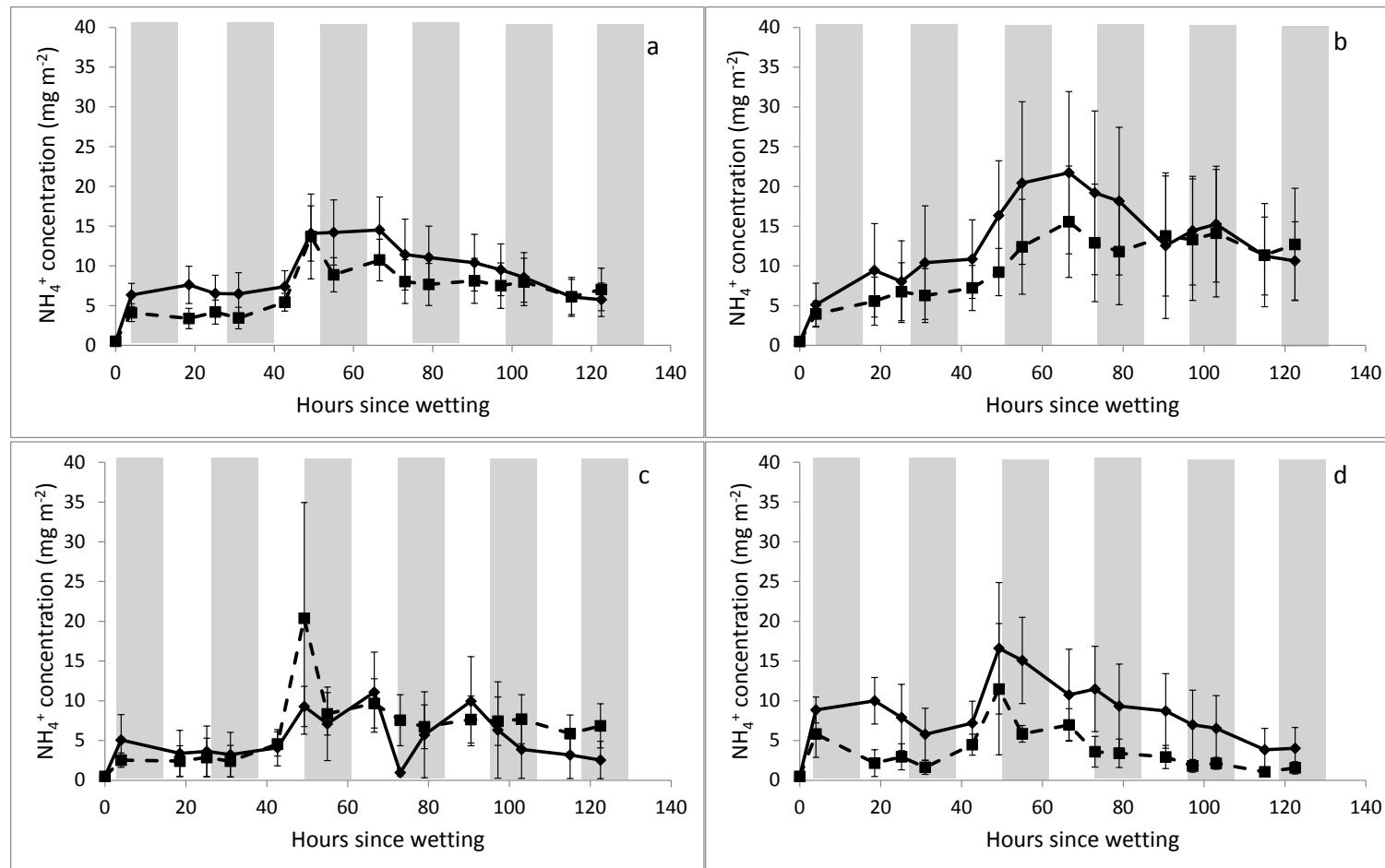
**Figure 6-4:** Examples of del patterns in dissolved oxygen concentrations from the a) natural light and b) light exclusion treatment mesocosms.

### 6.3.2 $\text{NH}_4^+$ and DOC dynamics

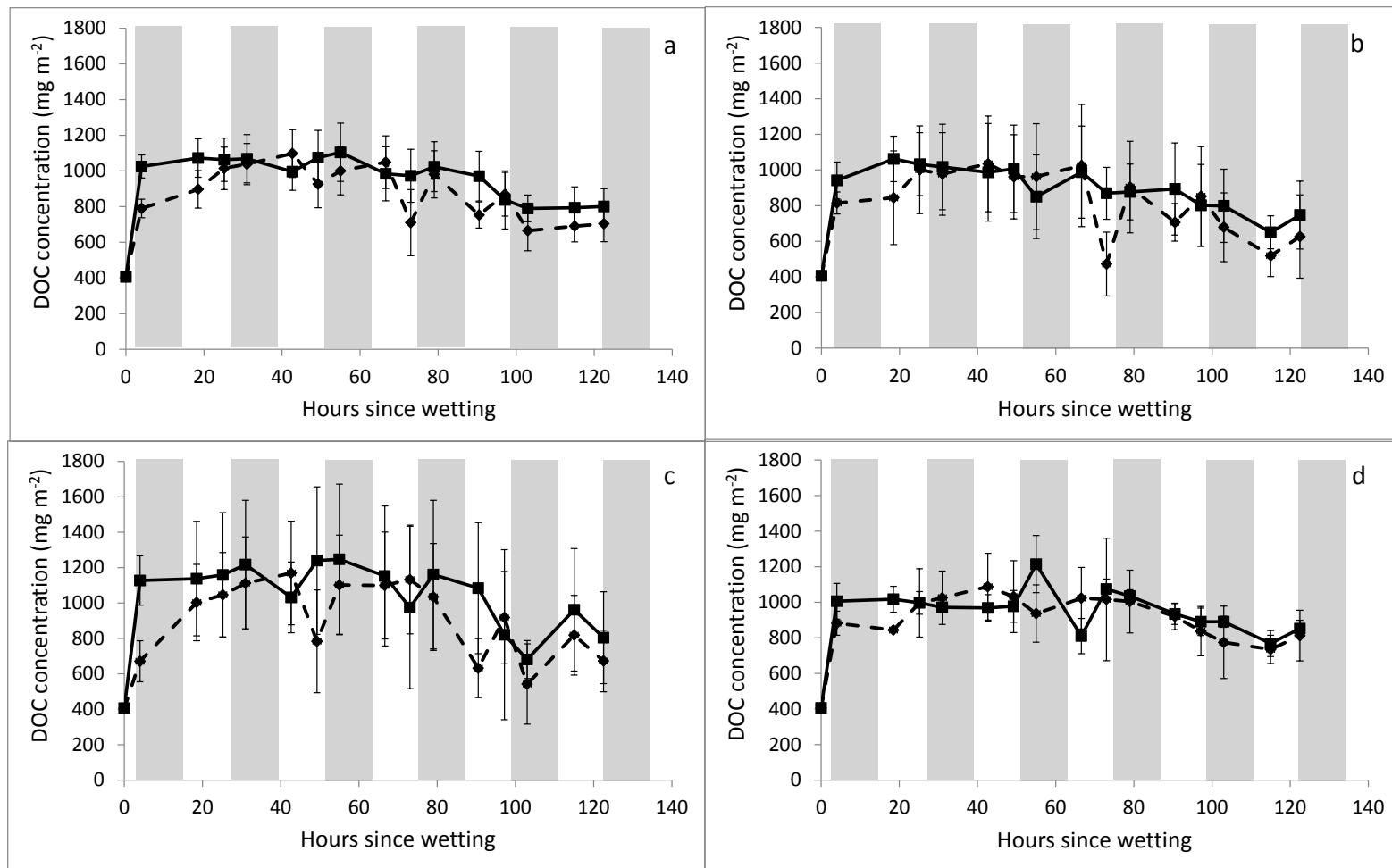
Application of river water to the soil resulted in an increase in  $\text{NH}_4^+$  concentration in the surface water across all positions in the landscape. In the light exclusion treatment, a maximum concentration of  $13.6 \text{ mg NH}_4^+ \text{ m}^{-2}$  was reached approximately 50 hours after inundation (Figure 6-4). In the natural light treatment, a maximum concentration of  $14.5 \text{ mg NH}_4^+ \text{ m}^{-2}$  was reached 65 hours after inundation. There was no evidence that  $\text{NH}_4^+$  concentrations decreased at night in the natural light treatment (Figure 6-4), therefore, no formal testing was carried out for differences in night and day time concentrations. However, the amount of  $\text{NH}_4^+$  in the surface water of the natural light treatment

mesocosms was significantly greater than that found in the light exclusion treatment when investigated across all of the levels in the landscape (Table 6-1). This difference was largely driven by the significant increase in  $\text{NH}_4^+$  concentration in the natural light treatment compared to the light exclusion treatments of floodplain level (Table 6-1). No significant treatment effect was found in the surface water above either the B1 or B2 levels. However, although not significant, concentrations in the light treatment of B1 were higher than those in the light exclusion treatment for the majority of the experimental period (Figure 6-4).

DOC concentrations increased after the application of the Gwydir River water to the soils. The river water DOC concentration before application to the soil was equivalent to 406.27 mg DOC  $\text{m}^{-2}$  in the mesocosms. Immediately following inundation DOC concentration increased to  $789.4 \pm 51.8$  and  $1024.7 \pm 64.7$  mg  $\text{m}^{-2}$  in the light exclusion and light treatments, respectively. There was no clear maximum DOC concentration during the experimental period and for most of its duration DOC concentrations hovered between 800 and 1000 mg  $\text{m}^{-2}$  in both treatments. However, concentrations did generally decline with time in both treatments (Figure 6-5). No significant difference was found in DOC concentration across all levels when comparing the light and light exclusion treatments, nor, for the individual levels in the landscape (Table 6-1).



**Figure 6-5:**  $\text{NH}_4^+$  concentration in the surface water averaged across all levels (a), over B1 (b), over B2 (c) and over the FP (d). The shaded bands signify night. The light exclusion treatment is shown in the dashed line and the full line is the light treatment. Error bars represent one standard error.



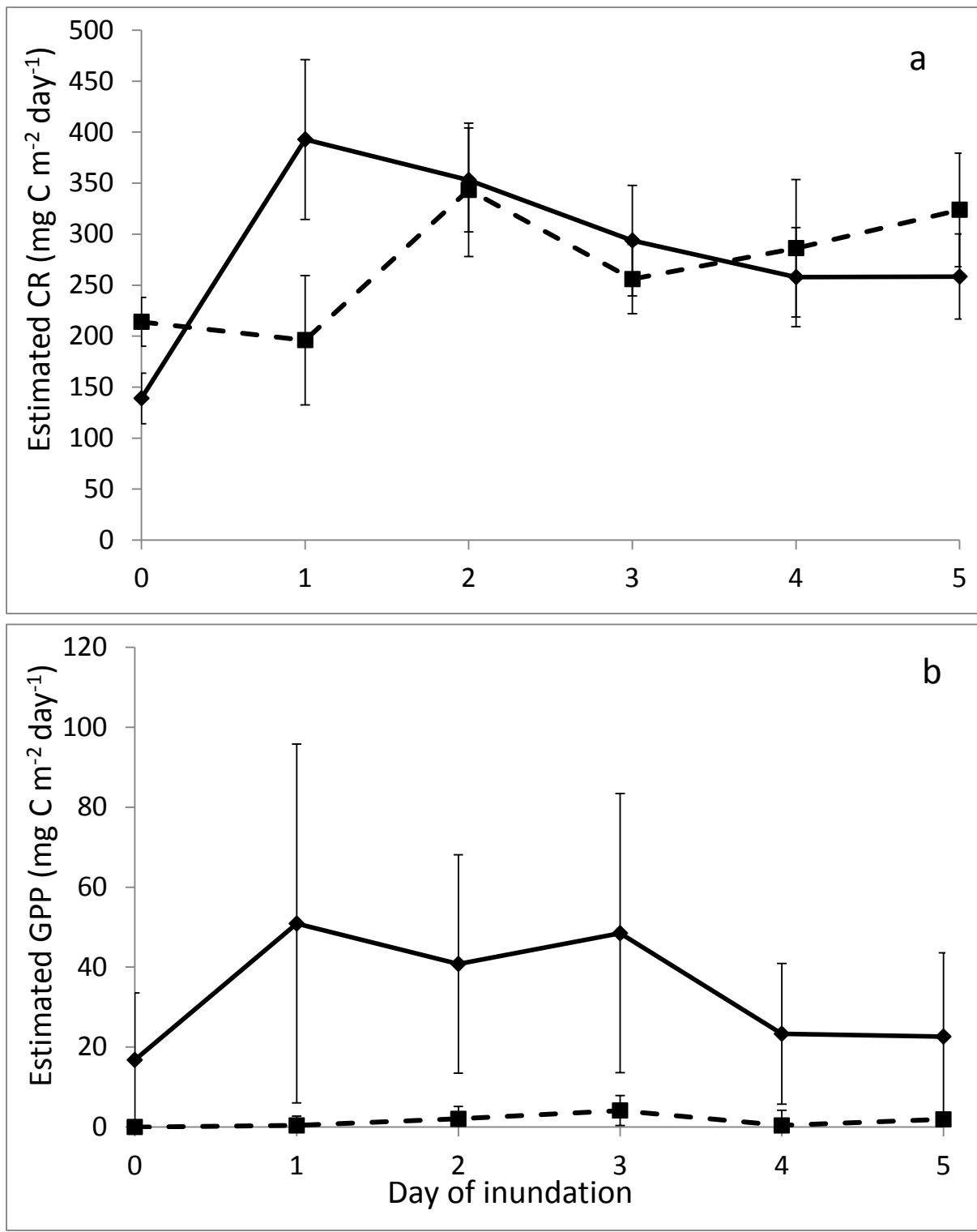
**Figure 6-6:** DOC concentration in the surface water averaged across all levels (a), over bench level 1 (b), over bench level 2 (c) and over the floodplain (d). The shaded bands signify night and light areas day. The light exclusion treatment is shown in the dashed line and the full line is the light treatment. Error bars represent one standard error.

**Table 6-1:** Summary of results for Analysis of Variance (PERMANOVA) for the effect of the light and light exclusion treatments on the mean  $\text{NH}_4^+$  and DOC concentration found in the surface water of the mesocosms. Significant differences were defined as  $p < 0.05$  and are denoted with \* and significance levels of  $p < 0.01$  are denoted with \*\*

		$\text{NH}_4^+$		DOC	
	Df	Pseudo F	$p$	Pseudo F	$p$
Overall	1	4.5102	0.037*	3.7161	0.056
B1	1	1.9159	0.171	1.0658	0.298
B2	1	1.0269	0.325	1.7629	0.190
FP	1	14.495	0.001**	1.0758	0.304

### 6.3.3 GPP and CR

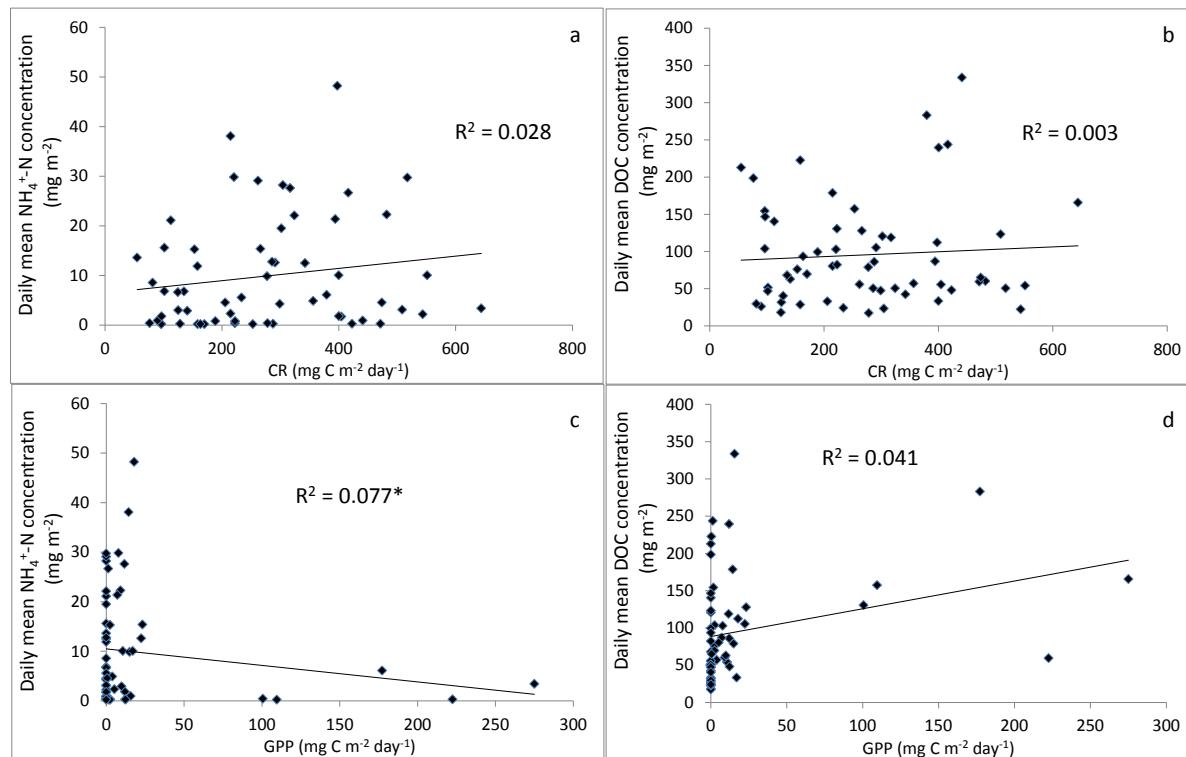
Rates of GPP were generally low, averaging  $33.9 \pm 11.2 \text{ mg C m}^{-2} \text{ d}^{-1}$  in the natural light treatment mesocosms and ranging from  $50.2 \pm 44.9 \text{ mg C m}^{-2} \text{ d}^{-1}$  on the second day of inundation to  $16.8 \pm 16.8 \text{ mg C m}^{-2} \text{ d}^{-1}$  on the first day of inundation (Figure 6-6). Unsurprisingly, rates of GPP in the light exclusion treatment were significantly less than those in the natural light treatment ( $\text{Pseudo F} = 8.386$ ,  $df = 1$ ,  $p = 0.001$ ). Rates of CR were an order of magnitude higher than GPP, averaging  $276.2 \pm 16.3 \text{ mg C m}^{-2} \text{ d}^{-1}$  across all monitored mesocosms (both natural light and light exclusion treatments). No significant difference was found between rates of CR between the treatments ( $\text{Pseudo F} = 0.146$ ,  $df = 1$ ,  $p = 0.698$ ). Average rates of CR in the natural light and light exclusion treatments were  $282.5 \pm 24.0 \text{ mg C m}^{-2} \text{ d}^{-1}$  and  $269.9 \pm 22.5 \text{ mg C m}^{-2} \text{ d}^{-1}$ , respectively. Across both treatments, rates of CR ranged from  $348.3 \pm 38.8 \text{ mg C m}^{-2} \text{ d}^{-1}$  on the third day of inundation to a low of  $176.5 \pm 24.9 \text{ mg C m}^{-2} \text{ d}^{-1}$  on the first day of inundation (Figure 6-6).



**Figure 6-7:** Rates of CR (a) and GPP (b) on each of the days of inundation for the light (dashed line) and light exclusion (full line) treatments. Error bars represent one standard error of the mean.

### 6.3.4 Relationships between GPP, CR and $\text{NH}_4^+$ and DOC

Rates of GPP and CR did not affect concentrations of DOC and  $\text{NH}_4^+$  in surface water of the mesocosms, with the exception of a weak negative relationship between GPP and  $\text{NH}_4^+$  concentration (Pseudo  $F = 4.921$ ,  $p = 0.030$ ) (Figure 6-7).



**Figure 6-8:** Relationships between daily rates of GPP and CR with the daily average DOC and  $\text{NH}_4^+$  concentration.  $r^2$  values have been reported with \* denoting a significant relationship at a probability of  $< 0.05$ .

## 6.4 Discussion

### 6.4.1 Can the diel pattern in $\text{NH}_4^+$ and DOC concentrations observed during the 2008 flow pulse in the Namoi River be replicated in the laboratory using inundated soil in mesocosms under a natural light regime?

The mesocosm experiment was unable to replicate the diel differences in  $\text{NH}_4^+$  and DOC concentrations observed during the high flow events in the Namoi River in December 2008 (Chapter 5) or the diel difference in DOC during the 2004 flooding event (Westhorpe et al. 2012). This inability to replicate these patterns may be due to lower light exposure during

the mesocosm experiment compared to during these flow events. The mesocosm experiment was conducted during May, in Brisbane, where the solar exposure is  $13.3 \text{ KJ m}^{-2}$ , comparatively, solar exposure in Walgett, located near the sampling area of the flow events, in December, the time of year of the flow events, is  $27.1 \text{ KJ m}^{-2}$  (Bureau of Meteorology: <http://www.bom.gov.au/climate/data/>). The lower levels of solar exposure during the mesocosm experiment may have reduced rates of GPP, which would have reduced the amount of bioavailable DOC produced by this process, reducing the potential for diel difference in DOC concentrations. Likewise, rates of photodegradation of DOM may also have been reduced by the lower solar exposure reducing the production of bioavailable DOC and  $\text{NH}_4^+$ .

The difference between average night and day temperatures was greater during the mesocosm experiment, at approximately  $2.5^\circ\text{C}$ , than the during the 2008 flow pulse in the Namoi River at  $0.15^\circ\text{C}$ . This greater difference in the mesocosms may have reduced rates of night time metabolism to a greater extent than during the flow events in the Namoi River, favouring the creation of a diel pattern in DOC and  $\text{NH}_4^+$ . The lack of diel patterns in either DOC or  $\text{NH}_4^+$  during this mesocosm experiment suggests that other factors were limiting rates of metabolism, possibly a supply of labile DOC either produced by the photodegradation of DOM or by algal production.

#### **6.4.2 Does the complete exclusion of light from the mesocosms affect the concentrations of $\text{NH}_4^+$ or DOC?**

The natural light treatment had significantly higher concentrations of  $\text{NH}_4^+$  compared to the light exclusion treatment, but no treatment effect was found on DOC concentrations. This suggests that the photodegradation of organic matter was influencing  $\text{NH}_4^+$  concentrations in the natural light treatment but rates of CR or GPP were not high enough to consume either the photolytically produced  $\text{NH}_4^+$  or DOC. Moreover, the warmer temperatures and greater light availability found in the light treatment mesocosms would favour increased rates of both CR and GPP compared with the light excluded mesocosms reducing concentrations of  $\text{NH}_4^+$  in this treatment. Strong links between light availability and  $\text{NH}_4^+$

concentration have been found in other systems; for example, in a Spanish headwater stream, increased light availability caused by riparian clearing was shown to increase algal production and  $\text{NH}_4^+$  uptake velocity (a measure of how fast a molecule of  $\text{NH}_4^+$  is removed from the stream) (Sabater et al. 2000). A similar finding was presented in nitrogen limited shaded mountain streams in the USA, where  $\text{NH}_4^+$  uptake velocity was positively related to both GPP and CR rates (Hall Jr and Tank 2003). Therefore, the increase in  $\text{NH}_4^+$  concentration in the light treatment compared to the light excluded mesocosms strongly suggests that photodegradation of DOM was occurring in this treatment and that rates of CR and GPP were not strong enough to influence the concentrations of either DOC or  $\text{NH}_4^+$

The non-significant difference in DOC concentration between the treatments does not rule out the possibility of photodegradation of organic matter; particularly, as there was no difference in the rates of CR between the light and light exclusion treatments. Alone, photodegradation of DOM alters the structure of DOC molecules, making them more bioavailable, and results in loss of some DOC as CO or  $\text{CO}_2$  (Wetzel 2006). However, these changes may not be detectable when measuring bulk DOC concentrations in freshly inundated soils due to the large amounts of DOC mobilised from the soil (Spencer et al. 2007). Only when the more bioavailable DOC produced by photodegradation is consumed by respiration are the effects of photodegradation likely to be observed on bulk DOC concentrations. Therefore, not finding a difference in DOC concentrations does not imply that photodegradation was not occurring, rather it suggests that the photometrically altered DOC was not being consumed by respiration in the natural light treatment mesocosms. It is also possible that this lack of difference in DOC concentrations may also have been caused by a small proportion of the DOC being photodegraded due to the reduced light exposure during the mesocosm experiment. However, given that proportionally less  $\text{NH}_4^+$  is produced by the photodegradation of DOM than DOC (Fellman et al. 2013), the significant difference that was found in  $\text{NH}_4^+$  concentration between the natural light and light exclusion treatments suggests that enough DOM was photodegraded to produce a significant difference in DOC concentration. Therefore, it is most likely that rates of CR not sufficient to create a significant difference in DOC between the light and light exclusion treatments.

### **6.4.3 Does the position in the landscape affect diel differences in DOC and NH<sub>4</sub><sup>+</sup> concentrations in either the light treatment or between the light and light exclusion treatments?**

When metabolism is not stimulated, and decreases in DOC concentration evident and without investigating the molecular structure of the DOC found in the mesocosms of each of the treatments, the production of NH<sub>4</sub><sup>+</sup> is the most reliable indicator of photodegradation. When each level in the landscape was investigated individually, significant increases in NH<sub>4</sub><sup>+</sup> concentration was only found on the floodplain level, suggesting that organic matter found on this level was more susceptible to photodegradation than that found on other levels. Fellman et al. (2013) recently suggested that the initial bioavailability of leaf litter leachate effects its photodegradability, with the more recalcitrant leachates from older leaves being more photodegradable. This age mediated increase in photodegradability may be attributed to greater proportions of conjugated and aromatic compounds in older leaves. These chemical groups are broken down into smaller more bioavailable compounds by sunlight resulting in an increase in the proportion of low molecular weight compounds (Helms et al. 2008). Therefore, it is likely that DOC mobilised from leaf litter and soil on the floodplain level, where the soil is older (Thoms and Olley 2004) and leaf litter in a greater state of decay (Chapter 3) makes its leachate more recalcitrant than litter from levels lower in the landscape and therefore more photodegradable, producing more labile photoproducts than levels closer to the river bed.

The greater susceptibility of floodplain organic matter to photodegradation may also help explain the larger diel changes in DOC concentration observed by Westhorpe et al. (2012) during the larger flooding event of 2004 compared with those found during the 2008 flow pulse event (Chapter 5). The 2004 flooding event inundated a greater area, including extensive areas of floodplain while the December 2008 flow pulse stayed in-channel (Chapter 5, Westhorpe et al. 2012). The organic matter inundated on the floodplain in 2004 was likely to be more susceptible to photodegradation, increasing the amount of bioavailable DOC produced during by photodegradation causing greater increases in heterotrophic bacterio-plankton respiration and, therefore, greater diel fluctuations in DOC

concentrations compared to the 2008 flow pulse. Additionally, the larger surface area to volume ratio of the larger 2004 flooding event would also increase the fraction of mobilised organic matter that is exposed to sunlight, again, leading to larger amounts of photodegradation and, therefore, greater consumption of DOC during the day resulting in greater diel fluctuation in DOC concentrations.

#### **6.4.4 Do rates of GPP and CR occurring in the flooded mesocosms affect the concentrations of $\text{NH}_4^+$ and DOC found in the surface water?**

Rates of GPP in the mesocosms had no effect on DOC concentrations and a significant but weak negative affect on  $\text{NH}_4^+$  concentrations, which is similar to the relationship found between GPP and  $\text{NH}_4^+$  in headwater streams (Sabater et al. 2000, Hall Jr and Tank 2003). However, this weak negative relationship implies that GPP is unlikely to be responsible for the diel patterns in  $\text{NH}_4^+$  observed during the 2008 flow pulse in the Namoi River (Chapter 5). The increased rates of GPP required to increase DOC concentration during the day would decrease daytime  $\text{NH}_4^+$  concentrations, which is the opposite pattern to that observed during the 2008 flow pulse in the Namoi River. The lack of relationship between GPP and DOC during the mesocosm experiment suggests that rates of GPP were too low to affect concentrations of DOC during the incubation period of the experiment.

Compared to other studies from Australian lowland rivers or rivers in arid areas from around the world, rates of GPP measured during the mesocosm experiment were low. Rates of GPP estimated by Fellows et al. (2007) in a disconnected waterhole in the Cooper Creek catchment were an order of magnitude greater than those found in the mesocosms of the inundated Gwydir River soils. Similarly, the rates of GPP measured in the mesocosms were also an order of magnitude lower than those reported by Burford et al. (2008) in the sediment and water column of an isolated waterhole in the Cooper Creek catchment following a flooding event. Rates of GPP measured from other desert rivers are generally much greater than those found in the mesocosms of inundated Gwydir River soils (e.g. Fisher et al. 1982, Uehlinger and Brock 2005).

With the methods used to measure GPP during this experiment it is not possible to partition the rates of GPP into benthic and water column productivity. However, given the large difference between rates of GPP found in this study compared to that found in other studies it is safe to assume that both benthic and water column GPP were low in the mesocosm experiment. These low rates of GPP may reflect the short duration of the experiment limiting the establishment of benthic algal communities. Bunn et al. (2006a) suggests such a mechanism limits rates of GPP during flow pulses in highly turbid rivers where the littoral zone moves faster than benthic algal communities can migrate limiting GPP. Rates of GPP in the mesocosms are unlikely to have been limited by turbidity as surface water was very clear (Figure 6-2). In fact, excess water column algal production is a possible consequence of the use of mesocosms due to reductions in flow and turbidity (Carpenter 1996). This experiment was carried out in May in Brisbane when solar exposure is less than half of that found in December in Walgett, a town close to the sampling points of the 2004 and 2008 flow events (Bureau of Meteorology: <http://www.bom.gov.au/climate/data/>). This reduction in solar exposure may have reduced the potential for GPP during this experiment when compared to that likely to be found during the flow events in the Namoi River.

Rates of CR found during the inundation of Gwydir River soils had no effect on  $\text{NH}_4^+$  or DOC concentrations (Figure 6-7) but were in the same order of magnitude although somewhat smaller than rates found from other studies in Australian lowland rivers. The rates of CR found in the mesocosms were approximately half of those presented by Fellows et al. (2007) who used a closed chamber method to estimate benthic respiration in a water hole on the Cooper Creek in western Queensland during a period of disconnection. In a related study also from a waterhole on Cooper Creek, Burford et al. (2008) separately estimated benthic and water column respiration, with the combined total rates of respiration higher than those found in the experimentally inundated Gwydir River soils. However, if it is assumed that most, if not all, of the measured respiration occurred in the inundated soil within the mesocosms, which is a reasonable assumption given their clear surface water (Figure 6-2), then rates of benthic respiration measured here are similar to those reported by Burford et al. (2008). Rates of water column CR are therefore suggested to be much lower than those

that have been presented for other Australian Rivers (Rees et al. 2005, Vink et al. 2005, Burford et al. 2008).

While mesocosms are a useful way of replicating field conditions they struggle with replicating the more dynamic hydrological conditions found in flowing rivers (Carpenter 1996). Increases in flow increase concentrations of suspended sediments (Chapter 5) and the bacteria attached to these sediments are much more metabolically active per cell than free living bacteria (Crump et al. 1998, Luef et al. 2007). Thus, periods of increased concentrations of suspended sediments have been linked with increases in rates of bacterial respiration in lowland rivers (Gawne et al. 2007, Ochs et al. 2010) and estuaries (Bent and Goulder 1981, Crump et al. 1998). Given this influence of hydrology on CR rates it is likely that measured rates of water column metabolism in the mesocosms were influenced by the homogeneous hydrology and lack of flow when compared with those during the flow events in the Namoi River.

Increases in turbidity associated with periods of increased flow may decrease light penetration, possibly reducing rates of DOM photodegradation, restricting CR during periods of increased flow. However, photodegradation of DOM is dominated by the UV and UVB spectrums (Moran and Zepp 1997), which is predominantly absorbed by DOM rather than by suspended particles (DeGrandpre et al. 1996, Williamson et al. 1996) and during the Australian summer UV and UVB are in the extreme range (Australian Bureau of Meteorology: <http://www.bom.gov.au/climate/data/>). Therefore, although suspended particles will compete with DOM for the absorption of UV and UVB light, the resulting reductions of biologically labile photoproducts is not predicted to be large (Moran and Zepp 1997). Moreover, the flow and turbulence that increases turbidity also continuously mixes the water column, a hydrological property that in Canadian wetlands has been shown to increase the photodegradation of DOM and the production of labile DOC photoproducts (Waiser and Robarts 2004). Therefore, the lack of high concentrations of suspended sediments during the mesocosm experiment may have reduced rates of CR compared to the flow events in the Namoi River when the high concentrations of suspended particles would

not have reduced photodegradation of DOM (Chapter 5) and the turbulence of flow during this event may have aided photodegradation by mixing the water column.

## 6.5 Conclusions

In comparison to the mesocosm experiment, summer flooding or flow pulses in Australian lowland rivers provide physical conditions conducive to photodegradation of DOM and high rates of respiration; with a continuous supply of organic matter that is mobilised in a well-mixed environment during a time when UV light is ‘extreme’ and there are high concentrations suspended solids providing a large and active population of bacteria to assess the photodegraded, labile DOC. Comparatively, the mesocosm experiment reduced the potential for both photodegradation of DOM and high rates of CR; with the reduced solar exposure and the static hydrological conditions both decreasing the potential for photodegradation of DOM and CR. The significant increases in  $\text{NH}_4^+$  concentrations in the light treatment mesocosms indicate that photodegradation was occurring during the experiment despite the lower light intensity and stable hydrological environments when compared to the flow events in the Namoi River. The role of photodegradation in increasing the availability of leaf leachate from common Australian riparian trees has recently been investigated using laboratory methods (Fellman et al. 2013) but to date no Australian field based work has been completed. Likewise, the role of bacteria attached to suspended particles has not been investigated in Australian rivers. Given the large amounts of carbon needed to be consumed or transformed to create the diel patterns in DOC observed in the Namoi River during the 2004 and 2008 flow events (Chapter 5, Westhorpe et al. 2012) these mechanisms may have significant implications for aquatic ecosystems and therefore warrant further investigation in both the laboratory and field.

# **Chapter 7. Patterns in river stage height and in-channel bench inundation under three different flow regimes in the Gwydir River**

## **7.1 Introduction**

Variability in the magnitude, duration, frequency, timing and predictability of flow (Table 1-1) has an overriding influence on riverine ecology (Lytle and Poff 2004) and channel geomorphology (Graf 1988, Thoms and Sheldon 1997, Naiman et al. 2008). Biota within riverine landscapes are adapted to the natural flow regime, including all aspects of its variability (Poff et al. 1997); therefore changing any aspect of this variability can affect riverine ecology through various mechanisms including reducing longitudinal and lateral connectivity (Bunn and Arthington 2002). Geomorphologically, flow variability shapes the physical habitat in riverine landscapes, at multiple scales; for example it organises soil and sediment particle sizes, both in the channel and on the floodplain (Walling and He 1998), it moves woody debris and other transportable items (Poff et al. 1997) and it forms or destroys in-channel features such as in-channel benches or anabranches (Graf 1988, Sheldon and Thoms 2006, Vietz et al. 2012). However, in many of the world's rivers this highly important natural variability in flow, which facilitates these functions, has been reduced by flow regulation with consequential impacts upon riverine ecology and geomorphology (Poff et al. 1997, Nilsson et al. 2005, Naiman et al. 2008) particularly in arid rivers (Thoms and Sheldon 2000a, b, 2002)

Arid rivers have more variable flow regimes compared with rivers in humid areas (Puckridge et al. 1998) which influences their geomorphology often making it more complex (Graf 1988). The in-channel geomorphology of rivers in humid areas, generally reaches an equilibrium condition that is facilitated by the near continuous level of stream flow (Graf 1988). Rivers with more variable flow regimes, often have channels that are characterised by highly variable or compound cross-sectional shapes (Graf 1988) enabling a larger range of flow volumes to be contained in-channel (Thoms and Walker 1993). This is achieved by having high flow channels, shaped by large, infrequent flows, and a series of lower flow channels that are all

contained within the larger channel (Thoms and Walker 1993). Changes to particular flows due to flow regulation can therefore alter specific components of in-channel geomorphology of rivers in arid areas (Graf 1988, Thoms and Walker 1993, Sheldon and Thoms 2006).

There is considerable evidence that altering the natural flow regime of rivers has a major impact on riverine ecosystems. Bunn and Arthington (2002) provide four principles that illustrate how riverine ecosystems are impacted by alterations to the natural flow regime; (i) physical changes to habitat can affect the distribution of aquatic plants, invertebrates and fish, (ii) altering the flow regime to which biota have adapted leads to recruitment failure and loss of biodiversity , (iii) changing the patterns of lateral and longitudinal connectivity restricts biota movements and leads to isolation of populations, failed recruitment and local extinctions, and (iv) altering the flow regime tends to increase the success of non-native species. The ecological response to flow regulation in a particular river or stream is dependent on how similar (or dissimilar) the natural flow regime is compared to the imposed and modified flow regime (Poff and Ward 1990). For example, flow regulation that increases the stability of flow will have different effects on a river that naturally had a highly variable flow regime compared with a river that naturally had a stable flow regime (Poff et al. 1997). Comparatively, the effects on the flow regime below a hydroelectric dam that produces a flow regime that is highly variable on a daily basis will be different to the impacts from flow regulation that increases flow stability for agricultural purposes (Poff et al. 1997).

In many Australian lowland rivers, particularly those of the Murray-Darling Basin, water resource development has reduced natural flow variability to secure water for irrigation based agriculture (Thoms and Sheldon 2000a). The frequency that in-channel features such as benches and anabranches are inundated has been reduced due to the loss of flow pulses, but as flow regulation does not affect larger flooding events, the frequency that the floodplain is inundated has remained relatively unchanged (Page et al. 2005). Consequently, many of these rivers are now in a precarious state of ecological health (Davies et al. 2010) and there is a recognition that flow restoration is required in this low to

moderate flow band to restore the connectivity of in-channel features (McGinness and Arthur 2011, Westhorpe and Mitrovic 2012). In an attempt to increase this connectivity, flow rules are often used to set flow thresholds for irrigator access, restricting the water available during reservoir spills or when high flows enter the river from unregulated tributaries (Westhorpe et al. 2008). Such rules have been set in the Gwydir River (Westhorpe et al. 2008) but their effectiveness at increasing the connectivity in the Gwydir River landscape has not been assessed.

This chapter uses modelled flow regimes to assess the potential for each of the in-channel bench levels found in the Gwydir River to be inundated ‘with flow rules’, ‘without flow rules’ and under a ‘natural’ flow regime, thereby assessing if flow regulation has affected the inundation patterns of these levels, and if so, has the introduction of flow rules re-introduced patterns of inundation of the in-channel benches found in the Gwydir River channel prior to flow regulation.

The specific research questions are;

1. If analysed in one metre incremental increases in river stage height, are the number and duration of events different under the three flow regimes and at what stage height are these differences most prominent during the 29 years of the modelled investigation period?
2. Do the number and duration of in-channel bench inundation events differ between the three different flow regimes over the 29 years of the modelled investigation period?

## 7.2 Methods

Three different flow regime scenarios were used to explore potential changes in floodplain and in-channel bench inundation; these scenarios included (i) a regulated flow regime with no flow rules in place, meaning abstraction for irrigation could occur during any part of a flow pulse, (ii) a regulated flow regime with flow rules in place that restricts abstraction,

allowing more frequent low-level inundation, and (iii) a modelled natural flow regime. The three flow regimes were generated using data from the IQQM flow model (DIPNR 2005). The ‘with flow rules’ scenario included the restriction of water extraction during reservoir spills or when high flows enter the river from unregulated tributaries, these rules were not included in the ‘without flows rules’ simulation. Comparing the patterns of inundation between these two flow regimes enabled an assessment of the effectiveness of flow rules at increasing connectivity within the Gwydir River channel by increasing the frequency or duration of in-channel bench inundation events. The ‘natural flow’ scenario was modelled based on the absence of major water impoundments and extractions and by comparison its inclusion allowed the assessment of the effects of flow regulation on patterns of inundation in the Gwydir River and whether the flow rules were able to introduce a more ‘natural flow’ regime. The IQQM model provided daily flow volume data for these flow regimes. This data was converted into river stage height to enable investigation of the patterns of in-channel bench inundation under each of the modelled flow regimes. This conversion was undertaken with river flow and stage height data sourced from the Pallamallawa gauging station that spanned 28/10/1980 to 20/11/2000 (New South Wales Office of Water:[http://realtimedata.water.nsw.gov.au/water.stm?ppbm=SURFACE\\_WATER&rs3&rskm\\_url](http://realtimedata.water.nsw.gov.au/water.stm?ppbm=SURFACE_WATER&rs3&rskm_url)).

The height of each in-channel bench level at each site above the standing river height was measured using a dumpy level (Chapter 2). These measured heights were added to the river stage height on the day of measurement to provide the in-channel bench height above gauging levels. The average in-channel bench height across the five sites was used to investigate the likely patterns of in-channel bench inundation in the lower Gwydir River under the three different flow regimes. Previous investigations into benches in the Murray-Darling River system have shown that in-channel benches occur at similar heights within different reaches of the river channel (Woodyer 1968) justifying using these averages as representative of in-channel bench levels in this region of the Gwydir River.

Average in-channel bench height for each level was compared to the calculated flow heights for each flow scenario. For each in-channel bench level the number of inundation events, defined as the number of occasions that the river stage height crossed the average height of each level (B1, B2 and FP) was quantified along with the total number of days the river was above this height. The average length of each of these inundation events was then calculated by dividing the total number of days that the river stage height was above each in-channel bench height by the number of times that it crossed this height. This same procedure was also carried out at 1 m height intervals allowing a more detailed investigation in the effects of flow regulation and flow rules on flow in the Gwydir River.

## 7.3 Results

### 7.3.1 In-channel bench heights

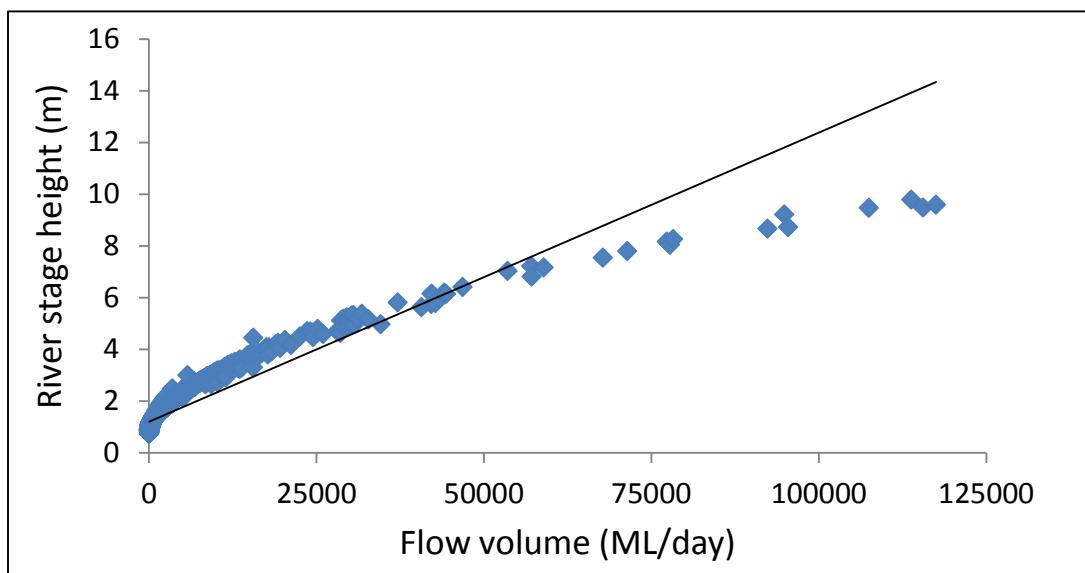
The height of the in-channel bench levels at each of the sites is presented in Table 7-1. Some variation was found in the height of the different levels between sites, with bench and floodplain levels at site 2 being higher than the equivalent levels other sites. The variation in level height increased from the CH level to the FP level as illustrated by the increasing standard error of each mean level height (Table 7-1).

**Table 7-1:** In-channel bench level heights (m) above gauging levels at the Pallamallawa gauging station at each of the sites and the average in-channel bench level height across the sites found in the Gwydir River ( $\pm$  one standard error of the mean).

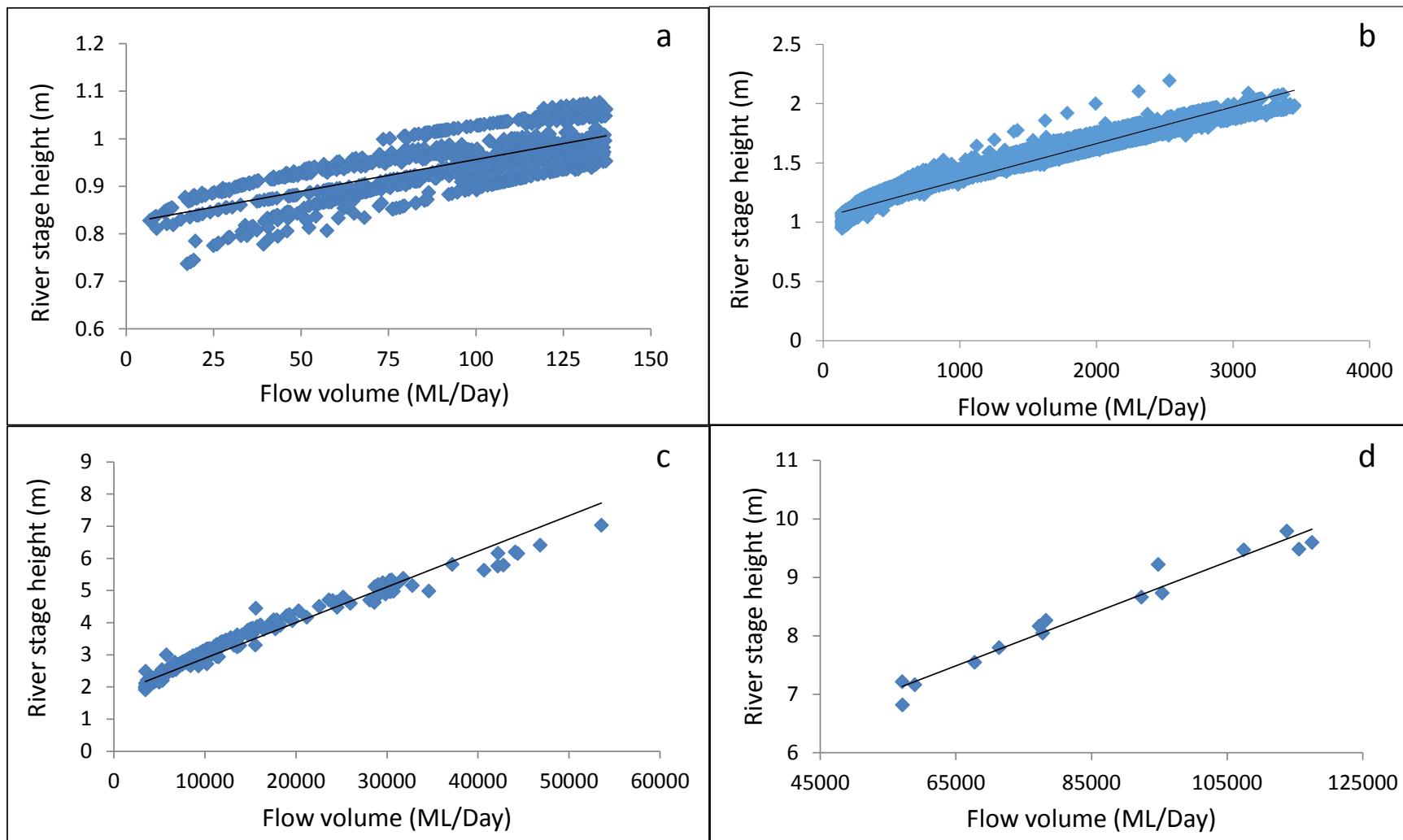
	Site 1	Site 2	Site 3	Site 4	Site 5	Average
CH	1.11	1.22	1.87	1.46	1.56	$1.44 \pm 0.13$
B1	3.94	3.94	3.14	2.27	2.24	$3.10 \pm 0.38$
B2	5.35	8.13	3.75	2.97	3.27	$4.69 \pm 0.95$
FP	8.25	11.19	4.9	5.55	7.14	$7.41 \pm 1.11$

### 7.3.2 Relationships between river flow and stage height

When the relationship between flow and stage height was analysed over the full range of river stage heights the relationship was not linear (figure xxx), therefore, multiple relationships that were partitioned between various stages heights were used. These smaller, partitioned, relationships improved linearity and were chosen to maximise the model fit ( $r^2$  value). The derived relationships were between rivers stages heights of 0.82 m - 1 m, 1 m - 2m, 2 m - 7.20 m and 7.21 m - 9.59 m (Figure xxxxx).



**Figure 7-1:** The relationship between flow and river stage height in the Gwydir River across all river stage height found during the study period. The line represents the linear line of best fit.



**Figure 7-2:** The relationship between flow and river stage height in the Gwydir River across the river stage heights selected to maximise the model fit. The line represents the linear line of best fit.

### **7.3.3 Modelled hydrographs**

#### **7.1.1.1 Difference in flow heights between the three flow regimes**

The three modelled flow scenarios resulted in different flow heights in the Gwydir River with differences in stage height and duration mostly found below 3 m in river stage height (Table 7-2). Above this height the average duration of flows >3 m was very similar between the different flow regimes; with both the ‘natural’ and ‘without flow rules’ regime having an average duration of 3.1 days and the ‘with flow rules’ scenario an average of 2.9 days. Over the 29 year analysis period flows >3 m were only separated by two flow events; one event caused the ‘without flow rules’ and ‘natural’ flow regimes to have an extra flow between 5 and 6 m in stage height while the second event was >7 m and occurred in the ‘with flow rules’ regimes but not the ‘without flow rules’ or ‘natural’ flow regimes (Table 7-2).

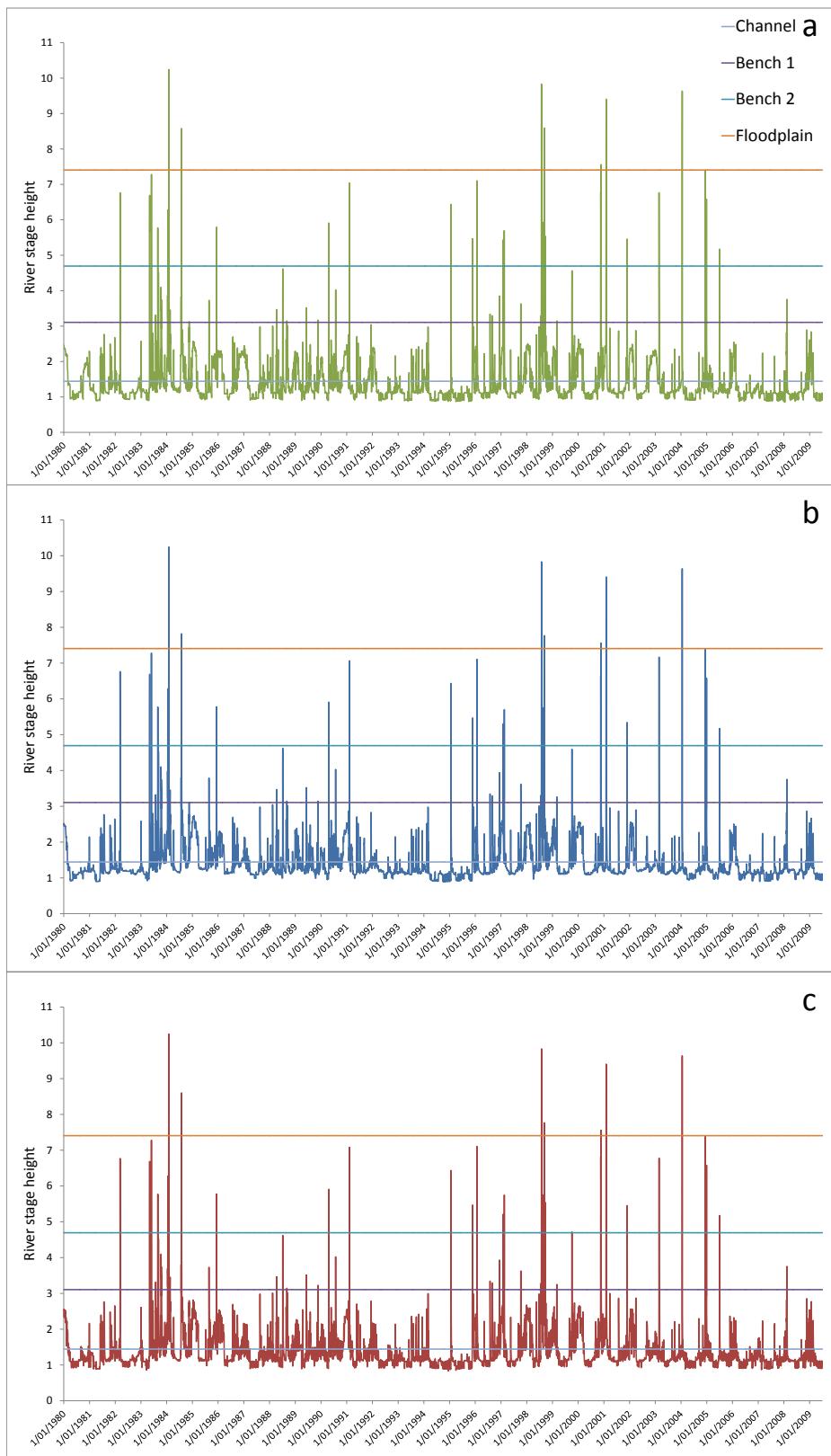
Comparing flows >2 m in river stage height between the ‘with’ and ‘without’ flow rules scenarios illustrates that the introduction of flow rules decreased the number of flow events in this category but increased their average duration. Comparatively, the ‘natural’ flow regime had the least number of flow events that were >2m in stage height but these events were longer in duration than under the ‘with’ or ‘without’ flow rules scenarios (Table 7-2).

The different flow regimes also affected the number and duration of events >1 m in river stage height. Under the ‘with flow rules’ scenario the number of events >1 m was reduced compared to the ‘without flow rules’ scenario. However, the duration of these events nearly tripled in the scenario ‘with flow rules’ compared to ‘without flow rules’. So, the introduction of flow rules decreased the number of flow events >1 m but increased their duration. The ‘natural’ flow regime had less days in total where flow was > 1 m compared to either the ‘with’ or ‘without’ flow rules scenarios and their duration was of similar length to the ‘without’ flow rules scenario (Table 7-2).

The number and duration of flow events with stage heights <1 m also varied between the three different flow regime scenarios. The ‘no flow rules’ regime had the greatest number of events that decreased to <1 m in stage height, however, the average duration of these events was shorter than under either of the other modelled flow regimes. The duration of <1 m high flow events was similar between the ‘with flow rules’ and ‘natural’ flow regimes but the ‘natural’ flow regime had over double the number of flow events <1 m in river stage height (Table 7-2).

**Table 7-2:** Simulated heights and lengths (days) of flows at the Pallawallawa gauging station under with flow rules, without flow rules and natural flow regimes broken down by 1m incremental increases in flow height.

Flow height		<1 m	>1 m	>2 m	>3 m	>4 m	>5 m	>6 m	>7 m
With flow rules	Events	101	102	98	53	31	26	17	11
	Average length	9.4	96.3	13.0	2.9	2.4	2	1.9	1.8
No flow rules	Events	261	262	122	51	32	27	17	10
	Average length	5.9	35.3	10.2	3.1	2.3	2	2	1.9
'Natural'	Events	205	206	85	53	32	27	17	10
	Average length	11	41.4	17.4	3.1	2.5	2.1	2.1	2.2



**Figure 7-3:** The hydrographs for the three different modelled flow regimes a) natural flow b) with flow rules c) without flow rules. .

### 7.3.3.1 Patterns of in-channel bench inundation under the three different flow regimes

Under the different flow regime scenarios there was little difference in the number or duration of inundation events of any level above the CH (Table 7-3). This is clearly illustrated when looking at the number of times that the B1 and B2 levels were inundated, this occurs only once less under ‘with flow rules’ flow regime compared to the other two flow regimes. Additionally, the FP level was only inundated once more under the ‘natural’ flow regime compared to either of the other flow regimes. The average length of inundation events of all of the levels in the Gwydir River channel was 0.1 days longer under the ‘natural’ regime compared to the other flow regimes (Table 7-3).

**Table 7-3:** The number of simulated inundation events and their length of each level in the Gwydir River landscape under the three different flow regimes.

Level		B1	B2	FP
Height (m)		3.14	4.73	7.44
Flow rules	Events	48	26	7
	Average length	2.8	2.1	1.3
No flow rules	Events	49	27	7
	Average length	2.8	2.1	1.3
'Natural'	Events	49	27	8
	Average length	2.9	2.2	1.4

## **7.4 Discussion**

### **7.4.1 If analysed in metre incremental increases in river stage height are the number and duration of events different in the three flow regimes and at what stage height are these differences most prominent during the 29 years of the modelled investigation period?**

There was little variation in flow heights between the different flow regimes above a river stage height of 3 m, with only two events separating the different flow regimes and the average duration of these events being within 0.5 days of each other. River regulation in Australia's dryland rivers is commonly found to affect flow in this way; decreasing the frequency of medium sized flows and having little effect on larger increases in flow (Maheshwari et al. 1995). Similar effects of flow regulation were presented by Thoms and Sheldon (2000b) in the Barwon-Darling river where they found that flow volumes exceeding the 10<sup>th</sup> and 25<sup>th</sup> percentile were on average 20% smaller under a modelled 'current' flow regime (where the 'current' regime in this study used water and catchment development conditions present in 1993–1994 combined with long-term mean climatic conditions) than flow under a 'natural' flow regime (which was similar to the 'natural' regime used here in that there is an absence of regulating structures, water extraction and catchment development). Similarly, Page et al. (2005) found flow regulation in the Murrumbidgee River reduced the frequency of flows with a return interval of 1.25 and 2 years more than flow with a return interval of between 5 and 20 years. In the Gwydir River, it is likely that these medium sized flows are either being stored in dams and weirs and the water is subsequently released to increase river flow during natural low flow periods or they are being extracted for on-farm storage and irrigation purposes.

The differences between the 'natural' and regulated flow regime scenarios means the 'natural' flow regime approximately doubled the number of days where flows were <1 m compared to the other flow regimes. Periods of low flow are natural features of Australian lowland rivers and their loss under flow regulation has ecological impacts (Lake 2003). Droughts or extended periods of low summer flow are a major force in maintaining

biodiversity (Everard 1996, Rolls et al. 2012). For example, flow regulation in Australian lowland rivers reduces seasonal variation in flow and maintaining a low flow throughout the year which thought to increase the success of exotic fish species such as carp (*Cyprinus carpio*) (Walker et al. 1995). The re-establishment of these low flow periods may not be possible in the Gwydir River given that flow regulation is intended to provide a more secure water source to the Gwydir Valley irrigators and low flow periods would interrupt this security.

Flows >1 m in stage height were dominant in all the flow regime scenarios investigated. Differences in either the duration or number of events meant that the ‘with’ and ‘without’ flow rules flow scenarios had 722 and 1300, respectively, more days of flow >1 m but less days >2 m compared to the ‘natural’ flow regime. Thus, these flow regimes were significantly more stable between 1 and 2 m in river stage height compared the ‘natural’ flow regime. This stability is likely to impact river ecology in ways such as increasing benthic algal production (Sheldon and Walker 1997) and altered fish assemblage structure (Gehrke et al. 1995). The increased flow stability under the ‘with’ and ‘without’ flow rules regimes may also have geomorphological consequences for the river with decreased in-channel complexity (Thoms and Sheldon 1997, Sheldon and Thoms 2006) and channel widening (Thoms and Walker 1993) cited as being caused by increased flow stability in other Australian lowland rivers.

The stability of flow events between 1 and 2 m in flow height of the regulated flow regimes was likely created by a reduction in the number of days that flow height was >2 m. When the ‘with’ and ‘without’ flow rules flow regimes are compared to the ‘natural’ flow regime the total number of days that river stage height was >2 m decreases from 1478 under the natural flow regime to 1278 and 1240 under the with and without flow rules regimes, respectively. This difference was mainly driven by a reduction in the duration of flow events >2 m rather than a reduction in the number of events. The introduction of flow rules increased the duration of these events from 10 days to 13 days which was more similar to the duration of these events under the natural flow regime of 17 days than without flow

rules. This illustrates that the flow rules are returning the flow regime in the Gwydir River in the direction of a more natural state, in some ways, but in-channel connectivity would be greater only if these the flow rules increased the number or duration of in-channel bench inundation events.

#### **7.4.2 Do the number and duration of in-channel bench inundation events differ between the three different flow regimes?**

The reduction in flow variability, specifically the reduction in the frequency of flow pulses and smaller flooding events, reduces in-channel connectivity (Thoms et al. 2005, McGinness and Arthur 2011), and is regarded as one of the drivers behind declines in the health of many rivers within the Murray-Darling River system (Davies et al. 2010). Therefore, a difference in the number of in-channel bench and floodplain inundation events under the three different modelled flow regimes in the heavily regulated Gwydir River would be expected, however, no such difference was found. This suggests that either a loss of connectivity between the terrestrial and aquatic ecosystems is not occurring in the highly regulated Gwydir River or that channel geomorphology has changed due to flow regulation causing flows that once would have inundated the lowest in-channel benches to no longer reach these levels.

Given the amount of scientific literature highlighting the importance of connectivity between aquatic and terrestrial ecosystems both internationally (Junk et al. 1989, Tockner et al. 1999) and within Australia (Robertson et al. 1999, Bunn and Arthington 2002, Leigh et al. 2010) and that flow regulation is widely acknowledged to reduce this connectivity (Poff et al. 1997, Thoms and Sheldon 2000b, Bunn and Arthington 2002, Thoms et al. 2005) it is unlikely that flow regulation in the Gwydir River has not impacted on in-channel connectivity. Therefore, the most likely reason for the similarity in the patterns of in-channel bench inundation between the modelled flow regimes is a geomorphological change in the river channel that has altered the height of the lowest in-channel bench level.

The geomorphology of river channels that have highly variable flow regimes adapts to changes in the rivers flow regime (Graf 1988) thus changes to flow variability, as a result of flow regulation, will alter the geomorphology of river channels. Such changes have been illustrated in an Australian context by Sheldon and Thoms (2006) who observed a reduction in-channel complexity, measured by the number of in-channel benches, when they compared regulated and un-regulated reaches of the Barwon-Darling River. Specifically, they found that the regulated river reach had lost up to three of its lowest in-channel bench levels when compared to the un-regulated reach. The lack of a difference in patterns of in-channel bench inundation in the Gwydir River may be explained if a similar geomorphological adaption to flow regulation, the loss of the lowest in-channel bench levels, has occurred.

In addition to flow regulation, the extraction of water during periods of increased flow can alter the shape of flow and flood hydrographs causing geomorphological changes to river channels. Thoms and Sheldon (1997) found that during a flooding event in the Barwon-Darling River water extractions doubled the rate of water level fall on the falling limb of the flood hydrograph and resulted in over 91 000 tonnes of sediment being eroded from the river banks, mostly from in-channel benches. It is likely that water extraction from the Gwydir River under the ‘no flow rules’ flow regime caused flows <3 m in height to be shorter in duration than similar sized flows under either of the other two modelled flow regime scenarios (Table 7-2). Prior to the introduction of flow rules in 1997 there was no restriction on the extraction of water during flow pulses or floods in the Gwydir River, it is therefore likely that there has been significant erosion of in-channels benches and conceivably their complete loss below 3m in height. Furthermore, in-channel benches below a river stage height of 3m have been reported by Woodyer (1968) throughout the Murray-Darling Basin, including in the Gwydir River, prior to flow regulation again suggesting the loss of low level in-channel benches due to flow regulation and water extraction.

## 7.5 Conclusions

The introduction of flow rules was undertaken to increase the connectivity between the aquatic and terrestrial ecosystems in the Gwydir River by facilitating the inundation of in-channel features. However, data presented in this chapter suggests that this connectivity may not have been increased, if measured by the number or duration of in-channel bench inundation events. This lack of increase in in-channel bench inundation is suggested to be due to the loss of the lowest in-channel bench levels from within the Gwydir river channel. The loss of in-channel benches is believed to be caused by long periods of stable flow conditions and increased rates of river stage fall during the falling limb of flow events (Thoms and Sheldon 1997, Sheldon and Thoms 2006). It is yet unclear if the introduction of flow rules that increase the duration of flow events between 2 and 3 m, perhaps reducing the rate of fall on the flow falling limbs, will result in the rebuilding of in-channel benches in the Gwydir River. Even if the introduction of flow rules is sufficient to begin re-building the lost in-channel bench level(s) it is likely to take years before they are established to a mature enough phase which will enable them to act as storage facility for terrestrially derived organic matter and increase the exchanges occurring during smaller more regular flow pulse events in the Gwydir River channel.

# **Chapter 8. General discussion: Setting a benchmark for environmental flows in a dryland lowland river**

## **8.1 Introduction**

More than 45 000 dams, greater than 15m in height, that hold more than 6 500 km<sup>3</sup> of water, have been constructed on rivers around the world (Avakyan and Iakovleva 1998). The construction of these dams, and the resulting regulation of river flow, is a consequence of the human demand for water. The impacts these dams have on river flow are diverse and dependent upon the purpose of the dam and the natural flow regime of the river being regulated (Poff et al. 1997). In Australia, the lowland reaches of many inland rivers have been regulated by the construction of headwater dams that stabilise flow, reducing flow variability and dampening the natural flow extremes in lowland areas (Puckridge et al. 1998, Thoms and Sheldon 2000a, Page et al. 2005). This has drastic geomorphological and ecological consequences, as both the natural variability and flow extremes inherent to these lowland rivers are important to their ecological health, thus the stabilising of their flow regimes has likely contributed to the declines in aquatic ecosystem health observed in many of these systems (Davies et al. 2010).

The stabilisation of flow and the loss of the extremely high and low flow periods in Australian lowland rivers, resulting from flow regulation, has created conditions that are favourable for the success of introduced species such as Carp (*Cyprinus carpio*) and Mosquito fish (*Gumbusia affinis*) (Faragherl and Harris 1994, Walker et al. 1995, Bunn and Arthington 2002). The success of these introduced species often results in reduced diversity of native fish (Bunn and Arthington 2002). The loss of periods of high and low flow through flow stabilisation also has a direct effect on native fish population as many native fish species recruit during these periods (Balcombe et al. 2006). Similar changes in the diversity of macroinvertebrate communities (Kingsford 2000) and littoral plant communities (Blanch et al. 2000) have been found to result from flow regulation in Australian lowland rivers.

The geomorphology of Australian lowland rivers is also affected by flow regulation. A series of 10 weirs constructed on the Lower River Murray have made the river wider and shallower in some areas and narrower and deeper in others, with the specific change dependent upon position relative to each weir and the surrounding environment (Thoms and Walker 1993). Geomorphological changes resulting from flow regulation have also been reported by Sheldon and Thoms (2006) where lower in-channel complexity, as measured by the number of in-channel benches, was found in a regulated reach of the Darling River when compared to a similar unregulated reach. The inundation of in-channel benches and other in-channel features is also affected by flow regulation. Thoms et al. (2005) used modelled flow regimes to illustrate flow regulation in the Macintyre River decreased the frequency and duration that in-channel features are inundated.

Increasing the frequency and duration that in-channel features such as anabranches and benches are inundated has been proposed as a management strategy aimed at rejuvenating ecosystem health in Australian lowland rivers (Thoms et al. 2005, Sheldon and Thoms 2006, McGinness and Arthur 2011, Westhorpe and Mitrovic 2012). One of the ecological roles facilitated by these in-channel features is to increase the connectivity between terrestrial and aquatic ecosystems. In-channel features provide a ‘floodplain’ like area that accumulates terrestrial organic matter during periods of low flow that can be released into the river during in-channel flow pulses, stimulating in-channel productivity (Sheldon and Thoms 2006, Westhorpe et al. 2010, McGinness and Arthur 2011).

In-channel features, when inundated, provide a source of DOC and inorganic nutrients to the river which is likely to increase aquatic productivity. Such exchanges are important as the availability of DOC has been found in a number of studies to be a limiting factor in heterotrophic productivity in Australian lowland rivers (Hadwen et al. 2010, Westhorpe et al. 2010) and increases in DOC concentrations. These increases in DOC concentration may result in increased heterotrophic productivity which may lead to increased zooplankton abundance eventually stimulating secondary production (Mitrovic et al. In Press). Likewise, autotrophic productivity in lowland rivers was found by Westhorpe et al. (2010) to be

limited by inorganic nutrient availability during bottle assays. Therefore, release of inorganic nutrients and DOC from the inundation of in-channel features may also result in increased autotrophic productivity and have carry on effects to higher in the food chain through increased zooplankton abundance (Mitrovic et al. In Press).

There has been much speculation about the exchanges facilitated by the inundation of in-channel benches during periods of increased flow in lowland Australian rivers (e.g. Thoms and Olley 2004, Sheldon and Thoms 2006, Southwell and Thoms 2011). However, there is little direct evidence regarding the quantity or quality of stores of mobile inorganic nutrients, organic carbon or its bioavailability in bench soils. Additionally, there is little information on how these stores vary across features of different heights in a river channel and how their release will be affected by processes occurring within the soil on inundation. Furthermore, there is a lack of knowledge regarding what is mobilised during flow pulses, when these features are inundated, a gap that has been highlighted by many authors (Davies et al. 1994, Puckridge et al. 1998, Sheldon 2005). The work presented in this thesis goes some way to filling these knowledge gaps and its major findings have been presented in two parts; (i) focussing on the soils of the different bench heights in the Gwydir River landscape and (ii) mobilisation and metabolism of solutes during a flow pulse. These parts are summarised below.

## **8.2 Bench soils – as sources and transformers of DOC and inorganic nutrients during periods of increased flow**

In-channel benches store large amounts of organic carbon and inorganic nutrients. When inundated, bench soils may be sources of organic carbon, stimulating in-stream heterotrophic productivity and inorganic nutrients stimulating both heterotrophic and autotrophic productivity (Hadwen et al. 2010, Westhorpe et al. 2010, Mitrovic et al. In Press). However, heterotrophic metabolism within the bench soil may affect the amount and form of inorganic nutrients mobilised while consuming organic carbon (Bostrom et al. 1988, Baker et al. 1999, Morrice et al. 2000). These heterotrophic processes are dependent

on the amount of carbon and electron acceptors that are stored in the bench soil prior to inundation and the type and rate of microbial processes that occur in the soil during inundation (Tiedje et al. 1984, Baker et al. 1999). These processes are likely to vary with inundation frequency and soil characteristics within a river channel.

## **8.3 The bench levels in the Gwydir channel**

### **8.3.1 Channel bed (CH)**

During sampling this level was found to be saturated due to its proximity to the standing water level in the Gwydir River itself. During periods of extreme low flow the sediments of this level may dry out, however, under the current regulated flow regime these are rare and short events (Chapter 7); thus, this level has been assumed to be permanently saturated. Investigation into the characteristics of the CH level were limited to its stores of water extractable DOC and inorganic nutrients, which were both found to be low (Chapter 3). The saturated state and low standing stocks of leaf litter were thought to be the cause of the low DOC and inorganic nutrient stocks found in this level. However, the CH level had high stocks of  $\text{NH}_4^+$  which may be due to the restriction of nitrification caused by the saturated nature of these sediments (Chapter 3). The potential for inundation of this level during flow events is high, given its low position in the river channel (Chapter 2); however, its ability to facilitate productivity via its frequent connectivity to the channel is limited due to the low stores of leaf litter, DOC and inorganic nutrients in CH soils (Chapter 3).

The types and rates of metabolism found when this level was inundated (as opposed to saturated) were prohibited due to their low saturated hydrological conductivity (Chapter 4) and therefore no conclusions can be drawn about the role that metabolism in the channel level plays during flow pulses when it is inundated. However, due to the saturated nature of this level it is unlikely that inundation, following short periods of desiccation, would either release large quantities of DOC or inorganic nutrients into the river or increase rates of metabolism enough to affect concentrations of DOC or inorganic nutrients in the river.

### **8.3.2 Bench 1 (B1)**

This level was the lowest in-channel bench level that was frequently exposed in the Gwydir River channel. When compared to the CH level the stocks of leaf litter, total soil carbon, the amount of mobile soil DOC,  $\text{NO}_3^-$  and DRP were significantly higher (Chapter 3). However, no difference was found in the amount of sand, silt or clay content between the CH and B1 levels (Chapter 3). This build-up of leaf litter and soil carbon suggests that the B1 level is more terrestrial than the CH level. It is likely that when increases in flow inundate the B1 level they connect more diverse soil patches facilitating larger releases of DOC,  $\text{NO}_3^-$  and DRP when compared to the CH level therefore inundation of the B1 level is likely to facilitate greater increases in production and respiration in the Gwydir channel when compared to the CH level (Hadwen et al. 2010, Westhorpe et al. 2010).

The increased amounts of soil carbon, DOC and leaf litter that make B1 more ‘terrestrial’ than the CH level, and the frequent inundation of this level, are likely to have contributed to the B1 level having the highest rates of inundated soil metabolism of any level in the Gwydir River channel. B1 soil metabolised the most organic C during experimental inundation (Chapter 4) and it seems likely these high rates of metabolism are responsible for reducing the FBDOC<sub>30</sub> found in the soil of this level (Chapter 3). The high rates of metabolism found during the inundation of the B1 level were suggested to be due to its microbial community being able to adapt to the conditions brought about with inundation relatively quickly by utilising a greater variety of alternative electron acceptors, often at higher rates, than other levels in the Gwydir River channel (Chapter 4). The high rates of metabolism and variety of metabolic pathways found in the B1 soil are likely to affect what is mobilised from this level during inundation. On inundation, soils of this level will quickly start consuming any  $\text{NO}_3^-$  in the pore water and then become a sink for surface water  $\text{NO}_3^-$ , while the production of  $\text{Fe}^{2+}$  by this soil after 40 hours of inundation (Chapter 4) suggests that it may be able to mobilise greater amounts of phosphate than what was extractable with river water (Chapter 3).

### **8.3.3 Bench 2 (B2)**

In terms of position in the channel the B2 level was the intermediate level between B1 and the FP levels and showed characteristics that reflected this position. This intermediate position was reflected in the amount of sand and silt, the amount of surface leaf litter, the total amount of soil carbon, DOC, DRP and  $\text{NO}_3^-$  (Chapter 3). However, the intermediate position of B2 was not reflected in the fraction of bioavailable DOC likely to be released on inundation, which was the highest of any level, nor in the amount of  $\text{NH}_4^+$  found in its soil, which was the lowest of any level (Chapter 3). The lower inundation frequency of the B2 level compared to B1 level leaves the soil aerobic for longer periods of time which increases the potential for nitrification to reduce stores of  $\text{NH}_4^+$  and increase  $\text{NO}_3^-$  (Chapter 3). The high FBDOC<sub>30</sub> found in the soils of the B2 level seems likely to result from a combination of a reduced inundation frequency at this height in the channel compared to the B1 level, reducing the frequency of increased soil metabolism associated with inundation (Valett et al. 2005, Wilson et al. 2011), and fresher inputs of organic carbon resulting from younger stores of surface leaf litter compared to the FP level (Chapter 3).

Chapter 4 illustrated that the amount of DOC consumed during artificial inundation of B2 soil, which is likely to be mostly from the stores of BDOC<sub>30</sub>, was found to be intermediate between the B1 and FP levels. The rate of soil metabolism during inundation of this level is likely to be high enough to affect water chemistry during a flow event, however, not as strongly as the B1 level. Denitrification within the soil of the B2 level began to consume the  $\text{NO}_3^-$  released into the pore waters within 12 hours of inundation (Chapter 4). If, at this point, the surface water over B2 soils contained  $\text{NO}_3^-$  diffusion would cause the net movement of  $\text{NO}_3^-$  into the soil where it would be denitrified and lost from the system (Hill 1996), thus the B2 level would become a sink for  $\text{NO}_3^-$ .

Given longer periods of inundation it is possible that this soil could further affect the exchanges occurring between aquatic and terrestrial ecosystems with the onset of other anaerobic soil processes. Although not observed during the 6 days of inundation used during the TEAPs experiment (Chapter 4) a number of other TEAPs such as  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$

reduction and methanogenesis could occur in these soils given longer periods of inundation found during larger flow pulses or floodplain inundation events. Therefore, these soils may, during longer periods of inundation, become a source of phosphate due to  $\text{Fe}^{3+}$  and  $\text{SO}_4^{2-}$  reduction occurring in the soils as well as a source of  $\text{CH}_4$ , a powerful greenhouse gas.

### 8.3.4 Floodplain (FP)

The FP level was the highest geomorphic level investigated in the Gwydir River, this position is reflected in many of its physical and biological properties. The FP level had the highest content of silt and clay, DOC, DRP and the largest standing stocks of leaf litter of any of the levels investigated (Chapter 3). An increasing amount of leaf litter, DOC and DRP was consistently found with increasing height in the Gwydir River landscape, including the floodplain (Chapter 3). However, in regard to  $\text{NH}_4^+$  and  $\text{NO}_3^-$  the floodplain level did not follow patterns established on other levels. On lower levels, an increase in level height resulted in lower soil  $\text{NH}_4^+$  and higher soil  $\text{NO}_3^-$ , but the FP level had more  $\text{NH}_4^+$  and less  $\text{NO}_3^-$  than would have been expected if this pattern had continued (Chapter 3). There are two likely causes that contributed to this variation (i) that the greater stores of leaf litter on the FP provided a greater source of  $\text{NH}_4^+$  than on other levels and (ii) that soil moisture on the level was governed by different factors compared with levels lower in the Gwydir River channel which restricted nitrification converting  $\text{NH}_4^+$  to  $\text{NO}_3^-$  in this soil. Therefore, when inundated the FP level is likely to be a large source of DOC, DRP and  $\text{NH}_4^+$  to the river, whereas other levels lower in the channel may not be able to provide exchanges of these elements that are as large.

For floodplain soils, the rate of soil metabolism during inundation was lower than in soils from either B1 or B2 levels. These lower rates may be due to the microbial community found in the soil of this level not being able to quickly adapt to the conditions brought about by inundation, perhaps due to the infrequency of inundation events at this level (Chapter 7). This suggests that unless inundated for periods longer than 6 days the biological activity occurring within FP soils is unlikely to affect the concentrations of DOC or inorganic nutrients found in the river.

## **8.4 Flow pulse**

### **8.4.1 Solute expression**

The complexities of undertaking research in river systems with high flow variability means that flows don't often occur when and where you want them to. The flow pulse studied here occurred in a different but adjacent river system, the Namoi River, to the investigation on soil properties of a lowland river channel which commenced in the Gwydir River. However, given the similar physical, hydrological, climatic and land use characteristics between the two catchments, using the findings from the investigations of soils in the Gwydir River to attempt to explain the expression of solute concentration during the Namoi River flow event is possible (Chapters 2 and 5). Particularly given that the major influence on stores of nutrients and carbon found in the soil of a riverine landscape are likely to be their organic content, soil texture and inundation frequency, which are likely to vary similarly across in-channel benches in both river systems (Chapter 3, Chapter 4, Reddy and Patrick 1984, Baldwin and Mitchell 2000, Valett et al. 2005)

It has been suggested by many authors that in-channel features are a major source of mobilised solutes during flow events in Australian lowland rivers (Sheldon and Thoms 2006, McGinness and Arthur 2011, Southwell and Thoms 2011, Westhorpe and Mitrovic 2012). If this is correct then the expression of solute concentrations in these rivers will be affected proportionally more by inundation of different bench levels within the channel than by catchment hydrology, which is the dominant controller of solute expression in high order streams (Boyer et al. 1997, Buffam et al. 2001, Inamdar et al. 2011). Additionally, the high infiltration and low runoff coefficient of Australian lowland rivers (Thoms and Sheldon 2000a) reduces the amount of water that reaches the river if these rainfall events occur in the lowland areas. During these events, the high infiltration rate and low runoff coefficient of lowland areas reduces the amount of water reaching the river and therefore, the affect that runoff flow path has on solute expression in the river. Thus, in an alloegenic river the mobilisation of material as the flow pulse moves downstream is likely to have a stronger

influence on the expression of solute concentrations than the flow path taken to reach the river.

The conceptual model presented in Chapter 1 divided the mechanisms of mobilisation into two categories; an initial flush known as the Birch effect and secondary mobilisation involving soil processes. Concentrations of solutes flushed from the soil are likely to peak either on the rising limb of the hydrograph or at peak flow, while concentrations of solutes mobilised by soil processes are likely to peak on the falling limb, when soils have been inundated for sufficient time for biological processes to be operating at rates high enough to affect surface water chemistry (Chapter 4, Chapter 5, Pacini and Gächter 1999, Banach et al. 2009b). During the sampled period of the flow event in the Namoi River, peaks of turbidity, TN, TON,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , TP and PP all occurred on the rising limb of the flow hydrograph suggesting that they were all flushed from the soils of in-channel features (Chapter 5). On the hydrograph falling limb peak concentrations of DOC and DRP were observed suggesting that they were mobilised by soil processes rather than flushed from the soils (Chapter 5).

From the investigation of soil properties (Chapter 3), levels B1 and B2 had the largest stores of  $\text{NO}_3^-$  suggesting that the peak in  $\text{NO}_3^-$  observed during the monitored period of the flow pulse in the Namoi River was likely a result of  $\text{NO}_3^-$  flushed from these low lying features. After the peak flow  $\text{NO}_3^-$  solute concentrations declined until late on the falling limb of the hydrograph (Chapter 5). This decline is likely to have been caused by either denitrification or dilution, but given the high denitrification rates found in Chapter 4 in the B1 and B2 level soils after inundation denitrification is likely to have played a key role. Concentrations of  $\text{NH}_4^+$  also peaked during the sampled period of the rising limb but concentrations of  $\text{NH}_4^+$ , found in B1 and B2 soils, were low making the soil an unlikely source. The B1 level did, however, have the largest stores of leaves in its leaf litter, which has been shown in headwater catchments to be a major source of  $\text{NH}_4^+$  to streams during storm events (Inamdar 2007). The dynamics of  $\text{NH}_4^+$  during the sampled period of the flow event were not solely determined by either flow or soil processes but rather exhibited a diel pattern in concentration (discussed below).

Concentrations of DRP during the flow pulse, studied in Chapter 5, suggested that DRP was both flushed from soil and released by soil processes. During this event concentrations of DRP increased during the sampled period of the rising limb, suggesting it was flushed from soils, however, peak concentrations were found on the falling limb, suggesting DRP was also affected by soil processes. Flushing of DRP from soils has previously been observed during the re-wetting of dried lake sediments (Qiu and McComb 1995) and given the increasing amounts of flushable DRP found with greater height in the Gwydir River channel (Chapter 3) increasing DRP concentrations with increased flow could be expected. The occurrence of peak DRP concentrations coincided with the lowest surface water DO concentrations suggesting the influence of anaerobic soil processes in mobilising DRP from inundated in-channel features (Chapter 5). The peak in DRP concentration after peak flow is likely to be caused by  $\text{SO}_4^{2-}$  and  $\text{Fe}^{3+}$  reduction, which are associated with the release of P bound to Fe oxides and oxyhydroxides (Bostrom et al. 1988, Roden and Edmonds 1997), rather than flushing from inundated soils. In the Gwydir River soils  $\text{Fe}^{3+}$  reduction was observed to begin in the B1 level soil and  $\text{SO}_4^{2-}$  reduction in all soils by this time at approximately the time that surface water DO concentrations were at their lowest suggesting their influence on DRP concentrations during the flow pulse in the Namoi River.

Like DRP, concentrations of DOC also peaked on the falling limb of the flow hydrograph suggesting they were not simply flushed from the inundated soils. Similarly to DRP the amount of DOC found in the soil of the different levels in the Gwydir River channel increased with greater height in the channel. Flushes from these levels with greater stores are likely to be the reason for the consistent increase in DOC concentration during the rising limb of the hydrograph (Chapter 5). However, unlike DRP, heterotrophic soil processes will consume DOC rather than release it from soil (Baker et al. 1999). This would cause concentrations of DOC in the surface water to reduce not increase as rates of soil biological processes increase with greater periods of inundation (Chapter 4). Using mesocosms filled with soil and leaf litter that were flooded with river water, Hladyz et al. (2011) showed that peak concentrations of DOC occurred after 4 days of inundation, suggesting that DOC is continually realised from soils after inundation which may partially explain peak DOC

concentrations occurring on the falling limb of the flow hydrograph (Chapter 5). This, combined with the increasing stores of leaf litter and soil carbon found with increasing height in the Gwydir River channel, may explain peak DOC concentration occurring after peak flow height.

## 8.5 Diel patterns in $\text{NH}_4^+$ and DOC during the flow pulse

The concentrations of  $\text{NH}_4^+$  and DOC during the flow pulse varied on a diel basis, a pattern which is unable to be explained by either flushing from soils or soil processes. Chapter 5 suggests that these diel patterns were caused by either the photodegradation of DOM increasing in-stream heterotrophic metabolism or increased rates of afternoon algal production. However, increased algal production is likely to be coupled to an increase in the uptake of  $\text{NH}_4^+$  (Sabater et al. 2000, Hall Jr and Tank 2003) reducing daytime  $\text{NH}_4^+$  concentrations, the opposite pattern to that observed during the flow pulse.

Photodegradation produces highly bioavailable forms of DOC that may be utilised in the water column by heterotrophic bacteria, driving down daytime DOC concentrations, which increase again after photodegradation ceases at night due to the leaching of DOC from inundated soil and leaf litter. Photodegradation of DOM also produces  $\text{NH}_4^+$  but, stoichiometrically, much less is produced per unit of DOM photodegraded (pers comm J.B. Fellman). This means that at night, photodegradation and the photolytic production of  $\text{NH}_4^+$  ceases but rates of heterotrophic metabolism may remain high due to the greater amounts of bioavailable DOC. This continued metabolism consumes the available  $\text{NH}_4^+$  causing the decline in  $\text{NH}_4^+$  concentrations observed during the evenings of the flow pulse.

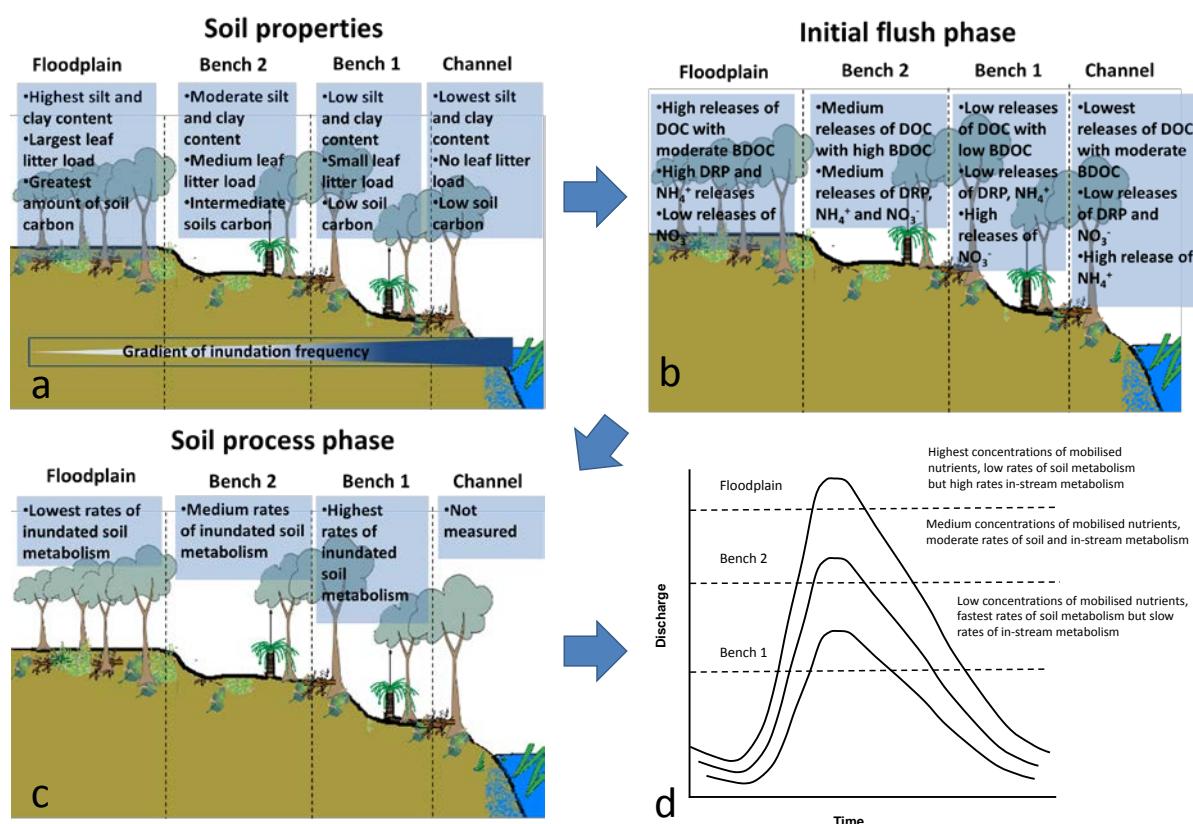
The evidence presented in Chapter 6, though not conclusive, suggests that it is photodegradation of DOM and the subsequent metabolism of the photoproducts rather than algal production that is responsible for the diel patterns in DOC and  $\text{NH}_4^+$  observed during the flow event in the Namoi River. The increase in  $\text{NH}_4^+$  concentrations and GPP rates, which were negatively correlated with  $\text{NH}_4^+$  concentrations (Chapter 6), found in mesocosms exposed to a natural light regime compared to the light excluded treatment suggest that photodegradation of DOM was occurring in the natural light treatment. The

lack of an increase in community respiration resulting from the photodegradation of DOM, consuming DOC and  $\text{NH}_4^+$ , was speculated to be caused by the use of mesocosms reducing flow velocities and therefore concentrations of suspended sediments and the bacterial population attached to them (Bent and Goulder 1981, Crump and Baross 1996, Ochs et al. 2010) which reduced rates of respiration in the surface water of the mesocosms.

Increased rates of sediment attached bacterial metabolism caused by photodegradation of DOM producing bioavailable DOC may provide a mechanism to increase retention of carbon and nutrients mobilised during flow pulse events. Sediment with its attached bacteria will fall out of suspension as flow decreases, thus retaining within the reach any carbon and nutrients assimilated by the bacteria during the flow pulse. To give some estimate of the size of this potential retention mechanism, it is possible to estimate the growth of bacteria from the observed diel changes in DOC load during the flow pulse. Night and day DOC loads were calculated using the mean DOC concentrations for each period (day and night) which was multiplied by the volume of flow in that period. These daily night and day DOC loads were then averaged across the 6 days of the flow pulse. The difference between the average day and night loads was 131 tonnes (Chapter 5). If this difference was caused by heterotrophic metabolism of the DOC we can apply bacterial growth efficiencies to estimate the resulting bacterial biomass. Del Giorgio and Cole (1998) reviewed the literature regarding bacterial growth efficiency in natural aquatic systems and reported an average in riverine systems of 0.22. Thus, an average of 29 tonnes of bacterial growth is estimated to have occurred each day in the flow pulse, if the diel changes in DOC were solely caused by heterotrophic metabolism. This is a very rough estimate, as DOC dynamics during the flow pulse would have been affected by many other factors including algal production, bacterial respiration and photolytic production of CO and  $\text{CO}_2$ . It does, however, provide some idea of the potential of bacterial utilisation of mobilised carbon and nutrients during the flow pulse.

## 8.6 A conceptual model for the role of in-channel benches and flow pulses in Australian lowland rivers

In-channel features such as benches, and the flow pulses that inundate them, play an important but little understood role in the ecology of lowland rivers. This thesis aimed to improve our understanding of the role that in-channel benches play in facilitating exchanges between terrestrial and aquatic ecosystems during flow pulses in lowland floodplain rivers. The conceptual model presented in Chapter 1 (Figure 1-6) has been updated with the findings from this thesis (Figure 8-1).



**Figure 8-1:** Updated conceptual model on the effects of inundation frequency on a) soil resources at different heights in a dryland river channel , b) release of carbon and nutrients on inundation, c) rates of soil metabolism during inundation, and d) concentrations of carbon and nutrients during flow events.

### **8.6.1 Key features of the updated conceptual model**

1. The amount of SRP, DOC and BDOC<sub>30</sub> found in the soil of the different bench levels in the Gwydir River landscape did fit the originally proposed model, increasing with height in the landscape. However, the amount of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and FBDOC<sub>30</sub> did not fit this model.

The distribution of NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> were affected by inundation frequency, with the saturated CH level having low stores of NO<sub>3</sub><sup>-</sup> and high stores of NH<sub>4</sub><sup>+</sup>. This pattern altered with greater bench height within the channel, with decreasing amounts of NH<sub>4</sub><sup>+</sup> and increasing amounts NO<sub>3</sub><sup>-</sup> on each successively higher level above the CH level. However, it did not hold on the highest level in the landscape, the FP, where large stores of NH<sub>4</sub><sup>+</sup> were found.

Stores of soil FBDOC<sub>30</sub> were not related to the amount of DOC found in the soil from each level or its height in the channel. Rather, it varied across the different levels in the landscape. The reason for this variation seems to be dependent upon each individual level rather than being caused by an overriding effect of distance from channel bed. For example, the B1 level had the lowest FBDOC<sub>30</sub> which was likely related to its high inundation frequency, while the B2 level which had the next highest inundation frequency had the highest FBDOC<sub>30</sub> of any of the levels in the Gwydir landscape. It is likely that the B2 level had the highest FBDOC<sub>30</sub> as it has a larger supply of leaf litter and lower inundation frequency than lower levels lower and its leaf litter was of a higher quality being younger than that found on the FP level (Baldwin 1999).

2. The original conceptual model predicted that rates of inundated soil metabolism were related to the amount of organic carbon found in the soil, however, results from the thesis suggest a soils inundation frequency determines the rate of soil metabolism during inundation. The FP level had the lowest rates of soil metabolism during inundation (Chapter 4) but the highest stores of soil carbon (Chapter 3).

These low rates of metabolism were considered to be caused by the inability of the microbial community of this level to adapt to the changing conditions caused by inundation. The B1 level, with the most frequently inundated soil, had the highest rates of inundated soil metabolism and was able to switch to a variety of alternative electron acceptors in order to achieve this rate of metabolism (Chapter 4). The ability of the resident microbial community in a terrestrial soil to adapt to periods of inundation was suggested to be related to the historical soil inundation frequency, where a history of greater inundation frequency increases the ability of a soils microbial community to adapt to the conditions brought about by inundation and lower inundation frequency decreases the soil microbial communities ability to adapt to inundation.

3. The flow pulse observed in the Namoi River mobilised large amounts of organic carbon and inorganic nutrients. However, unlike the predictions in the original conceptual model the highest concentrations of solutes occurred both on the rising limb and falling limb of the hydrograph rather than at the flow peak. In the original conceptual model peak flow was predicted to have the highest solute concentrations due to the largest land area being inundated. However, possibly due to an uneven distribution of both inorganic nutrients in the channel, as described in Chapter 3, and the process which mobilised these solutes from the inundated in-channel features, peak concentrations of DOC and inorganic carbon occurred at various points during the flow hydrograph.

The original conceptual model did not include any metabolism occurring in-stream during a flow pulse. However, diel patterns in DOC and  $\text{NH}_4^+$  found during the flow pulse are suggestive that high rates of in-stream metabolism occurred during the passage of the flow pulse. Although the mechanism causing these patterns was not clearly identified, chapters 5 and 6 suggest that the driving mechanism behind these patterns was photodegradation of terrestrially derived DOM into  $\text{NH}_4^+$  and labile forms of DOC. The labile forms of DOC fuel increases in in-stream metabolism consuming DOC during the day decreasing concentrations compared to those

observed at night. Due to a larger production of labile DOC compared to  $\text{NH}_4^+$ , due to the stoichiometry of DOM (pers comm J.B. Fellman), rates of in-stream metabolism continue to be elevated into the evening due to the larger supply of DOC after the photolytic production of  $\text{NH}_4^+$  has ceased causing  $\text{NH}_4^+$  concentrations to decline in the early evening. Given the large quantities of carbon that seem to have been metabolised during the flow event and its potential role in retaining organic carbon in these systems, further investigation into these diel patterns is warranted.

## 8.7 River management and environmental flows

This thesis has shown that in-channel benches contain large stores of organic carbon and inorganic nutrients that are able to be mobilised during periods of inundation. However, flow regulation of many lowland rivers in Australia (Thoms and Sheldon 2000a) has reduced the frequency of flow events, particularly the more frequent small flow events such as the one described above for the Namoi River. In an attempt to increase the magnitude and frequency of small to medium sized flow pulses, the ones most impacted by flow regulation, flow rules have been introduced into the Gwydir and Namoi Rivers. These flow rules restrict the water available to irrigators during reservoir spills or when high flows enter the river from unregulated tributaries (Westhorpe et al. 2008). Chapter 7 suggests that these flow rules do not significantly increase the frequency or duration that any in-channel bench in the Gwydir River channel is inundated. This lack of an increase in bench inundation with flow rules was suggested to be caused by a geomorphological change to the Gwydir River channel, increasing the height of the lowest bench, rather than the flow rules not increasing flow height and/or frequency of flow pulses. However, flow rules did increase the duration of flow pulses below the lowest remaining bench level in the Gwydir River which, in time, may re-build in-channel benches at this level that were proposed to have been lost due to flow regulation. But whether the flow rules are sufficient to re-create the allegedly lost in-channel bench levels requires further investigation.

## **8.8 Conclusions**

In-channel benches and the flow pulses that inundate them are part of the ecology of Australian lowland rivers. Their loss due to flow regulation is likely to have contributed to the declines in aquatic ecosystem health recently noted by Davies et al. (2010). This thesis has shown that in-channel benches store large amounts of DOC and inorganic nutrients that are released into the river during inundation events. Rates of metabolism during inundation within the soil of in-channel benches was found to be relative to in-channel bench inundation frequency, with rates of metabolism higher in in-channel benches that are frequently inundated compared to less frequently inundated in-channel benches. The thesis has also suggested that during these events rates of in-stream metabolism increase to rates sufficient to cause the observed diel pattern in the concentration of DOC and  $\text{NH}_4^+$  observed during the flow pulse in the Namoi River, the ecological consequences of which requires further investigation.

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"Diel variation of dissolved organic carbon during large flow events in a lowland river", by Douglas P. Westhorpe, Simon M. Mitrovic, k. Benjamin Woodward, in "Limnologica" 42 (2012) 220-226.

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