Phosphorus retention and metabolism: indicators of stream deterioration across a rural-urban gradient?

by

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List of abbreviations

Benthic organic matter	BOM
Coarse particulate organic matter	CPOM
Community respiration	CR
Decay coefficient	•
Dispersion coefficient	D
Dissolved organic carbon	DOC
Filterable reactive phosphorus	FRP
Fine particulate organic matter	FPOM
Gross primary production	GPP
Mass transfer coefficient	v_f
Net ecosystem production	NEP
Net primary production	NPP
Production rate	•
Retardation factor	R
Stream velocity	v
Total carbon	TC
Total nitrogen	TN
Total phosphorus	TP
Uptake length	S_w

Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I consent to the thesis being made available for photocopying and loan if accepted for the award of the degree.

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Kane Thomas Aldridge

27th October 2005

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Summary

Much attention has been paid to the effects of anthropogenic impacts upon physical and chemical conditions in freshwater ecosystems. However, impacts upon the functioning of these ecosystems and services that they provide remain relatively unknown. The objective of this thesis was to examine the validity of the general hypothesis that the deterioration of ecosystems may be reflected in their capacity to process resources.

Changes in stream phosphorus retention and metabolism were investigated across a rural-urban gradient in the Torrens River Catchment, South Australia, where channel structures of rural reaches are less modified than urban reaches. In a stream with an intact upper rural catchment (First Creek), a reach with an un-modified channel structure retained 60% $\pm$ 12.1 filterable reactive phosphorus (FRP) and had an average uptake length of 79 m $\pm$ 3.4. In comparison, degraded and engineered reaches of First Creek retained less FRP and had longer uptake lengths. In Fourth Creek, which is influenced by agriculture, there were no differences in FRP retention between the reaches. Reduced FRP retention in impacted reaches were a result of decreased contact time, reduced period of continuous flow and increased nutrient availability. Although abiotic benthic FRP uptake rates (up to 6.8 •g m^{-2} s^{-1} $\pm$ 0.36) were consistently greater than biotic uptake rates (up to 3.6 •g m^{-2} s^{-1} $\pm$ 0.52), decreased total benthic uptake rates in impacted reaches were mainly due to decreased biotic uptake.

Metabolic rates were measured within benthic chambers containing rocks and gravel and scaled up to the stream reach. At chamber and reach scales, metabolic rates in the un-modified reach of First Creek were consistently low (community respiration (CR) up to 113 mg O_2 m^{-2} day^{-1} $\pm$ 47.4 and gross primary production (GPP) up to 234 mg O_2 m^{-2} day^{-1} $\pm$ 89.5), with a positive net ecosystem production (NEP). In comparison, the degraded reach of First Creek switched between having a negative and positive NEP. Reaches of Fourth Creek also experienced considerable variation and had higher metabolic rates than First Creek (CR up to 371 mg O_2 m^{-2} day^{-1} $\pm$ 62.1 and GPP up to 847 mg O_2 m^{-2} day^{-1} $\pm$ 66.1). Increased metabolic rates in impacted reaches were attributed to increased light availability and reduced grazing by higher trophic levels, promoting autotrophic organisms.

The altered ecosystem functions were considered to reflect a reduced capacity of deteriorated streams to process resources. However, the addition of coarse particulate organic matter to a degraded-urban stream reach increased CR and reduced NEP to levels more akin to those experienced within pristine streams. Furthermore, percent FRP retention increased, primarily through increased demand for phosphorus of the microbial community.

Although this demonstrated that rehabilitation of in-stream attributes might restore important ecosystem functions in impacted streams, successful restoration will only be achieved if the over-riding causes of in-stream degradation are addressed.

Foreword

This thesis has been prepared as a series of chapters in a format that will be suitable for future publication in scientific journals. To maintain the sense of individual chapters, this has inevitably led to some repetition between chapters.

Chapter one

1 General introduction

1.1 Ecosystem services and functions and biological diversity

Human existence depends upon the services that ecosystems provide. These services include; maintaining conditions favourable to humans, such as regulation of the Earth's climate; and allowing practices essential for survival, such as food production (Costanza *et al.* 1997). Freshwater ecosystems provide a substantial portion of the total global value of Earth's ecosystem services, despite the relatively small area that they cover (Costanza *et al.* 1997). These services are provided through functional processes, such as primary production and organic matter breakdown, which provide a basal energy source for lotic food-webs, allowing removal of a fishable resource for human consumption (Meyer *et al.* In press). Another functional process is nutrient and contaminant uptake, which improves water quality so that water is available for human consumption, the production of food and the protection of downstream ecosystems, such as estuarine and marine ecosystems (Meyer *et al.* In press).

The ability of an ecosystem to carry out such functions is dependant upon the species and functional diversity (Naeem *et al.* 1994; Hulot *et al.* 2000; Tilman 2000; Engelhardt and Ritchie 2001; Cardinale *et al.* 2002a; Mulder *et al.* 2002). This diversity also provides ecosystems with resistance and resilience against perturbations (Van Voris *et al.* 1980; Harris 1994; Tilman and Downing 1994; Naeem and Li 1997). Optimal biological diversity will be reached when an ecosystem experiences an intermediate level of disturbance, since no individual species or group of species will be favoured (Connell 1978; Townsend and Scarsbrook 1997). This diversity may result in multiple pathways of resource interception and transformation (Brookes *et al.* In press). An example of this is shown in Figure 1.1, which highlights how the diversity of stream ecosystems provides multiple pathways of resource interception and transformation.

When ecosystems experience persistent high or low disturbances, biological diversity declines, the resistance and resilience of that ecosystem declines (Harris 1994) and ecosystem functions may be altered. Brookes *et al*. (In press) proposed that in developed catchments, the replacement of native vegetation with agriculture and urban areas has resulted in reduced physical and biological diversity and a reduced number of pathways of resource interception and transformation (Figure 1.2). Consequently, resources are channelled into terminal water bodies with little processing. In addition, flow regulation creates a low disturbance environment, thus favouring the dominance of particular functional groups. An example of this is in Torrens Lake, South Australia, where a large amount of nutrients enter the artificially created lake following rainfall. This combined with the regulated water regime favour phytoplankton and bacterial communities leading to toxic algal blooms (Ganf *et al*. 1999) and deoxygenation (Wallace Unpublished data).

1.2 Impacts of changes in land-use on stream ecosystems

Freshwater ecosystems have experienced a reduction in their biological diversity via the removal of native vegetation and its replacement with agricultural and urban areas (Lake *et al*. 2000). A major impact of urbanisation is an increase in the area of impervious surfaces, which intensifies the connection between streams and their surrounding catchment (Booth and Jackson 1997; Walsh *et al*. 2004). This has reduced the amount of water infiltration through soil profiles and increased the amount of water entering streams as run-off, resulting in increased peak-flows and reduced base-flows (Walsh *et al*. 2004). Consequently, stream channels have been severely eroded, with simplification of stream habitats (Paul and Meyer 2001). This is also done directly by humans, with streams 'channelised' for flood mitigation (Lepori *et al*. 2005) and in some cases natural substrata are replaced with impervious surfaces. Urban streams also experience; increased inputs of contaminants, including heavy metals and nutrients (Paul and Meyer 2001; Hatt *et al*. 2004); altered water temperatures due to water inputs from impervious surfaces and removal of riparian vegetation (Paul and Meyer 2001; Walsh *et al*. 2004); reduced standing stocks of organic matter due to a reduced capacity of channelised streams to retain organic matter (Lepori *et al*. 2005) and reduced inputs from riparian vegetation.

These impacts are also experienced in streams in agricultural regions. However, the harvesting of water for agricultural purposes has reduced the magnitudes of peak-flows and reduced the amount of water passing through streams (Savadamuthu 2003). This may be particularly detrimental in regions that experience mediterranean or arid climates, where water harvesting may reduce the period of stream flow (Savadamuthu 2003).

While stream ecosystems have adapted to the extremely variable conditions that they experience (Boulton and Lake 1990; Bunn and Arthington 2002), changes in land-use have resulted in persistent low and high disturbance environments. For example, river regulation may reduce river flow (Bunn and Arthington 2002), while removal of riparian vegetation may increase river peak-flows (Walsh *et al*. 2004). These changes will act as low and high disturbances, respectively, and favour a fewer number of species than an intermediate flow regime (Townsend and Scarsbrook 1997). Consequently, in developed areas the structural integrity and functions of stream ecosystems are likely to be compromised. Without proper management there may be a loss of pathways of resource interception and transformation and a subsequent decrease in the efficiency of resource processing of the system (Figure 1.2).

1.3 Stream resource interception and transformation

Minor tributaries collect a majority of the water entering freshwater ecosystems (Peterson *et al*. 2001) and so act as important linkages between terrestrial environments and terminal water bodies. Consequently, interception and transformation of resources will have significant implications for downstream ecosystems and for control of problems associated with anthropogenic contaminant inputs. The efficiency of resource processing of streams may be reflected by ecosystem functions, such as nutrient retention and stream metabolism. Nutrient retention reflects the ability of a stream to intercept resources and stream metabolism provides an indication of the transformation of resources within various functional groups.

1.3.1 Nutrient retention

It is well documented that streams have the capacity to retain nutrients (McColl 1974; Meyer and Likens 1979; Newbold *et al*. 1981; Stream Solute Workshop 1990; Hart *et al*. 1991; Davis and Minshall 1999; Mulholland *et al*. 2001; Webster *et al*. 2003). Therefore streams may alter the amount and bioavailability of nutrients, in addition to slowing the rate of nutrient delivery to downstream ecosystems. Studies of nutrient retention have revealed considerable variation in the amount of nutrients retained within streams on spatial and temporal scales. This variation is attributed to differences in the environmental conditions that control biotic and abiotic pathways of nutrient uptake (Figure 1.1), including; temperature, light intensity, discharge and nutrient availability.

Early investigations of stream nutrient retention implied that the biological assimilation was the sole pathway (McColl 1974; Elwood *et al.* 1983) (Figure 1.1). Much of this assimilation was attributed to biofilms. Biofilms contain significant proportions of the total biomass of streams and consist of assemblages of algae, bacteria, fungi and protists within a polysaccharide matrix on the surfaces of inorganic and organic substrates (Lock *et al.* 1984). However, Hart *et al.* (1991) demonstrated that abiotic uptake contributed almost entirely to total phosphorus retention in an Australian stream, and Haggard *et al.* (1999) demonstrated that abiotic uptake resulted in 28-50 % of total sorption in three American streams. In comparison, Munn and Meyer (1990) suggested that abiotic uptake was less important than biotic uptake for phosphorus retention. Abiotic uptake of nutrients includes adsorption to the surfaces of sediment particles (Webster *et al.* 2001; House and Denison 2002) and surfaces of dead and living organisms (Sanudo-Wilhelmy *et al.* 2004), including biofilms (Lock *et al.* 1984; Flemming 1995).

The multiple impacts of changes in land-use upon stream ecosystems are likely to cause a reduction in the number and/or activity of biotic and abiotic pathways of nutrient retention. Consequently, the ability of a stream to retain nutrients may be used as an indicator of the efficiency of resource interception.

1.3.2 Stream metabolism

Stream metabolism encompasses the biological and chemical processes that stream organisms carry out in order to sustain life. At the ecosystem level, measurements of stream metabolism include, gross primary production, community respiration and net ecosystem production. Primary production and respiration of organic matter may convert resources that are retained within the stream into forms that are available to higher organisms (Rounick *et al.* 1982; Rounick and Winterbourn 1983; Stock and Ward 1989) (Figure 1.1). The utilisation of retained resources and transfer to higher trophic levels may represent efficient resource processing.

Much of the metabolism that occurs in streams is attributed to biofilms and so the metabolism of these communities will have major implications for stream ecosystems. A number of the factors that are influenced by changes in land-use have been shown to be important determinants of stream metabolism, including; light (Bunn *et al.* 1999), temperature (Bott *et al.* 1985), water regime (Uehlinger 2000; Acuna *et al.* 2004), nutrient availability (Tank and Webster 1998; Mosisch *et al.* 2001; Mulholland *et al.* 2001), organic matter (Tank and Webster 1998; Crenshaw *et al.* 2002; Stelzer *et al.* 2003; Acuna *et al.* 2004) and grazing (Rounick *et al.* 1982; Rounick and Winterbourn 1983). Consequently, alterations to stream metabolism are likely.

Measurements of metabolism may reflect the partitioning of resources within stream ecosystems, with high rates of primary production and respiration indicating a dominance of autotrophic and heterotrophic organisms, respectively. A dominance of functional groups has been shown to be reflective of inefficient transformation of resources as few resources are passed onto higher organisms (Bunn *et al.* 1999). Consequently, measurements of metabolism may be an indicator of the efficiency of resource transformation.

1.4 The project

The objective of this thesis was to examine the validity of the general hypothesis proposed by Brookes *et al.* (In press) that the deterioration of ecosystems may be reflected in their capacity to process resources. This was done by examining changes in nutrient retention and stream metabolism across a rural-urban gradient in the Torrens River Catchment, South Australia. In the Torrens River Catchment, the separation between rural and urban environments traverses five streams, representing a gradient from streams with un-modified channel structures in the rural environment to degraded and engineered channel structures in the urban environment.

Differences in the capacities of un-modified, degraded and engineered reaches to intercept resources are examined (chapters three and four). This was done by determining whether there are differences in the capacities of un-modified, degraded and engineered reaches to retain phosphorus (chapter three) and whether there are differences in abiotic and biotic pathways of phosphorus uptake among the reaches (chapter four). Differences in stream metabolism among the reaches are examined to determine whether they reflect differences in resource transformation (chapters five and six). This was examined using re-circulating benthic chambers (chapter five) containing different substrates, which allowed measurements to be scaled up to the stream reach (chapter six). Finally, it was examined whether there is potential to improve the efficiency of resource processing in degraded streams through the restoration of attributes of un-modified stream reaches (chapter seven). This was done by measuring phosphorus retention and stream metabolism in a degraded-urban stream, following the addition of coarse particulate organic matter.

While much attention has been paid to the effects of anthropogenic impacts upon physical and chemical conditions in freshwater ecosystems, impacts upon ecosystem functions have been overlooked (Boulton 1999). As the area of land affected by urbanisation and agriculture continues to grow, an understanding of the causes of differences in stream ecosystem functions between rural and urban streams is of paramount importance. An understanding will assist in management of these ecosystem functions, allowing the ecosystems to carry out services for humans. Costanza (1997) identified water treatment to be an essential ecosystem service provided by functions of freshwater ecosystems. Consequently, management of ecosystem functions associated with resource processing in streams will improve in-stream and downstream water quality, increase the amenity and recreational value of streams and promote the preservation of biological diversity. In fact, the restoration of ecosystem functions of freshwater systems may be a more appropriate procedure for the preservation of biological diversity than the preservation of individual species (Ward *et al*. 1999; Moss 2000).

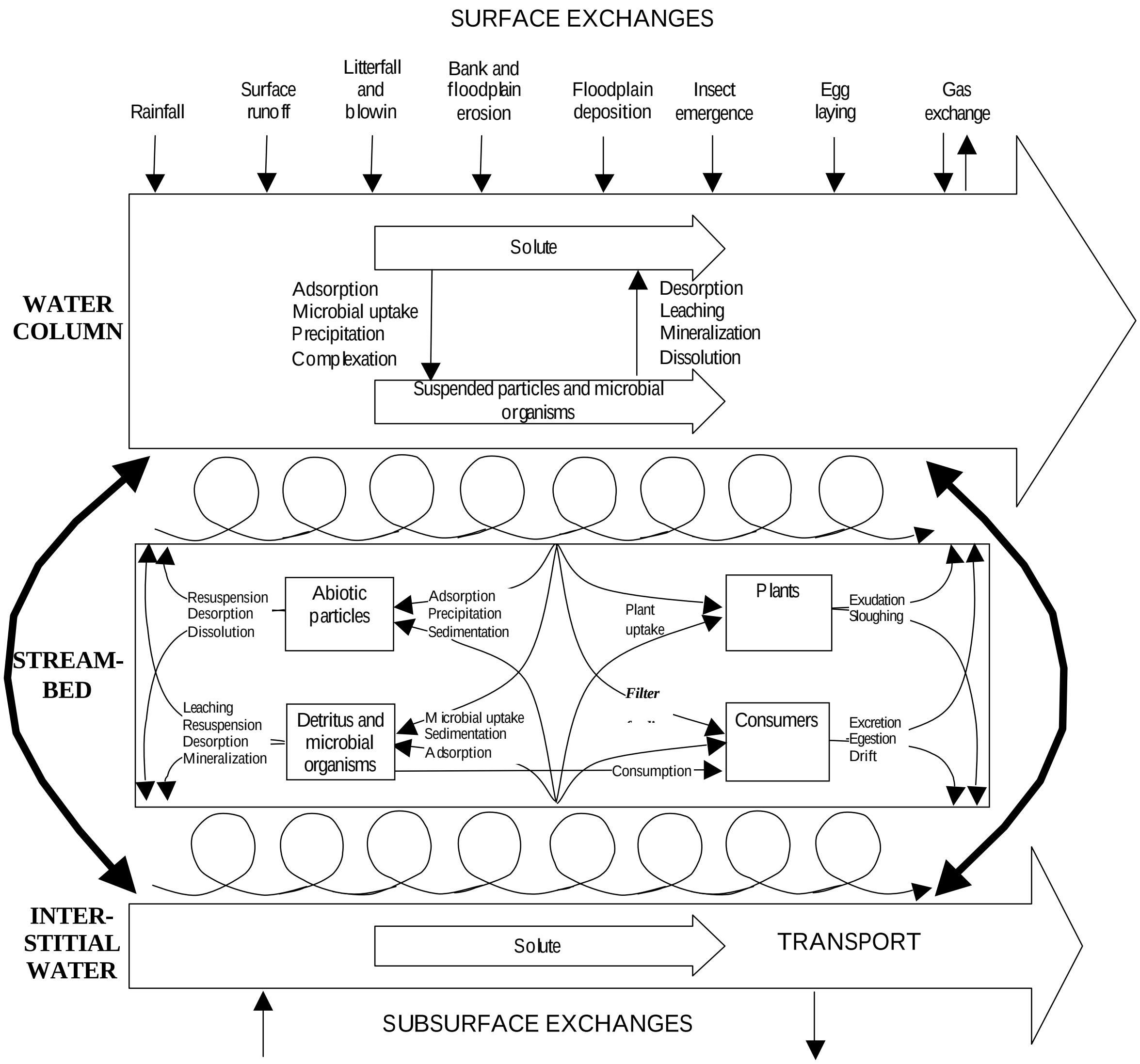
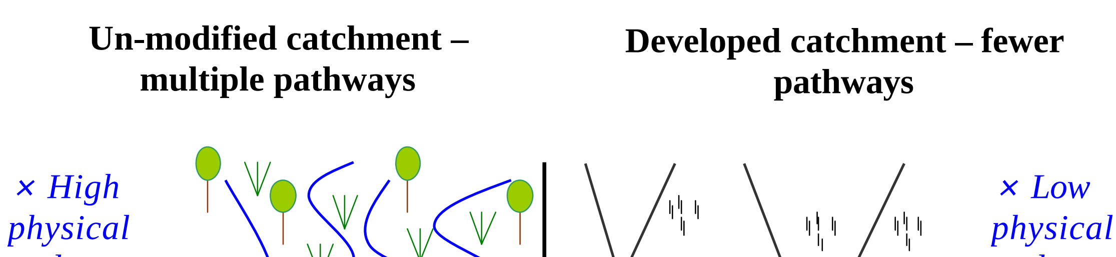


Figure 1.1. Conceptual diagram of solute processes in streams. The two spirals represent the continuous exchange of solutes and particle-bound chemicals between the streambed and water column and between the streambed and interstitial water. Materials in the water column and interstitial water are moving downstream, while the streambed materials are stationary (Stream Solute Workshop 1990).



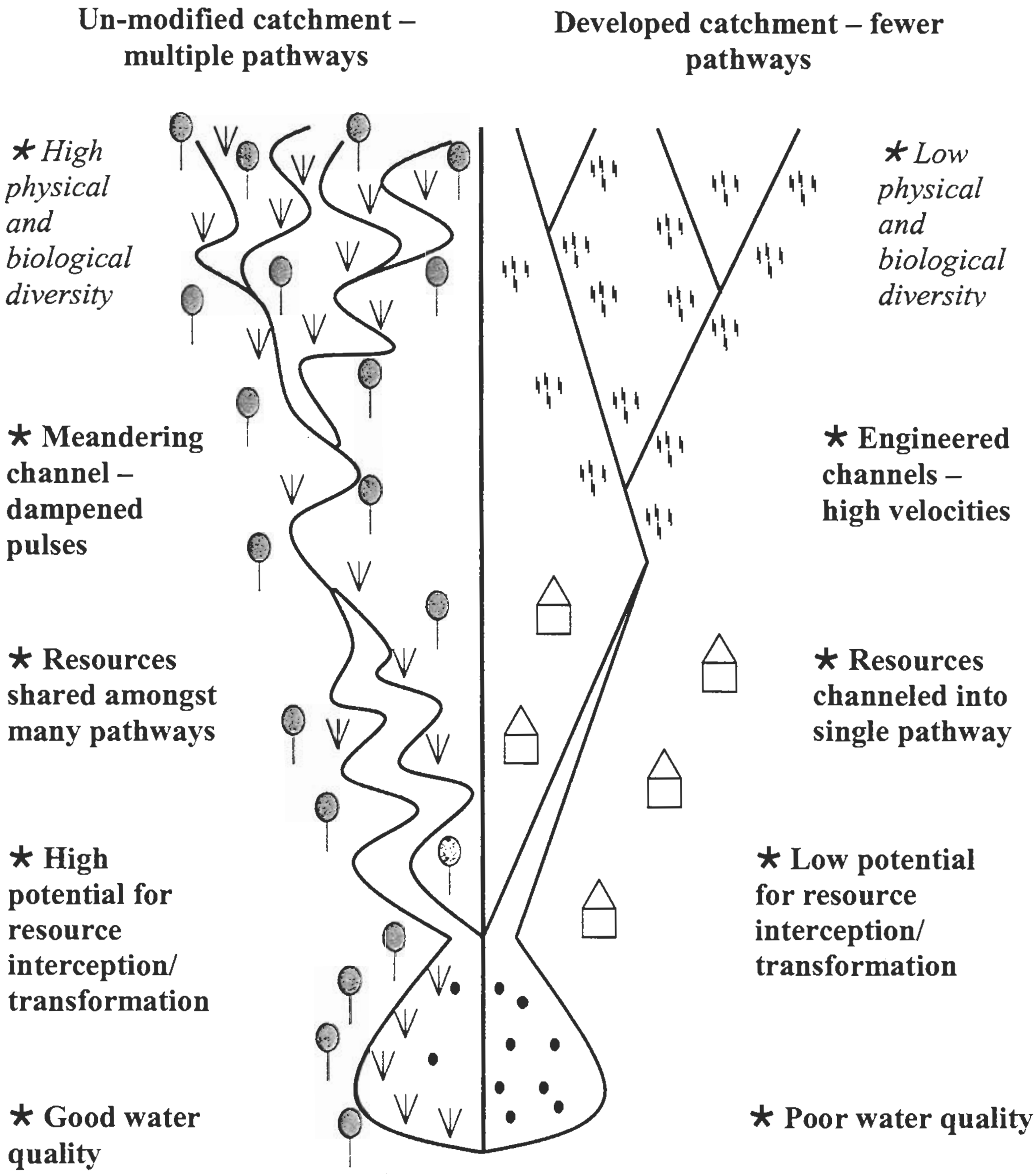


Figure 1.2. Conceptual diagram of resource dynamics in un-modified and developed catchments (Brookes *et al.* In press). The un-modified catchment has a complex physical structure and high biological diversity, as indicated by riparian and aquatic vegetation. This promotes multiple pathways of resource interception and transformation. The developed catchment has experienced habitat simplification and a reduction in biological diversity, with replacement of native vegetation with agricultural and urban areas. Consequently, there is a reduction in the number of pathways of resource interception and transformation.

Chapter two

2 Study site and general methods

2.1 Study site

Water quality is the biggest single factor affecting the future water supply and prosperity of South Australia (Department for Water Resources 2000). Algal blooms are a common occurrence in terminal water bodies of South Australia due to increased nutrient levels, particularly phosphorus (Department for Water Resources 2000). The Torrens River Catchment is an important area of South Australia, as it contains a majority of metropolitan Adelaide, the capital city, and supplies up to 60% of South Australia's domestic water (Tonkin Consulting 2002). The catchment is approximately 495 km^2 and accommodates approximately 500 000 people (Tonkin Consulting 2002). It is highly modified and supports multiple land-uses. It is dominated by urban and agricultural areas, with less than 15% of the area remaining as native vegetation (Tonkin Consulting 2002).

Within the lower rural-urban sub-catchment there is a distinct separation between urban and rural environments (Figure 2.1). This traverses five streams, representing a gradient from stream reaches with un-modified channel structures in rural areas to degraded and engineered channel structures in urban areas. Three reaches, 100 m in length, were chosen in each of First and Fourth Creeks to represent the shift in channel structure; a rural-un-modified, an urban-degraded and an urban-engineered (Figures 2.1-2.10). For chapter seven, an additional urban-degraded reach was chosen, which bifurcates into two discrete streams with approximately equal dimensions (Figures 2.11-2.12).

These streams are well mixed owing to the rapid, turbulent stream flow, shallow water and few pools. Flow in the rural section of Fourth Creek is impacted by the presence of upstream agricultural dams and flow ceases during summer and for most of autumn. Flow in the rural section of First Creek (Figure 2.13A) is not impacted by the presence of dams. Stream flow is highly variable; however, a majority occurs during winter and spring (Figure 2.13), reflecting the mediterranean climate of the region. Urban reaches experience reduced base-flow, a reduced period of continuous flow and increased peak-flows (Figure 2.13B).

Streambeds are typically dominated by rock and cobble substrates, with attached biofilms appearing to dominate production.

2.1.1 Landscape

The five streams of the lower sub-catchment begin in the Mount Lofty Ranges within narrow, steep-sided valleys. The streams follow a north-westerly path through the hills face zone and into the Torrens River on the Adelaide Plains, which now form suburbs of Adelaide (Figure 2.1).

The rocks of the Mount Lofty Ranges were laid down during the Precambrian era. A little less than five million years ago, this sediment, which was converted to sedimentary rock, was raised and formed a high mountain belt. This was followed by a period of weathering and erosion, which rounded the hills and then by another period of uplifting (tertiary period). This uplifting occurred along fault-lines and the fault-blocks were uplifted differentially. Consequently, the Mount Lofty Ranges now consist of steep fault-scarps rising abruptly on a flat-topped, titled, fault blocks.

During the Quaternary period (last two million years) the Adelaide Plains have been built up from material eroded from the hills and deposited by the streams of lower sub-catchment. The initial material came from a thin Tertiary cover overlying the hills and the clays were deposited on the plains over Tertiary marine rocks. The clays are overlain by more sandy material from the eroded Precambrian bedrock of the Mount Lofty Ranges. More coarse gravels were deposited in the alluvial fans of the foot-hills (sandstone, quartzite, shale, limestone and dolomite) and finer sediments were carried out on the plain (soft sand and limestone overlying sandy-clay).

Early accounts of vegetation in the region are lacking in detail. It appeared that much of the Adelaide Plains surrounding the five streams was an open savanna woodland, which was heavily timbered with River Red Gum (*Eucalyptus camaldulensis*) and Blue Gum (*Eucalyptus leucoxylon*) with a diverse understorey (Kraehenbuehl 1978). Accounts of vegetation along Second Creek and current vegetation along First Creek were used by Kraehenbuehl (1978) to gain an understanding of the vegetation that may have surrounded First Creek. Other dominant plants probably included Peppermint Gums (*Eucalyptus rostrata*), Golden Wattle (*Acacia pycnantha*), Native Pine (*Callitris preissii*), Sheoak (*Casuarina stricta*), Native Cherry (*Exocarpos cupressiformis*) and the South Australian

Christmas Bush (*Bursaria spinosa*). The diverse understorey probably consisted of a range of shrubs and smaller perennials and bulbous plants, orchids and grasses (Kraehenbuehl 1978). Within the stream beds there probably existed the common reed (*Phragmites communis*) and small sedges (*Scirpus cernuus*, *Schoenus breviculmis*, *Juncus caespiticius* and *Cyperus tenellus*).

Kraehenbuehl (1978) also suggests that the area surrounding Fourth Creek was also classified as an open savanna woodland, which was heavily timbered with River Red Gums and Blue Gums. Other dominant plants may have included the White Bottlebrush (*Callistemon salignus*), Blackwood (*Acacia melanoxylon*), *Bursaria spinosa*, *Casuarina stricta*, *Dodonaea viscosa* and *Acacia rotundifolia* and *Cyperus vaginatus* within the stream bed.

First and Fourth Creek sub-catchments have experienced considerable modification. In 2003, approximately half of the total area of the First Creek sub-catchment was contained within metropolitan Adelaide (Table 2.1). The remaining half was rural and approximately 83% of this area was protected native vegetation. The remaining 17% consisted of grazed native vegetation, residential, recreational and cultural areas. In 2003, approximately 33% of the Fourth Creek sub-catchment was contained within metropolitan Adelaide (Table 2.1). Unlike the sub-catchment of First Creek, the rural area of Fourth Creek contained significant development. Only 26% of the total rural area existed as protected native vegetation and almost half was grazed (Table 2.1). Other rural land-uses within the Fourth Creek sub-catchment included, residential, irrigated perennial horticulture, irrigated vine fruits, public services, softwood plantation and irrigated cropping and recreation and culture.

2.1.2 Channel structure

Each reach was surveyed to determine differences in channel structures (Table 2.2). To do this each reach was divided into cells 10 m in length and a 1 m by 1 m grid was randomly placed within each cell. Within the grid, percent cover of substrate (boulder, rock, gravel, sand, or cement) was estimated. In addition, the percent cover of coarse particulate organic matter (CPOM) was estimated. Stream width, stream depth at 10 cm intervals across stream width and bank height were also measured. Sinuosity was measured as the total reach length divided by the direct distance between the upper and lower points. Stream slope (reach length divided by fall distance) was measured using a Sokkisha TTL5 (Sokkisha, Tokyo, Japan) theodolite and staff.

Un-modified reaches have a complex meandering nature and natural substrate (Table 2.2, Figures 2.2 and 2.6). Erosion in the degraded reach of First Creek (Figure 2.3) has resulted in a wider channel structure, higher bank height, a greater cover of gravel/sand substrate and lower cover of coarse particulate organic matter than the un-modified reach (Table 2.2). One bend within the degraded reach of First Creek resulted in a high sinuosity. In the degraded reach of Fourth Creek (Figure 2.7), erosion has resulted in greater stream bank height, a greater cover of gravel/sand substrate and lower cover of CPOM than the un-modified reach (Table 2.2). The degraded reach of Fourth Creek has a narrower, channelised structure in comparison to the un-modified reach (Table 2.2).

To mitigate against erosion and flooding, the beds of engineered reaches have been replaced with cement-cobble or cement-slate substrates (Figures 2.4-2.5 and 2.8-2.9). Three pools were created in the engineered reach of Fourth Creek (Figure 2.10), but these reaches have retained little of their natural-channel structure, contain a small amount of their natural substrate and contain no CPOM (Table 2.2). The engineered reaches take the shape of the permanent substrate and so their channel structures are not influenced by erosion.

2.2 General methods

2.2.1 Filterable reactive phosphorus and dissolved organic carbon

Water samples (approximately 70 mL) were collected at the mid-point of the reach width and water depth. These samples were considered to be representative of the water column as the streams are well mixed and measurements of water temperature revealed no thermal discontinuities. Immediately following collection, samples were stored in the dark on ice. On return to the laboratory samples were filtered through a 0.45-••m Millipore® membrane filter. Filters were not pre-rinsed as analyses of filtered samples revealed undetectable concentrations, suggesting that there was an insignificant amount of phosphorus leached from the filters. Within 24 h, samples were analysed for filterable reactive phosphorus (FRP, also described as soluble reactive phosphorus) following the molybdenum blue technique (Mackereth *et al.* 1978). This was conducted using a Hitachi U-2000 spectrophotometer (Hitachi Ltd., Tokyo, Japan) with a path length of 10 mm. This analysis has a reported detection limit of 10 •g L^{-1}, however, with careful procedure an accuracy of 5 •g L^{-1} was achieved. Nevertheless, concentrations below the reported detection limit were treated with caution. Dissolved organic carbon concentrations were analysed using an SGE ANATOC II total organic carbon analyser (SGE, Melbourne, Australia). This was carried out in non-purgeable organic carbon mode using titanium dioxide as a catalyst in the presence of near-UV light. Prior to analysis samples were adjusted to pH 2.8 with 0.1 M perchloric acid and 0.1 M sodium hydroxide.

The number of moles of DOC and FRP in a given volume of water were calculated by dividing the mass of each molecule in that volume by the atomic weight. The DOC to FRP molar ratio was then calculated to indicate the relative availability of FRP and DOC molecules.

2.2.2 Benthic organic matter and chlorophyll *a*

Material attached to the surfaces of rocks was removed and temporarily suspended in reverse-osmosis water. Benthic organic matter (BOM) was measured as volatile solids ignited at 550°C following standard method 2540E (Eaton *et al.* 1995). Two sub-samples were concentrated onto pre-combusted Whatman International GF-C filters. One was dried to a constant weight at 105°C, which was achieved after 1 h. It was then weighed, combusted for 1 h at 550°C, placed in a dehydration chamber for 0.5 h and weighed again. The mass of organic matter was calculated as the difference between the dry weight and combusted weight. The other sample was placed in 99.8% methanol, stored for 24 h in the dark at 3°C, centrifuged for 10 min and chlorophyll *a* concentration was determined using a Hitachi U-2000 spectrophotometer (Hitachi Ltd., Tokyo, Japan). The chlorophyll *a* concentration was determined by measuring the absorbance at 665 and 750 nm, following the procedures of Golterman *et al.* (1978).

2.2.3 Phosphorus, nitrogen and carbon tissue concentrations

Benthic organic matter and leaf litter were collected and analysed for total phosphorus (TP), total carbon (TC) and total nitrogen (TN) concentrations. For TP analysis, suspended samples were analysed using the persulphate digestion method of standard method 4500-N C (Eaton *et al.* 1995). For TC and TN, BOM was concentrated onto pre-combusted Whatman International GF-C filters and leaf litter was ground with a mortar and pestle.

Samples were then analysed using LECO TruSpec Carbon/Hydrogen/Nitrogen Determinator (LECO, St. Joseph, USA).

The number of moles of phosphorus, nitrogen and carbon were calculated by dividing the mass of each molecule within a sample by the atomic weight of the molecule. The TP, TN and TC molar ratios were then calculated to indicate the relative availability of phosphorus, nitrogen and carbon.

2.2.4 Rock surface area

The total surface area of rocks were determined by wrapping the rocks in aluminium foil, removing excess aluminium foil and measuring the surface area of the aluminium foil using a •T Area Meter (Delta-T Devices, Cambridge, England).

2.2.5 Light intensity and water temperature

Underwater light intensity (photosynthetic-active radiation) was measured over the course of each experiment. Instantaneous measurements were taken every 5 s using a LI-1000 Data-logger and LI-192SA-Underwater-Quantum Sensor (LI-COR Inc., Lincoln, USA). The sensor was placed randomly within the stream reach, 5 cm below the water surface. For chapters three and four, reported light intensities are the average underwater instantaneous light intensities during each experiment. For chapters five and six, reported light intensities are the average underwater instantaneous light intensities during daylight hours. Light intensities and the number of daylight hours were used to calculate daily incident light. Measurements of ambient water temperature were taken every 10 min using a TPS WP-82 Dissolved Oxygen-Temperature meter (TPS Pty. Ltd., Brisbane, Australia), which was placed randomly within the stream reach, 5 cm below the water surface.

2.2.6 Hydrology

Stream discharge was measured as the product of average stream velocity and cross-sectional area. Velocity was measured at three positions across the stream cross-section using a BFM002 Open Channel Flow Meter and 0012B Impeller Control Display Unit (Valeport Ltd., Dartmouth, UK). Cross-sectional area was calculated as the product of stream width and average stream depth, measured at 5 cm intervals across the stream. For each year the period of continuous flow was determined by making observations on when each reach was flowing and when it ceased to flow. In chapter six, experiments were conducted over two years and the period of continuous flow was calculated separately for each year.

2.2.7 Day number

January 1st was identified as day one and December 31st as day 365 for each year. In chapter six, experiments were conducted over two years and day number was calculated separately for each year.

Table 2.1. Land-use of rural areas of First and Fourth Creek sub-catchments in 2003. Land-use areas were calculated using ArcGIS (ERSI Inc, Redlands, USA) and data supplied by Department of Water, Land and Biodiversity Conservation, the Government of South Australia.

Land-use	First Creek			Fourth Creek		
	Area (m^2)	Percent total area	Percent rural area	Area (m^2)	Percent total area	Percent rural area
Protected - natural vegetation	9236376	40.9	83.3	4028605	17.5	25.9
Grazing - natural vegetation	1386283	6.1	12.5	4600463	19.9	29.5
Rural residential	451337	2.0	4.1	2518262	10.9	16.2
Grazing - modified pastures	---	---	---	2924228	12.7	18.8
Irrigated perennial horticulture	---	---	---	1091175	4.7	7.0
Irrigated vine fruits	---	---	---	204534	0.9	1.3
Public services				164631	0.7	1.1
Softwood plantation	---	---	---	2114	0.1	0.1
Recreation and culture	7552	0.0	0.1	16690	0.1	0.1
Irrigated cropping	---	---	---	6169	0.0	0.0
Total rural	11081548	49.0	100.0	15575951	67.5	100.0
Total urban	11514286	51.0	---	7495814	32.5	---
Total area	22595834	100.0	---	23071764	100.0	---

Table 2.2. Geomorphic measurements of un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks. Stream slope was measured as direct length divided by fall distance. Sinuosity was measured as stream length divided by direct length. Mean ± standard error.

Geomorphic measurement	First Creek			Fourth Creek		
	Un-mod	Deg	Eng	Un-mod	Deg	Eng
Stream slope	20.0	57.2	218.2	30.3	68.5	58.2
Sinuosity	1.09	1.20	1.02	1.05	1.01	1.02
Depth (m)	0.06 ± 0.007	0.06 ± 0.010	0.07 ± 0.002	0.08 ± 0.010	0.06 ± 0.009	0.03 ± 0.012
Width (m)	1.5 ± 0.13	2.2 ± 0.30	2.5 ± 0.01	2.2 ± 0.17	1.6 ± 0.10	2.1 ± 0.16
Bank height (m)	0.6 ± 0.06	1.3 ± 0.16	0.9 ± 0.02	0.7 ± 0.10	0.9 ± 0.04	0.6 ± 0.07
Percent boulder/ rock/cobble	94 ± 1.9	85 ± 3.6	2 ± 0.6	90 ± 8.0	80 ± 3.5	12 ±8.4
Percent gravel/sand	6 ± 1.9	15 ± 3.6	1 ± 0.5	10 ± 8.0	20 ± 3.5	2 ± 2.0
Percent cement-cobble/slate	0	0	97 ± 1.0	0	0	86 ± 10.2
Percent coarse particulate organic matter	3 ± 1.1	1 ± 0.5	0.0	2 ± 0.5	0.0	0.0

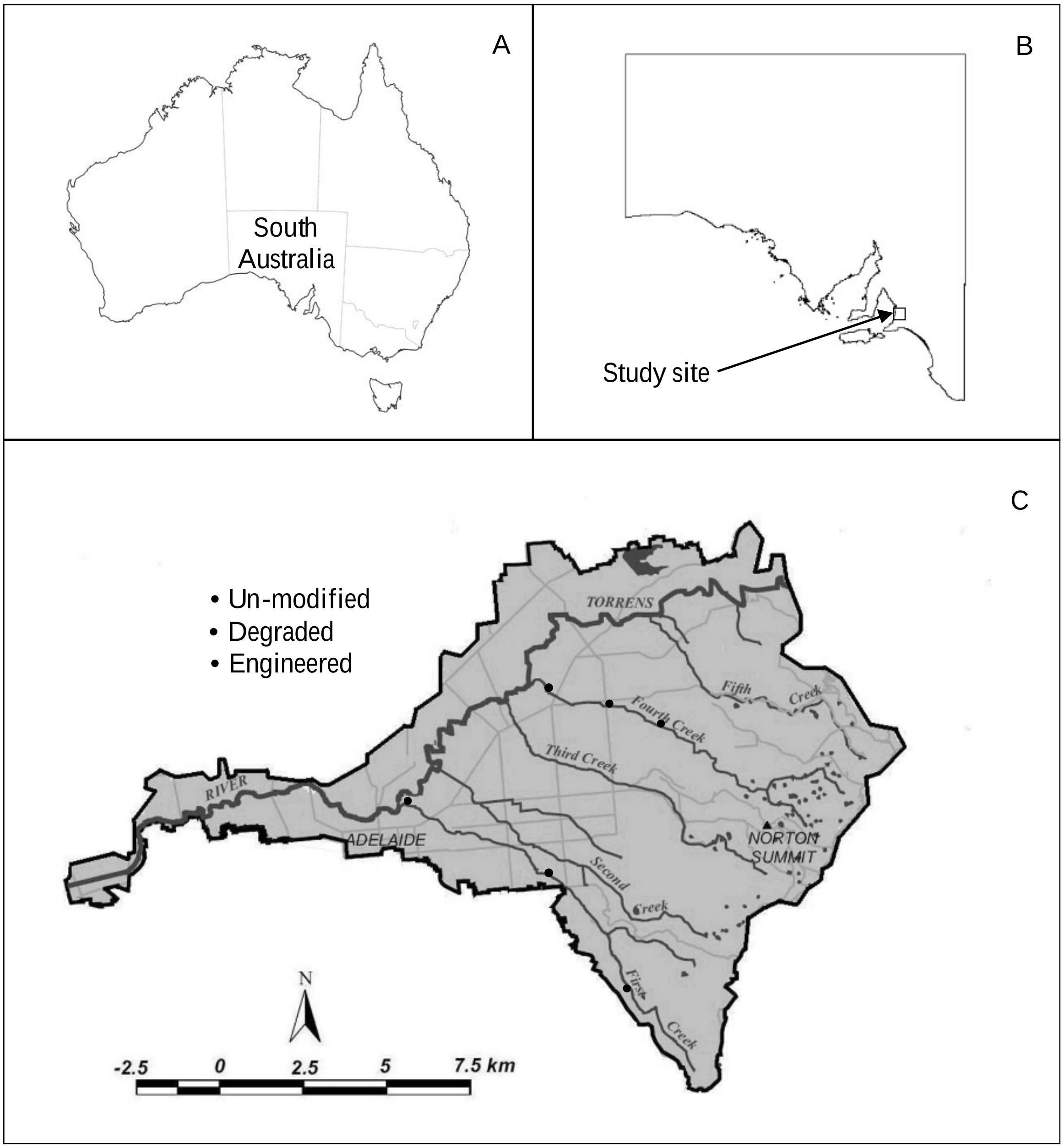


Figure 2.1. Location of South Australia within Australia (A), Torrens River Catchment within South Australia (B) and studied stream reaches within First and Fourth Creeks (C, modified from Tonkin Consulting (2002). In C, faint lines represent major roads, dark lines denote water bodies, including farm dams concentrated in the eastern area of Fourth Creek. Squares denote un-modified reaches, diamonds denote degraded reaches and circles denote engineered reaches. For chapter seven, an additional urban-degraded reach was chosen, which is located immediately upstream of the engineered reach of Fourth Creek.

Figure 2.2. Photo of the un-modified reach of First Creek. In the foreground is a re-circulating benthic chamber. Note little evidence of stream bed and bank erosion.

Figure 2.3. Photo of the degraded reach of First Creek. Note increased levels of stream bed and bank erosion in comparison to the un-modified reach of First Creek.

Figure 2.4. Photo of the engineered reach of First Creek. Note the replacement of natural substrates with a cement-rock substrate and the increased level of bank erosion.

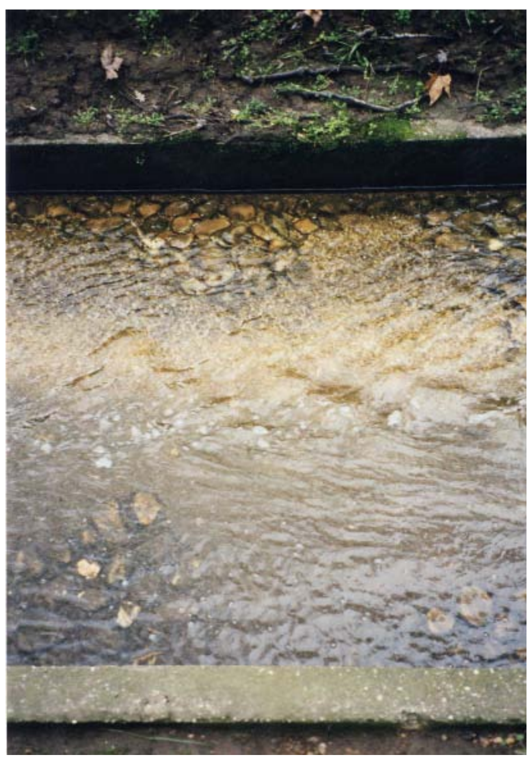


Figure 2.5. Photo of the stream bed (aerial view) of the engineered reach of First Creek. Note the replacement of natural substrates with a cement-rock substrate.

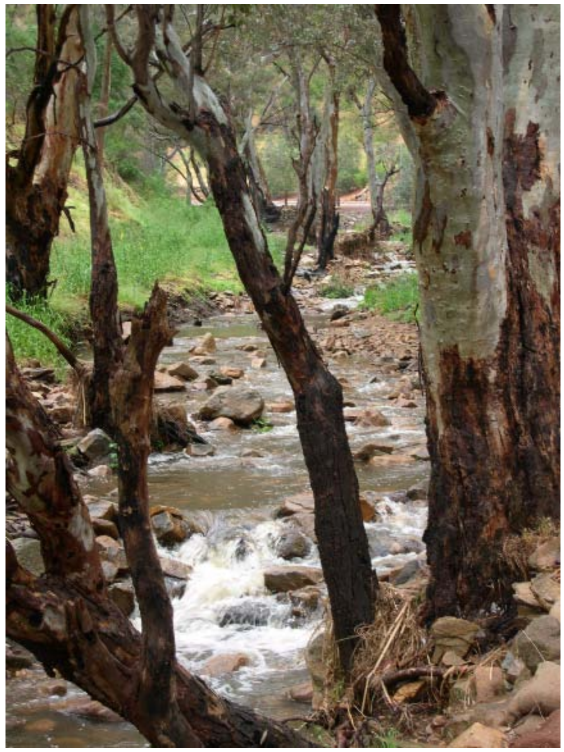


Figure 2.6. Photo of the un-modified reach of Fourth Creek. Note the low level of stream bed and bank erosion.

Figure 2.7. Photo of the degraded reach of Fourth Creek. Note the increased level of stream bank erosion and the channelised structure of the reach.

Figure 2.8. Photo of the engineered reach of Fourth Creek. Note the replacement of natural substrates with a cement-slate substrate.

Figure 2.9. Photo of the stream bed (aerial view) of the engineered reach of Fourth Creek. Note the replacement of natural substrates with a cement-slate substrate.

Figure 2.10. Photo of one of three pools within the engineered reach of Fourth Creek.

Figure 2.11. Photo of the upstream end of the urban reach of Fourth Creek studied in chapter seven (looking west). Note the bifurcation of the stream into two channels of approximately equal dimensions.

Figure 2.12. Photo of the downstream end of the urban reach of Fourth Creek studied in chapter seven (looking east). Note the bifurcation of the stream into two channels of approximately equal dimensions.

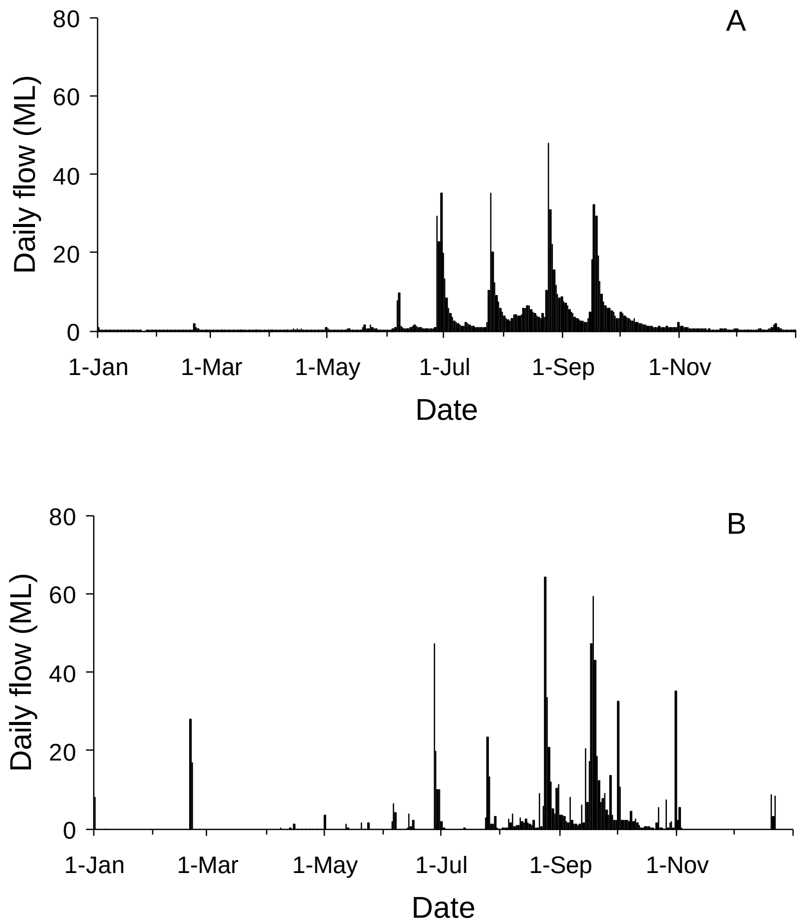


Figure 2.13. Daily flow in the (A) un-modified reach of First Creek and (B) downstream of the engineered reach of First Creek during 2003. Data provided by the Department of Water, Land and Biodiversity Conservation, the Government of South Australia.

Chapter three

3 Phosphorus retention in stream reaches with varying channel structure across a rural-urban gradient

Abstract. In developed catchments, streams experience simplification of their channel structure, which may reduce the number of pathways for nutrient interception and transformation. The aim of this study was to assess the ability of stream reaches with varying channel structure to retain phosphorus. This was investigated through a series of filterable reactive phosphorus (FRP)-sodium chloride-addition experiments in two streams in the Torrens River Catchment, South Australia. In First Creek, which has a predominately intact upper catchment, the reach with an un-modified channel structure retained more FRP (60% ± 12.1) and had a shorter uptake length (79 m ± 3.4) than the degraded (21% ± 3.4, 106 m ± 23.8) and engineered reaches (5% ± 2.2, 158 m ± 48.3). In contrast, in Fourth Creek, which has significant agricultural development in the upper catchment, there were no differences in percent FRP retention or uptake lengths between the un-modified (27% ± 7.9, 107 m ± 11.9), degraded (24% ± 3.2, 141 m ± 20.3) and engineered reaches (18% ± 4.1, 113 m ± 21.7). Hydrology (contact time, velocity, period of continuous flow) and phosphorus availability were the major factors determining differences in FRP retention. This project demonstrated that a decreased capacity of impacted streams to intercept nutrients might contribute to elevated nutrient levels in streams in developed catchments.

Key words: *Stream, reach, filterable reactive phosphorus, retention, uptake length, mass transfer coefficient, urbanisation, agriculture, channel structure, hydrology, nutrient availability*

3.1 Introduction

Streams are important linkages between terrestrial environments and terminal water bodies since they collect a majority of the resources that enter freshwater ecosystems (Peterson *et al*. 2001). Streams may intercept and transform nutrients (Mulholland 2004) and reduce the amount and bioavailability of nutrients, which may be significant for the control of anthropogenic nutrient inputs. McColl (1974) demonstrated that a New Zealand stream retained 62-97% of phosphorus inputs and Hart *et al*. (1992) and Hart *et al*. (1991) demonstrated that an Australian stream retained 22-84% of phosphorus inputs. Although a portion may be re-released (Meals *et al*. 1999), this still acts to slow nutrient transport.

Previous studies have developed an understanding of the biotic and abiotic processes that provide multiple pathways for nutrient interception and transformation. This understanding was developed in relatively pristine streams, but few have investigated nutrient retention in impacted streams. In urban areas, stream morphology has been altered due to increased surface run-off, flood severity and erosion (Walsh *et al*. 2004). In addition, humans have simplified stream morphology for flood mitigation. Streams in developed rural areas experience other impacts. For example, the period of stream flow may be reduced due to water harvesting for agricultural purposes (Savadamuthu 2003), which may impact upon stream communities.

Elevated nutrient levels are common in urban (Hatt *et al*. 2004; Brett *et al*. 2005) and rural streams influenced by agriculture (Harris 2001). This is generally attributed to increased nutrient inputs. Brookes *et al*. (In press) proposed that deterioration of ecosystems may reduce their capacity to process resources. Consequently, elevated nutrient levels may be the result of a reduced number and/or activity of pathways of nutrient interception and transformation. This project tested the hypothesis that urban stream reaches with simplified channel structures would have a lower capacity to intercept phosphorus than rural stream reaches with more natural channel structures.

This was conducted within the Torrens River Catchment, where impacted streams may provide few pathways for nutrient interception and transformation. This is evident in the Torrens Lake, where algal blooms are a common occurrence because of modification of the natural hydrology and increased nutrient loads, particularly phosphorus (Ganf *et al*. 1999). Phosphorus retention was compared in un-modified, degraded and engineered reaches of First and Fourth Creeks (chapter two). The conditions controlling differences in the capacity of these reaches to retain phosphorus were also investigated.

3.2 Methods

3.2.1 Phosphorus-addition experiments

During winter 2003, spring 2003 and winter 2004, filterable reactive phosphorus (FRP)-sodium chloride (NaCl)-addition experiments were carried out in each reach (Table 3.1). Short-term addition experiments were employed because the aim was to assess the potential for phosphorus removal from stream water at the particular time (Stream Solute Workshop 1990) and not to assess the response to extended phosphorus addition. Sodium chloride was used as a conservative tracer, as changes in its concentration (conductivity) reflected dilution and dispersion. If there was no FRP uptake, observed-FRP concentrations would match changes in conductivity. However, if observed-FRP concentrations diverged from expected-FRP concentrations, the stream acted as a sink or a source. Observed- and expected-FRP concentrations, if there was no uptake, were compared over time and percent FRP retention was calculated by comparing the area beneath the curves (between the time when expected-FRP concentrations began to rise and returned to background).

Prior to each experiment, 50 L of stream water was removed and enriched with di-potassium hydrogen orthophosphate (K_2HPO_4) and NaCl. The desired FRP concentration at the point of addition after dilution with stream water was below 150 •g L^{-1}, which is at the upper end of concentrations experienced in these streams. The desired peak conductivity at 100 m downstream was double the background conductivity (300-500 •S cm^{-1}). Four measurements of conductivity of the mixed tracer solution were taken using a TPS WP-84 Conductivity-Salinity-Temperature meter (TPS Pty. Ltd., Brisbane, Australia) and four samples were taken for determination of FRP concentration (chapter two). The solution was pumped into the stream over 2 min. At 35 m and 100 m downstream, conductivity and time were logged and 70 mL grab samples taken, from the time of addition until conductivity returned to background. The 35 m sampling point was not used during winter 2004. Conductivity measurements and water samples were taken at the mid-point of the reach width and water depth at intervals that would allow suitable coverage of changes in FRP over time, usually between 10 s and 1 min. These samples were considered to be representative of the water column as the streams were well mixed and measurements of water temperature revealed no thermal discontinuities.

Prior to each experiment, four grab samples were taken for analysis of dissolved organic carbon (DOC) and FRP concentrations and DOC to FRP molar ratios were calculated (chapter two). Measurements were also taken for stream discharge, light intensity, water temperature, period of continuous flow and day number, as described in chapter two. Reported light intensities are the average underwater instantaneous light intensities during each addition experiment. Four groups of four rocks were randomly selected and the amount of benthic organic matter (BOM) and benthic chlorophyll *a* per unit surface area were determined, as described in chapter two.

3.2.2 Solute transport modelling

Hydrological and FRP retention properties were calculated using Matlab (version 5.0.0.4073, The Mathworks Inc, Natwick, USA) and the governing equation of solute transport (equation 1).

Equation 1:

$$R\frac{\delta c}{\delta t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\delta c}{\delta x} - \mu c + \gamma$$

Where R is the retardation factor, c is the solute concentration, t is the time, D is the dispersion coefficient, x is the downstream distance, v is the stream velocity, • is the decay coefficient and • is the production rate.

Stream velocity (v) and dispersion coefficient (D) were calculated by modelling measurements of conductivity with the analytical solution (equation 2) of the governing equation of solute transport with no decay or production (van Genuchten and Alves 1982). Values were calculated by adjusting v, D and the conductivity at the point of addition during the addition of the tracer solution, until the least sum of squares difference was attained between observed and modelled data. An example of this is shown in Figure 3.1.

Filterable reactive phosphorus retardation factor (R), production rate (•) and decay coefficient (•) were calculated by modelling measurements of observed-FRP concentrations with the analytical solution (equation 3) of the governing equation of solute transport with decay and production (van Genuchten and Alves 1982). Values were calculated by adjusting R, • and •, until the least sum of squares difference was attained between observed and modelled data. An example of this is shown in Figure 3.2.

Equation 2:

$$c(x,t) = C_i + (C_o - C_i)A(x,t) \qquad \mathbf{0 < \mathit{t} </= \mathit{t_o}}$$

$$c(x,t) = C_i + (C_o - C_i)A(x,t) - C_o A(x,t-t_o) \qquad \mathbf{\mathit{t} > \mathit{t_o}}$$

Where

$$A(x,t) = 0.5\text{erfc}\left(\frac{Rx - vt}{2\sqrt{DRt}}\right) + 0.5\exp\left(\frac{vx}{D}\right)\text{erfc}\left(\frac{Rx + vt}{2\sqrt{DRt}}\right)$$

and C_i is the background conductivity, C_o is conductivity at the point of addition during the addition of the tracer solution, t_o is the time of tracer addition, exp is the exponential function and erfc is the complementary error function.

<u>Equation 3:</u>

$$c(x,t) = \frac{\gamma}{\mu} + \left(C_i - \frac{\gamma}{\mu}\right)A(x,t) + \left(C_o - \frac{\gamma}{\mu}\right)B(x,t) \qquad \mathbf{0 < t </= t_o}$$

$$c(x,t) = \frac{\gamma}{\mu} + \left(C_i - \frac{\gamma}{\mu}\right)A(x,t) + \left(C_o - \frac{\gamma}{\mu}\right)B(x,t) - C_o B(x,t-t_o) \qquad \mathbf{t > t_o}$$

Where

$$A(x,t) = \exp\left(\frac{-\mu t}{R}\right)\left[1 - 0.5\text{erfc}\left(\frac{Rx - vt}{2\sqrt{DRt}}\right) - 0.5\exp\left(\frac{vx}{D}\right)\text{erfc}\left(\frac{Rx + vt}{2\sqrt{DRt}}\right)\right]$$

$$B(x,t) = 0.5\exp\left(\frac{(v-m)x}{2D}\right)\text{erfc}\left(\frac{Rx - mt}{2\sqrt{DRt}}\right) + 0.5\exp\left(\frac{(v+m)x}{2D}\right)\text{erfc}\left(\frac{Rx + mt}{2\sqrt{DRt}}\right)$$

and

$$m = v\sqrt{\left(1 + \frac{4\mu D}{v^2}\right)}$$

<u>Equation 4:</u>

$$S_w = \frac{v}{\mu}$$

<u>Equation 5:</u>

$$v_f = \mu h$$

Where h is the average water depth.

The FRP uptake length (S_w) and FRP mass transfer coefficient (v_f) were calculated using equations 4 and 5 (Stream Solute Workshop 1990). The S_w represents the average longitudinal distance a molecule will travel before it is removed from water column and the v_f represents a molecule's average vertical speed of movement through the water column (Stream Solute Workshop 1990). These FRP retention properties are generally calculated when plateau concentrations are reached following long-term nutrient additions (Stream Solute Workshop 1990). Since short-term additions were employed in this study, comparisons between the modelled FRP retention properties of this and other studies are not made. Instead, the FRP retention properties are only used to compare sites of this study.

3.2.3 Statistical analyses

Statistical analyses were restricted to FRP retention properties at 100 m. Filterable reactive phosphorus retention properties include; retardation factor, production rate, decay coefficient, uptake length, mass transfer coefficient and percent retention. To summarise differences in FRP retention properties, a two-dimensional non-metric multidimensional scaling (NMS) ordination was conducted using PC-ORD (Version 4.10, MjM software, Oregon, USA). A main matrix containing FRP retention properties was overlaid with the same matrix to determine the directional effects of FRP retention properties on the two-dimensional distributions. This revealed a final stress of 3.87 and was suitable for a two-dimensional ordination. Environmental parameters could not be included since complete data sets were not available.

Univariate analyses were performed using JMP-IN (Version 3.2.1, SAS Institute Inc., Cary, USA) to examine differences in individual FRP retention properties. Since differences in the measured parameters between the degraded and un-modified and the engineered and un-modified reaches were of interest, paired-comparisons were used. All samples were tested for homogeneity (O'Brien, Brown-Forsythe, Levene and Bartlett tests) and normality (Shapiro-Wilk test). When variances were equal, parametric t-tests were performed. When variances were unequal, Mann-Whitney non-parametric analyses were performed. Relationships between environmental parameters and FRP retention properties were analysed by regression analysis. Statistically significant relationships were accepted if p values were less than 0.05. Variability between replicates is reported as standard errors.

3.3 Results

3.3.1 Environmental conditions

The variable nature of these streams was reflected by discharge, which ranged from 15 to 238 L s^{-1} with no consistent pattern across seasons and reaches (Table 3.2). The un-modified reach of First Creek flowed for longer than all other reaches and DOC and FRP were generally lower in un-modified reaches (Table 3.2). Water temperature and light intensity were generally higher in spring than winter and higher in Fourth Creek than First Creek. Benthic organic matter ranged between 2 and 14 g m^{-2} and benthic chlorophyll *a* between 1 and 14 mg m^{-2}.

3.3.2 Solute behaviour

Solute behaviour varied among reaches. In winter 2003, in the un-modified and degraded reaches of First Creek, the tracer solution had contact times at 100 m of 27.9 and 28.6 min, respectively (Figures 3.3A-B). In comparison, in the engineered reach the contact time was 6.8 min (Figure 3.3C). In the degraded reach observed-FRP concentrations were below expected concentrations (Figure 3.3B), but the difference was greater in the un-modified reach (Figure 3.3A). In the engineered reach observed-FRP concentrations closely followed expected concentrations (Figure 3.3C). In Fourth Creek, higher discharge (Table 3.2) and stream velocity (v, Table 3.3) caused expected-FRP concentrations to rise and fall more rapidly than in First Creek (Figures 3.4A-C). The un-modified and degraded reaches of Fourth Creek had contact times of 11.6 min at 100 m, while the engineered reach had a contact time of 5.7 min. At 35 m in all reaches of Fourth Creek, observed-FRP concentrations closely followed expected concentrations, while at 100 m observed concentrations were slightly below expected concentrations (Figures 3.4A-C).

Overall, engineered reaches experienced greater variation in v and D than un-modified reaches (Table 3.3). While the values of v were not different between reaches and streams, in First Creek D was greater in the degraded and engineered reaches than in the un-modified reach (p = 0.0495, • = 0.05, df = 1 for both analyses).

3.3.3 FRP retention properties

Differences in FRP retention properties between reaches were evident. The two-dimensional distribution of FRP retention properties of the un-modified reach of First Creek were clustered together (Figure 3.5) and separated from that of impacted reaches. Furthermore, the distribution of FRP retention properties of the un-modified reach of First Creek was closely associated with high percent FRP retention and short uptake lengths (S_w) (Figure 3.5). The distribution of FRP retention properties of the degraded reach of First Creek was associated with lower percent FRP retention and longer S_w than the un-modified reach, particularly during winter 2003 (Figure 3.5). This pattern was more pronounced for the engineered reach of First Creek (Figure 3.5), which also had a broader distribution (Figure 3.5) owing to the variation in FRP retention properties (Table 3.3).

These differences in First Creek were exemplified by differences in percent FRP retention (Table 3.3). During each season, the un-modified reach retained a greater percent of FRP than impacted reaches (Table 3.3). Percent retention was also influenced by season, with the un-modified and degraded reaches retaining most FRP during spring 2003 and all reaches retaining less during winter 2004 (Table 3.3). Overall, the un-modified reach retained 60% ± 12.1 of the FRP, which was greater than the degraded (21% ± 3.4, p = 0.0367, • = 0.05, df = 4) and engineered reaches (5% ± 2.2, p = 0.0111, • = 0.05, df = 4) (Figure 3.6). In addition, the engineered reach had greater production rates and S_w than the un-modified reach (p = 0.0223, • = 0.05, df = 1 and p = 0.0495, • = 0.05, df = 1, respectively) (Table 3.3, Figure 3.6). However, there were no differences in mass transfer coefficients (Table 3.3).

During spring 2003 and winter 2004, v and D were similar in both streams (Table 3.3) and the distribution of FRP retention properties of the un-modified reach of Fourth Creek was associated with that of First Creek (Table 3.3, Figure 3.5). Furthermore, in spring 2003, the un-modified reach of Fourth Creek had higher percent FRP retention and shorter S_w than the degraded and engineered reaches of Fourth Creek (Table 3.3). However, in winter 2003 v was elevated in the un-modified reach of Fourth Creek and S_w and percent FRP retention were similar to that of the degraded and engineered reaches (Table 3.3, Figure 3.5). Consequently, there were no differences in FRP retention properties between the reaches of Fourth Creek (Figure 3.6), although the engineered reach had a broader distribution of FRP retention properties (Figure 3.5) owing to the variation in FRP retention properties (Table 3.3).

3.3.4 Causes of differences in FRP uptake and retention

Percent FRP retention had significant relationships with a range of factors (Table 3.4). It was strongly related to nutrient availability, with positive relationships with the molar ratio of background DOC to FRP molar ratio during winter and spring (Table 3.4, Figure 3.7). Percent FRP retention was also strongly related to hydrological parameters including, the period of continuous flow (Table 3.4, Figure 3.8) and contact time (Table 3.4, Figure 3.9). In addition, percent FRP retention had an inverse relationship with S_w (p = 0.0349, r^2 = 0.2492, • = 0.05, df = 17). Uptake length was only related to background FRP concentrations (Figure 3.10) and retardation factor (Table 3.4). Differences in v_f were explained by differences in hydrological parameters, with positive relationships with v, D and discharge and an inverse relationship with contact time (Table 3.4).

3.4 Discussion

Nutrient exports to terminal water bodies have increased due to anthropogenic changes (Vollenweider 1968; Wahl *et al.* 1997; Sharpley *et al.* 2001). This may reflect not only increased inputs, but also alterations to in-stream nutrient processing. Only a few studies have compared nutrient retention in pristine and impacted streams. Moyer (1995) and Sabater *et al*. (2000) demonstrated increased retention in impacted streams, while others demonstrated lower nutrient retention in urban streams compared with rural streams (Grimm *et al.* In press; Groffman *et al.* In press; Meyer *et al.* In press). This project demonstrated greater FRP retention in a reach with an un-modified channel structure compared with degraded and engineered reaches in a stream with an intact upper catchment (First Creek). In fact, FRP retention decreased longitudinally despite nutrient demand increasing longitudinally in streams (Mulholland *et al.* 1995).

Percent retention is influenced by hydrological parameters and is not a measure of stream solute affinity. The mass transfer coefficient (v_f) may account for hydrological differences. While Meyer *et al.* (In press) demonstrated lower ammonium and phosphate v_f in urban streams than rural streams, no differences were detected in this project. The close association of v_f with hydrological parameters suggested that differences were caused by changes in the contact of phosphorus with stream compartments. This may be due to the shallow, turbulent nature of these streams, making v_f unsuitable for assessing uptake potential. Uptake length (S_w) was not related to hydrological parameters and was lower in the un-modified reach than impacted reaches (see Figure 3.11 for conceptual model). Percent retention does incorporate all impacts of changes in land-use, including hydrological parameters, which were found to be a major factor determining percent FRP retention.

Urban streams experience increased peak-flows. This may decrease the contact time of molecules with streams and decrease the likelihood that biotic or abiotic pathways will retaining that molecule (Triska *et al.* 1989; D'Angelo and Webster 1991; Butturini and Sabater 1998; Hall Jr. *et al.* 2002). Meyer *et al.* (In press) suggested that increased peak-flows in urban streams removes organic matter, and thus abiotic and biotic pathways of nutrient interception and transformation. In this study, FRP retention was not related to organic matter, but hyporheic organic matter and coarse particulate organic matter were not measured. In fact, coarse particulate organic matter has been shown to be the most active site for nitrogen immobilisation by microbial organisms (Sanzone *et al.* 2001).

The results of this project suggest that rehabilitation of First Creek could reduce phosphorus exports by 132 kg y^{-1}, or 44%. This assumes that;

- Un-modified, degraded and engineered reaches are equal in length.
- The total annual phosphorus load is 300 kg (Arup Stokes 1999) and each reach receives a load of 140 kg.
- Un-modified, degraded and engineered reaches retain 60%, 21% and 5% of phosphorus inputs, respectively.
- Rehabilitated reaches will retain 60%.
- Phosphorus is readily available.

Although a portion of the retained phosphorus may be re-released, Mulholland (2004) demonstrated that in-stream processes resulted in 30% retention of all FRP inputs. Even if retention was temporary, rehabilitated reaches would convert dissolved nutrients to fine particulate material (Meyer and Likens 1979), which pristine streams have a high capacity to retain (Hall Jr. *et al.* 1998).

In Fourth Creek, which has significant agricultural development (chapter two), there were no differences in FRP retention properties between reaches. The reduced period of continuous flow in Fourth Creek may have reduced the activity of abiotic and biotic pathways of phosphorus retention, as percent FRP retention increased with the period of continuous flow. While Maltchik *et al.* (1994) demonstrated greater nutrient demand following re-wetting, extended periods of desiccation may adversely affect biotic and abiotic pathways of nutrient retention (Gasith and Resh 1999; Baldwin and Mitchell 2000).

Agriculture may also reduce the microbial demand for phosphorus by increasing phosphorus availability, which was a major factor determining phosphorus retention and has been observed elsewhere (Munn and Meyer 1990; Martí and Sabater 1996; Davis and Minshall 1999). Within the Torrens River Catchment, FRP concentrations in run-off from native vegetation are approximately three times lower than from agriculture (Tonkin Consulting 2002). Indeed, the un-modified reach of First Creek experienced low background FRP concentrations, higher background DOC to FRP molar ratios and retained most of the added FRP. Merseburger *et al.* (2005) found that agricultural nutrient inputs overwhelmed a stream's capacity to retain nutrients. In addition, the availability of organic carbon exerts a strong control over heterotrophic metabolism and nutrient uptake (Mulholland *et al.* 1997; Bernhardt and Likens 2002; Crenshaw *et al.* 2002).

In this study, the most pristine reach maintained a relatively stable response that indicated efficient nutrient interception. In contrast, the response of impacted reaches was highly variable indicating decreased ecosystem resistance to perturbations. It is becoming evident that biological diversity and physical heterogeneity play important roles in maintaining ecosystem resilience and functions, such as enhanced resource interception (Hutchinson and Webster 1998; Hulot *et al.* 2000; Cardinale *et al.* 2002a; Mulder *et al.* 2002; Brookes *et al.* In press). Preservation and rehabilitation of stream ecosystem functions, such as nutrient retention, requires the identification of the processes causing deterioration. The manner in which water is delivered from urban catchments appears to be the overriding cause of in-stream degradation (Booth and Jackson 1997; Walsh *et al.* 2004) and management strategies are required to address this at in-stream and catchment scales. It is evident from this project that management of hydrology and nutrient availability will have important implications for phosphorus retention. This will not only benefit freshwater biota, but may also provide important ecosystem services to humans, such as improved resource processing.

Table 3.1. Dates, times and period of continuous flow during FRP addition experiments in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks in winter 2003 (W03), spring 2003 (S03) and winter 2004 (W04).

Parameter	Season	First Creek			Fourth Creek		
		Un-mod	Deg	Eng	Un-mod	Deg	Eng
Time and date	W03	12:31 16 Jul.	10:47 9 Jul.	11:23 19 Aug.	11:46 6 Aug.	11:51 30 Jul.	12:48 28 Aug.
	S03	12:25 15 Oct.	13:30 9 Oct.	10:03 14 Oct.	10:45 5 Nov.	14:33 23 Oct.	10:34 30 Oct.
	W04	13:12 22 Jun.	11:43 22 Jun.	9:54 22 Jun.	11:44 23 Jun.	9:28 23 Jun.	10:29 23 Jun.
Period of continuous flow (days)	W03	198	50	91	78	71	100
	S03	288	142	147	169	156	163
	W04	173	36	36	37	37	37

Table 3.2. Environmental parameters in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks in winter 2003 (W03), spring 2003 (S03) and winter 2004 (W04). Mean ± standard error.

Parameter	Season	First Creek			Fourth Creek		
		Un-mod	Deg	Eng	Un-mod	Deg	Eng
Background FRP (•g L^{-1})	W03	4 ± 1.0	12 ± 0.0	5 ± 0.0	14 ± 1.1	6 ± 0.8	10 ± 0.6
	S03	4 ± 0.0	9 ± 0.5	32 ± 2.0	7 ± 0.7	9 ± 1.5	20 ± 0.0
	W04	4 ± 0.3	11 ± 0.6	13 ± 0.8	5 ± 0.0	7 ± 0.0	7 ± 0.4
Added FRP (mg L^{-1})	W03	8.3 ± 0.01	6.5 ± 0.12	4.8 ± 0.04	12.0 ± 0.15	7.0 ± 0.05	10.0 ± 0.07
	S03	3.9 ± 0.10	9.6 ± 0.02	0.9 ± 0.03	4.2 ± 0.08	3.3 ± 0.0	1.9 ± 0.01
	W04	4.2 ± 0.11	5.1 ± 0.0	3.6 ± 0.0	5.1 ± 0.07	5.1 ± 0.06	6.8 ± 0.06
FRP at point of addition (mg L^{-1})	W03	2.5	1.3	0.1	0.6	0.5	0.1
	S03	0.2	0.2	0.1	0.1	0.2	0.1
	W04	0.1	0.1	0.1	0.1	0.1	0.2
DOC (mg L^{-1})	W03	---	---	---	6.6 ± 0.04	6.3 ± 0.04	8.6 ± 0.04
	S03	4.9 ± 0.02	7.5 ± 0.30	---	6.9 ± 0.14	7.4 ± 0.11	6.9 ± 1.6
	W04	9.0 ± 0.03	7.4 ± 0.04	7.2 ± 0.02	8.4 ± 0.14	4.7 ± 0.01	5.7 ± 0.18
Discharge (L s^{-1})	W03	30	31	52	153	107	238
	S03	26	62	15	44	20	23
	W04	128	198	109	116	72	84
Water temperature (°C)	W03	10.9 ± 0.02	10.1 ± 0.01	9.8 ± 0.01	10.3 ± 0.01	11.5 ± 0.02	11.9 ± 0.02
	S03	12.8 ± 0.02	12.5 ± 0.02	16.0 ± 0.03	15.0 ± 0.03	22.2 ± 0.02	14.5 ± 0.01
	W04	11.0 ± 0.01	11.9 ± 0.04	12.3 ± 0.01	11.3 ± 0.00	10.8 ± 0.01	12.3 ± 0.01
Light intensity (•mol m^{-2} s^{-1})	W03	86 ± 6.2	72 ± 7.7	---	210 ± 0.7	243 ± 55.1	---
	S03	438 ± 53.7	25 ± 2.8	---	1072 ±16.8	1007 ±50.3	---
	W04	82 ± 4.2	33 ± 3.1	42 ± 6.8	92 ± 5.7	52 ± 5.5	75 ± 3.2
Benthic organic matter (g m^{-2})	W03	---	---	---	---	---	---
	S03	4 ± 0.4	6 ± 0.4	3 ± 0.6	4 ± 0.1	3 ± 0.4	2 ± 0.2
	W04	13 ± 2.9	5 ± 0.6	2 ± 0.5	14 ± 2.4	2 ± 0.4	4 ± 0.7
Benthic chlorophyll *a* (mg m^{-2})	W03	---	---	---	---	---	---
	S03	11 ± 1.6	14 ± 2.4	7 ± 0.4	7 ± 1.4	8 ± 1.4	3 ± 0.3
	W04	5 ± 2.1	2 ± 0.3	1 ± 0.1	8 ± 1.7	2 ± 0.3	2 ± 0.5

Table 3.3. Hydrological and FRP retention properties in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks in winter 2003 (W03), spring 2003 (S03) and winter 2004 (W04). Properties were calculated using the analytical solution of the governing equation of solute transport (van Genuchten and Alves 1982).

Property	Season	First Creek			Fourth Creek		
		Un-mod	Deg	Eng	Un-mod	Deg	Eng
Stream velocity ($m\ min^{-1}$)	W03	7.8	7.2	32.9	18.3	20.8	70.7
	S03	8.1	11.5	11.3	6.9	6.9	17.3
	W04	11.5	15.6	30.0	8.4	11.8	16.1
Dispersion ($m^2\ min^{-1}$)	W03	8.5	18.5	24.0	29.0	23.0	169.8
	S03	10.6	20.7	28.0	8.3	8.5	92.0
	W04	11.6	35.2	58.6	16.8	10.7	6.6
Retardation factor	W03	1.00	1.10	1.04	1.03	1.00	1.06
	S03	1.02	1.06	1.17	1.04	1.03	1.21
	W04	1.04	1.02	1.07	1.02	1.00	1.00
Production rate (•g $L^{-1}\ min^{-1}$)	W03	0.37	1.11	4.68	3.79	1.60	13.01
	S03	0.04	1.44	3.33	0.59	0.83	4.56
	W04	0.80	3.58	7.81	0.73	1.16	1.67
Decay coefficient (min^{-1})	W03	0.097	0.048	0.251	0.140	0.115	1.000
	S03	0.112	0.116	0.045	0.072	0.055	0.122
	W04	0.137	0.228	0.332	0.089	0.102	0.126
Uptake length (m)	W03	80.4	150.0	131.1	130.7	180.9	70.7
	S03	72.3	99.1	251.1	95.8	125.5	141.8
	W04	83.9	68.4	90.4	94.4	115.7	127.8
Mass transfer coefficient ($cm\ min^{-1}$)	W03	1.23	0.56	1.49	2.18	1.61	10.00
	S03	1.21	1.16	0.13	0.68	0.38	0.86
	W04	1.92	2.89	2.08	0.86	0.83	1.27
Percent retention	W03	65	19	9	14	18	16
	S03	78	28	5	41	28	11
	W04	37	16	1	28	26	25

Table 3.4. Statistics and relationships obtained for effects of environmental parameters on percent FRP retention, uptake length and mass transfer coefficient. Relationships include natural log (ln) transforms of parameters (x) and percent FRP retention (y). Only significant effects are shown (p less than 0.05). For all analyses df = 17, except for background DOC to FRP ratios during winter and spring, where df = 8 and 4, respectively.

Parameter	Statistic and relationship	Percent retention	Uptake length	Mass transfer coefficient
Background FRP concentration	p	0.0014	0.0017	---
	r^2	0.4795	0.4685	---
	Relationship	Inverse ln(x)	Positive linear	---
Background DOC to FRP molar ratio - winter	p	0.0147	---	---
	r^2	0.5964	---	---
	Relationship	Positive linear	---	---
Background DOC to FRP molar ratio - spring	p	0.0382	---	---
	r^2	0.8075	---	---
	Relationship	Positive linear	---	---
Period of continuous flow	p	0.0013	---	---
	r^2	0.4856	---	---
	Relationship	Positive linear	---	---
Discharge	p	---	---	0.0001
	r^2	---	---	0.6145
	Relationship	---	---	Positive linear
Contact time	p	0.0039	---	0.0268
	r^2	0.4152	---	0.2708
	Relationship	Positive linear	---	Inverse linear
Stream velocity	p	0.0160	---	<0.0001
	r^2	0.3121	---	0.8183
	Relationship	Inverse ln(x)	---	Positive linear
Dispersion coefficient	p	0.0086	---	<0.0001
	r^2	0.3592	---	0.7031
	Relationship	Inverse ln(x)	---	Positive linear
Retardation factor	p	---	0.0372	---
	r^2	---	0.2440	---
	Relationship	---	Positive linear	---
Production rate	p	0.0088	---	---
	r^2	0.3574	---	---
	Relationship	Inverse ln(y)	---	---

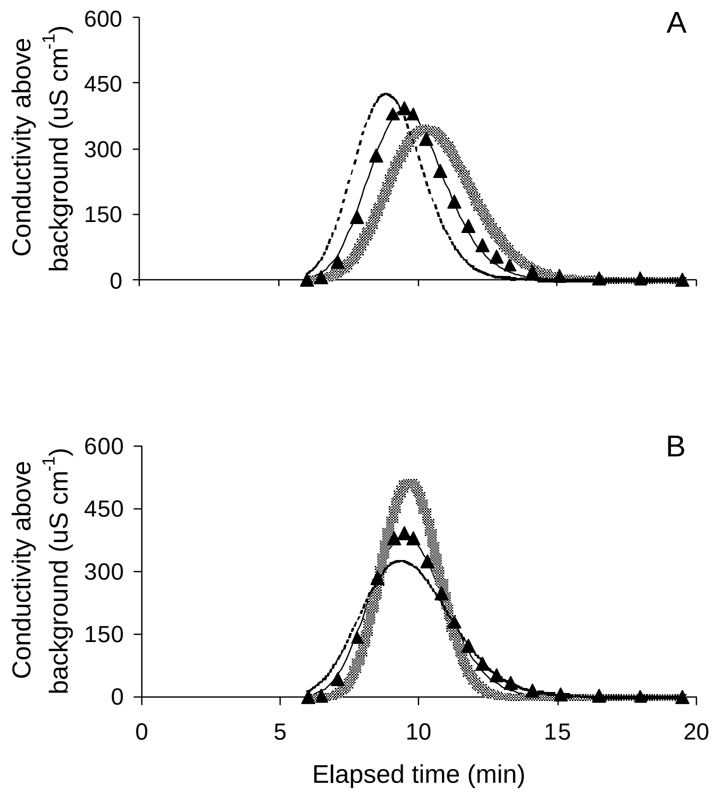


Figure 3.1. Influence of changes in (A) stream velocity, v, and (B) dispersion, D, on the modelled fit of observed conductivity in the un-modified reach of First Creek, winter 2004. Triangles are observed data. Fitted thin full line in A is the modelled fit with least sum of squares difference (LSSD, v of 11.5 m min^{-1}), while dashed and thicker lines are fits with v of 12.5 and 10.5 m min^{-1}, respectively. Fitted thin full line in B is the modelled fit with LSSD (D of 11.6 m^2 min^{-1}), while dashed and thicker lines are fits with D of 18.0 and 5.0 m^2 min^{-1}, respectively.

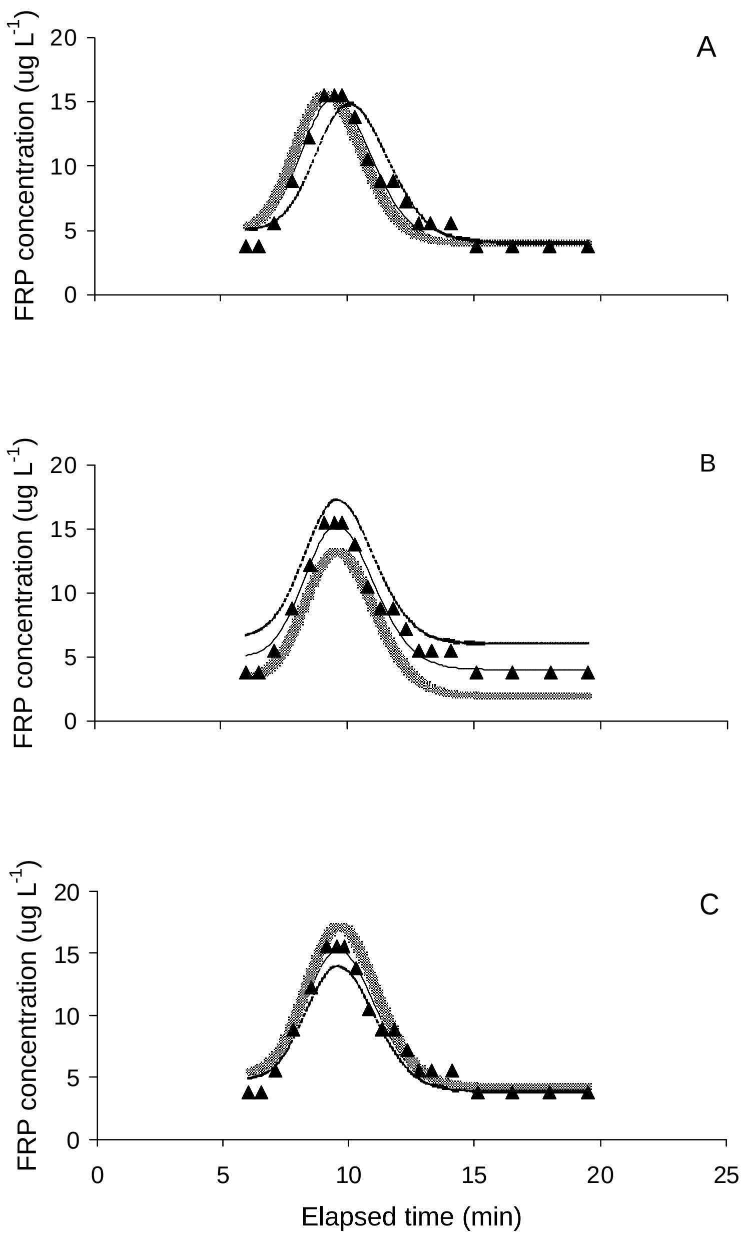


Figure 3.2. Influence of changes in (A) retardation factor, *R*, (B) production rate, •, and (C) decay coefficient, •, on the modelled fit of observed FRP concentrations in the un-modified reach of First Creek, winter 2004. Triangles are observed data. Fitted thin full line in (A) is the modelled fit with least sum of squares difference (LSSD, *R* of 1.04), while dashed and thick lines are modelled fits with *R* of 1.10 and 1.00, respectively. Fitted thin full line in (B) is the modelled fit with LSSD (• of 0.80 •g L^{-1} min^{-1}), while dashed and thick lines are modelled fits with • of 1.20 and 0.4 •g L^{-1} min^{-1}, respectively. Fitted thin full line in (C) is the modelled fit with LSSD (• of 0.137 min^{-1}), while dashed and thick lines are modelled fits with • of 0.15 and 0.12 min^{-1}, respectively.

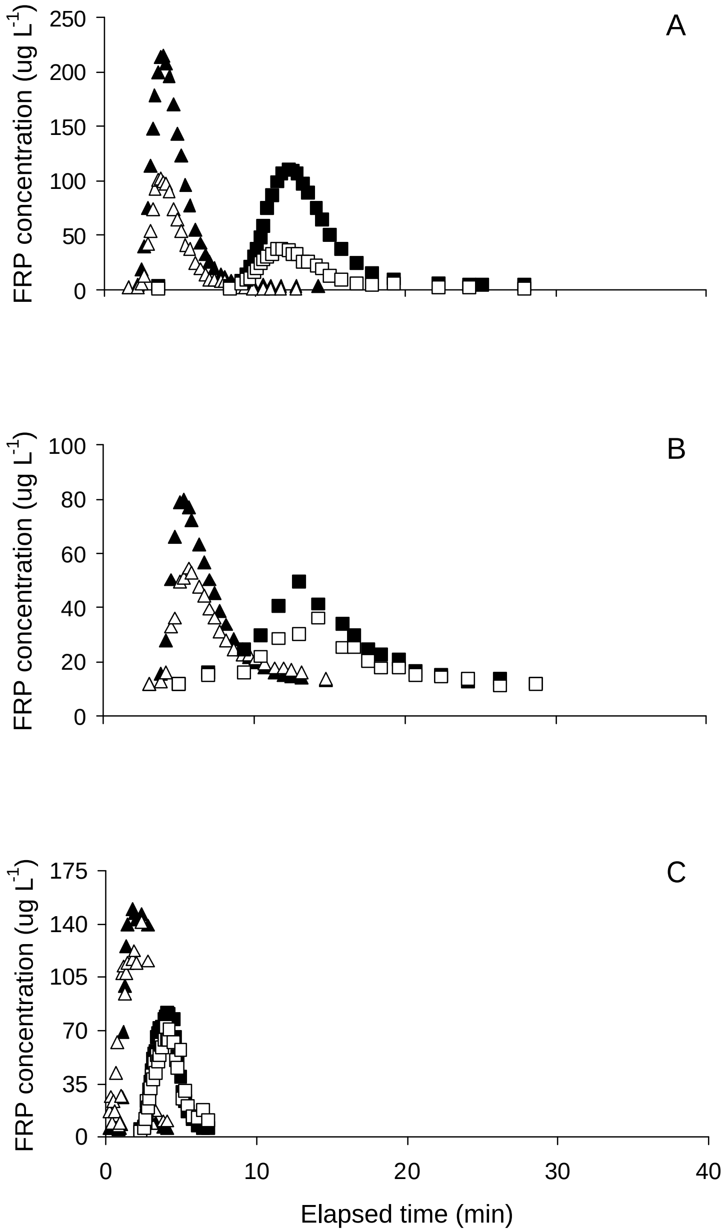


Figure 3.3. Expected and observed filterable reactive phosphorus (FRP) concentrations in (A) un-modified, (B) degraded, and (C) engineered reaches of First Creek during winter 2003. Black shapes denote expected-FRP concentrations if there is no FRP uptake and clear shapes denote observed-FRP concentrations at 35 m (triangles) and 100 m (squares).

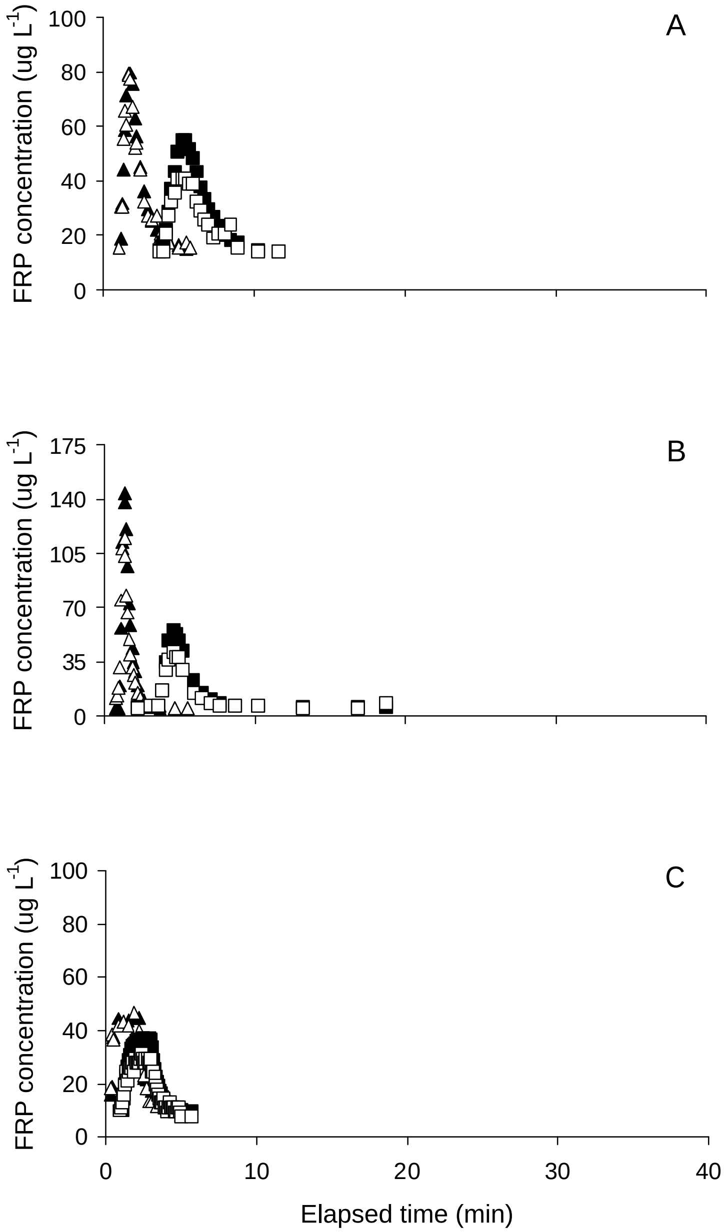


Figure 3.4. Expected and observed filterable reactive phosphorus (FRP) concentrations in (A) un-modified, (B) degraded, and (C) engineered reaches of Fourth Creek during winter 2003. Black shapes denote expected-FRP concentrations if there is no FRP uptake and clear shapes denote observed-FRP concentrations at 35 m (triangles) and 100 m (squares).

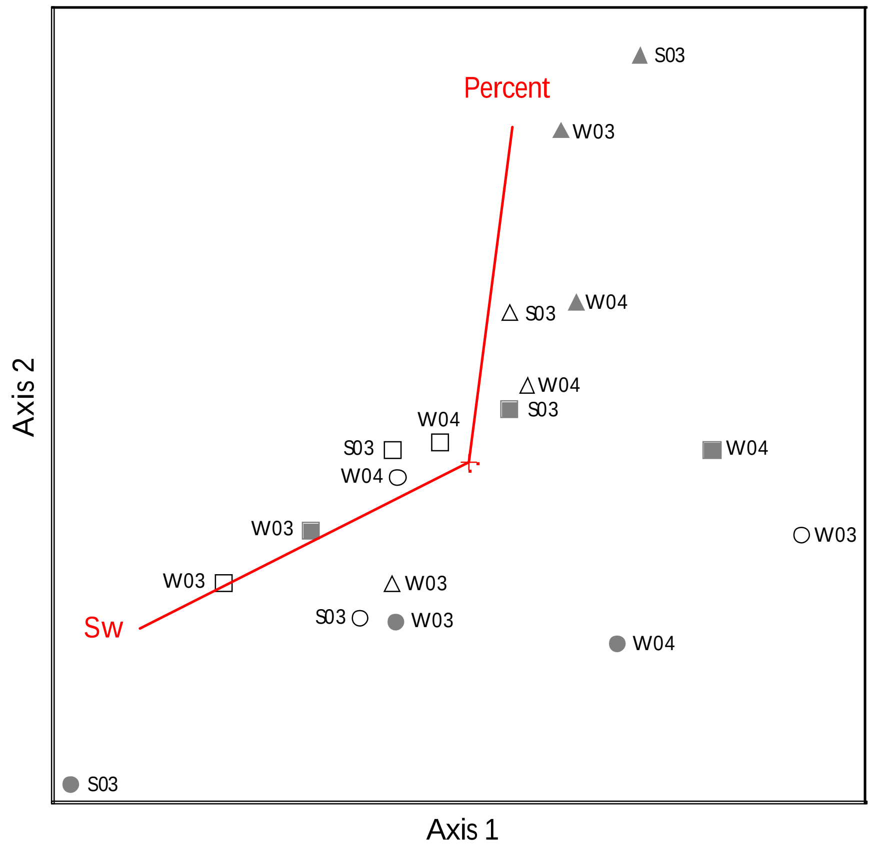


Figure 3.5. Two-dimensional NMS ordination of FRP retention properties. Measurements in un-modified (triangles), degraded (squares) and engineered (circles) reaches of First Creek (shaded shapes) and Fourth Creek (un-shaded shapes) in winter 2003 (W03), spring 2003 (S03) and winter 2004 (W04). Red vectors show the direction of increase in percent FRP retention (percent) and FRP uptake length (S_w) at a cut-off r^2 value of 0.600.

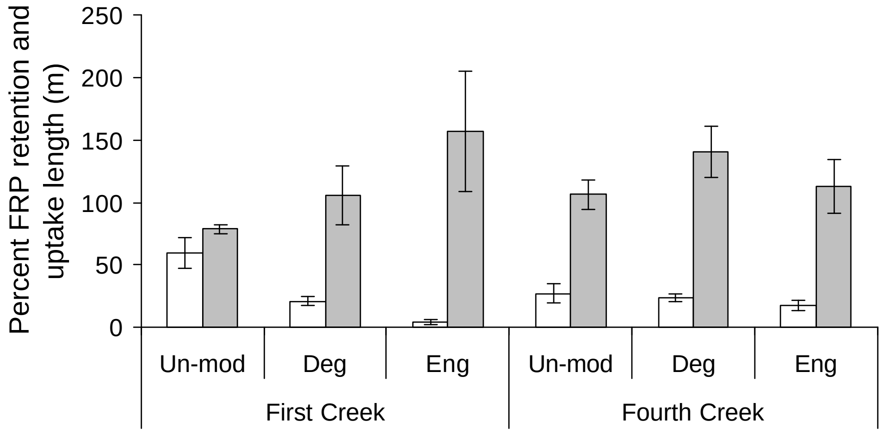


Figure 3.6. Percent filterable reactive phosphorus (FRP) retention and uptake length at 100 m in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks. Clear bars denote percent retention and shaded bars denote uptake length. Error bars are standard errors.

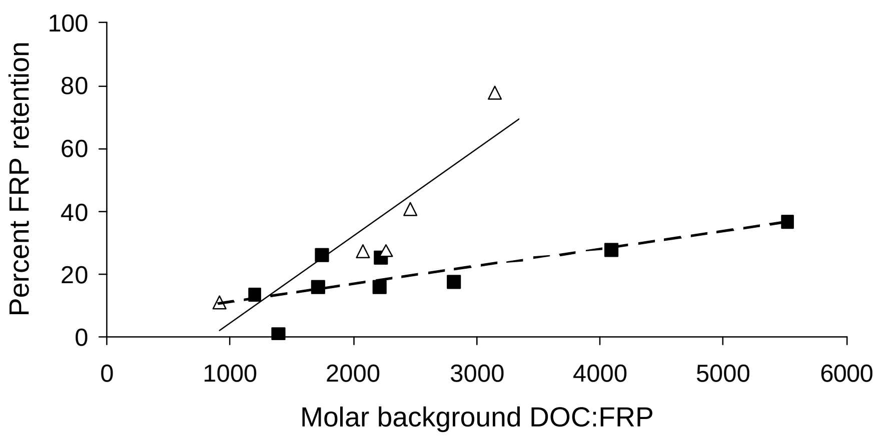


Figure 3.7. Influence of background dissolved organic carbon (DOC) to filterable reactive phosphorus (FRP) molar ratio on percent FRP retention at 100 m in un-modified, degraded and engineered reaches of First and Fourth Creeks. Triangles and squares denote spring and winter experiments, respectively. Full and dashed lines denote fitted linear regressions for spring (p = 0.0382, • = 0.05, r^2 = 0.8075, df = 4) and winter experiments (p = 0.0147, • = 0.05, r^2 = 0.5964, df = 8).

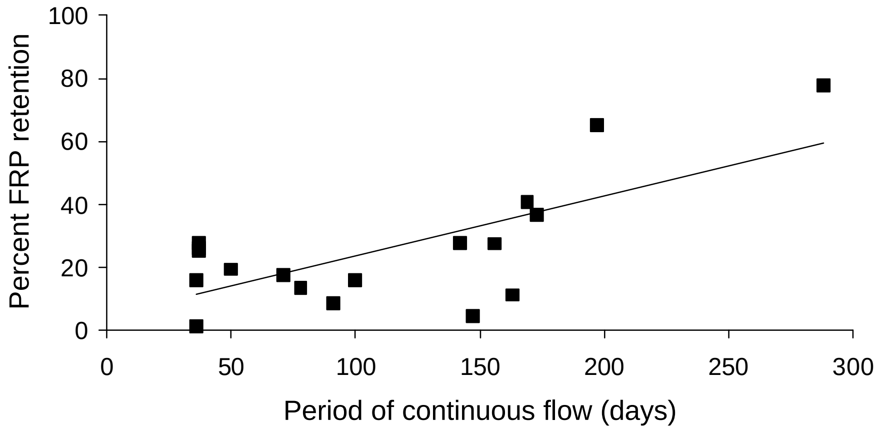


Figure 3.8. Influence of period of continuous flow on percent filterable reactive phosphorus (FRP) retention at 100 m in un-modified, degraded and engineered reaches of First and Fourth Creeks. Full line denotes fitted linear regression (p = 0.0013, • = 0.05, r^2 = 0.4856, df = 17).

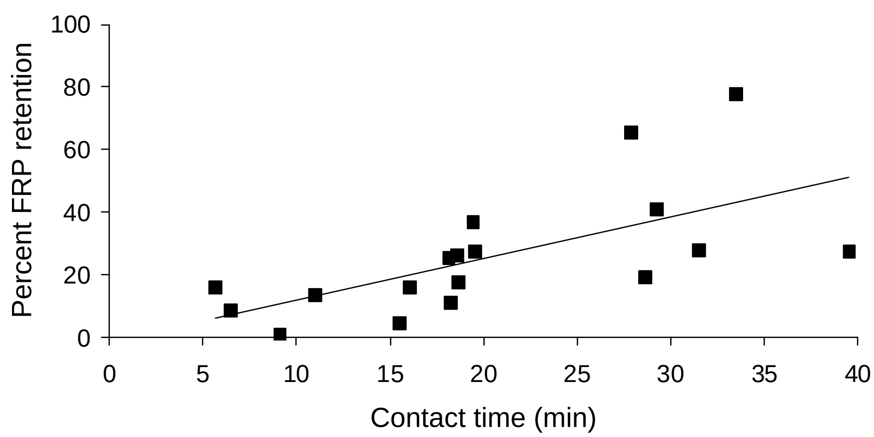


Figure 3.9. Influence of contact time on percent filterable reactive phosphorus (FRP) retention at 100 m in un-modified, degraded and engineered reaches of First and Fourth Creeks. Full line denotes fitted linear regression (p = 0.0039, • = 0.05, r^2 = 0.4152, df = 17).

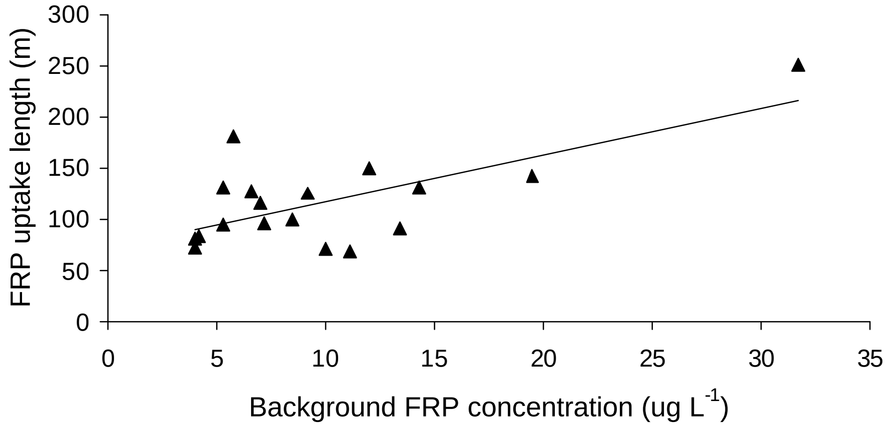


Figure 3.10. Influence of background filterable reactive phosphorus (FRP) concentration on FRP uptake length in un-modified, degraded and engineered reaches of First and Fourth Creeks. Fitted line denotes linear regression (p = 0.0017, • = 0.05, r^2 = 0.4685, df = 17).

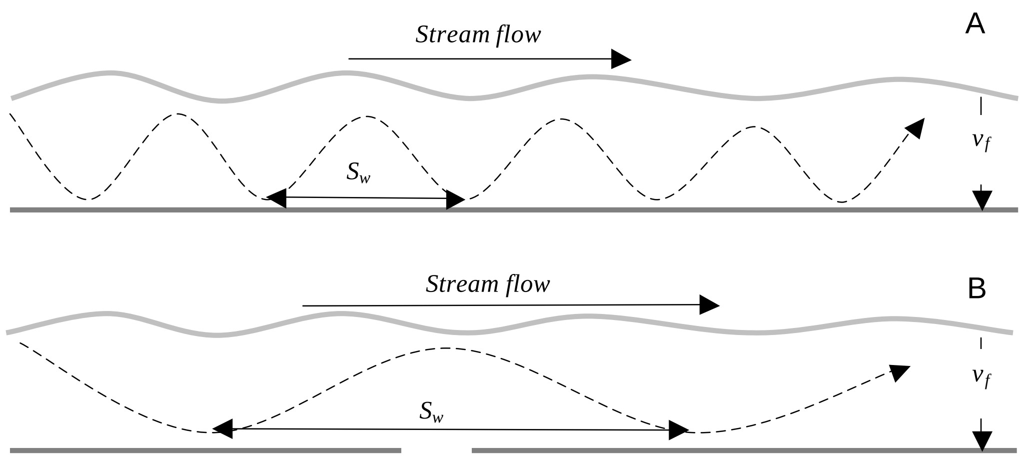


Figure 3.11. Conceptual model of phosphorus cycling in the (A) un-modified and (B) impacted reaches of First Creek. Greater phosphorus demand in the un-modified reach results in a shorter uptake length (S_w) and higher percent FRP retention than in impacted reaches. However, there is no difference in mass transfer coefficient (v_f) because differences in the affinities of the reaches for phosphorus are counteracted by increased contact of molecules with stream compartments in impacted streams due to altered hydrological parameters.

Chapter four

4 Abiotic and biotic benthic phosphorus uptake in stream reaches with varying channel structure across a rural-urban gradient

Abstract. Lower phosphorus retention has been observed in stream reaches with modified channel structures than un-modified reaches. The aim of this project was to investigate the relative importance of abiotic and biotic pathways of phosphorus uptake of benthic rock communities in un-modified and modified reaches. This was investigated through a series of filterable reactive phosphorus (FRP)-uptake experiments. Total benthic FRP uptake was the loss of FRP to un-sterilised rocks, abiotic uptake was the loss to sterilised rocks and biotic uptake was the difference between total and abiotic uptake. Abiotic FRP uptake rates varied between 1.3 and 6.8 •g m^{-2} s^{-1} and were consistently greater than biotic FRP uptake rates, which varied between -5.1 and 3.6 •g m^{-2} s^{-1}. Total and biotic FRP uptake were greatest in the un-modified reaches in two of three seasons and abiotic FRP uptake was greater in the un-modified and degraded reaches than the engineered reaches. Abiotic and biotic uptake rates were closely associated with the availability of sorption sites. Furthermore, biotic FRP uptake was also influenced by the period of continuous flow.

Key words: *Stream, reach, abiotic, biotic, benthic, filterable reactive phosphorus, uptake, rural, urban, channel structure, hydrology, ecological stoichiometry*

4.1 Introduction

The processing of nutrients within streams may be significant for the control of problems associated with anthropogenic nutrient inputs. The ability of streams to retain nutrients is a consequence of a range of biotic and abiotic processes, which provide multiple pathways for nutrient interception and transformation (Brookes *et al.* In press). Early investigations of nutrient retention in streams implied that biological assimilation was the sole pathway (McColl 1974; Elwood *et al.* 1983). This was attributed to biofilms, which have a high nutrient affinity and respond rapidly to nutrient inputs (Pelton *et al.* 1998; Scinto and Reddy 2003). While abiotic uptake of nutrients is considered to be important for nutrient retention (Davis and Minshall 1999; Hall Jr. *et al.* 2002), only a few studies have demonstrated its importance (Munn and Meyer 1990; Hart *et al.* 1991; Haggard *et al.* 1999). Abiotic uptake of nutrients includes adsorption to the surfaces of sediment particles (Webster *et al.* 2001; House and Denison 2002) and surfaces of dead and living organisms (Sanudo-Wilhelmy *et al.* 2004), including biofilms (Lock *et al.* 1984; Flemming 1995).

The multiple impacts of changes in land-use upon stream ecosystems (Paul and Meyer 2001; Walsh *et al.* 2004) are likely to cause a reduction in the number and/or activity of biotic and abiotic pathways of nutrient retention. For example alterations to stream temperature may influence biotic activity (McColl 1974; Martí and Sabater 1996); riparian vegetation may influence light intensity and autotrophic activity (McColl 1974; Martí and Sabater 1996); stream discharge may remove organic matter and reduce biotic activity (Meyer *et al.* In press); water permanency may alter the biotic community (Gasith and Resh 1999); and nutrient availability may influence nutrient demand. Brookes *et al.* (In press) proposed that deterioration of ecosystems may be reflected in their capacity to process resources. Indeed, in chapter three a stream reach within an intact catchment and an un-modified channel structure was shown to retain more phosphorus than impacted reaches.

This project tested the hypothesis that the reduced capacity of urban stream reaches with simplified channel structures to retain phosphorus is a result of a reduced activity of abiotic and biotic pathways of phosphorus uptake. In doing so, the relative importance of abiotic and biotic pathways of phosphorus uptake were compared. This was conducted in un-modified, degraded and engineered reaches of First and Fourth Creeks within the Torrens River Catchment, South Australia (chapter two). Since these pathways are likely to experience considerable seasonal variation, this was investigated on a seasonal basis. The conditions important for controlling abiotic and biotic phosphorus uptake were also investigated.

4.2 Methods

4.2.1 Phosphorus uptake experiments

One experiment was conducted within each reach in the autumn-winter and winter-spring transitions and late spring of 2004 (Table 4.1). During late spring, some reaches were dry and so rocks were collected and the experiment was conducted in the nearest reach containing water. During winter-spring and late spring, a storm event prevented access of equipment to the un-modified reach of First Creek. Consequently, rocks and water were collected and the experiments were conducted in the degraded reach of First Creek.

Benthic rocks were chosen for uptake experiments because they were the dominant substrate of these streams (chapter two). For each experiment, 24 rocks, with diameters of 2-7 cm, were randomly collected. Twelve were placed in an autoclave (R. L. Smith and Co. Ltd., Buckinghamshire, UK) for 25 min at 126ºC to sterilise the attached biofilms, while the remaining 12 were stored in stream water in the dark at 3ºC. Care was taken in collecting rocks, however some loss of loosely attached material was un-avoidable. The following day, three un-sterilised rocks were placed in each of four containers, three sterilised rocks were placed in another four containers and four containers remained without rocks (control). Into each container, 0.5 L of stream water, enriched with di-potassium hydrogen orthophosphate (K_2HPO_4), was introduced. The desired initial filterable reactive phosphorus (FRP) concentration was 70 •g L^{-1}, which is between the upper and background concentrations experienced in these streams.

Four groups of containers were placed randomly in the reach within a 5 m radius so that each group consisted of a container of each treatment (un-sterilised, sterilised, control). The containers were placed so that the surrounding water level was just below the container water level. Water samples of 20 mL were collected from each container with a syringe at 5, 15, 30, 60 and 120 min for analysis of FRP concentration, as described in chapter two. Initial concentrations were considered to be that of the enriched stream water.

Uptake rates over the course of the experiments were calculated as the initial mass of FRP minus the final mass of FRP within each chamber, divided by the surface area of rocks (chapter two), divided by the time (120 min). These rates were corrected for the mass of FRP removed by previous samples and the changes in the control concentration, although these were negligible. Total benthic FRP uptake was measured as the loss of FRP to un-sterilised rocks (and associated biofilm). Abiotic benthic uptake was measured as the loss of

FRP to sterilised rocks, corrected for the control. Biotic benthic uptake was the difference between total and abiotic uptake.

Material attached to the surfaces of rocks was removed and samples were taken for determination of benthic organic matter (BOM) and benthic chlorophyll *a*, as described in chapter two. The material was removed from an additional six rocks and three samples were analysed for total phosphorus (TP) and three for total carbon (TC) and total nitrogen (TN) (chapter two). Molar ratios were calculated, as described in chapter two. Three grab samples were taken from the stream and analysed for background FRP and dissolved organic carbon (DOC) concentrations and molar ratios were calculated, as described in chapter two. Measurements were also taken for stream discharge, period of continuous flow, light intensity, water temperature and day number (chapter two). Reported light intensities are the average underwater instantaneous light intensities during each experiment.

4.2.2 Statistical analyses

To summarise differences in FRP uptake rates (total, abiotic and biotic benthic FRP uptake) a two-dimensional NMS ordination was conducted using PC-ORD (Version 4.10, MjM software, Oregon USA). A main matrix containing all measurements of total, abiotic and biotic benthic FRP uptake rates was overlaid with the same data set in addition to the measured environmental parameters. This revealed a final stress of 3.04 and was suitable for a two-dimensional ordination.

Univariate analyses were performed using JMP-IN (Version 3.2.1, SAS Institute Inc., Cary, USA) to examine the differences in individual FRP uptake rates between the reaches. All samples were tested for homogeneity (O'Brien, Brown-Forsythe, Levene and Bartlett tests) and normality (Shapiro-Wilk test). Differences were compared through three-way analysis of variance with creek, reach and season as fixed effects (model 1). Interaction effects between two or three parameters herein are denoted with *. When interactions were tested, significant effects were accepted if p values were less than 0.01 because interactions place doubt over the F-ratio of the main effects. In all other analyses, statistically significant relationships were accepted if p values were less than 0.05. Differences in BOM and benthic chlorophyll *a* between sterilised and un-sterilised samples were compared through one-way analysis of variance. Relationships between environmental conditions and

FRP uptake rates were analysed by regression analysis. Variability between replicates is reported as standard errors.

4.3 Results

4.3.1 Environmental conditions

The un-modified reach of First Creek had a greater period of continuous flow than all other reaches (Table 4.1). During spring, the engineered reach of First Creek and degraded and engineered reaches of Fourth Creek had ceased to flow. Discharge was highly variable, with maximum discharge during winter-spring (Table 4.2). Water temperature was generally higher in the urban reaches (including the un-modified reach of First Creek in autumn-winter and late spring) and highest during late spring. Light intensity was higher in Fourth Creek than First Creek and highest in late spring in all reaches of Fourth Creek and the engineered reach of First Creek (Table 4.2). Background FRP concentrations and DOC concentrations varied considerably and were lowest in the un-modified reaches (Table 4.2).

4.3.2 Benthic organic matter

Benthic organic matter was variable (0.8-14.9 mg m^{-2}), but was not different between sterilised and un-sterilised rocks (Table 4.3). In general, BOM was highest during autumn-winter. Benthic chlorophyll *a* ranged between 0.3 and 28.4 mg m^{-2} and was higher on un-sterilised than sterilised rocks (Table 4.3, p = 0.0189, • = 0.05, df = 17), owing to cell lysis. Benthic TP, TC and TN were lowest in un-modified reaches (Table 4.4) and lowest during winter-spring in all reaches except for the engineered reach of First Creek for TP and the degraded reach of Fourth Creek for TP, TC and TN (Table 4.4). In First Creek, benthic TC to TP and TN to TP molar ratios were highest in the un-modified reach and lowest in the engineered reach (Table 4.4). In Fourth Creek, there was little difference between the reaches. Benthic TC to TN molar ratios decreased during the experimental period and were highest in the un-modified reaches during autumn-winter and winter-spring.

4.3.3 Benthic FRP uptake

Changes in FRP uptake during the experiments varied between the reaches, as shown by Figures 4.1 and 4.2 for autumn-winter. In the un-modified reaches, abiotic and biotic uptake increased for the duration of the experiment and abiotic uptake was greater than biotic uptake (Figures 4.1A and 4.2A). This was similar for the degraded reaches and the engineered reach of Fourth Creek, although abiotic and biotic uptake was lower (Figures 4.1B, 4.2B, 4.2C). In the engineered reach of First Creek, FRP uptake increased until 30 min, after which time there was no further FRP uptake (Figure 4.1C).

These differences exemplified differences in benthic FRP uptake rates between the reaches. There was a transition in the two dimensional distributions of uptake rates from engineered reaches to degraded reaches to un-modified reaches (Figure 4.3). This transition was associated with changes in total and biotic benthic FRP uptake rates and background FRP concentrations. Un-modified reaches were associated with higher uptake rates and lower FRP concentrations than the degraded and engineered reaches. The engineered reaches also had broader distributions than the un-modified and degraded reaches due to the variability in uptake rates observed in engineered reaches (Figures 4.4-4.6). Despite the differences in the distributions, there was considerable over-lap (Figure 4.3), suggesting that differences were not consistent across seasons and creeks.

4.3.4 <u>Total benthic FRP uptake rates</u>

Although un-modified reaches were associated with high total benthic FRP uptake rates (Figure 4.3), differences between reaches were not consistent across seasons and creeks (Figure 4.4). Combining the results of both creeks, in autumn-winter and late spring, the un-modified reaches had greater rates than degraded and engineered reaches. However, during winter-spring the degraded reaches had greater rates than the un-modified reaches and so the effect of reach was dependant upon the effect of season (Table 4.5). Similarly, the effect of reach was also dependant upon the effect of creek (Table 4.5). Combining all seasons, in First Creek rates were greatest in the un-modified reach and lowest in the engineered reach. In Fourth Creek rates were not different in the degraded and engineered reaches (Figure 4.4). Since the effect of reach was dependant upon creek and season, there was an effect of reach*season*creek (Table 4.5).

Differences in total benthic FRP uptake rate were dependant upon a number of factors (Table 4.6). A majority of the variation was explained by differences in nutrient availability, including, background FRP concentration, background DOC to FRP molar ratio (Figure 4.7) and benthic TC to TP molar ratio (Table 4.6). For the latter, the value of the un-modified reach of First Creek during winter-spring was removed, as the molar ratio was greater than one order of magnitude higher than all other values.

4.3.5 Biotic benthic FRP uptake rates

Differences in biotic benthic FRP uptake rates were similar to those of total uptake rates, with the influence of reach not consistent across seasons and creeks (Figure 4.4). In autumn-winter and late spring, un-modified reaches had the greatest uptake rates, but during winter-spring rates were greater in degraded reaches than un-modified reaches (Figure 4.5). Also, in First Creek uptake rates were greatest in the un-modified reach and lowest in the engineered reach, but in Fourth Creek rates were greater in the engineered reach than the degraded reach (Figure 4.5). Since the effect of reach was dependant upon creek and season, there was also an effect of reach*season*creek (Table 4.5).

Biotic benthic FRP uptake rates were dependant upon a number of factors (Table 4.6). Much of the variation was explained by differences in nutrient availability, including, background FRP concentration and background DOC to FRP molar ratio (Table 4.6). In addition, biotic benthic FRP uptake rate had a positive relationship with the period of continuous flow (Table 4.6, Figure 4.8).

4.3.6 Abiotic benthic FRP uptake rates

Differences in abiotic benthic FRP uptake rates between reaches were not as evident as total and biotic uptake rates (Figure 4.6). Combining both creeks, although engineered reaches had lowest uptake rates in all seasons, the reach with the highest uptake rates varied seasonally; un-modified reaches in autumn-winter; degraded reaches in late spring; and un-modified and degraded reaches in winter-spring. Consequently, the effect of reach was dependant upon the effect of season (Table 4.5). In addition, the effect of season was dependant upon creek (Table 4.5) because in First Creek rates were lowest in winter-spring, whereas in Fourth Creek rates were lowest in late spring (Figure 4.6). Since the effect of reach was dependant upon season and the effect of season was dependant upon creek, there was an effect of reach*season*creek (Table 4.5).

Differences in abiotic benthic FRP uptake rates were only significantly explained by differences in BOM (Table 4.6) and the TC to TP molar ratio of BOM (Table 4.6, Figure 4.9). For the latter, the value of the un-modified reach of First Creek in winter-spring was removed, as the molar ratio was greater than one order of magnitude higher than all other values.

4.3.7 Summary

There were differences in total, abiotic and biotic benthic FRP uptake rates between the reaches, but the response was dependant upon the effects of creek and season. In general, total and biotic benthic FRP uptake rates were greatest in the un-modified reaches, except in winter-spring. Biotic benthic FRP uptake rates were most dependant upon the phosphorus availability in the water column and the period of continuous flow. Abiotic benthic FRP uptake rates were greater in the un-modified and degraded reaches than the engineered reaches and were most dependant upon the amount and phosphorus availability of BOM.

4.4 Discussion

Chapter three demonstrated that percent FRP retention decreased and uptake lengths increased in reaches with varying channel structures across a rural-urban gradient, despite nutrient demand increasing longitudinally in streams (Mulholland *et al.* 1995). However, percent FRP retention and uptake lengths do not necessarily reflect the affinity of stream compartments for phosphorus. In this project, the affinity of abiotic and biotic benthic pathways for phosphorus varied between un-modified, degraded and engineered reaches. Abiotic benthic FRP uptake rates were greater than biotic uptake rates, which was also found in another Australian stream (Hart *et al.* 1991), but not in American streams (Munn and Meyer 1990; Haggard *et al.* 1999). However, a majority of the difference in total benthic FRP uptake was attributed to biotic pathways. In two of three seasons, biotic and total uptake rates were greatest in un-modified reaches, reflecting more efficient resource interception.

Rates of phosphorus uptake in this study were substantially higher than those elsewhere, including in intact headwater streams (Munn and Meyer 1990; Davis and Minshall 1999) and impacted streams (Kronvang *et al.* 1999) and were greater than ammonium uptake rates across a range of biomes in North America (Webster *et al.* 2003). Furthermore, uptake rates were at the upper end of the range of an Australian river (Webster *et al.* 2001) and were far greater than those of a benthic community per unit algal biomass (Planas *et al.* 1996). A potential explanation is the relatively high light intensities and water temperatures of these streams, which would stimulate microbial activity. However, uptake rates had inverse relationships with light intensity and temperature. This is thought to be an artefact of lower uptake rates in urban reaches, which also had higher light intensities and temperatures.

The high uptake rates were most likely due to the low phosphorus availability within the water column and organic matter, which biotic and abiotic phosphorus uptake were dependant upon. This has been observed elsewhere (McColl 1974; Hart *et al.* 1992; Martí and Sabater 1996; Bernhardt and Likens 2002; Dodds *et al.* 2004). Frost *et al.* (2002) suggested that changes in land-use may influence the relative abundances of different elements and that ecological stoichiometry, that is the relative proportions of chemical elements in ecosystems, is important in determining the transformation of resources to higher organisms. Indeed, biotic benthic FRP uptake was greatest in those reaches where phosphorus was most limiting; in the un-modified reach of Fourth Creek, where water column phosphorus availability was low and in the un-modified reach of First Creek, where water column phosphorus and BOM phosphorus availability were low.

Abiotic phosphorus uptake appeared to be dependant upon the number of interception pathways available, since it showed a strong relationship with the amount of BOM and the TC to TP molar ratio of BOM. Abiotic phosphorus uptake was lowest in winter-spring when there was lowest BOM, which coincides with the greatest number of rain-events, which may re-set abiotic pathways through the removal of organic material (Acuna *et al.* 2004). Meyer *et al.* (In press) demonstrated that lower nutrient retention in urban streams than rural streams was related to reduced BOM as a result of increased peak-flows in urban streams.

Shortening of the wet period may also reduce the capacity of the biotic community to respond to nutrient inputs, as biotic FRP uptake was explained by the period of continuous flow. Although partial drying of substrates may increase their affinity for nutrients (Baldwin and Mitchell 2000), the length of dry periods may alter community composition (Peterson and Boulton 1999; Gottlieb *et al.* 2005) and complete desiccation may lead to death of bacteria. Subsequent re-wetting may then cause an initial flush of nutrients (Baldwin and Mitchell 2000), as was observed in this study when reaches had been dry and were re-wet.

The uptake of nutrients by biotic and abiotic pathways will have important implications for downstream ecosystems, such as reducing nutrient concentrations (Mulholland 2004) and converting dissolved nutrients to fine particulate nutrients (Meyer and Likens 1979). It is also likely that there are important interactions that occur between the abiotic and biotic pathways and removal of either pathway will have implications for the other. Therefore, although biotic FRP uptake accounted for a majority of the difference in total uptake, it is essential that both pathways are preserved and rehabilitated to enhance resource interception. It is evident from this study that changes in land-use that alter the hydrology and nutrient availability in streams will have implications for the functioning of in-stream communities. It is therefore important that management practices are carried out to address these impacts, which will enhance resource interception and transformation.

Table 4.1. Dates, times and period of continuous flow in autumn-winter (AW), winter-spring (WS) and late spring (S) in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks during 2004.

Parameter	Season	First Creek			Fourth Creek		
		Un-mod	Deg	Eng	Un-mod	Deg	Eng
Time and date	AW	12:00 12 May	11:00 21 May	11:30 25 May	10:30 11 June	10:20 4 June	10:40 28 May
	WS	11:05 25 Aug.	10:00 19 Aug.	10:00 31 Aug.	10:00 10 Sep.	10:10 3 Sep.	10:00 16 Sep.
	S	10:00 26 Oct.	10:30 25 Oct.	10:00 27 Oct.	09:30 3 Nov.	09:35 1 Nov.	09:40 2 Nov.
Period of continuous flow (days)	AW	134	4	8	25	48	11
	WS	230	94	106	116	109	122
	S	292	161	-30	170	-15	-7

Table 4.2. Environmental parameters in autumn-winter (AW), winter-spring (WS) and late spring (S) in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks. Mean ± standard error.

Parameter	Season	First Creek			Fourth Creek		
		Un-mod	Deg	Eng	Un-mod	Deg	Eng
Discharge ($L\ s^{-1}$)	AW	17	7	13	81	20	8
	WS	112	273	48	1674	52	421
	S	16	9	0	3	0	0
Water temperature (°C)	AW	11.5	15.2	15.7	13.3	13.2	15.0
	WS	13.0	10.4	13.0	11.1	12.7	12.7
	S	17.0	16.8	17.9	15.5	22.3	16.5
Light intensity (•mol $m^{-2}\ s^{-1}$)	AW	121 ± 3.4	98 ± 18.3	51 ± 4.6	229 ± 50.2	246 ± 9.2	115 ± 12.4
	WS	83 ± 10.5	73 ± 3.7	239 ± 39.7	89 ± 14.8	123 ± 18.8	214 ± 27.4
	S	25 ± 1.8	28 ± 7.8	566 ± 66.6	223 ± 26.2	992 ± 53.9	355 ± 57.4
Background FRP (•g L^{-1})	AW	3 ± 0.5	18 ± 1.4	5 ± 0.4	7 ± 1.0	34 ± 0.6	16 ± 0.6
	WS	5 ± 0.6	16 ± 1.5	13 ± 0.0	16 ± 0.6	9 ± 0.6	11 ± 1.5
	S	2 ± 2.2	13 ± 0.6	83 ± 0.6	1 ± 0.0	50 ± 0.6	8 ± 0.0
Initial FRP (•g L^{-1})	AW	82 ± 0.7	76 ± 1.3	54 ± 1.7	66 ± 0.4	70 ± 0.4	75 ± 1.2
	WS	60 ± 0.4	71 ± 1.1	44 ± 0.5	68 ± 0.5	62 ± 0.7	74 ± 0.5
	S	61 ± 1.6	71 ± 0.5	126 ± 1.2	65 ± 0.8	80 ± 0.4	87 ± 0.8
DOC (mg L^{-1})	AW	2.4 ± 0.05	16.3 ± 0.77	28.3 ± 0.89	4.1 ± 0.14	10.4 ± 0.21	9.0 ± 0.14
	WS	5.9 ± 0.05	5.8 ± 0.19	18.8 ± 1.27	7.2 ± 0.05	11.9 ± 1.77	7.8 ± 0.02
	S	4.0 ± 0.26	18.5 ± 0.26	4.2 ± 0.46	4.1 ± 0.44	10.8 ± 1.75	17.9 ± 1.90

Table 4.3. Benthic organic matter and benthic chlorophyll *a* on un-sterilised and sterilised rocks in autumn-winter (AW), winter-spring (WS) and late spring (S) in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks. Mean ± standard error.

Creek	Reach	Season	Benthic organic matter ($g\ m^{-2}$)		Benthic chlorophyll a ($mg\ m^{-2}$)	
			Un-sterilised	Sterilised	Un-sterilised	Sterilised
First	Un-mod	AW	4.5 ± 0.92	14.9 ± 5.14	9.9 ± 1.76	2.9 ± 0.96
		WS	1.1 ± 0.25	0.8 ± 0.11	0.3 ± 0.04	0.1 ± 0.01
		S	2.7 ± 0.25	2.1 ± 0.3	2.5 ± 0.36	0.9 ± 0.11
	Deg	AW	7.3 ± 1.2	13.8 ± 3.48	0.6 ± 0.02	0.4 ± 0.09
		WS	1.4 ± 0.13	1.5 ± 0.3	1.6 ± 0.18	0.3 ± 0.02
		S	2.3 ± 0.47	2.0 ± 0.12	6.3 ± 1.34	1.7 ± 0.10
	Eng	AW	2.2 ± 0.49	3.6 ± 1.73	0.9 ± 0.13	0.6 ± 0.10
		WS	4.0 ± 0.23	2.5 ± 0.2	26.0 ± 3.22	3.6 ± 1.00
		S	4.1 ± 0.42	2.6 ± 0.17	2.7 ± 0.5	1.4 ± 0.27
Fourth	Un-mod	AW	2.6 ± 0.26	3.8 ± 0.58	5.2 ± 0.71	1.4 ± 0.31
		WS	1.6 ± 0.10	1.3 ± 0.13	0.8 ± 0.06	0.2 ± 0.02
		S	2.2 ± 0.38	1.3 ± 0.19	6.8 ± 1.35	0.9 ± 0.25
	Deg	AW	2.0 ± 0.2	7.4 ± 3.01	0.9 ± 0.23	0.3 ± 0.04
		WS	4.3 ± 0.79	3.0 ± 0.18	28.4 ± 3.88	2.5 ± 0.24
		S	4.5 ± 0.46	2.2 ± 0.5	1.4 ± 0.31	0.6 ± 0.14
	Eng	AW	7.2 ± 3.04	30.5 ± 6.91	1.4 ± 0.11	0.6 ± 0.15
		WS	2.7 ± 0.24	1.8 ± 0.26	15.4 ± 3.84	3.0 ± 0.78
		S	2.0 ± 0.16	1.8 ± 0.15	2.2 ± 0.3	0.6 ± 0.09

Table 4.4. Benthic total phosphorus (TP), total carbon (TC) and total nitrogen (TN) and molar ratios in autumn-winter (AW), winter-spring (WS) and late spring (S) in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks. Mean ± standard error.

Parameter	Season	First Creek			Fourth Creek		
		Un-mod	Deg	Eng	Un-mod	Deg	Eng
Benthic TP ($mg\ m^{-2}$)	AW	0.9 ± 0.89	5.8 ± 0.61	11.8 ± 1.30	7.1 ± 1.48	3.5 ± 0.21	12.4 ± 2.10
	WS	0.04 ± 0.01	4.1 ± 0.19	15.8 ± 2.37	2.5 ± 0.25	13.0 ± 2.32	5.0 ± 0.98
	S	1.1 ± 1.00	8.7 ± 2.02	12.1 ± 2.75	5.0 ± 0.56	6.3 ± 0.59	5.7 ± 0.64
Benthic TC ($mg\ m^{-2}$)	AW	814 ± 66.1	2056 ± 585.5	1167 ± 262.9	1306 ± 302.2	595 ± 40.0	2315 ± 446.4
	WS	537 ± 29.0	662 ± 172.4	966 ± 98.6	354 ± 12.7	1288 ± 284.8	868 ± 215.4
	S	564 ± 46.5	1378 ± 88.4	1913 ± 610.5	828 ± 69.4	3491 ± 584.2	907 ± 124.3
Benthic TN ($mg\ m^{-2}$)	AW	34 ± 20.1	144 ± 49.0	77 ± 30.5	72 ± 28.2	49 ± 16.5	258 ± 28.9
	WS	33 ± 10.5	62 ± 9.1	117 ± 16.7	23 ± 22.4	140 ± 34.9	127 ± 28.6
	S	73 ± 9.9	171 ± 2.9	212 ± 46.7	129 ± 12.9	279 ± 56.3	222 ± 82.3
Benthic TC to TP (molar)	AW	2216.6	913.6	254.5	471.2	439.2	482.9
	WS	36350.0	415.7	157.6	364.2	243.4	444.9
	S	1350.7	409.4	407.1	425.7	1440.0	411.9
Benthic TC to TN (molar)	AW	27.6	16.6	17.7	21.1	14.1	10.5
	WS	19.1	12.5	9.6	18.0	10.2	8.0
	S	9.1	9.4	10.5	7.5	14.6	4.8
Benthic TN to TP (molar)	AW	80.2	55.0	14.3	22.4	31.1	46.2
	WS	1901.8	33.2	16.4	20.3	23.8	55.9
	S	149.0	43.6	38.7	56.8	98.8	86.6

Table 4.5. P-values obtained for effects of reach, season and creek (and interactions) on total, abiotic and biotic benthic FRP uptake rates. For the effect of creek, reach, season, creek*reach and creek*season *df* = 2. For the effect of reach*season and creek*reach*season *df* = 4. Significant effects are those with *p* less than 0.01.

Effect	Total benthic FRP uptake rate	Abiotic benthic FRP uptake rate	Biotic benthic FRP uptake rate
Reach	<0.0001	<0.0001	<0.0001
Season	<0.0001	<0.0001	0.0001
Creek	0.2951	0.0397	0.0546
Reach*season	<0.0001	0.0109	<0.0001
Reach* creek	<0.0001	0.2387	0.0009
Creek*season	0.1373	<0.0001	0.3191
Reach*season * creek	<0.0001	<0.0001	<0.0001

Table 4.6. Statistics and relationships obtained for influence of environmental parameters on benthic FRP uptake rates. Relationships include exponential (exp) and natural log (ln) transforms of parameters (x) and FRP uptake rates (y). For all analyses df = 17. Only significant effects are shown.

Parameter	Statistic and relationship	Total benthic FRP uptake rate	Abiotic benthic FRP uptake rate	Biotic benthic FRP uptake rate
Light intensity	p	0.0115	---	0.0047
	r^2	0.3375	---	0.4020
	Relationship	Inverse linear	---	Inverse linear
Water temperature	p	---	---	0.0338
	r^2	---	---	0.2519
	Relationship	---	---	Inverse linear
Period of continuous flow	p	---	---	0.0007
	r^2	---	---	0.5244
	Relationship	---	---	Positive ln(x)
Background FRP	p	<0.0001	---	0.0001
	r^2	0.6879	---	0.6195
	Relationship	Inverse linear	---	Inverse linear
Initial FRP	p	0.0269	---	0.0002
	r^2	0.2706	---	0.5932
	Relationship	Inverse linear	---	Inverse linear
Background DOC to FRP molar ratio	p	0.0074	---	0.0015
	r^2	0.3698	---	0.4755
	Relationship	Positive ln(x)	---	Positive ln(x)
Benthic organic matter	p	---	0.0499	---
	r^2	---	0.2194	---
	Relationship	---	Positive exp(x)	---
Benthic TC to TP molar ratio	p	0.0010	<0.0001	---
	r^2	0.5277	0.6537	---
	Relationship	Positive exp(y)	Positive exp(y)	---

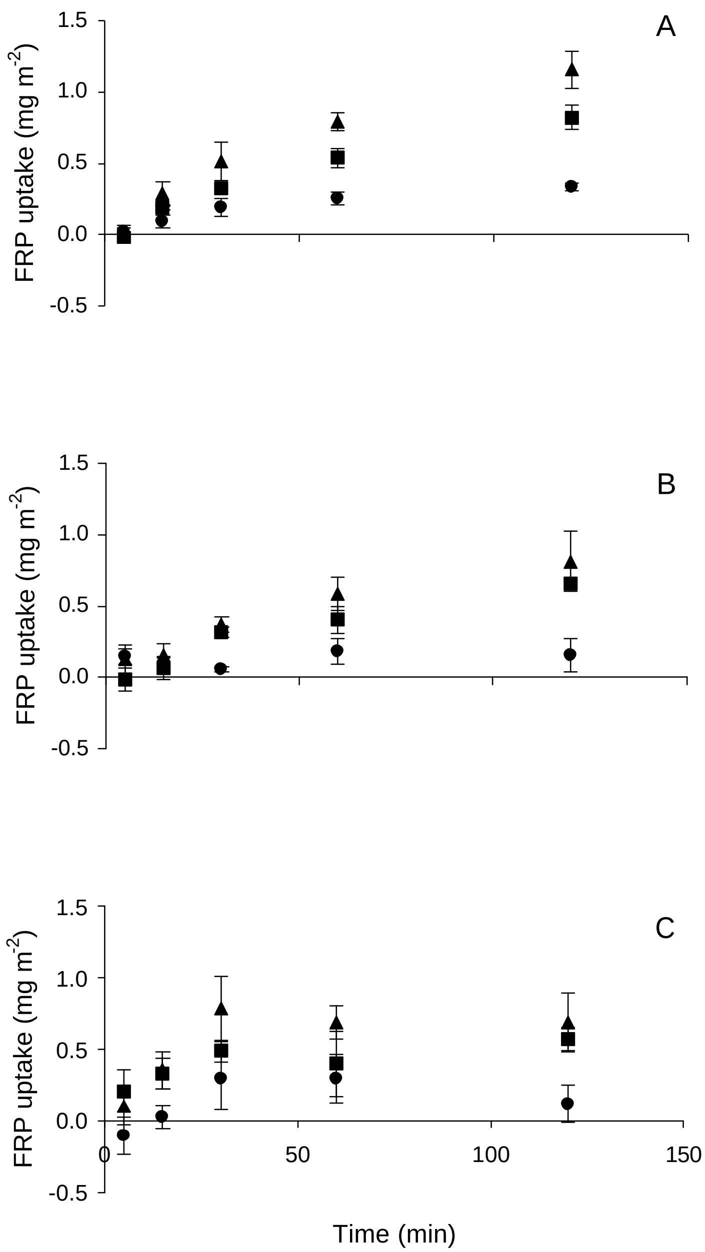


Figure 4.1. Total, abiotic and biotic benthic FRP uptake in First Creek during autumn-winter in (A) un-modified, (B) degraded and (C) engineered reaches. Triangles denote total benthic FRP uptake, squares denote abiotic benthic FRP uptake and circles denote biotic benthic FRP uptake. Error bars are standard errors.

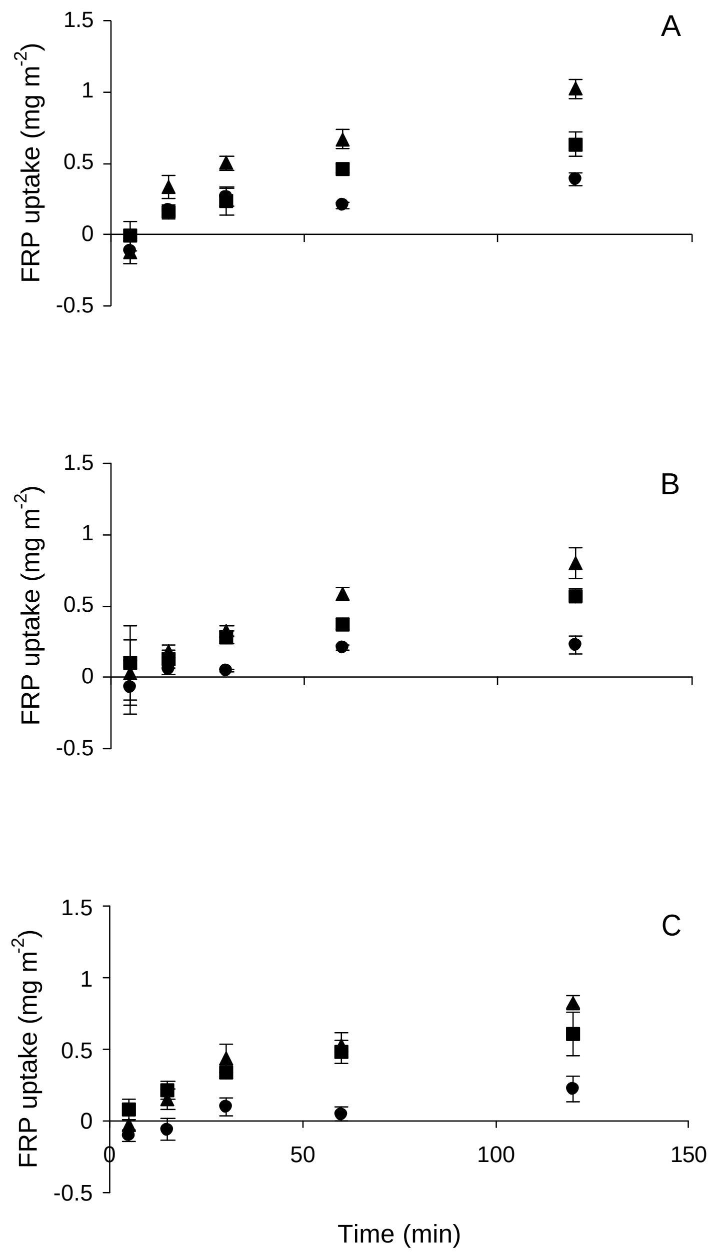


Figure 4.2. Total, abiotic and biotic benthic FRP uptake in Fourth Creek during autumn-winter in (A) un-modified, (B) degraded and (C) engineered reaches. Triangles denote total benthic FRP uptake, squares denote abiotic benthic FRP uptake and circles denote biotic benthic FRP uptake. Error bars are standard errors.

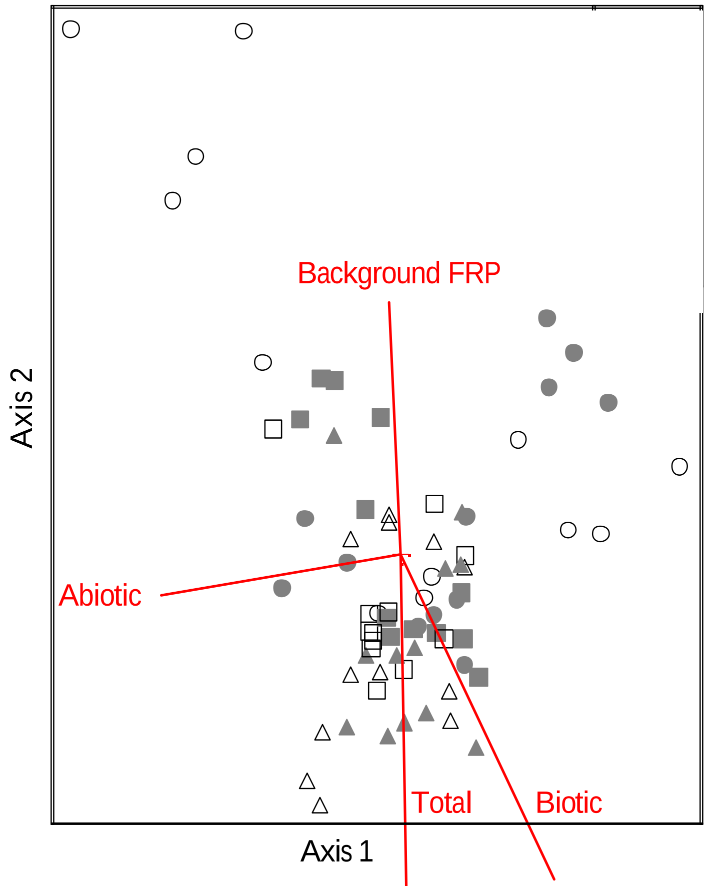


Figure 4.3. Two-dimensional NMS ordination of total, abiotic and biotic benthic FRP uptake rates. Triangles denote measurements in un-modified reaches, squares denote degraded reaches and circles denote engineered reaches in First Creek (un-shaded shapes) and Fourth Creek (shaded shapes). Red vectors show the direction of increase in benthic FRP uptake rates and background FRP concentrations and their association with the two-dimensional distribution, at a cut-off r^2 value of 0.650.

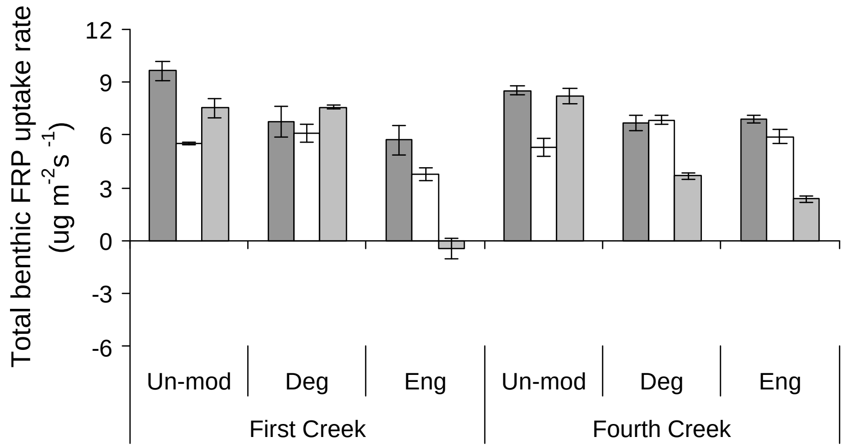


Figure 4.4. Total benthic FRP uptake rates in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks during autumn-winter (dark shaded), winter-spring (un-shaded) and late spring (light shaded). Error bars are standard errors.

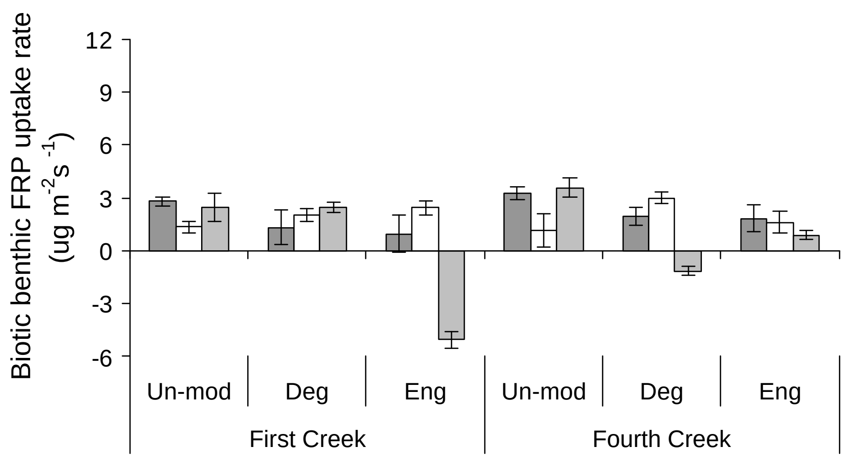


Figure 4.5. Biotic benthic FRP uptake rates in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks during autumn-winter (dark shaded), winter-spring (un-shaded) and late spring (light shaded). Error bars are standard errors.

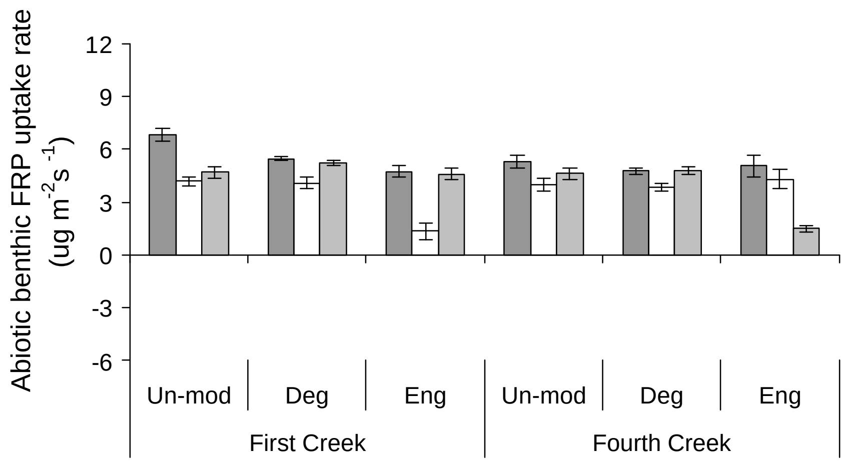


Figure 4.6. Abiotic benthic FRP uptake rates in un-modified (Un-mod), degraded (Deg) and engineered (Eng) reaches of First and Fourth Creeks during autumn-winter (dark shaded), winter-spring (un-shaded) and late spring (light shaded). Error bars are standard errors.

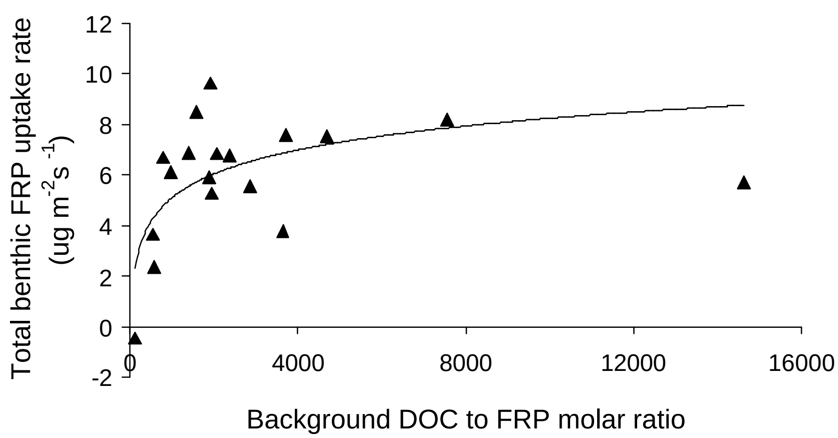


Figure 4.7. Influence of background dissolved organic carbon (DOC) to filterable reactive phosphorus (FRP) molar ratio on total benthic FRP uptake rate in un-modified, degraded and engineered reaches of First and Fourth Creeks. Full line denotes regression with natural log transform of background DOC to FRP molar ratio (p = 0.0015, • = 0.05, r^2 = 0.3698, df = 17).

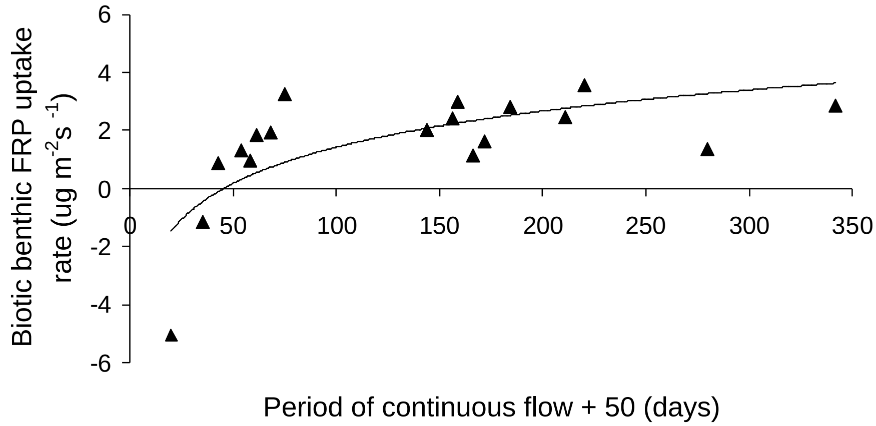


Figure 4.8. Influence of period of continuous flow on biotic benthic FRP uptake rate in un-modified, degraded and engineered reaches of First and Fourth Creeks. Full line denotes regression, with natural log transform of period of continuous flow plus 50 (p = 0.0007, • = 0.05, r^2 = 0.5244, df = 17).

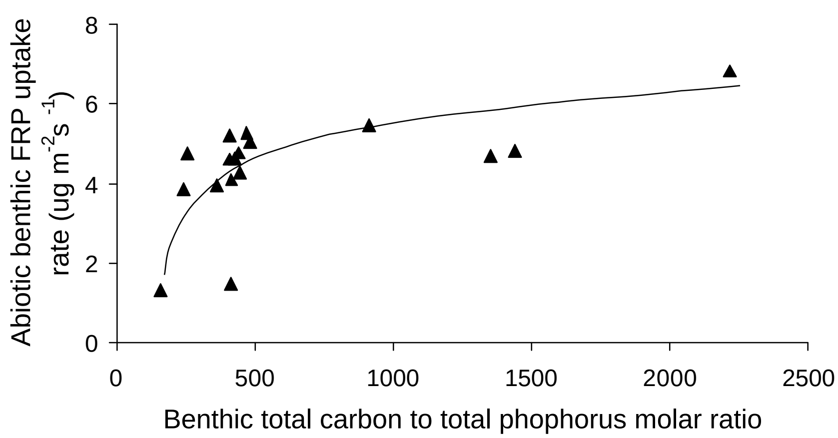


Figure 4.9. Influence of benthic total carbon to total phosphorus molar ratio on abiotic benthic FRP uptake rate in un-modified, degraded and engineered reaches of First and Fourth Creeks. Full line denotes regression, with exponential transform of abiotic benthic FRP uptake rate (p = <0.0001, • = 0.05, r^2 = 0.6537, df = 17).

Chapter five

5 Changes in metabolism of stream reaches with varying channel structure across a rural-urban gradient

Abstract. The aim of this project was to assess differences in stream metabolism in reaches with varying channel structure. Gross primary production (GPP), community respiration (CR) and net ecosystem production (NEP) were assessed across a rural-urban gradient within two streams. In First Creek, which has a predominately intact upper catchment, the un-modified rural reach showed little seasonal variation in metabolic rates and had a positive NEP. In contrast, the degraded-urban reach of First Creek showed greater variation and NEP switched between negative and positive. In Fourth Creek, which has a predominately agricultural upper catchment, un-modified, degraded and engineered reaches had higher CR and GPP than the un-modified reach of First Creek and experienced considerable seasonal variation. In general, there was an effect of reach upon metabolic rates, but the effect changed seasonally, with greater metabolic rates in the degraded reach than un-modified reach later in warmer seasons. However, metabolic rates within the engineered reach were generally lower than that of the degraded reach. Metabolism in the un-modified reach of First Creek, which was the most pristine, was more resilient to perturbations and reflected more efficient resource transformation than in impacted reaches.

Keywords: *Stream, reach, metabolism, gross primary production, community respiration, net ecosystem production, urbanisation, agriculture, channel structure*

5.1 Introduction

Stream metabolism encompasses the biological and chemical processes that stream organisms carry out in order to sustain life. At the ecosystem level, stream metabolism includes gross primary production (GPP), community respiration (CR) and net ecosystem production (NEP). Much of the metabolism that occurs in streams is attributed to biofilms, which contain autotrophic and heterotrophic organisms that act as important energy sources for higher organisms (Rounick *et al.* 1982; Rounick and Winterbourn 1983; Stock and Ward 1989; Hall Jr. and Meyer 1998). Consequently, biofilms provide sites for the transformation, decomposition and storage of metabolites and nutrients.

The replacement of native vegetation with developed areas has greatly altered conditions within streams (Paul and Meyer 2001). A number of these conditions have been shown to be important determinants of stream metabolism, including: water regime (Elosegui and Pozo 1998; Acuna *et al.* 2004), stream morphology (Cardinale *et al.* 2002b), organic matter (Acuna *et al.* 2004), nutrients (Mulholland *et al.* 2001; Stelzer *et al.* 2003) and light availability (Bunn *et al.* 1999; Mosisch *et al.* 2001; Mulholland *et al.* 2001). Consequently, changes to stream metabolism are likely, which may have implications for the efficiency of resource transformation and for the condition of downstream ecosystems (Brookes *et al.* In press). A dominance of stream metabolism by particular functional groups has been shown to be reflective of inefficient transformation of resources as few resources are passed onto higher organisms. Bunn *et al.* (1999) demonstrated that high GPP coincided with the dominance of autotrophic organisms that did not enter higher trophic levels. A dominant heterotrophic community may also be perceived as a decline in stream condition since it may lead to deoxygenation and an un-suitable habitat for a range of organisms (Wu *et al.* 2003; Connolly *et al.* 2004).

The aim of this project was to assess differences in metabolism between stream reaches with varying channel structures across a rural-urban gradient. This was conducted within the un-modified and degraded reaches of First and Fourth Creeks and the engineered reach of Fourth Creek within the Torrens River Catchment (chapter two). It was hypothesised that metabolic rates within stream reaches impacted by changes in land-use would be dominated by individual functional groups, which would reflect inefficient transformation of resources. Stream metabolism was studied on a seasonal basis and the conditions important for controlling differences in stream metabolism were investigated.

5.2 Methods

5.2.1 Stream metabolism

Stream metabolism was measured in each reach during winter 2003, spring 2003 and the transitions between autumn-winter 2004 and winter-spring 2004 (Table 5.1). Metabolism was measured using re-circulating benthic chambers. Open water measurements were not suitable due to the turbulent nature of these streams, which prevents accurate measurements of re-aeration rates (Bott *et al.* 1985; Bott *et al.* 1997). Benthic rocks were used within the chambers as they are the principal substrate within the streams (chapter two). During winter-spring 2004, a storm-event prevented access of equipment to the un-modified reach of First Creek. Consequently, rocks were removed and the experiment was conducted in the degraded reach of First Creek. Although these measures do not include hyporheic metabolism or metabolism upon other substrates, the combined effect of benthic rock and pelagic metabolism was considered to be indicative of stream reach metabolism and is referred to as stream metabolism.

Benthic rocks were randomly chosen within a stream reach and placed within three or four sealed chambers that also contained stream water. Chambers were randomly placed at a known depth within the 100 m reach and dissolved oxygen levels were recorded at 10 min intervals over 36 h to capture a complete day-night cycle. Measurements of dissolved oxygen concentration and temperature were recorded using TPS WP-82 Dissolved oxygen-Temperature meters (TPS Pty. Ltd., Brisbane, Australia). Chambers consisted of a Perspex dome with an internal base diameter of 28.5 cm and volume of approximately 10 L. The chambers were sealed with bucket lids and a 12 V pump re-circulated water through the chamber and over the surface of the dissolved oxygen probe, which was inserted at the top of the chamber.

Community respiration was calculated as the nocturnal change in dissolved oxygen concentration (Figure 5.1), extrapolated to 24 h and was assumed to be equal during the day and night. Net production (NP) over 24 h was calculated using the change in dissolved oxygen concentrations during the day (Figure 5.1). Gross primary production (GPP) over 24 h was calculated as the addition of NP and the predicted CR during the day. Net ecosystem production (NEP) was calculated as the difference between GPP and CR over 24 h. Metabolic rates were adjusted for the volume of the chamber (total volume minus the volume displaced by enclosed substrates) and the total surface area of the rocks, which was measured as described in chapter two.

From each chamber, initial and final water samples were taken for analysis of filterable reactive phosphorus (FRP) and dissolved organic carbon (DOC) concentrations and molar ratios were calculated (chapter two). Measurements were also taken for stream discharge, day number, period of continuous flow, light intensity and water temperature (chapter two). Reported light intensities are the average underwater instantaneous light intensities during daylight hours. The number of daylight hours was recorded and along with average daily light intensities, were used to calculate daily incident light.

Material attached to rocks was removed and samples were taken for determination of benthic organic matter (BOM) and benthic chlorophyll *a* (chapter two). Attached material from the un-modified reach of First Creek consisted of inorganic and organic debris with the occasional presence of pinnate diatoms and very occasional presence of blue-green, unicellular green and filamentous green algae. Attached material from the degraded reach of First Creek also consisted of inorganic and organic debris, but contained a high abundance of filamentous green algae in the later seasons of each year. In the reaches of Fourth Creek, attached material was generally dominated by filamentous green algae.

5.2.2 Statistical analyses

To summarise differences in metabolic rates a two-dimensional NMS ordination was conducted using PC-ORD (Version 4.10, MjM software, Oregon USA). A main matrix containing all measurements of CR, GPP and NEP was overplayed with the same data set to determine the directional effects of CR, GPP and NEP on the two-dimensional distribution. Environmental parameters could not be included since complete data sets were not available. The analysis revealed a stress of 5.33 and was suitable for an ordination.

Univariate analyses were performed using JMP-IN (Version 3.2.1, SAS Institute Inc., Cary, USA) to examine the differences in individual metabolic rates between the reaches. All samples were tested for homogeneity (O'Brien, Brown-Forsythe, Levene and Bartlett tests) and normality (Shapiro-Wilk test). Differences were compared through two-way analysis of variance with reach and season as fixed effects (model 1). Interaction effects between reach and season are denoted with *. When interactions were tested, significant effects were accepted if p values were less than 0.01 because interactions place doubt over the F-ratios of the main effects. In all other analyses, statistically significant relationships were accepted if p values were less than 0.05. Differences between streams were not included in a three-way analysis of variance due loss of degrees of freedom. Relationships between environmental conditions and metabolic rates were analysed by regression analysis. Variability between replicates is reported as standard errors.

5.3 Results

5.3.1 Environmental conditions

The un-modified reach of First Creek had a greater period of continuous flow than all other reaches (Table 5.1). Overall, un-modified reaches also had lower water temperature, lower FRP and DOC concentrations, lower benthic chlorophyll *a* and higher BOM than impacted reaches (Table 5.2). However, these differences varied seasonally with highest discharge, DOC and benthic chlorophyll *a* in winter-spring 2004. Water temperature and daily light intensity were highest in spring 2003 and BOM was highest in autumn-winter 2004 (Table 5.2).

5.3.2 Metabolic rates

The two-dimensional distribution of metabolic rates of the un-modified reach of First Creek was narrow and aligned with low community respiration (CR), gross primary production (GPP) and net ecosystem production (NEP) (Figure 5.2). During one or more seasons, the distributions of measurements of the degraded reach of First Creek and all reaches of Fourth Creek were associated with that of the un-modified reach of First Creek and low metabolic rates. However, in the remaining seasons they were associated with high metabolic rates and so their distributions were broader than that of the un-modified reach of First Creek (Figure 5.2).

5.3.3 Community respiration

The un-modified reach of First Creek maintained low CR (Figure 5.3), which was consistent with the ordination (Figure 5.2). While all other reaches experienced low CR in one or more seasons, in the remaining seasons CR was higher than in the un-modified reach of First Creek. In First Creek, CR was greater in the degraded reach than in the un-modified reach in all seasons except for winter-spring 2004 (Figure 5.3) and so the effect of reach was dependant upon the interaction with season (Table 5.3). Community respiration was generally higher in Fourth Creek than First Creek. However, in Fourth Creek there was no effect of reach (Table 5.3) because in the earlier seasons of each year CR was greatest in the un-modified reach, but in winter-spring 2004 CR was greatest in the degraded reach (Figure 5.3). Consequently, there was an effect of reach*season (Table 5.3).

Season had the same effect on both creeks, with CR lowest in autumn-winter 2004 and greatest in spring 2003 (Figure 5.3). Consequently, CR was related to day number (Figure 5.4) and light availability (Table 5.4), which was highest in spring 2003 (Table 5.2). In addition, CR had significant positive relationship with benthic chlorophyll *a* (Table 5.4), with CR equal to 116 mg m^{-2} day^{-1} when benthic chlorophyll *a* was zero according to the linear regression (CR = 116 + 5.6 x benthic chlorophyll *a*, Figure 5.5). The high CR values at low benthic chlorophyll *a* (Figure 5.5) were measurements during spring 2003 when light availability and GPP were high.

5.3.4 Gross primary production

The un-modified reach of First Creek also experienced less seasonal variation in GPP than all other reaches (Figure 5.6). Furthermore, GPP was generally higher in Fourth Creek than First Creek. In Fourth Creek, while GPP was greatest in the un-modified reach in the earlier season of each year, there were greater rates in the degraded reach in the later seasons (Figure 5.6). Consequently, the effect of reach was dependant upon an interaction with season (Table 5.3). In all seasons apart from winter-spring 2004 the engineered reach had the lowest GPP (Figure 5.6).

In First Creek, GPP was greatest in the un-modified reach during autumn-winter 2004, greatest in the degraded reach during spring 2003 and approximately equal in winter 2003 and winter-spring 2004 (Figure 5.6). Consequently, there was no overall difference between the reaches, but there was an effect of season (Table 5.3) with an increase in GPP through the year. This was the case in a majority of reaches and so GPP was related to day number (Table 5.4). Furthermore, GPP was related to daily light intensity, daily incident light (Figure 5.7) and benthic chlorophyll *a* (Figure 5.8).

5.3.5 Net ecosystem production

The association of NEP with GPP (Figure 5.2) suggested that differences in NEP were more strongly related to GPP than CR. Indeed, NEP was higher in Fourth Creek than First Creek (Figure 5.9). In the un-modified reach of First Creek, NEP was close to zero and positive except in winter-spring 2004 (Figure 5.9). However, in the degraded reach NEP increased from below zero to above zero during both years (Figure 5.9) owing to the increase in GPP (Figure 5.6) and decrease in CR (Figure 5.3). Consequently, NEP was greatest in the un-modified reach in earlier seasons, but greatest in the degraded reach in later seasons and the effect of reach was dependant upon an interaction with season (Table 5.3). There was also an effect of season on NEP, with rates lowest in autumn-winter 2004 and greatest in spring 2003 suggesting a general increase in the dominance of GPP over CR through the year. In Fourth Creek, NEP was similar in the degraded reach and engineered reaches, except in winter-spring 2004 when NEP was more positive in the degraded reach. The degraded reach had greatest NEP during the later seasons of both years and the un-modified reach had greater NEP during the earlier seasons. Consequently, the effect of reach was dependant upon the interaction with season, which also had an effect (Table 5.3).

Net ecosystem production was most strongly related to light availability, but also had relationships with benthic chlorophyll *a* and final DOC to FRP molar ratio (Table 5.4).

5.4 Discussion

Rates of NP in streams of the Torrens River Catchment are equivalent to 0 to 0.3 g C m^{-2} day^{-1}, assuming a photosynthetic quotient of one and that 1 g of oxygen is equal to 0.375 g of carbon (Bunn *et al.* 1999). This is lower than most other aquatic ecosystems (Bunt *et al.* 1975). Furthermore, GPP and CR were lower than that measured in other streams elsewhere (Bunn *et al.* 1999; Mulholland *et al.* 2001; Acuna *et al.* 2004). However, rates were similar to that of a stream where scouring limits the accumulation of organic material (Rier and King 1996). Indeed, these streams experience high stream velocities which may remove benthic organisms and much of the organic matter that heterotrophic organisms are dependant upon (Acuna *et al.* 2004; Meyer *et al.* In press).

Although NEP was generally positive, respiration by heterotrophic organisms appeared to be the main contributor to CR, since the average CR was 162 mg O_2 m^{-2} day^{-1} and CR was equivalent to 116 mg O_2 m^{-2} day^{-1} when autotrophic organisms were absent (when chlorophyll *a* was zero, as calculated by Cohen (1990)). In other reported cases, un-disturbed forested streams were found to have negative NEP (Bott *et al.* 1985; King and Cummins 1989; Molla *et al.* 1996; Rier and King 1996; Bunn *et al.* 1999; Young and Huryn 1999; Mulholland *et al.* 2001; Acuna *et al.* 2004) with importance being placed on allochthonous carbon sources (Vannote *et al.* 1980). The discrepancy with this project may have been due to several factors. Firstly, the inclusion of metabolism associated with coarse particulate organic matter and in the hyporheic zone in this project would have made NEP more negative because the metabolism of these compartments is generally heterotrophic (Tank and Webster 1998; Crenshaw *et al*. 2002). Secondly, the assumption that CR is equal during the day and night may have also led to underestimates of CR (Parkhill and Gulliver 1999) because phytoplankton respiration is enhanced by light as a result of increased carbohydrate production (Stone and Ganf 1981; Yallop 1982; Markager *et al*. 1992)

However, Minshall (1978) suggested that not all pristine running waters have negative NEP. The streams of this project, and indeed in much of Australia, have characteristics that may favour autotrophic organisms, including: a limited canopy cover, high light availability and low inputs of allochthonous organic material (Boulton and Suter 1986; Boulton and Lake 1988). Light availability was an important factor controlling GPP, which has been observed elsewhere (Bunn *et al*. 1999; Young and Huryn 1999; Mosisch *et al*. 2001; Mulholland *et al*. 2001; Acuna *et al*. 2004). While GPP was associated with benthic chlorophyll *a*, GPP was relatively high during spring 2003 when chlorophyll *a* was low. During this period, light availability was high, highlighting its importance in controlling metabolic rates. Streams of this region are also dominated by rock substrates and riffle habitats (chapter two), which have been shown to favour autotrophic communities (Bott *et al*. 1985; Brown and King 1987; Stock and Ward 1989; Rier and King 1996; Whitledge and Rabeni 2000).

Rates of NEP were greater in Fourth Creek than First Creek. Fourth Creek has the additional influence of agriculture (chapter two), which has been observed to enhance metabolic rates elsewhere (King and Cummins 1989; Bunn *et al*. 1999; Wagner and Bretschko 2002). Bunn *et al*. (1999) demonstrated that the increased GPP and NEP in agricultural streams coincided with a dominance of filamentous green algae that did not appear to enter the food-web. This reflects an inefficient transfer of resources to higher trophic levels. Indeed, in this study it was observed that rates of GPP and NEP were highest in impacted reaches where organic matter was dominated by filamentous algae. Although the shortened period of continuous flow in Fourth Creek may influence the structure of algal communities (Peterson and Boulton 1999; Gottlieb *et al*. 2005) it was not shown to influence metabolic rates. The increased metabolic rates in Fourth Creek were attributed to the removal of riparian vegetation and subsequent increased light availability. Although grazing of microbial organisms was not investigated, the increased metabolic rates in impacted reaches would have been unlikely if higher trophic levels were consuming microbial organisms. This suggests that fewer resources were passed on to higher trophic levels in impacted reaches. Fewer species of higher trophic levels have been observed in urban streams (Paul and Meyer 2001), but changes in the transfer of resources to higher trophic levels in impacted streams requires further investigation.

This project demonstrated that the un-modified reach of First Creek, which was the most pristine in this study, maintained relatively low metabolic rates, which may reflect the stability of stream ecosystems against perturbations (Uehlinger 2000). However, because of the seasonal variation in metabolic rates within the impacted reaches, differences between reaches varied seasonally. Consequently, generalisations about differences in metabolic rates between pristine and impacted reaches are difficult. In First Creek, CR was greater in the degraded reach in three of four seasons and NEP was lower in the degraded reach early in the year owing to higher rates of CR. In Fourth Creek CR, GPP and NEP were greater in the degraded urban reach than the un-modified reach later in each year. However, metabolic rates also differed between the two urban reaches, with the engineered reach generally having lower rates of CR, GPP and NEP than the degraded reach. This difficulty in making generalisations is also revealed in comparisons of previous studies. While Wang *et al*. (2003) demonstrated lower CR, GPP, and NEP in an urban stream than an agricultural stream, Ball *et al*. (1973) (in Paul and Meyer 2001) observed higher CR and GPP in an urban river than a forested river. Paul (1999) (in Meyer *et al*. In press) also demonstrated higher GPP in urban streams than forested streams, but little difference between CR and NEP.

It is evident that the response of stream metabolism to changes in land-use is variable between regions, streams and seasons. Consequently, to accurately predict changes in stream metabolism across broad spatial or temporal scales, extensive measurements may be required. There was evidence to suggest that stream metabolism varied between stream reaches in ways that reflected less efficient resource transformation in impacted reaches. This was observed as increased GPP and NEP and dominance of algal communities, due to increased light availability and perhaps reduced grazing. Inclusion of measurements of the transfer of resources to higher trophic levels would enhance the usefulness of measurements of stream metabolism in future investigations.

Table 5.1. Date and period of continuous flow at time of stream metabolism measurements in winter 2003 (W03), spring 2003 (S03), autumn-winter 2004 (AW04) and winter-spring 2004 (WS04) in un-modified (Un-mod) and degraded (Deg) reaches of First and Fourth Creeks and engineered (Eng) reach of Fourth Creek.

Parameter	Season	First Creek		Fourth Creek		
		Un-mod	Deg	Un-mod	Deg	Eng
Date	W03	16 July	9 July	7 Aug.	31 July	28 Aug.
	S03	14 Oct.	8 Oct.	4 Nov.	22 Oct.	29 Oct.
	AW04	11 May	20 May	10 June	3 June	27 May
	WS04	25 Aug.	18 Aug.	9 Sept.	2 Sep.	15 Sep.
Period of continuous flow (days)	W03	198	50	79	72	100
	S03	287	141	168	155	162
	AW04	133	3	24	17	10
	WS04	238	93	115	108	121

Table 5.2. Environmental parameters in winter 2003 (W03), spring 2003 (S03), autumn-winter 2004 (AW04) and winter-spring 2004 (WS04) in un-modified (Un-mod) and degraded (Deg) reaches of First and Fourth Creeks and engineered (Eng) reach of Fourth Creek. Mean ± standard error.

Parameter	Season	First Creek		Fourth Creek		
		Un-mod	Deg	Un-mod	Deg	Eng
Discharge (L s^{-1})	W03	29.9	31.3	153.2	107.0	238.4
	S03	25.5	62.2	43.7	20.2	22.5
	AW04	17.3	7.3	80.6	19.7	7.7
	WS04	112.4	273.3	1674.2	52.5	420.8
Water temperature (°C)	W03	10.6 ± 0.03	11.5 ± 0.02	10.0 ± 0.03	10.1 ± 0.02	11.1 ± 0.02
	S03	11.2 ± 0.02	12.7 ± 0.02	13.1 ± 1.34	16.0 ± 0.07	14.2 ± 0.03
	AW04	11.0 ± 0.03	13.9 ± 0.02	12.8 ± 0.01	14.3 ± 0.07	12.9 ± 0.05
	WS04	12.9 ± 0.03	10.5 ± 0.01	10.9 ± 0.03	12.3 ± 0.01	11.7 ± 0.03
Daily light intensity (•mol m^{-2} s^{-1})	W03	98 ± 4.0	94 ± 8.6	201 ± 21.7	306 ± 19.4	122 ± 33.9
	S03	415 ± 29.1	50 ± 3.6	697 ± 93.9	828 ± 89.7	---
	AW04	43 ± 6.9	---	56 ± 6.4	112 ± 11.3	---
	WS04	49 ± 5.2	69 ± 8.4	44 ± 3.7	152 ± 15.4	74 ± 8.4
Daily incident light (mol m^{-2})	W03	3.9	3.7	8.7	12.5	5.0
	S03	20.4	2.4	36.0	41.7	---
	AW04	1.7	---	2.2	4.4	---
	WS04	2.1	2.9	1.9	6.7	3.3
Initial FRP (•g L^{-1})	W03	3.8 ± 1.11	61.2 ± 25.07	17.2 ± 1.07	6.1 ± 0.56	15.8 ± 0.42
	S03	16.1 ± 6.41	6.8 ± 0.96	4.4 ± 0.56	33.4 ± 1.47	15.6 ± 0.56
	AW04	3.2 ± 0.48	17.8 ± 1.42	6.7 ± 0.96	34.0 ± 0.48	15.9 ± 0.56
	WS04	14.7 ± 0.00	8.0 ± 0.00	15.6 ± 0.80	11.7 ± 0.00	8.5 ± 0.68
Final FRP (•g L^{-1})	W03	1.0 ± 0.00	7.3 ± 1.47	10.7 ± 0.68	6.1 ± 0.56	8.3 ± 0.42
	S03	4.9 ± 3.64	5.7 ± 0.56	7.7 ± 0.56	8.4 ± 1.47	9.5 ± 0.00
	AW04	2.3 ± 0.00	16.9 ± 0.42	4.2 ± 0.48	18.6 ± 2.39	18.1 ± 1.11
	WS04	10.5 ± 0.83	8.0 ± 0.00	6.0 ± 0.48	6.7 ± 0.00	6.4 ± 0.42
Initial DOC (mg L^{-1})	W03	---	---	6.6 ± 0.04	6.3 ± 0.04	8.6 ± 0.04
	S03	4.9 ± 0.02	7.5 ± 0.29	6.9 ± 0.14	7.4 ± 0.11	6.9 ± 1.59
	AW04	2.7 ± 0.05	11.0 ± 0.25	4.5 ± 0.09	4.4 ± 0.04	7. 2± 1.44
	WS04	11.8 ± 1.08	5.9 ± 0.04	7.9 ± 0.03	12.8 ± 1.18	8.8 ±0.00
Final DOC (mg L^{-1})	W03	---	---	6.8 ± 0.20	8.4 ± 1.47	8.8 ± 0.04
	S03	5.3 ± 0.07	6.2 ± 0.90	7.2 ± 0.28	11.9 ± 1.94	6.0 ± 1.90
	AW04	2.8 ± 0.03	10.8 ± 0.44	4.5 ± 0.03	5.6 ± 1.44	8.7 ± 0.46
	WS04	11.6 ± 0.74	6.3 ± 0.45	7.7 ± 0.13	13.5 ± 1.02	8.0 ± 0.21

Table 5.2 continued.

Parameter	Season	First Creek		Fourth Creek		
		Un-mod	Deg	Un-mod	Deg	Eng
Benthic organic matter (g m^{-2})	W03	---	---	---	---	---
	S03	3.7 ± 0.35	6.2 ± 0.10	2.6 ± 0.05	2.8 ± 0.35	1.9 ± 0.11
	AW04	12.6 ± 2.92	4.9 ± 0.56	13.6 ± 2.40	2.1 ± 0.38	4.2 ± 0.92
	WS04	1.4 ± 0.40	1.6 ± 0.42	2.0 ± 0.88	4.4 ± 0.60	2.8 ± 0.51
Benthic chlorophyll *a* (mg m^{-2})	W03	---	---	---	---	---
	S03	1.1 ± 0.06	1.2 ±0.28	0.7 ± 0.07	0.8 ± 0.05	0.3 ± 0.03
	AW04	5.4 ± 2.05	1.7 ± 0.27	7.8 ± 1.70	1.5 ± 0.26	2.5 ± 0.55
	WS04	0.4 ± 0.07	1.2 ± 0.19	1.2 ± 0.69	23.3 ± 5.65	23.1± 5.95
Chamber depth (m)	W03	22.8 ± 0.60	22.3 ± 0.73	21.8 ± 1.01	26.3 ± 0.88	24.8 ± 2.30
	S03	20.3 ± 0.88	22.7 ± 0.33	24.7 ± 0.88	21.3 ± 1.45	23.7 ± 1.86
	AW04	21.1 ± 0.43	23.3 ± 0.48	18.3 ± 0.48	15.0 ± 0.70	22.3 ± 0.88
	WS04	23.5 ± 0.87	23.3 ± 1.03	18.0 ± 0.71	22.0 ± 0.82	30.5 ± 4.97

Table 5.3. P-values obtained for effects of reach, season and the interaction between reach and season on community respiration (CR), gross primary production (GPP) and net ecosystem production (NEP) in First and Fourth Creeks. In First Creek, for the effect of reach $df = 1$, for the effect of season and season*reach $df = 3$. In Fourth Creek, for the effect of reach $df = 2$, for the effect of season $df = 3$, for the effect of season*reach $df = 6$. Significant effects are those with p less than 0.01.

Effect	First Creek			Fourth Creek		
	CR	GPP	NEP	CR	GPP	NEP
Reach	<0.0001	0.2717	0.0160	0.0128	0.0001	0.0056
Season	<0.0001	<0.0001	0.0006	0.0001	<0.0001	<0.0001
Reach*season	0.0002	0.0547	0.0081	0.0015	<0.0001	<0.0001

Table 5.4. Statistics and relationships obtained for the influence of environmental parameters on community respiration (CR), gross primary production (GPP) and net ecosystem production (NEP). Relationships include natural log (ln) transforms of parameters (x). Only significant effects are shown (p less than 0.05). For final DOC to FRP molar ratio, the value of one chamber in the un-modified reach of First Creek during winter-spring 2003 was removed from the analysis since it value was an order of magnitude higher than all other values.

Parameter	Statistic and relationship	CR	GPP	NEP
Day number	p	0.0100	0.0167	---
	r^2	0.3150	0.2789	---
	df	19	19	---
	Relationship	Positive linear	Positive linear	---
Daily light intensity	p	0.0207	0.0131	0.0328
	r^2	0.3083	0.3453	0.2692
	df	16	16	16
	Relationship	Positive ln(x)	Positive ln(x)	Positive ln(x)
Daily incident light	p	0.0155	0.0121	0.0353
	r^2	0.3320	0.3520	0.2629
	df	16	16	16
	Relationship	Positive ln(x)	Positive ln(x)	Positive ln(x)
Benthic chlorophyll *a*	p	0.0075	0.0005	0.0005
	r^2	0.1294	0.2086	0.2106
	df	53	53	53
	Relationship	Positive linear	Positive linear	Positive linear
Final DOC	p	0.0023	0.0189	---
	r^2	0.1401	0.0858	---
	df	63	63	---
	Relationship	Positive linear	Positive linear	---
Initial DOC to FRP molar ratio	p	0.0032	0.0464	---
	r^2	0.1296	0.0615	---
	df	64	64	---
	Relationship	Positive linear	Positive linear	---
Final DOC to FRP molar ratio	p	0.0002	0.0008	0.0123
	r^2	0.2008	0.1673	0.0968
	df	63	63	63
	Relationship	Positive linear	Positive linear	Positive linear

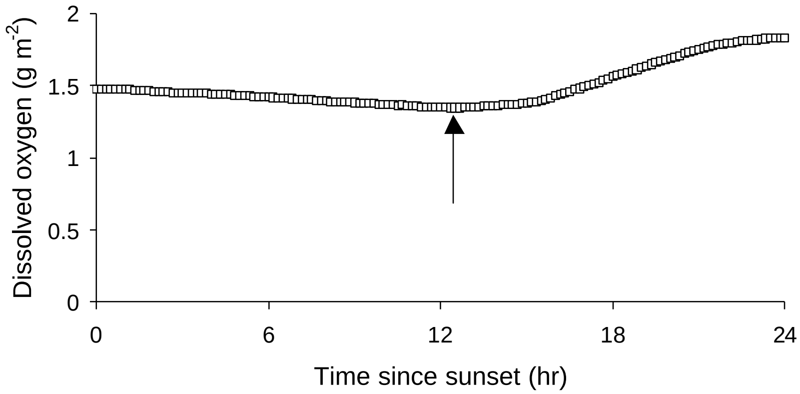


Figure 5.1. Change in dissolved oxygen levels in a re-circulating benthic chamber after sunset in the un-modified reach of First Creek, spring 2003. Note the constant oxygen consumption through the night and oxygen production (net production) between sunrise (arrow) and the following sunset (hour 24).

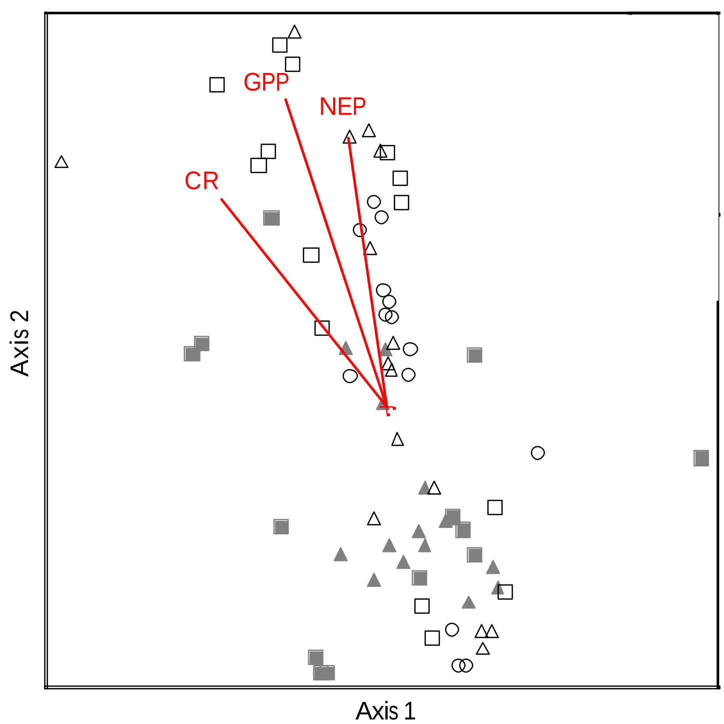


Figure 5.2. NMS ordination of community respiration (CR), gross primary production (GPP) and net ecosystem production (NEP) in un-modified (triangles), degraded (squares) and engineered reaches (circles) of First (shaded shapes) and Fourth Creeks (un-shaded shapes). Red vectors show direction of increase of metabolic rates in the two-dimensional distribution, at a cut-off r^2 value of 0.800.

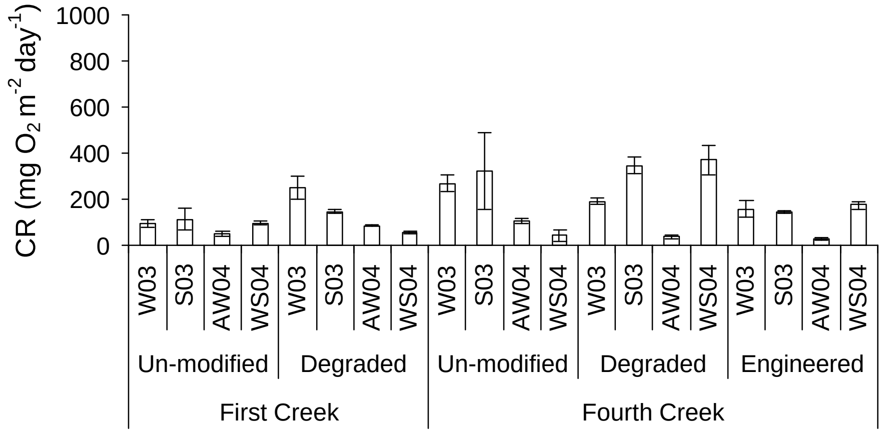


Figure 5.3. Community respiration (CR) in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek during winter 2003 (W03), spring 2003 (S03), autumn-winter 2004 (AW04) and winter-spring 2004 (WS04). Error bars represent standard errors.

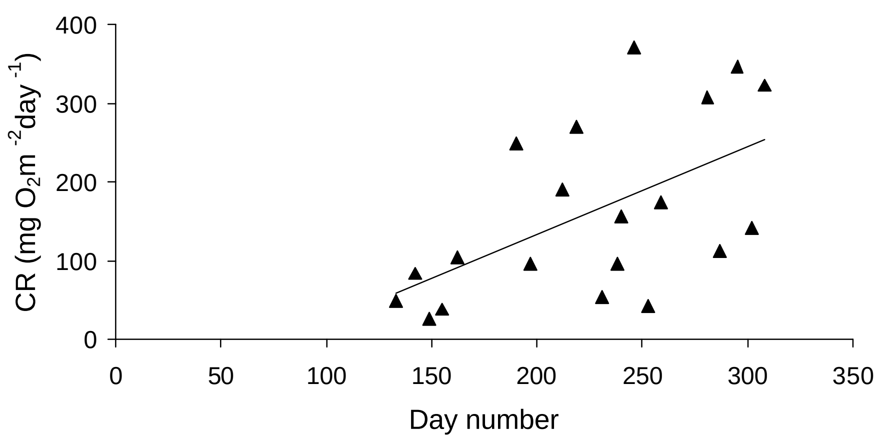


Figure 5.4. Influence of day number on community respiration (CR) in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek. Full line denotes linear regression (p = 0.0100, • = 0.05, r^2 = 0.3150, df = 19).

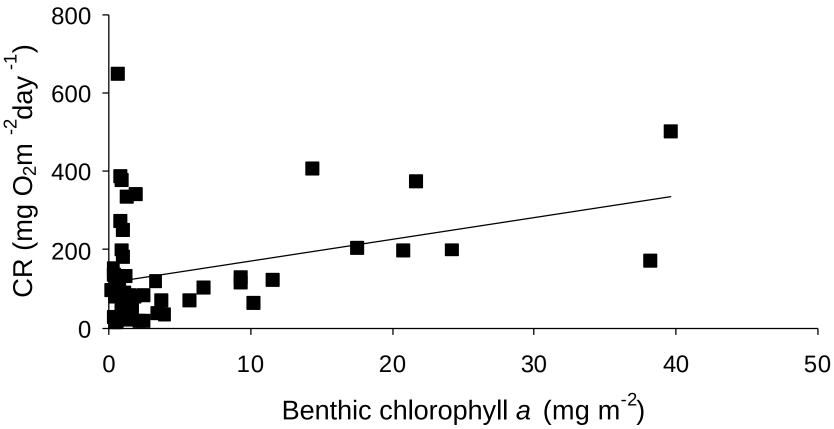


Figure 5.5. Influence of benthic chlorophyll *a* on community respiration (CR) in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek. Full line denotes linear regression (p = 0.0075, • = 0.05, r^2 = 0.1294, df = 53).

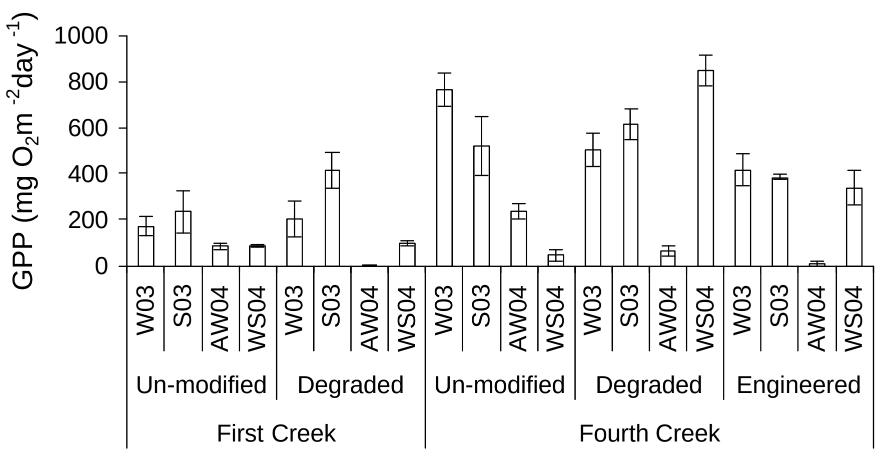


Figure 5.6. Gross primary production in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek during winter 2003 (W03), spring 2003 (S03), autumn-winter 2004 (AW04) and winter-spring 2004 (WS04). Error bars represent standard errors.

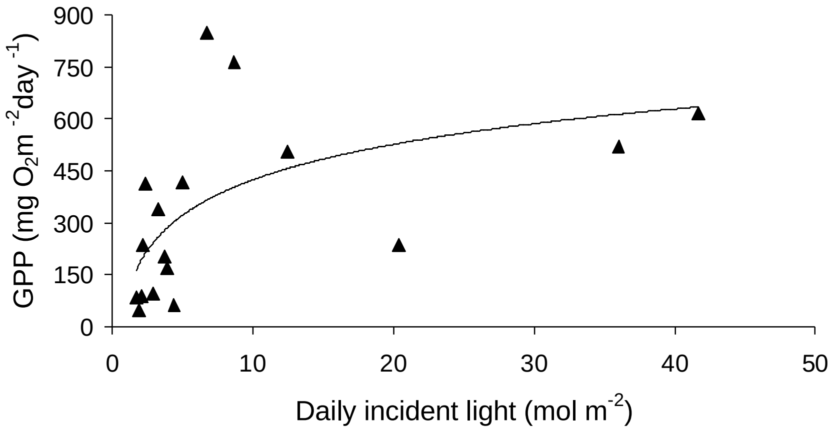


Figure 5.7. Influence of daily incident light on gross primary production (GPP) in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek. Full line denotes regression with natural log transform of daily incident light (p = 0.0121, • = 0.05, r^2 = 0.3520, df = 16).

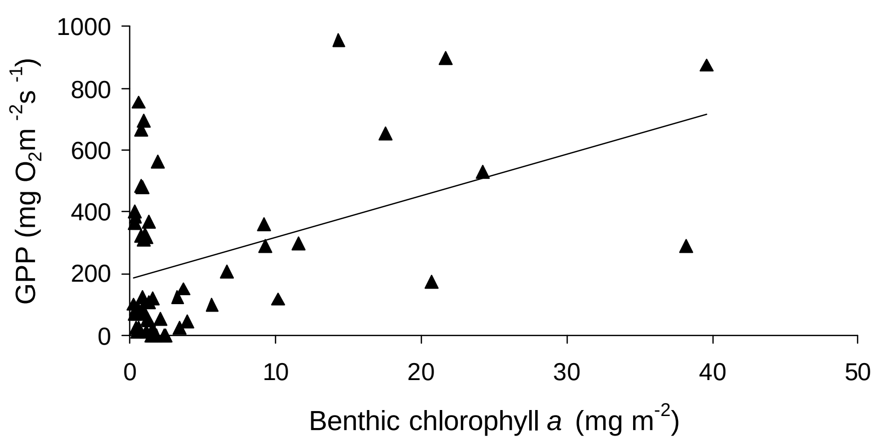


Figure 5.8. Influence of benthic chlorophyll *a* on gross primary production (GPP) in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek. Full line denotes linear regression (p = 0.0005, • = 0.05, r^2 = 0.2086, df = 53).

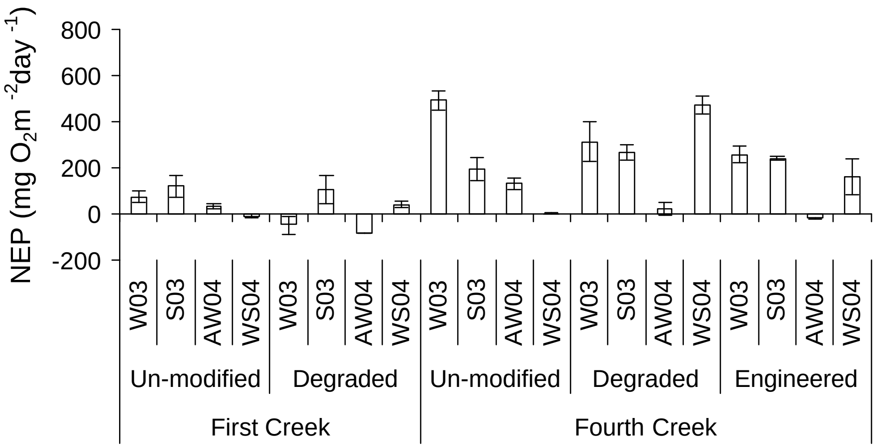


Figure 5.9. Net ecosystem production in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek during winter 2003 (W03), spring 2003 (S03), autumn-winter 2004 (AW04) and winter-spring 2004 (WS04). Error bars represent standard errors.

Chapter six

6 Scaling up chamber metabolic rates to stream reaches: changes across a rural-urban gradient

Abstract. Benthic chambers were used to investigate metabolic rates across a rural-urban gradient. The aim was to compare the metabolism associated with rocks, gravel and open water and by scaling up, relate these data to stream reaches. The combination of rock and pelagic metabolism was generally amenable to scaling up. This was because reaches were dominated by rock substrates and the combination of rock and pelagic metabolism was greater than that of the combination of gravel and pelagic metabolism. However, in reaches with diverse substrates the scaling up of chamber rates did not predict reach metabolic rates. This suggests that the application of measurements of stream metabolism using benthic chambers to larger scales must be done with caution to ensure samples are representative of the whole stream response.

Keywords: *Stream, reach, metabolism, gross primary production, net production, community respiration, rock, gravel, pelagic, urbanisation, agriculture*

6.1 Introduction

Primary production and respiration of organic matter provide basal energy sources for lotic food-webs (Rounick *et al.* 1982; Rounick and Winterbourn 1983; Stock and Ward 1989; Hall Jr. and Meyer 1998). Stream metabolism responds to anthropogenic changes with increased activity of autotrophic organisms (King and Cummins 1989; Bunn *et al.* 1999). Using benthic chambers, chapter five demonstrated that the combination of benthic rock and pelagic metabolism changed across a rural-urban gradient within the Torrens River Catchment. Impacted reaches experienced more seasonal variation in metabolic rates and at times had greater gross primary production (GPP) and community respiration (CR) than a more pristine reach. This was hypothesised to reflect inefficient transformation of resources in impacted streams, which will have significant implications for downstream ecosystems (Brookes *et al*. In press). Although rocks are the dominant benthic substrate within these streams (chapter two), these measurements of metabolism are not necessarily reflective of those at the scale of the stream reach because: reaches may vary in the quantities of different sized substrates; smaller substrates may possess distinct biotic assemblages and contribute disproportionately to stream metabolism (Brown and King 1987); and reaches may have different wetted surface areas.

The aim of this project was to compare the metabolism associated with benthic rocks, benthic gravel and open water and by scaling up, relate these data to reaches. This was conducted within the un-modified and degraded reaches of First and Fourth Creeks and the engineered reach of Fourth Creek in the Torrens River Catchment (chapter two). The conditions important for controlling differences in metabolism at the various scales were also investigated.

6.2 Methods

6.2.1 Benthic metabolism

Metabolism was measured in each reach during the transitions of autumn-winter and winter-spring 2004 (Table 6.1). A storm event prevented access of equipment to the un-modified reach of First Creek in winter-spring. Consequently, rocks were relocated to the degraded reach of First Creek. Inorganic particles with diameters less than 15 mm were assigned to gravel and larger particles to rocks. Rocks were placed in four chambers, which were placed randomly within a reach of 100 m at a known depth. Gravel was placed within three chambers alongside chambers containing rocks. For each chamber containing rocks, all rocks within a randomly placed 0.04 m^2 quadrat were collected. Gravel was collected in a similar manner, to a depth of 0.5 cm. Metabolic rates were measured as described in chapter five. Gravel surface was determined by taking a sub-sample and measuring the radius of 100 randomly chosen gravel particles (surface area assumed to be equal to that of a sphere) and counting the number of gravel particles within 10 smaller sub-samples.

The chamber data reflects both substrate and pelagic metabolism and is referred to as substrate-pelagic metabolism. Data presented for rock-pelagic metabolism were also presented in chapter five.

6.2.2 Scaling to level of the reach

Reach metabolic rates were the product of substrate-pelagic metabolic rates and the total surface area of each substrate within the reach. To estimate surface area, each 100 m long reach was divided into 10 m cells. Within each cell, a 1 m by 1 m quadrat was placed randomly and the percent cover of rock and gravel were estimated. Stream width and water depth were measured within each cell at 10 cm intervals across the stream width. The total surface area of rock and gravel of each 100 m reach was estimated by multiplying the aerial cover of the substrate by the surface area per unit aerial cover. The latter was estimated from the surface area within the 0.04 m^2 quadrat.

6.2.3 Pelagic metabolism

Approximately 100 mL of stream water was transferred to eight Pyrex jars, four wrapped in aluminium foil. Initial measurements of dissolved oxygen concentration were taken (chapter two) at approximately 10:00 am. Jars were sealed and light and dark pairs were placed alongside chambers. After 5 h, final measurements of dissolved oxygen concentrations were taken. Community respiration over 24 h was calculated as the rate of change in dissolved oxygen concentrations within the dark jars and was considered to be constant over the 24 h period. Net production (NP) over 24 h was calculated as the change in dissolved oxygen concentrations within the light jars and was adjusted for the number of daylight hours. Gross primary production was calculated as the addition of NP and the predicted CR during the day. Net ecosystem production (NEP) was calculated as the difference between GPP and CR over 24 h.

6.2.4 Environmental conditions

Measurements of filterable reactive phosphorus (FRP) concentration, dissolved organic carbon (DOC) concentration, stream discharge, period of continuous flow, day number, daily light intensity, daily incident light, water temperature, benthic organic matter (BOM) and benthic chlorophyll *a* were made as outlined in chapters two and five. Water samples from jars were returned to the laboratory and also analysed for chlorophyll *a* concentration.

6.2.5 Statistical analyses

To determine the association of reach metabolic rates and those measured within chambers and jars, a two-dimensional NMS ordination was conducted using PC-ORD (Version 4.10, MjM software, Oregon USA). For this analysis the main matrix contained measurements of reach CR, GPP and NEP and was overlaid with the same data set and rock-pelagic, gravel-pelagic and pelagic CR, GPP and NEP. This revealed a stress of 1.25 and was suitable for a two-dimensional ordination.

Univariate analyses were performed using JMP-IN (Version 3.2.1, SAS Institute Inc., Cary, USA) to examine differences in metabolic rates of the various components between reaches. All samples were tested for homogeneity (O'Brien, Brown-Forsythe, Levene and Bartlett tests) and normality (Shapiro-Wilk test). Differences were compared through two-way analysis of variance with reach and season as fixed effects (model 1). Interaction effects between reach and season are denoted with *. Differences between First and Fourth Creeks were not included in a three-way analysis of variance due to the loss of degrees of freedom. When interactions were tested, significant effects were accepted if p values were less than 0.01 because interactions place doubt over the F-ratios of the main effects. In all other analyses, statistically significant relationships were accepted if p values were less than 0.05. Relationships between environmental conditions and metabolic rates were analysed by regression analysis. Variability between replicates is reported as standard errors.

6.3 Results

6.3.1 Environmental conditions

The wetted surface area was highest in the un-modified and degraded reaches of Fourth Creek in winter-spring (Table 6.2) as a result of elevated discharge (Table 6.3). Stream surface areas were dominated by rock substrate, but in both streams gravel cover was highest in the degraded reaches (Table 6.2). Benthic organic matter and chlorophyll *a* associated with rocks was higher than that associated with gravel (Table 6.3). Although there was considerable seasonal variation, BOM and pelagic chlorophyll *a* were highest in the un-modified reaches, while benthic chlorophyll *a* was highest in the degraded and engineered reaches of Fourth Creek in winter-spring (Table 6.3). In addition, un-modified reaches had lower water temperature and lower FRP and DOC concentrations (Table 6.3).

6.3.2 Reach metabolic rates

Reach metabolic rates in the un-modified reach of First Creek were consistently low (Figure 6.1). In comparison, all other reaches experienced more seasonal variation and had broader distributions that were associated with higher metabolic rates than the un-modified reach of First Creek in one of the two seasons (Figure 6.2).

In Fourth Creek, metabolic rates varied between reaches, but the variation was not consistent between seasons (Table 6.4); CR, GPP and NEP were greatest in the un-modified reach during autumn-winter and greatest in the degraded reach during winter-spring; the engineered reach had lowest rates in autumn-winter but were greater than the un-modified reach in winter-spring (Figure 6.1). In First Creek, CR was greater in the degraded reach than the un-modified reach in both seasons (Figure 6.1) and so there was an effect of reach alone (Table 6.4). While NEP was lower in the degraded reach than the un-modified reach in autumn-winter, the reverse was true during winter-spring and so there was no effect of reach, but there was an effect of season and reach*season (Table 6.4).

Reach CR and GPP had significant relationships with a range of environmental conditions, but was most closely related to light availability, reach BOM and reach chlorophyll *a* (Table 6.6).

6.3.3 Rock-pelagic metabolic rates

Similarities between rock-pelagic and reach metabolic rates were evident with consistently low metabolic rates in the un-modified reach of First Creek and considerable seasonal variation in all other reaches (Figure 6.3). This was substantiated by the ordination with the vectors of rock-pelagic CR, GPP and NEP directly aligned with their reach counterparts (Figure 6.2). As at the scale of the reach, rock-pelagic metabolic rates were generally greater in Fourth Creek than First Creek (Figure 6.3). In Fourth Creek, rock-pelagic metabolic rates experienced the same patterns as those at the scale of the reach. Similarly, in First Creek, rock-pelagic GPP and NEP experienced the same pattern as those at the scale of the reach. However, the response of rock-pelagic CR was different than that at the scale of the reach; while reach CR was greater in the degraded reach in both seasons, rock-pelagic CR was greater in the degraded reach than the un-modified reach during autumn-winter and the reverse was true during winter-spring (Figure 6.3). Consequently, there was no effect of reach or season but there was an effect of reach*season (Table 6.4).

As with reach CR and GPP, rock-pelagic CR and GPP also had strong relationships with a number of environmental conditions, including, light availability, BOM and chlorophyll *a* (Table 6.7).

6.3.4 Gravel-pelagic metabolic rates

Gravel-pelagic metabolic rates were approximately two orders of magnitude lower than rock-pelagic metabolic rates (Figure 6.4). Gravel-pelagic CR and GPP contributed to less than 25% of reach CR and GPP, except in the degraded reach of Fourth Creek during autumn-winter (Table 6.5). Furthermore, gravel-pelagic metabolic rates displayed different patterns to that of reach metabolic rates. This was substantiated by the ordination with the vectors of gravel-pelagic CR, GPP and NEP having no relationship with the two-dimensional distribution of reach metabolic rates (Figure 6.2).

There were few differences in gravel-pelagic metabolic rates between reaches or seasons. In Fourth Creek, there was considerable in-stream variation in metabolic rates (Figure 6.4) and no significant effects of reach, season or reach*season were detected (Table 6.4). In First Creek, GPP was greater in the un-modified than the degraded reach during autumn-winter and this was reversed in autumn-winter and so there was an effect of reach*season (Table 6.4). As a result, NEP was lower in the degraded reach during autumn-winter and lower in the un-modified reach during winter-spring (Figure 6.4).

Unlike reach CR and GPP, gravel-pelagic CR and GPP were only weakly related to environmental conditions, including, FRP concentrations and light availability (Table 6.7).

6.3.5 Pelagic metabolic rates

The response of pelagic metabolic rates (Figure 6.5) was also different than that of the reach (Figure 6.1). This was substantiated by the ordination with the vectors of pelagic CR, GPP and NEP having no relationship with the two-dimensional distribution of reach metabolic rates (Figure 6.2). In comparison with reach metabolic rates, pelagic CR was generally greater than GPP, resulting in a negative NEP. In addition, there were no apparent differences between First and Fourth Creeks (Figure 6.5). Also, there was considerable variation in pelagic CR and NEP in all reaches, except for the un-modified reach of Fourth Creek.

In Fourth Creek, CR increased in all reaches between autumn-winter and winter-spring and was lowest in the un-modified reach during both seasons. In autumn-winter, CR was slightly higher in the degraded reach than the engineered reach but there was little difference in winter-spring. Consequently, there was an effect of reach, season and reach*season (Table 6.4). In each reach, NEP was more negative in winter-spring than autumn-winter owing to the seasonal changes in CR (Figure 6.5). In both seasons NEP was greater in the un-modified reach autumn-winter, but not different in the degraded and engineered reaches. Consequently, there was an effect of reach and season but no effect of reach*season (Table 6.4).

In First Creek, rates of CR were greater in the un-modified reach than the degraded reach in both seasons and increased in both reaches between autumn-winter and winter-spring. Consequently, there was an effect of reach and season but no effect of reach*season (Table 6.7). Since there was little difference in GPP between the reaches, the reverse was observed for NEP in First Creek (Table 6.7, Figure 6.5).

Unlike reach CR and GPP, pelagic CR was weakly related to environmental conditions. Pelagic CR had significant positive relationships with initial DOC concentrations and initial DOC to FRP molar ratio (Table 6.7), but GPP did not have significant relationships with any environmental parameters.

6.4 Discussion

Chamber rock-pelagic metabolic rates predicted general trends in reach metabolic rates. Pelagic and gravel-pelagic metabolic rates did not. The un-modified reach of First Creek maintained low reach CR, GPP and NEP, which reflects the stability of this ecosystem against perturbations (Uehlinger 2000). Impacted reaches experienced significant seasonal shifts in metabolism. In the degraded reach of First Creek, NEP shifted from negative to positive through the year. However, reach CR was greater in the degraded reach than the un-modified reach in both seasons, unlike rock-pelagic CR. Consequently, the response of rock-pelagic CR was slightly different from that of the reach.

Enhanced metabolic rates were observed in Fourth Creek, which is influenced by agriculture (chapter two). This has been observed elsewhere in streams impacted by agriculture (King and Cummins 1989; Bunn *et al.* 1999; Wagner and Bretschko 2002). In Fourth Creek, metabolic rates were different between reaches, but the difference varied with season with greatest rates in the un-modified reach during autumn-winter and in the degraded reach during winter-spring. The difference in GPP between reaches of First Creek also varied with season. Consequently, generalisations about the difference in metabolic rates within and between streams are problematic, a conclusion reached in comparing other studies. For example, lower CR, GPP and NEP in an urban stream than a stream in an agricultural catchment (Wang *et al*. 2003); higher CR and GPP in an urban river than a forested river (Ball *et al*. 1973 in Paul and Meyer 2001); and higher GPP in urban streams than rural streams (Paul 1999 in Meyer *et al*. In press).

Un-disturbed forested streams generally have negative NEP (Rier and King 1996; Bunn *et al*. 1999; Young and Huryn 1999; Mulholland *et al*. 2001; Acuna *et al*. 2004). Streams of this region have relatively high light availability and low inputs of allochthonous organic material (Boulton and Suter 1986; Boulton and Lake 1988). This may increase the importance of autochthonous sources of carbon for these ecosystems. Indeed, reach NEP was generally positive owing to the abundance of rock substrates that had predominantly positive NEP, which has been observed elsewhere (Bott *et al*. 1985; Brown and King 1987; Stock and Ward 1989).

Although gravel-pelagic metabolism generally had negative NEP, the low abundance of gravel meant it had little influence on the reach metabolism. The low gravel-pelagic metabolic rates may have been due to the higher disturbance level experienced by smaller substrates (Downes *et al*. 1998), which has been observed to reduce invertebrate abundance (Matthaei and Townsend 2000). Changes in the relative abundance of different substrates will affect whole stream metabolism. Indeed, degraded reaches had a greater gravel cover, perhaps due to greater erosion and deposition in urban streams (Paul and Meyer 2001). Whitledge (2000) found that streams dominated by pool habitats, which contained finer sediments, were heterotrophic due to lower rates of GPP.

The relative contributions of pelagic and benthic compartments to stream metabolism were not calculated because pelagic CR was often greater than that of benthic-pelagic CR. While this may demonstrate that a majority of the CR was pelagic, it may also be a result of measurements of CR within chambers during the night underestimating CR over 24 h. In fact, respiration of autotrophic organisms is enhanced by light as a result of increased carbohydrate production (Stone and Ganf 1981; Yallop 1982; Markager *et al*. 1992). Bunn *et al*. (1999) found negligible pelagic metabolism in forested streams and most other studies imply that this is the case (Bott *et al*. 1985; Brown and King 1987; Naimo and Layzer 1988;

King and Cummins 1989; Rier and King 1996; Bott *et al*. 1997; Whitledge and Rabeni 2000). It is apparent from this study that the importance of pelagic metabolism, particularly CR, warrants further investigation. Wallace (Unpublished data) found that pelagic oxygen consumption was greater in urban reaches of First and Fourth Creeks than rural reaches following rain; this may lead to oxygen depletion of the water column of urban streams (Paul and Meyer 2001).

As in chapter five, it is difficult to make generalisations about differences in stream metabolism across the rural-urban gradient due to seasonal variation. There was evidence to suggest that metabolism varied between reaches in ways that reflected less efficient resource transformation in impacted reaches (chapter five). The combination of benthic chambers and measurements of stream morphology allowed metabolic rates at larger scales to be obtained. However, the scaling up did not assess whole reach metabolism, since metabolism associated with coarse particulate organic matter and the hyporheic zone were not included. Consequently, in turbulent streams where open water measurements are not accurate (Bott *et al*. 1985; Bott *et al*. 1997), scaling up would be more accurate when all compartments are included. Rock-pelagic metabolism measured within re-circulating benthic chambers reflected general changes in the calculated reach metabolism, but was not able to predict all differences accurately. Consequently, the application of these conclusions to larger scales should only be done with caution, following validation that measurements within chambers reflect those of larger scales.

Table 6.1. Dates and period of continuous flow at time of measurements of stream metabolism in autumn-winter (AW) and winter-spring (WS) in un-modified (Un-mod) and degraded (Deg) reaches of First and Fourth Creeks and engineered (Eng) reach of Fourth Creek.

Parameter	Season	First Creek		Fourth Creek		
		Un-mod	Deg	Un-mod	Deg	Eng
Date	AW	11 May	20 May	10 June	3 June	27 May
	WS	25 Aug.	18 Aug.	9 Sept.	2 Sep.	15 Sep.
Period of continuous flow (days)	AW	133	3	24	17	10
	WS	238	93	115	108	121

Table 6.2. Morphological parameters during measurements of stream metabolism in autumn-winter (AW) and winter-spring (WS) in un-modified (Un-mod) and degraded (Deg) reaches of First and Fourth Creeks and engineered (Eng) reach of Fourth Creek. Mean ± standard error.

Parameter	Season	First Creek		Fourth Creek		
		Un-mod	Deg	Un-mod	Deg	Eng
Stream width (m)	AW	1.5 ± 0.13	2.2 ± 0.30	2.2 ± 0.17	1.6 ± 0.10	2.1 ± 0.05
	WS	1.6 ± 0.12	3.2 ± 0.26	3.0 ± 0.29	2.3 ± 0.05	2.1 ± 0.04
Water depth (m)	AW	0.06 ± 0.007	0.06 ± 0.010	0.08 ± 0.010	0.06 ± 0.009	0.03 ± 0.012
	WS	0.15 ± 0.011	0.15 ± 0.023	0.20 ± 0.015	0.09 ± 0.010	0.11 ± 0.049
Percent gravel cover	AW	6.0 ± 1.91	14.5 ± 3.61	9.5 ± 2.52	20.5 ± 3.53	2.0 ± 2.00
	WS	5.0 ± 1.42	1.9 ± 0.69	5.0 ± 1.76	12.0 ± 2.49	1.0 ± 1.00
Percent rock cover	AW	94.0 ± 1.91	85.5 ± 3.61	90.5 ± 2.52	79.5 ± 3.53	98.0 ± 2.00
	WS	95.0 ± 1.42	98.1 ± 0.69	95.0 ± 1.76	88.0 ± 2.49	99.0 ± 1.00
Wetted area (m^2)	AW	3034.3	7647.1	3555.5	7152.0	1285.8
	WS	2407.9	3110.5	19957.3	19022.6	1876.0

Table 6.3. Environmental parameters during measurements of rock, gravel and pelagic metabolism in autumn-winter (AW) and winter-spring (WS) in un-modified (Un-mod) and degraded (Deg) reaches of First and Fourth Creeks and engineered (Eng) reach of Fourth Creek. Mean ± standard error.

Parameter	Substrate	Season	First Creek		Fourth Creek		
			Un-mod	Deg	Un-mod	Deg	Eng
Discharge (L s^{-1})	All	AW	17.3	7.3	80.6	19.7	7.7
		WS	112.4	273.3	1674.2	52.5	420.8
Daily light intensity (•mol m^{-2} s^{-1})	All	AW	43 ± 6.9	---	56 ± 6.4	112 ± 11.3	---
		WS	49 ± 5.2	69 ± 8.4	44 ± 3.7	152 ± 15.4	74 ± 8.4
Daily incident light (mol m^{-2})	All	AW	1.7	---	2.2	4.4	---
		WS	2.1	2.9	1.9	6.7	3.3
Water temperature (°C)	Rock	AW	11.0 ± 0.03	13.9 ± 0.02	12.8 ± 0.01	14.3 ± 0.07	12.9 ± 0.05
		WS	12.9 ± 0.03	10.5 ± 0.01	10.9 ± 0.03	12.3 ± 0.01	11.7 ± 0.03
	Gravel	AW	11.0 ± 0.01	13.9 ± 0.02	12.8 ± 0.05	14.2 ± 0.05	12.7 ± 0.21
		WS	12.9 ± 0.01	10.5 ± 0.01	10.9 ± 0.01	12.3 ± 0.02	12.3 ± 0.00
Initial FRP (•g L^{-1})	All	AW	3.2 ± 0.48	17.8 ± 1.42	6.7 ± 0.96	34.0 ± 0.48	15.9 ± 0.56
		WS	14.7 ± 0.00	8.0 ± 0.00	15.6 ± 0.80	11.7 ± 0.00	8.5 ± 0.68
Final FRP (•g L^{-1})	Rock	AW	2.3 ± 0.00	16.9 ± 0.42	4.2 ± 0.48	18.6 ± 2.39	18.1 ± 1.11
		WS	10.5 ± 0.83	8.0 ± 0.00	6.0 ± 0.48	6.7 ± 0.00	6.4 ± 0.42
	Gravel	AW	6.3 ± 3.99	19.3 ± 1.11	6.7 ± 1.67	24.3 ± 4.55	19.8 ± 1.47
		WS	13.0 ± 0.96	8.0 ± 0.00	7.9 ± 1.47	7.8 ± 1.11	6.8 ± 0.00
Initial DOC (mg L^{-1})	All	AW	2.7 ± 0.05	11.0 ± 0.25	4.5 ± 0.09	4.4 ± 0.04	7. 2± 1.44
		WS	11.8 ± 1.08	5.9 ± 0.04	7.9 ± 0.03	12.8 ± 1.18	8.8 ± 0.00
Final DOC (mg L^{-1})	Rock	AW	2.8 ± 0.03	10.8 ± 0.44	4.5 ± 0.03	5.6 ± 1.44	8.7 ± 0.46
		WS	11.6 ± 0.74	6.3 ± 0.45	7.7 ± 0.13	13.5 ± 1.02	8.0 ± 0.21
	Gravel	AW	2.7 ± 0.02	10.2 ± 0.39	4.4 ± 0.16	6.3 ± 2.08	5.2 ± 0.62
		WS	11.7 0.78	5.9 ± 0.04	7.5 ± 0.15	15.3 ± 0.64	7.9 ± 0.12

Table 6.3 continued

Parameter	Substrate	Season	First Creek		Fourth Creek		
			Un-mod	Deg	Un-mod	Deg	Eng
Benthic organic matter (g m^{-2})	Rock	AW	12.63 ± 2.922	4.86 ± 0.560	13.58 ± 2.422	2.10 ± 0.376	3.85 ± 0.738
		WS	1.37 ± 0.404	1.56 ± 0.404	2.02 ± 0.877	4.35 ± 0.563	2.82 ± 0.506
	Gravel	AW	0.18 ± 0.030	0.23 ± 0.012	0.24 ± 0.064	0.04 ± 0.011	0.12 ± 0.063
		WS	0.02 ± 0.004	0.02 ± 0.004	0.02 ± 0.006	0.01 ± 0.002	0.01± 0.002
Benthic chlorophyll *a* (mg m^{-2})	Rock	AW	5.00 ± 2.047	1.68 ± 0.270	7.80 ± 1.703	1.46 ± 0.260	2.23 ± 0.455
		WS	0.40 ± 0.071	1.15 ± 0.187	1.20 ± 0.693	23.28 ± 5.648	23.09± 5.954
	Gravel	AW	0.020 ± 0.017	0.006± 0.002	0.015 ± 0.002	0.007 ± 0.002	0.018 ± 0.010
		WS	0.001 ± 0.000	0.003 ± 0.000	0.004 ± 0.001	0.012 ± 0.002	0.020 ± 0.004
Chlorophyll *a* (•g L^{-1})	Water column	AW	4.3 ± 0.31	4.8 ± 0.08	7.9 ± 2.97	3.9 ± 0.32	4.1 ± 0.58
		WS	5.5 ± 0.52	3.2 ± 0.41	7.7 ± 0.43	4.3 ± 0.33	7.7 ± 0.88
Chamber depth (m)	Rock	AW	21.1 ± 0.43	23.3 ± 0.48	18.3 ± 0.48	15.0 ± 0.70	22.0 ± 0.71
		WS	23.5 ± 0.87	23.3 ± 1.03	18.0 ± 0.71	22.0 ± 0.82	30.5 ± 4.97
	Gravel	AW	21.3 ± 0.88	22.8 ± 0.60	19.0 ± 1.00	15.0 ± 1.53	21.0 ± 0.58
		WS	22.7 ± 0.33	22.7 ± 0.88	17.7 ± 0.33	21.7 ± 0.88	31.0 ± 5.51

Table 6.4. P-values for the effect of reach (R), season (S) and the interaction between reach and season (R*S) on community respiration (CR), gross primary production (GPP) and net ecosystem production (NEP). For analyses of First Creek, for the effect of reach *df* = 1, for the effect of season *df* = 1, for the effect of reach*season *df* = 1. For analyses of Fourth Creek, for the effect of reach *df* = 2, for the effect of season *df* = 1, for the effect of reach*season *df* = 2. Significant effects are considered to be those with p less than 0.01.

Measure	Effect	First Creek			Fourth Creek		
		CR	GPP	NEP	CR	GPP	NEP
Reach	R	0.0002	0.0295	0.3318	<0.0001	<0.0001	0.0012
	S	0.1915	0.0012	0.0065	<0.0001	<0.0001	0.0024
	R*S	0.9485	0.0003	0.0007	<0.0001	<0.0001	<0.0001
Rock-pelagic	R	0.6179	0.0043	0.0047	0.0009	<0.0001	0.0003
	S	0.2706	0.0005	0.0011	<0.0001	<0.0001	<0.0001
	R*S	0.0002	0.0008	<0.0001	<0.0001	<0.0001	<0.0001
Gravel-pelagic	R	0.9866	0.0198	0.3389	0.0823	0.0408	0.0219
	S	0.1129	0.0198	0.4128	0.3186	0.4881	0.9189
	R*S	0.0995	0.0002	0.0024	0.2585	0.0714	0.0423
Pelagic	R	<0.0001	0.2959	<0.0001	<0.0001	0.0231	<0.0001
	S	<0.0001	0.3092	<0.0001	<0.0001	0.0111	<0.0001
	R*S	0.0261	0.5400	0.0220	0.0045	0.0126	0.2362

Table 6.5. Percent of reach community respiration (CR) and gross primary production (GPP) attributed to rock-pelagic and gravel-pelagic CR and GPP in autumn-winter (AW) and winter-spring (WS) in un-modified (Un-mod) and degraded (Deg) reaches of First and Fourth Creeks and engineered (Eng) reach of Fourth Creek. Mean ± standard error.

Parameter	Substrate	Season	First Creek		Fourth Creek		
			Un-mod	Deg	Un-mod	Deg	Eng
Percent of reach CR	Gravel-pelagic	AW	16 ± 2.9	21 ± 5.9	3 ± 0.5	45 ± 7.7	6 ± 0.5
		WS	9 ± 1.3	2 ± 0.1	15 ± 3.9	6 ± 3.0	2 ± 0.6
	Rock-pelagic	AW	84 ± 2.9	79 ± 5.9	97 ± 0.5	55 ± 7.9	94 ± 0.5
		WS	91 ± 1.3	98 ± 0.1	85 ± 3.9	94 ± 3.0	98 ± 0.6
Percent of reach GPP	Gravel-pelagic	AW	8 ± 0.6	0 ± 0.0	1 ± 0.3	46 ± 11.8	8 ± 0.0
		WS	0 ± 0.0	1 ± 0.2	14 ± 7.1	4 ± 1.9	1 ± 0.4
	Rock-pelagic	AW	92 ± 0.6	100 ± 0.0	99 ± 0.3	54 ± 11.8	92 ± 0.0
		WS	100 ± 0.0	99 ± 0.2	86 ± 7.1	96 ± 1.9	99 ± 0.4

Table 6.6. Statistics and relationships obtained for effects of environmental parameters on reach community respiration (CR), gross primary production (GPP) and net ecosystem production (NEP). Relationships include natural log (ln) transforms of parameters (x) and metabolic rates (y). Only significant effects are shown (p less than 0.05).

Parameter	Statistic and relationship	Reach CR	Reach GPP
Daily light intensity	p	<0.0001	<0.0001
	r^2	0.5823	0.6210
	df	23	23
	Relationship	Positive linear	Positive linear
Daily incident light	p	<0.0001	<0.0001
	r^2	0.6590	0.6886
	df	23	23
	Relationship	Positive linear	Positive linear
Initial DOC	p	0.0163	---
	r^2	0.1891	---
	df	29	---
	Relationship	Positive linear	---
Initial DOC to FRP molar ratio	p	0.0018	0.0144
	r^2	0.2979	0.1955
	df	29	29
	Relationship	Positive ln(y)	Positive linear
Reach chlorophyll *a*	p	<0.0001	<0.0001
	r^2	0.6267	0.6006
	df	29	29
	Relationship	Positive ln(x)	Positive ln(x)
Reach BOM – autumn-winter	p	0.0041	0.0001
	r^2	0.4818	0.6956
	df	14	14
	Relationship	Positive linear	Positive linear
Reach BOM – winter-spring	p	0.0204	0.0219
	r^2	0.3491	0.3424
	df	14	14
	Relationship	Positive linear	Positive linear
Wetted area	p	0.0151	0.0144
	r^2	0.1931	0.2031
	df	29	29
	Relationship	Positive linear	Positive linear

Table 6.7. Statistics and relationships obtained for effects of environmental parameters on rock-pelagic, gravel-pelagic and pelagic community respiration (CR), gross primary production (GPP) and net ecosystem production (NEP). Relationships include natural log (ln) transforms of parameters (x) and metabolic rates (y). Only significant effects are shown (p less than 0.05).

Parameter	Statistic and relationship	Rock-pelagic		Gravel-pelagic		Pelagic	
		CR	GPP	CR	GPP	CR	GPP
Daily light intensity	p	<0.0001	<0.0001	---	0.0375	---	---
	r^2	0.4601	0.5489	---	0.1823	---	---
	df	31	31	---	23	---	---
	Relationship	Positive linear	Positive linear	---	Positive linear	---	---
Daily incident light	p	<0.0001	<0.0001	---	0.0312	---	---
	r^2	0.5342	0.6213	---	0.1941	---	---
	df	31	31	---	23	---	---
	Relationship	Positive linear	Positive linear	---	Positive ln(x)	---	---
Initial FRP	p	---	---	---	0.0135	---	---
	r^2	---	---	---	0.1989	---	---
	df	---	---	---	29	---	---
	Relationship	---	---	---	Positive linear	---	---
Final FRP	p	---	---	0.0166	0.0281	---	---
	r^2	---	---	0.1947	0.1663	---	---
	df	---	---	28	28	---	---
	Relationship	---	---	Positive linear	Positive linear	---	---
Initial DOC	p	0.0007	0.0138	---	---	0.0049	---
	r^2	0.2709	0.1530	---	---	0.1901	---
	df	38	38	---	---	39	---
	Relationship	Positive linear	Positive linear	---	---	Positive linear	---
Final DOC	p	<0.0001	0.0047	---	---	---	---
	r^2	0.3497	0.1962	---	---	---	---
	df	38	38	---	---	---	---
	Relationship	Positive linear	Positive linear	---	---	---	---

Table 6.7 continued.

Parameter	Statistic and relationship	Rock-pelagic		Gravel-pelagic		Pelagic	
		CR	GPP	CR	GPP	CR	GPP
Initial DOC to FRP molar ratio	p	<0.0001	0.0002	---	---	0.0035	---
	r^2	0.3694	0.3186	---	---	0.2029	---
	df	38	38	---	---	39	---
	Relationship	Positive ln(y)	Positive linear	---	---	Positive linear	---
Final DOC to FRP molar ratio	p	<0.0001	<0.0001	---	---	---	---
	r^2	0.5789	0.5914	---	---	---	---
	df	38	38	---	---	---	---
	Relationship	Positive linear	Positive linear	---	---	---	---
Chamber chlorophyll *a*	p	<0.0001	<0.0001	---	---	---	---
	r^2	0.6200	0.5562	---	---	---	---
	df	38	38	---	---	---	---
	Relationship	Positive linear	Positive linear	---	---	---	---
Chamber BOM – autumn-winter	p	0.0289	0.0013	---	---	---	---
	r^2	0.2509	0.4671	---	---	---	---
	df	18	18	---	---	---	---
	Relationship	Positive linear	Positive linear	---	---	---	---
Chamber BOM – winter-spring	p	0.0019	0.0010	---	---	---	---
	r^2	0.4233	0.4595	---	---	---	---
	df	19	19	---	---	---	---
	Relationship	Positive linear	Positive linear	---	---	---	---

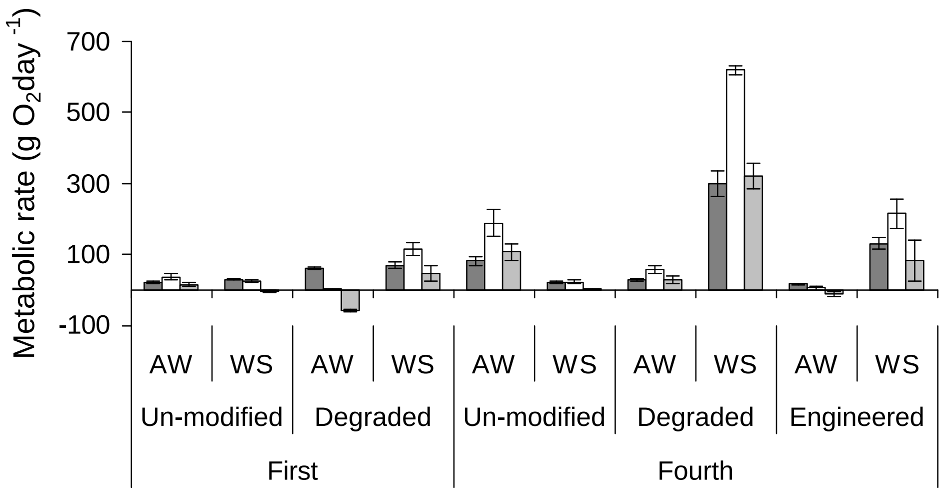


Figure 6.1. Reach community respiration (dark shaded), gross primary production (un-shaded) and net ecosystem production (light shaded) in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek during autumn-winter (AW) and winter-spring (WS). Error bars represent standard errors.

Figure 6.2. A two-dimensional NMS ordination of reach (Tot) community respiration (CR), gross primary production (GPP) and net ecosystem production (NEP). Measurements in un-modified (triangles), degraded (squares) and engineered (circles) reaches of First (un-shaded) and Fourth Creeks (shaded). Red vectors show the direction of increase in reach and rock-pelagic (Rock) metabolic rates at a cut-off r^2 value of 0.750.

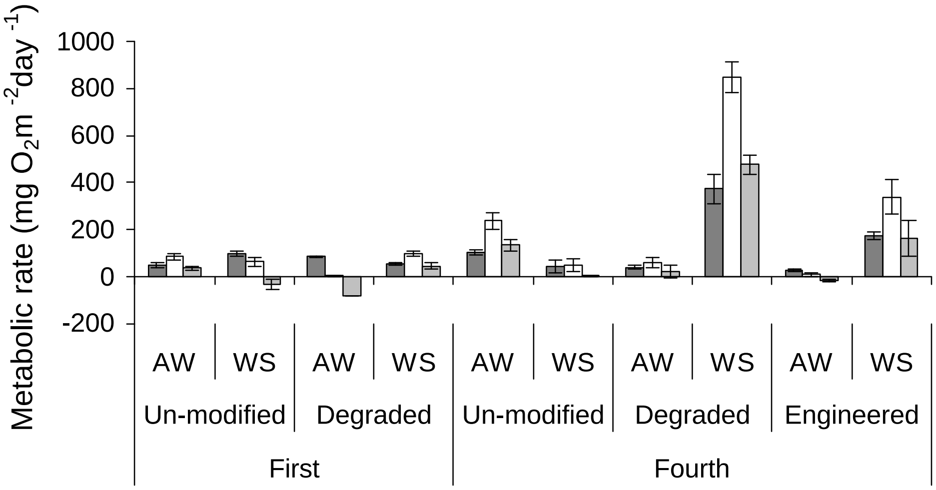


Figure 6.3. Rock-pelagic community respiration (dark shaded), gross primary production (un-shaded) and net ecosystem production (light shaded) in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek during autumn-winter (AW) and winter-spring (WS). Error bars represent standard errors.

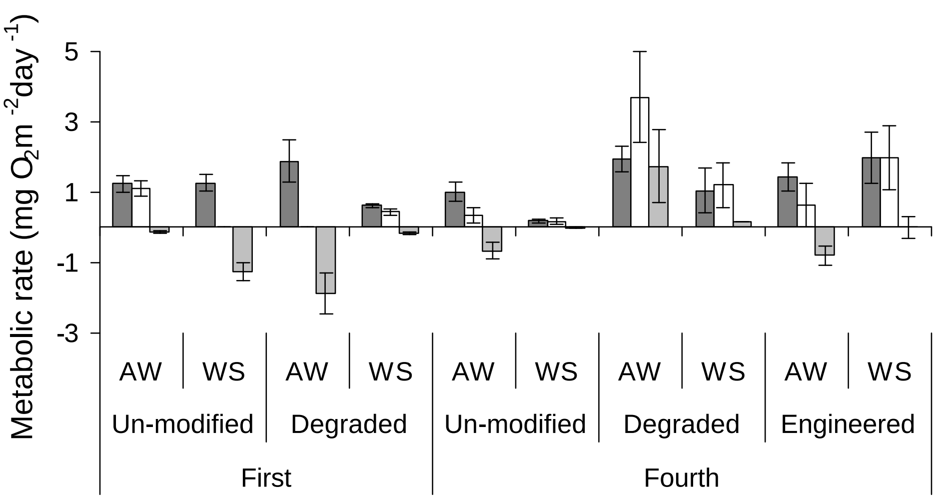


Figure 6.4. Gravel and pelagic community respiration (dark shaded), gross primary production (un-shaded) and net ecosystem production (light shaded) in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek during autumn-winter (AW) and winter-spring (WS). Error bars represent standard errors.

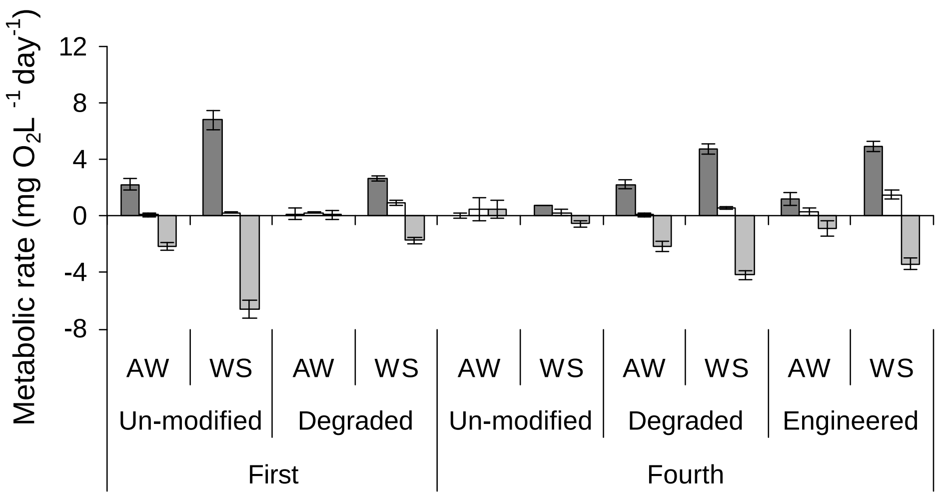


Figure 6.5. Pelagic community respiration (dark shaded), gross primary production (un-shaded) and net ecosystem production (light shaded) in un-modified and degraded reaches of First and Fourth Creeks and engineered reach of Fourth Creek during autumn-winter (AW) and winter-spring (WS). Error bars represent standard errors.

Chapter seven

7 Restoration of two ecosystem functions in a degraded-urban stream following the addition of coarse particulate organic matter

Abstract. In urban areas, the removal of riparian vegetation and subsequent increase in peak-flows within streams has resulted in lower standing stocks of coarse particulate organic matter (CPOM). The aim of this study was to investigate whether the addition of CPOM, in the form of leaf litter, into an urban stream altered ecosystem functions in ways that reflect more efficient processing of resources. Two ecosystem functions were chosen to assess this; stream metabolism and nutrient retention. Stream metabolism was measured by monitoring oxygen consumption and production within re-circulating benthic chambers. The addition of CPOM increased community respiration and decreased levels of net ecosystem production, to levels more akin to those within less impacted streams. Phosphorus retention was measured through a series of filterable reactive phosphorus (FRP)-sodium chloride addition experiments. The addition of CPOM increased the percent FRP retention, but did not alter the uptake length or mass transfer coefficient. The increased percent retention was attributed to increased phosphorus limitation of the CPOM and increased demand for phosphorus of the microbial community. This suggests that the re-introduction of CPOM into degraded streams may be an important step in the management of the functioning of stream ecosystems.

Keywords: *Coarse particulate organic matter, leaf litter, community respiration, gross primary production, net primary production, phosphorus, retention, stream, urbanisation, ecological stoichiometry*

7.1 Introduction

Coarse particulate organic matter (CPOM) plays a pivotal role in resource processing within ecosystems (Moore *et al.* 2004). In streams it may act as a surface area for biofilm attachment. Perhaps more importantly, it is also an energy source for microbial heterotrophs and macroinvertebrates and so forms a basal resource for stream ecosystems (Hicks 1997; Wallace *et al.* 1999). However, changes in land-use, including urbanisation, have greatly altered standing stocks of CPOM within streams through several mechanisms. Firstly, the removal of riparian vegetation has reduced CPOM deposition. Furthermore, changes in land-use have resulted in streams with channelised structures that have a reduced capacity to retain CPOM (Lepori *et al.* 2005). In addition, increased peak-flows that are experienced within urban streams (Booth and Jackson 1997; Walsh *et al.* 2004) are likely to remove CPOM directly, since CPOM retention is highly dependant upon hydrological factors (Webster and Meyer 1997).

A reduction in CPOM may alter resource interception and transformation. Meyer *et al.* (In press) demonstrated that a reduction in organic matter in urban streams resulted in reduced nutrient retention. It is also likely to reduce the activity of microbial heterotrophs and invertebrates that rely upon CPOM (Tank *et al.* 1998; Wallace *et al.* 1999). Most pristine streams throughout the world are heterotrophic (Rier and King 1996; Bunn *et al.* 1999; Young and Huryn 1999; Mulholland *et al.* 2001; Acuna *et al.* 2004) and are dependant upon allochthonous sources of carbon (Vannote *et al.* 1980). Consequently, a reduction in CPOM may cause a shift towards a community dominated by autotrophic organisms, which was observed in impacted stream reaches in chapters five and six.

Urban stream reaches in the Torrens River Catchment, South Australia, have lower standing stocks of CPOM than rural reaches (chapter two). While urbanisation was shown to impact on phosphorus processing (chapters three and four) and stream metabolism (chapters five and six), there is not, as yet, equivalent information of the impacts of restoration of CPOM standing stocks on these ecosystem functions in urban streams. The aim of this study was two fold. The first aim was to demonstrate the influence of CPOM on stream metabolism and phosphorus retention. Secondly, to examine whether the restoration of in-stream attributes of degraded streams can improve the efficiency of resource processing to reflect the functioning of more pristine streams. It was hypothesised that if CPOM was added to a degraded urban stream, it would act as an energy source for microbial communities and thus increase stream metabolic rates, increased demand for nutrients and increase the removal of phosphorus from stream water.

7.2 Methods

For this study an urban reach of Fourth Creek was chosen, which has experienced considerable erosion and bifurcates into two streams with approximately equal dimensions (chapter two). Stream metabolism and filterable reactive phosphorus (FRP) retention were measured before and after the addition of CPOM to the southern reach, herein referred to as the manipulated reach, M. The un-manipulated reach acted as the control, C.

7.2.1 Coarse particulate organic matter

Coarse particulate organic matter consisted of fresh *Eucalyptus camaldulensis* Dehnh (River Red Gum) leaves, which is the dominant riparian tree in the region. The dry weight of the leaf litter was estimated by determining the relationship of fresh and dry weights within sub-samples. The dry weight of these sub-samples was measured following drying to a constant weight at 60•C. On 14 November 2004, 140 g (dry weight) of leaf litter was separated into twenty groups of approximately equal mass and distributed evenly along M. The litter was packed into 0.5 m x 0.5 m plastic mesh and placed below the water surface. On 15, 17, 19 and 23 November 2004, leaf samples were collected for analysis of total phosphorus (TP), total carbon (TC) and total nitrogen (TN) concentrations and the molar ratios were calculated (chapter two). To control for the addition of the leaf packs, garden netting was also placed in C.

7.2.2 Stream metabolism

Stream metabolism was measured prior to CPOM addition and one and eight days after CPOM addition (Table 7.1). Stream metabolism was measured by placing substrates within re-circulating benthic chambers and monitoring dissolved oxygen consumption and production. Community respiration (CR), gross primary production (GPP) and net ecosystem production (NEP) were calculated as described in chapter five. Stream metabolic rates were adjusted for rock surface area as rocks form the benthic surface area of the stream. Although these are not absolute measurements of stream reach metabolism, these measurements do reflect general changes in reach metabolic rates (chapter six).

Prior to the addition of CPOM, rocks were randomly chosen within each reach and placed within three chambers with stream water. Chambers were randomly placed within the 100 m reach at a known depth. This was also done in C following the addition of CPOM to M. However, at this time in M, benthic rocks, stream water and leaf litter from leaf peaks were placed in three chambers. In addition, leaf litter was placed in another three chambers without rocks. Metabolic rates of biofilms attached to rocks (rock metabolism) and leaf litter (leaf metabolism) were calculated to determine the origin of changes in stream metabolism. To do this, metabolic rates in chambers containing both rocks and leaf litter were corrected for rates in chambers containing only leaf litter. Leaf metabolism was assumed to be equal with and without the presence of rocks.

Material attached to the surfaces of rocks was removed and sub-samples were taken for determination of benthic organic matter (BOM) and benthic chlorophyll *a* (chapter two). Measurements of organic matter and chlorophyll *a* attached to the surfaces of leaf litter were also calculated. Material attached to the leaf surfaces was removed by running fingers along leaf surfaces. From each chamber, initial and final water samples were taken for analysis of filterable reactive phosphorus (FRP) and dissolved organic carbon (DOC) concentrations and the molar ratios were calculated (chapter two). Measurements were also taken for stream discharge at three locations in each reach (chapter two).

7.2.3 Phosphorus retention

Prior to the addition of CPOM, three phosphorus-addition experiments were carried out concurrently in each reach (Table 7.1) using methods described in chapter three. Following addition of CPOM, another four experiments were carried out in each reach (Table 7.1). Percent FRP retention was calculated by plotting expected and observed FRP concentrations against elapsed time and comparing the area beneath the curves (between the time when expected-FRP concentration began to rise and returned to background). Data from the phosphorus-addition experiments was modelled to calculate hydrological and FRP retention properties. This was done using Matlab (Version 5.0.0.4073, The Mathworks Inc, Natwick, USA) and analytical solutions of the governing equation of solute transport (van Genuchten and Alves 1982), as described in chapter three. The FRP uptake length (S_w) and

FRP mass transfer coefficient (v_f) were calculated using equations of the Stream Solute Workshop (1990), as described in chapter three.

Prior to each phosphorus-addition experiment, four samples were collected from each reach for analysis of DOC and FRP concentrations and the DOC to FRP molar ratios were calculated (chapter two). Measurements of discharge were also recorded at three locations in each reach (chapter two).

7.2.4 Statistical analysis

Statistical analyses were performed using JMP-IN (Version 3.2.1, SAS Institute Inc., Cary, USA). All samples were tested for homogeneity (O'Brien, Brown-Forsythe, Levene and Bartlett tests) and normality (Shapiro-Wilk test). Metabolic rates of the two reaches prior to CPOM addition were compared with t-tests. Metabolic rates after CPOM addition were compared through two-way analysis of variance with reach and time as fixed effects (model 1). The interaction between reach and time is referred to herein as reach*time. Differences in rock metabolic rates and leaf metabolic rates were also compared through two-way analysis of variance with substrate and time as fixed effects (model 1). The interaction between substrate and time is referred to herein as substrate*time. When interactions were tested, significant effects were accepted if p values were less than 0.01 because interactions place doubt over the F-ratios of the main effects. In all other analyses, statistically significant relationships were accepted if p values were less than 0.05. Filterable reactive phosphorus retention properties of both reaches were compared prior to and following the addition of CPOM through t-tests. Relationships of metabolic rates and FRP retention properties with environmental conditions were analysed by regression analysis. Differences in environmental conditions between the two reaches were compared through one-way analysis of variance. Variability between replicates is reported as standard errors.

7.3 Results

7.3.1 Stream metabolism

Before and after CPOM addition, there were no differences in environmental conditions experienced between the two reaches (Table 7.2). On 15 November, there appeared to be higher final DOC concentration in M than C suggesting release of DOC, however this was not significant due the variation experienced in M. After the addition of CPOM, there was an increase in attached organic matter per unit rock surface area in M (p = <0.0001, • = 0.05, df = 9), owing to the increased organic matter attached to leaf surfaces (Table 7.2). However, there was no change in organic matter per unit rock surface area in C (Table 7.2).

Stream metabolic rates were similar between the two reaches prior to CPOM addition (Figure 7.1). Following CPOM addition there was no change in stream GPP, but stream CR was greater in M than C on days one and eight (Table 7.3, Figure 7.1). Consequently, NEP was lower in M than C one and eight days after CPOM addition (Table 7.3, Figure 7.1). Differences in CR and NEP were only explained by difference in the total amount of organic matter (p = <0.0001, • = 0.05, r^2 = 0.7962, df = 16 and p = 0.0020, • = 0.05, r^2 = 0.4816, df = 16, respectively) (Figure 7.2).

The altered stream metabolic rates were predominately a result of metabolism upon leaf litter. While there were no differences between leaf and rock GPP, one day after CPOM addition, leaf CR was greater than rock CR (Figure 7.3). Although by day eight there was no apparent difference, overall leaf CR was greater than that of rocks (Table 7.4). The reverse was true for NEP, with higher CR upon leaf litter than rocks resulting in reduced NEP upon leaf litter (Table 7.4, Figure 7.3). While the addition of CPOM appeared to increase rock CR in M in comparison to C on day eight (Figure 7.3), the difference was not statistically different (Table 7.5). Overall there was no difference in rock NEP between M and C, but on day eight rock NEP in M was lower than rock NEP in C, meaning there was an effect of reach*time (Table 7.5, Figure 7.3).

7.3.2 Phosphorus retention

Environmental conditions were similar within both reaches during the phosphorus-addition experiments (Tables 7.6 and 7.7). While discharge was generally higher in C, this difference was not significant and both reaches experienced discharges between approximately 4 and 95 L s^{-1} (Table 7.6). However, C experienced lower background FRP concentrations (Table 7.6) and higher background DOC to FRP molar ratios than M (p = 0.0008, • = 0.05, df = 12 and p = 0.0006, • = 0.05, df = 12, respectively).

During the experiment FRP uptake properties were controlled by hydrological parameters; FRP uptake length (S_w) had a positive relationship with stream velocity (v); mass transfer coefficient (v_f) had positive relationships with discharge, v and dispersion (D);

percent FRP retention had inverse relationships with discharge, *v* and *D* (Table 7.8). In addition, v_f had a positive linear relationship with DOC concentration (Table 7.8).

Prior to CPOM addition, M generally had longer S_w, lower v_f and retained less FRP (Table 7.7), but these differences were not significant. Uptake length progressively decreased in M with the number of days since CPOM addition (Table 7.8, Figure 7.4) and the difference in v_f between C and M became smaller (Table 7.7). However, following CPOM addition there were no statistical differences in S_w or v_f between C and M.

Following the addition of CPOM, the percent of FRP retained in M was greater than in C, but this was not statistically significant. However, the difference in percent FRP retention between C and M before and after CPOM addition was significant (p = 0.0163, • = 0.05, df = 6). Before the addition of CPOM, M retained on average 6.8% ± 0.97 less FRP than C. After the addition of CPOM, M retained 7.7% ± 2.75 more FRP than C (Figure 7.5). The increase in the percent FRP retention in M in comparison to C coincided with decreasing phosphorus availability of the CPOM. In fact, following CPOM addition, percent FRP retention had an inverse relationship with leaf TP concentration (Figure 7.6) and positive relationships with leaf TC to TP molar ratio and leaf TN to TP molar ratio (Table 7.8), but was not related to hydrological parameters.

7.4 Discussion

The addition of CPOM increased percent FRP retention. While FRP uptake length (S_w) shortened in M and mass transfer coefficient (v_f) decreased at a slower rate in M than C following CPOM addition, there were no significant differences in S_w and v_f between M and C. Chapter three also demonstrated that changes in S_w and particularly v_f across a rural-urban gradient were less responsive than percent FRP retention. Given the variable nature of these streams, increased replication through time may have allowed differences to be detected. Chapter three also demonstrated that v_f was not a suitable measure of phosphorus uptake potential across a rural-urban gradient because of its close association with hydrological parameters.

The addition of CPOM did increase CR, which has also been found for stream sediments (Crenshaw *et al.* 2002). The increased CR in this study did not coincide with increased GPP, resulting in a switch from a positive NEP to a negative NEP. Chapter five demonstrated that a degraded-urban reach of the same stream had considerably higher NEP than a more pristine reach within the Torrens River Catchment. The higher NEP was considered to reflect inefficient transformation of resources, as the autotrophic community was not consumed by higher trophic levels. Although the more pristine reach had a slightly positive NEP (chapter five), the NEP following CPOM addition is more similar to that of the pristine reach than that of the degraded reach prior to CPOM addition. In fact, a majority of pristine streams have been shown to have a negative NEP (Rier and King 1996; Bunn *et al.* 1999; Young and Huryn 1999; Mulholland *et al*. 2001; Acuna *et al.* 2004).

Leaves of *E. camaldulensis* leach DOC into the overlying water column (Baldwin 1999) and would have acted as an energy source for microbial organisms (Crenshaw *et al*. 2002; Wiegner *et al.* 2005), resulting in elevated metabolic rates. Meyer *et al*. (1998) demonstrated that DOC concentrations are directly related to leaf litter standing stocks. In this study, there was little difference detected in DOC concentrations following CPOM addition, suggesting that most of the leached DOC was incorporated into the microbial community. Indeed, following the addition of CPOM there was an increase in the total amount of attached organic matter per unit rock surface area.

Following the addition of CPOM there were no differences in FRP concentration either, suggesting that leached FRP was incorporated into the microbial community. Indeed, a majority of the phosphorus leached from *E. camaldulensis* leaves is in dissolved, readily available forms (Baldwin 1999) and would be available for microbial organisms. Microbial assimilation of CPOM is often limited by nutrients (Rosemond *et al.* 2002; Gulis and Suberkropp 2003; Stelzer *et al.* 2003) and the nutrient ratios of CPOM in this study suggested this was the case. In general, CPOM TC to TP molar ratios were between 1600 and 2700, which exceeds those of microbial organisms that have TC to TP molar ratios below 100 (Stelzer *et al.* 2003). Consequently, increased rates of CR in this study could only have continued if nutrient sources became available.

Indeed, following the addition of CPOM there was an increase in the percent of FRP retained, reflecting an increase in the capacity of resource interception. Subsequently, as phosphorus was preferentially lost from CPOM, FRP retention continued to increase, probably because microbial heterotrophs required more water column phosphorus to sustain their increased rates of respiration. These results are consistent with Crenshaw *et al*. (2002) and Bernhardt and Likens (2002) who demonstrated that carbon availability has a strong influence on nutrient retention. Frost *et al*. (2002) proposed that the development of different elemental compositions of freshwater organisms, or the ecological stoichiometry, may play an important role in controlling ecosystem processes. In this study, the importance of ecological stoichiometry to FRP retention appeared to override hydrological parameters, which had controlled FRP retention properties over the experimental period and have previously been shown to be important determinants of nutrient retention (D'Angelo and Webster 1991; Butturini and Sabater 1998; Hall Jr. *et al.* 2002).

It is not clear whether the increased microbial activity and FRP retention was directly or indirectly associated with CPOM. A likely direct cause was that the CPOM acted as surface for attachment and a nutritional substrate of microbial organisms, thus increasing microbial activity and FRP retention. However, Boulton (1991) demonstrated that microbial biomass associated with Eucalypt leaves did not increase until 20 days after submergence. Consequently, it is also likely that the increased CR was indirectly caused by an increased capacity of the stream to retain fine particulate organic matter (FPOM), which would contain an active microbial community. Microbial organisms associated with FPOM have been shown to be less important for nutrient uptake than those associated with CPOM (Sanzone *et al.* 2001) and so the source of the observed changes requires further investigation.

Whatever the case, this study demonstrated that CPOM addition to degraded-urban streams has the potential to restore at least two important ecosystem functions in ways that reflect efficient resource processing. It is likely that the benefits of rehabilitation of CPOM standing stocks would cascade through the stream community since microbial heterotrophs and CPOM will contribute to higher trophic levels (Hall Jr. and Meyer 1998) and microbial heterotrophs render CPOM more palatable to other invertebrates (Suberkropp and Klug 1980). Indeed, the presence of terrestrial detrital inputs has been shown to increase the abundance and biomass of macroinvertebrates (Wallace *et al.* 1999). Moore *et al.* (2004) suggested that these multiple pathways of energy inputs into food-webs that detritus provides, increases biological diversity and provides ecosystem stability. While Lepori *et al.* (2005) demonstrated that rehabilitation of stream structures successfully increased standing stocks of CPOM, the effect is unlikely to be sustained unless the over-riding effect of changes in stream structure are addressed through management at the catchment scale.

Table 7.1. Dates of stream metabolism and phosphorus-addition experiments and in the manipulated and control reaches. Leaf litter was added to the manipulated reach on 14 November 2004.

Experiment	Time relative to leaf addition	Experiment number	Date
Stream metabolism	Before	1	8 Nov.
	After	2	15 Nov.
		3	23 Nov.
Phosphorus-addition	Before	1	8 Nov
		2	10 Nov.
		3	12 Nov.
	After	4	15 Nov.
		5	17 Nov.
		6	19 Nov.
		7	23 Nov.

Table 7.2. Environmental parameters during measurements of stream metabolism in manipulated and control reaches, before and after leaf addition. Mean ± standard error.

Parameter	Time relative to leaf addition	Date	Manipulated	Control
Discharge (L s^{-1})	Before	8 Nov.	10.4 ± 2.87	23.1 ± 3.88
	After	15 Nov.	49.5 ± 17.29	73.0 ± 9.15
		23 Nov.	4.1 ± 1.46	5.6 ± 3.56
Water temperature (°C)	Before	8 Nov.	14.7 ± 0.42	14.9 ± 0.13
	After	15 Nov.	16.9 ± 0.06	16.6 ± 0.03
		23 Nov.	18.6 ± 0.32	16.8 ± 0.15
Initial FRP (• g L^{-1})	Before	8 Nov.	11.1 ± 1.11	9.4 ± 0.56
	After	15 Nov.	10.3 ± 0.67	8.9 ± 0.67
		23 Nov.	11.6 ± 0.56	13.8 ± 1.92
Final FRP (• g L^{-1})	Before	8 Nov.	5.6 ± 0.56	6.1 ± 1.47
	After	15 Nov.	12.3 ± 2.40	8.3 ± 0.67
		23 Nov.	13.8 ± 6.94	8.8 ± 1.92
Initial DOC (mg L^{-1})	Before	8 Nov.	6.9 ± 1.14	7.8 ± 1.89
	After	15 Nov.	5.4 ± 0.38	5.7 ± 1.07
		23 Nov.	7.5 ± 1.72	7.1 ± 1.48
Final DOC (mg L^{-1})	Before	8 Nov.	7.7 ± 0.54	9.2 ± 0.71
	After	15 Nov.	11.8 ± 3.01	4.7 ± 0.16
		23 Nov.	7.4 ± 1.01	5.4 ± 0.51
Benthic organic matter (g m^{-2})	Before	8 Nov.	1.8 ± 0.25	2.2 ± 0.28
	After	15 Nov.	1.5 ± 0.17	1.8 ± 0.13
		23 Nov.	2.0 ± 0.33	2.0 ± 0.30
Benthic chlorophyll *a* (mg m^{-2})	Before	8 Nov.	5.0 ± 1.25	5.6 ± 0.18
	After	15 Nov.	3.5 ± 0.39	4.0 ± 0.24
		23 Nov.	2.7 ± 1.38	3.4 ± 0.58
Chamber depth (m)	Before	8 Nov.	22.7 ± 1.67	23.0 ± 1.00
	After	15 Nov.	22.3 ± 0.88	23.3 ± 0.67
		23 Nov.	22.0 ± 0.00	23.3 ± 0.67
Leaf attached organic matter (g m^{-2})	After	15 Nov.	1.9 ± 0.44	---
		23 Nov.	1.6 ± 0.06	---
Leaf attached chlorophyll *a* (mg m^{-2})	After	15 Nov.	0.2 ± 0.04	---
		23 Nov.	0.8 ± 0.23	---

Table 7.3. P-values obtained for effects of reach, time and reach*time on stream gross primary production, community respiration and net ecosystem production, following the addition of coarse particulate organic matter to a manipulated reach. For all effects *df* = 1. Significant effects are those with *p* less than 0.01.

Effect	Gross primary production	Community respiration	Net ecosystem production
Reach	0.9994	0.0001	0.0004
Time	0.5140	0.1030	0.8350
Reach*time	0.1396	0.5987	0.1157

Table 7.4. P-values obtained for effects of substrate, time and substrate*time on leaf and rock gross primary production, community respiration and net ecosystem production, following the addition of coarse particulate organic matter to a manipulated reach. For all effects *df* = 1. Significant effects are those with *p* less than 0.01.

Effect	Gross primary production	Community respiration	Net ecosystem production
Substrate	0.4578	0.0071	0.0051
Time	0.2472	0.0860	0.6524
Substrate*time	0.6935	0.0108	0.0123

Table 7.5. P-values obtained for effects of reach, time and reach*time on rock gross primary production, community respiration and net ecosystem production, following the addition of coarse particulate organic matter to a manipulated reach. For all effects *df* = 1. Significant effects are those with *p* less than 0.01.

Effect	Gross primary production	Community respiration	Net ecosystem production
Reach	0.3075	0.1187	0.0198
Time	0.6798	0.6273	0.1908
Reach*time	0.2002	0.1185	0.0095

Table 7.6. Environmental parameters during phosphorus-addition experiments in manipulated and control reaches, before and after leaf addition. Mean ± standard error.

Parameter	Time relative to leaf addition	Date	Manipulated	Control
Discharge (L s^{-1})	Before	8 Nov	10.4 ± 2.87	23.1 ± 3.88
		10 Nov.	10.2 ± 1.47	17.8 ± 1.58
		12 Nov.	93.2 ± 22.82	90.2 ± 22.64
	After	15 Nov.	49.5 ± 17.29	73.0 ± 9.15
		17 Nov.	17.4 ± 9.25	37.5 ± 7.25
		19 Nov.	14.5 ± 2.57	17.3 ± 4.60
		23 Nov.	4.1 ± 1.46	5.6 ± 3.56
Water temperature (°C)	Before	8 Nov	14.0 ± 0.05	14.4 ± 0.03
		10 Nov.	16.1 ± 0.04	16.0 ± 0.02
		12 Nov.	15.4 ± 0.01	15.6 ± 0.02
	After	15 Nov.	15.5 ± 0.01	15.5 ± 0.02
		17 Nov.	17.7 ± 0.08	17.4 ± 0.03
		19 Nov.	15.1 ± 0.06	15.6 ± 0.04
		23 Nov.	15.6 ± 0.16	16.7 ± 0.07
Background FRP (• g L^{-1})	Before	8 Nov	6.5 ± 0.68	13.2 ± 0.96
		10 Nov.	8.3 ± 0.48	14.7 ± 0.42
		12 Nov.	8.4 ± 0.42	11.8 ± 1.25
	After	15 Nov.	8.6 ± 0.58	11.6 ± 1.98
		17 Nov.	9.2 ± 0.48	11.1 ± 0.56
		19 Nov.	6.4 ± 0.42	10.2 ± 0.48
		23 Nov.	9.7 ± 0.48	10.1 ± 0.42
Added FRP (• g L^{-1})	Before	8 Nov	1888 ± 8.3	1997 ± 13.6
		10 Nov.	2181 ± 9.2	2067 ± 23.6
		12 Nov.	1887 ± 0.0	1853 ± 19.2
	After	15 Nov.	2273 ± 113.1	2103 ± 16.7
		17 Nov.	1967 ± 33.3	2117 ± 16.7
		19 Nov.	1773 ± 0.0	1957 ± 16.7
		23 Nov.	2270 ± 161.9	2370 ± 87.7

Table 7.6 continued.

Parameter	Time relative to leaf addition	Date	Manipulated	Control
FRP at point of addition (• g L^{-1})	Before	8 Nov	165.2	111.6
		10 Nov.	322.4	167.0
		12 Nov.	42.1	57.6
	After	15 Nov.	125.6	53.7
		17 Nov.	232.3	93.3
		19 Nov.	158.2	173.0
		23 Nov.	441.1	225.5
DOC (mg L^{-1})	Before	8 Nov	4.1 ± 0.08	4.1 ± 0.07
		10 Nov.	4.3 ± 0.09	4.1 ± 0.04
		12 Nov.	5.2 ± 0.03	5.1 ± 0.05
	After	15 Nov.	4.6 ± 0.06	4.5 ± 0.10
		17 Nov.	4.4 ± 0.03	4.3 ± 0.05
		19 Nov.	4.2 ± 0.05	4.3 ± 0.15
		23 Nov.	4.3 ± 0.07	4.4 ± 0.22
Leaf total phosphorus (mg g^{-1})	After	15 Nov.	0.78 ± 0.164	---
		17 Nov.	0.65 ± 0.091	---
		19 Nov.	0.49 ± 0.54	---
		23 Nov.	0.46 ± 0.064	---
Leaf total carbon (mg g^{-1})	After	15 Nov.	497.3 ± 4.4	---
		17 Nov.	478.6 ± 9.5	---
		19 Nov.	500.4 ± 5.4	---
		23 Nov.	487.6 ± 5.4	---
Leaf total nitrogen (mg g^{-1})	After	15 Nov.	11.2 ± 1.0	---
		17 Nov.	16.5 ± 0.5	---
		19 Nov.	16.2 ± 1.4	---
		23 Nov.	16.3 ± 0.7	---

Table 7.7. Hydrological and filterable reactive phosphorus (FRP) retention properties during phosphorus-addition experiments in manipulated and control reaches of Fourth Creek before and after leaf addition. Average measurements ± standard error. All parameters apart from percent FRP retention were calculated using the analytical solution of the governing equation for solute transport described by van Genuchten and Alves (1982).

Parameter	Time relative to leaf addition	Date	Manipulated	Control
Stream velocity (m min^{-1})	Before	8 Nov	4.5	4.8
Stream velocity (m min^{-1})	Before	10 Nov.	2.4	3.1
Stream velocity (m min^{-1})	Before	12 Nov.	13.6	7.8
Stream velocity (m min^{-1})	After	15 Nov.	6.7	8.2
Stream velocity (m min^{-1})	After	17 Nov.	3.0	4.9
Stream velocity (m min^{-1})	After	19 Nov.	3.6	2.2
Stream velocity (m min^{-1})	After	23 Nov.	1.7	1.4
Dispersion (m^2 min^{-1})	Before	8 Nov	7.5	8.2
Dispersion (m^2 min^{-1})	Before	10 Nov.	5.2	5.8
Dispersion (m^2 min^{-1})	Before	12 Nov.	21.9	16.2
Dispersion (m^2 min^{-1})	After	15 Nov.	7.8	12.2
Dispersion (m^2 min^{-1})	After	17 Nov.	3.6	8.8
Dispersion (m^2 min^{-1})	After	19 Nov.	4.4	5.4
Dispersion (m^2 min^{-1})	After	23 Nov.	3.5	3.0
Retardation factor	Before	8 Nov	1.01	1.04
Retardation factor	Before	10 Nov.	1.03	1.04
Retardation factor	Before	12 Nov.	1.00	1.32
Retardation factor	After	15 Nov.	1.02	1.10
Retardation factor	After	17 Nov.	1.07	1.03
Retardation factor	After	19 Nov.	1.04	1.22
Retardation factor	After	23 Nov.	1.14	1.00
FRP production (• g L^{1} min^{-1})	Before	8 Nov	0.50	1.03
FRP production (• g L^{1} min^{-1})	Before	10 Nov.	0.50	0.99
FRP production (• g L^{1} min^{-1})	Before	12 Nov.	1.98	1.43
FRP production (• g L^{1} min^{-1})	After	15 Nov.	1.03	1.57
FRP production (• g L^{1} min^{-1})	After	17 Nov.	0.45	1.08
FRP production (• g L^{1} min^{-1})	After	19 Nov.	0.49	0.40
FRP production (• g L^{1} min^{-1})	After	23 Nov.	0.36	0.38

Table 7.7 continued.

Parameter	Time relative to leaf addition	Date	Manipulated	Control
FRP decay coefficient (min^{-1})	Before	8 Nov	0.039	0.061
		10 Nov.	0.034	0.055
		12 Nov.	0.148	0.079
	After	15 Nov.	0.061	0.078
		17 Nov.	0.028	0.059
		19 Nov.	0.040	0.035
		23 Nov.	0.029	0.028
FRP uptake length (m)	Before	8 Nov	115.4	78.7
		10 Nov.	70.6	56.4
		12 Nov.	91.9	98.7
	After	15 Nov.	109.8	105.1
		17 Nov.	107.1	83.1
		19 Nov.	90.0	62.9
		23 Nov.	58.6	50.0
FRP mass transfer coefficient (cm min^{-1})	Before	8 Nov	0.241	0.475
		10 Nov.	0.210	0.429
		12 Nov.	0.916	0.616
	After	15 Nov.	0.378	0.608
		17 Nov.	0.173	0.460
		19 Nov.	0.248	0.273
		23 Nov.	0.180	0.218
Percent FRP retention	Before	8 Nov	8.5	16.2
		10 Nov.	6.0	10.9
		12 Nov.	0.6	8.4
	After	15 Nov.	7.7	1.6
		17 Nov.	11.0	0.9
		19 Nov.	23.4	24.1
		23 Nov.	27.4	12.0

Table 7.8. Statistics and relationships obtained for effects of environmental parameters on FRP uptake length, FRP mass transfer coefficient and percent FRP retention. Relationships include natural log (ln) and square root (sqrt) transforms of parameters (x) and FRP retention properties (y). Only significant effects are shown (p less than 0.05). For all analyses df = 13, except for leaf nutrient concentrations, leaf nutrient molar ratios and number of days after leaf addition, where df = 3.

Parameter	Statistic and relationship	FRP uptake length	FRP mass transfer coefficient	Percent FRP retention
Discharge	p	---	<0.0001	0.0094
	r^2	---	0.8115	0.4430
	Relationship	---	Positive linear	Inverse ln(y)
Velocity	p	0.0058	<0.0001	0.0027
	r^2	0.4836	0.8540	0.5419
	Relationship	Positive ln(x)	Positive linear	Inverse linear
Dispersion coefficient	p	---	<0.0001	0.0046
	r^2	---	0.9001	0.5007
	Relationship	---	Positive linear	Inverse linear
DOC	p	---	0.0044	---
	r^2	---	0.5055	---
	Relationship	---	Positive linear	---
Number of days after leaf addition	p	0.0207	---	---
	r^2	0.9590	---	---
	Relationship	Inverse linear	---	
Leaf total phosphorus	p	---	---	0.0061
	r^2	---	---	0.9879
	Relationship	---	---	Inverse ln (y)
Leaf total carbon to phosphorus molar ratio	p	---	---	0.0066
	r^2	---	---	0.9869
	Relationship			Positive linear
Leaf total nitrogen to phosphorus molar ratio	p	---	---	0.0446
	r^2	---	---	0.9129
	Relationship	---	---	Positive sqrt(y)
Leaf total carbon to nitrogen molar ratio	p	---	0.0313	---
	r^2	---	0.9384	---
	Relationship	---	Positive linear	---

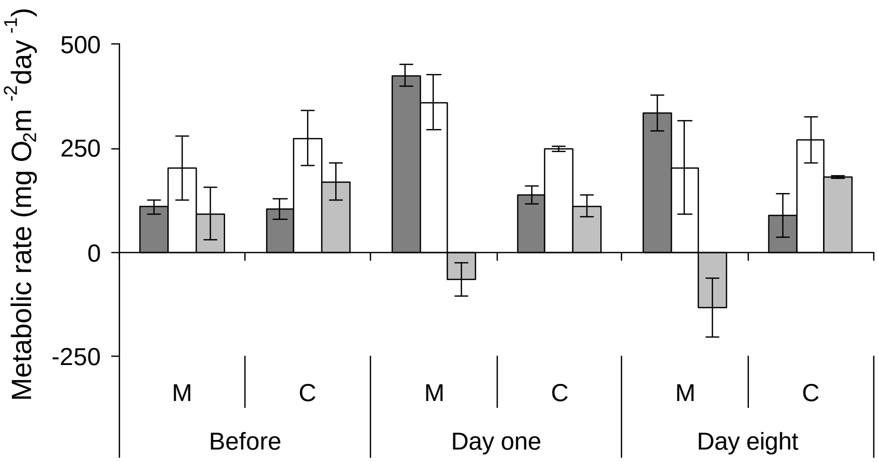


Figure 7.1. Stream community respiration (dark shaded), gross primary production (un-shaded) and net ecosystem production (light shaded) in manipulated (M) and control (C) reaches, before, one day and eight days after the addition of leaf litter. Rates are given as per unit surface area of rock substrate. Error bars represent standard errors.

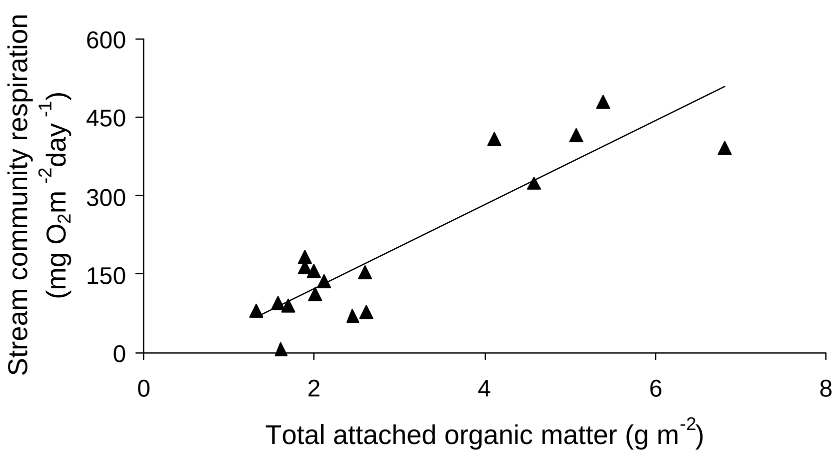


Figure 7.2. Influence of total attached organic matter per unit rock surface area on community respiration in manipulated and control reaches of Fourth Creek following the addition of leaf litter. Full line denotes fitted linear regression (p = <0.0001, • = 0.05, r^2 = 0.7962, df = 16).

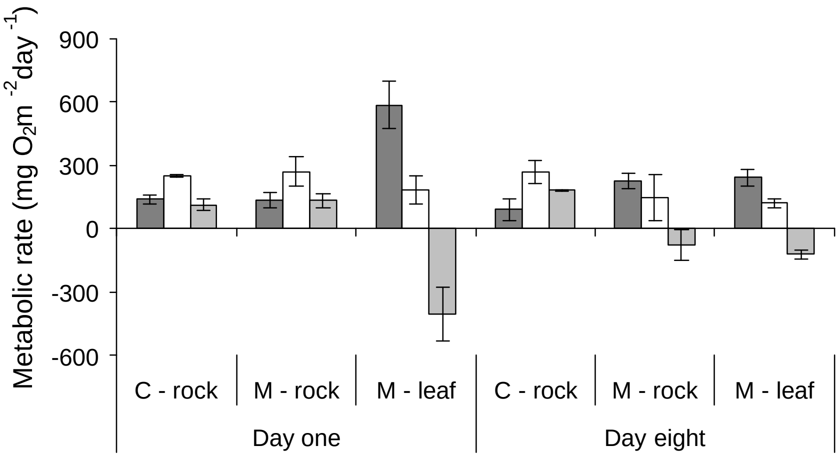


Figure 7.3. Rock and leaf community respiration (dark shaded), gross primary production (un-shaded) and net ecosystem production (light shaded) in control (C) and manipulated (M) reaches, one and eight days after the addition of leaf litter. Rates are given as per unit surface area of rock and leaf. Error bars represent standard errors.

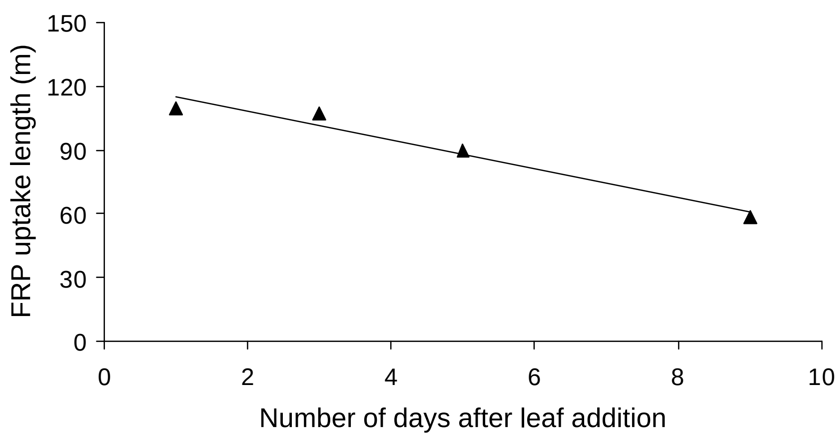


Figure 7.4. Influence of number of days since leaf addition on FRP uptake length in manipulated reach. Full line denotes fitted linear regression (p = 0.0207, • = 0.05, r^2 = 0.9590, df = 3).

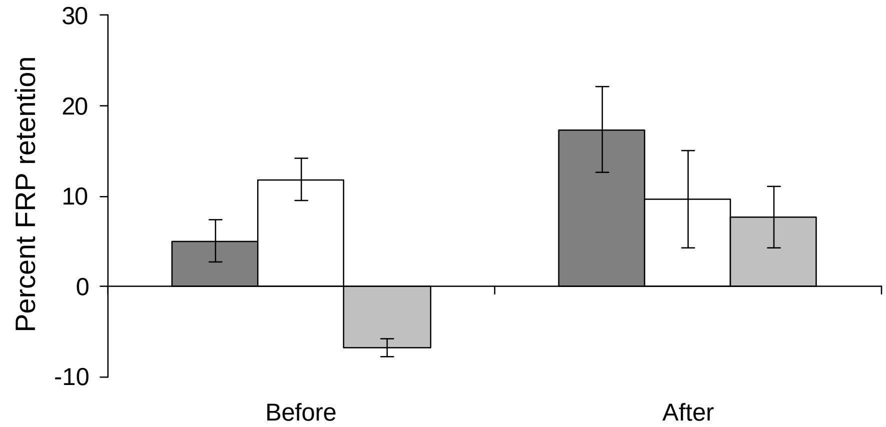


Figure 7.5. Percent FRP retention in manipulated (dark shaded) and control (un-shaded) reaches of Fourth Creek and the difference between manipulated and control reaches (light shaded) before and after the addition of leaf litter. Differences were calculated as the percent FRP retention in the manipulated reach minus the percent FRP retention in the control reach. Error bars represent standard errors.

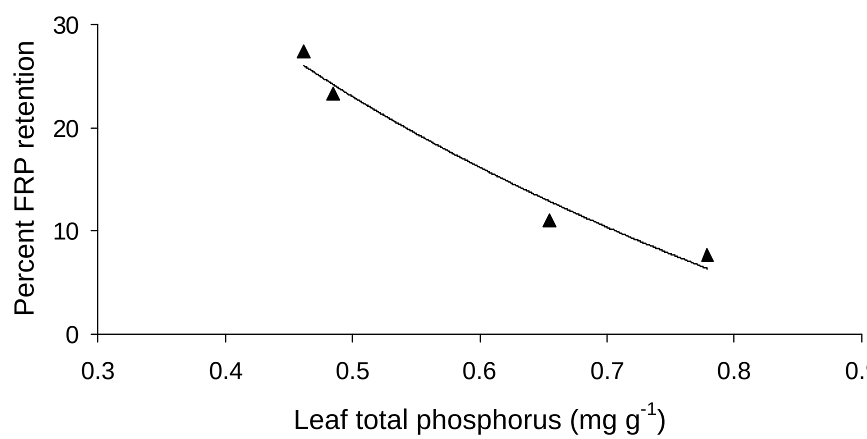


Figure 7.6. Influence of leaf total phosphorus concentration on percent FRP retention in manipulated reach following the addition of leaf litter. Full line denotes fitted regression with natural log transform of percent FRP retention (p = 0.0031, • = 0.05, r^2 = 0.9879, df = 3).

Chapter eight

8 General discussion

8.1 Changes in ecosystem functions across a rural-urban gradient

The capacity of stream ecosystems to process resources reflected the level of deterioration of streams within the Torrens River Catchment. This was demonstrated by:

- Reduced phosphorus retention in impacted reaches due to altered hydrological conditions and higher phosphorus availability than in the un-modified reach of First Creek (chapter three).
- Reduced biotic benthic phosphorus uptake in impacted reaches in two of three seasons. This was due to a reduced period of continuous flow and high phosphorus availability in impacted reaches (chapter four).
- Increased metabolic rates and a dominance of autotrophic communities in impacted streams due to increased light availability (chapters five and six).

The altered conditions were thought to reduce the number and/or activity of pathways of resource interception and transformation. Within the most pristine reach, the un-modified reach of First Creek, the greater number of interception and transformation pathways reduced the amount of resources passing downstream (Figure 8.1). Although the transfer of resources from microbial organisms to higher trophic levels was outside the scope of this project, enhanced grazing pressure upon microbial organisms was thought to maintain low metabolic rates and increase nutrient turn-over (Steinman *et al*. 1995).

Ecosystem functions of impacted reaches were more variable, reflecting reduced ecosystem stability (Harris 1994; Carpenter *et al*. 1996). A high disturbance environment was thought to result in low microbial abundances and activity and so fewer resources were intercepted and transformed (Figure 8.2A). When a major disturbance was absent for some time, the availability of resources, such as light and nutrients, was thought to favour an autotrophic community and result in increased metabolic rates (Figure 8.2B). The enhanced metabolic rates would not be possible if higher trophic levels were consuming microbial organisms, suggesting that fewer resources were passed on to higher trophic levels, as observed by Bunn *et al.* (1999). Since there were sufficient resources, additional resources were not intercepted or transformed, with a majority passing downstream.

8.2 Implications for management of ecosystem functions

Biotic benthic and total phosphorus interception were dependent upon the period of continuous flow, with release of phosphorus following drying (chapter four). Baldwin and Mitchell (2000) also found this, but demonstrated partial drying increased the affinity of sediments for nutrients. Consequently, water extractions for agricultural purposes should be managed to allow natural fluctuations in water levels and prevent reductions in the period of flow. This may be achieved by: limiting the amount of water captured by dams; constructing dam bypasses that allow water to enter streams, particularly during drier months; and periodically releasing water from dams.

Slowing water flow would also enhance stream phosphorus retention, since it was positively related to contact time. This is particularly relevant in urban streams, which experience increased peak-flows (Booth and Jackson 1997; Walsh *et al.* 2004). This may be achieved through principles of water sensitive urban design (Wong *et al.* 1999) such as; capturing storm-water and slowly releasing it into streams; removing direct storm-water inputs into streams; and diverting storm-water over vegetated areas to promote soil infiltration. In addition, the rehabilitation of stream physical complexity will prevent the more laminar flow that is experienced within channelised streams.

A reduction in surface run-off entering streams directly will also reduce scouring of coarse particulate organic matter (CPOM) and increase resource interception. As demonstrated by chapter seven, CPOM increased phosphorus retention because of reduced phosphorus availability and increased phosphorus demand. This is a likely explanation for the observed benefits of straw in preventing algal growth (Caffrey and Monahan 1999). Chapters three and four also demonstrated that phosphorus availability was important in a controlling biotic and total phosphorus interception. Consequently, as inputs from the surrounding catchment are reduced, the ability of streams to intercept additional resources will be enhanced. This may be achieved through reduced nutrient application (fertilisers etc.), the construction of artificial wetlands and rehabilitation of riparian vegetation.

Riparian vegetation is known to be an important step in management of stream ecosystems (Tabacchi *et al.* 1998). Not only will it maintain CPOM standing stocks and reduce nutrient inputs, but it will also limit light availability, which was important in determining the dominance of autotrophic communities in impacted reaches (chapters five and six). However, autochthonous carbon sources appear be important in the food-webs of these streams. Therefore, management should not aim to limit autotrophic communities altogether, but instead encourage a range of species that are native to the region.

The increased dominance of autotrophic communities was also thought to be a result of decreased grazing pressure. It is probable that the management strategies described above would also provide benefits to higher trophic levels. For example, the increased abundance of microbial heterotrophs upon CPOM may contribute to higher trophic levels (Hall Jr. and Meyer 1998) and render the CPOM available to other invertebrates (Suberkropp and Klug 1980). Similarly, the rehabilitation of the physical structure and flow regimes of degraded streams may also provide refuge for a range of organisms (Boulton and Lake 1988; Townsend and Scarsbrook 1997) which are in low abundance and diversity in degraded streams (Paul and Meyer 2001).

8.3 Ecosystem services

The rehabilitation techniques described above would require a major overhaul of developed areas and would be costly. Although the primary beneficiary would be in-stream biota, the importance of various functional processes of ecosystems to the well-being of humans is gaining some understanding (Costanza *et al.* 1997). Short-term monetary costs of such rehabilitation must be weighted against the long-term benefits that rehabilitation will provide, such as improved water quality and reduced water treatment costs. Similarly, future development of pristine areas must accurately match the long-term costs with short-term benefits if sustainable development is to be achieved.

Anthropogenic impacts upon ecosystem services are not well understood. This project demonstrated altered ecosystem functions in impacted streams that reflected a reduction in the efficiency of resource processing. Consequently, alterations to ecosystem services are likely, such as lower resource transfer to higher organisms and poorer water quality. This may increase costs incurred elsewhere, such as, in the operation of water treatment plants.

This project has also demonstrated that there is potential for restoration of these ecosystem services. Rehabilitation will not only provide humans with resources, but will also provide humans with aesthetic and recreational benefits (Bolund and Hanhammar 1999). This is particularly relevant in developed areas where ecosystems provide people with an appreciation of the environment, which may be a powerful educational tool. Consideration of the benefits of rehabilitation to the environment, economy and society must all be considered to make large rehabilitation projects feasible.

8.4 Knowledge gaps

The understanding of stream ecology in the region of this project is limited. It is evident these streams are different to temperate streams that have been studied in detail. A major difference is the flow regimes that these streams experience. These vary from streams with permanent flow; to temporary streams with regular seasonal intermittent flow; and temporary streams that only flow immediately following unpredictable rain (Boulton and Suter 1986). This provides a unique opportunity for research along a continuum of flow regimes and will provide not only important information for current management practices, but also insight into the impacts of climate change upon stream ecosystems. Other questions that require investigation include; what is the relative importance of autochthonous and allochthonous carbon sources to food-webs? What factors control community structure? How does community structure influence ecosystem functions?

A limitation of this project was that resources transferred to higher organisms were not investigated. This would add substantially to studies investigating resource processing within pristine and impacted ecosystems. Decreased resource transfer has been demonstrated in streams impacted by agriculture (Bunn *et al.* 1999). While fewer consumers have been observed in urban streams (Collier and Winterbourn 1986; Walsh *et al.* 2001), alterations to resource transfers to higher trophic levels has not been demonstrated in urban streams. Ecological stoichiometric and isotopic studies can provide substantial insight into the transfer of resources between various trophic levels and will help identify some of the important pathways of resource transformation. Since carbon is a stable resource that is shared between trophic levels, it provides a good basis for studies of resource processing at ecosystem and landscape scales (Cole and Caraco 2001).

Although this project used the conceptual model of Brookes *et al.* (In press) (Figure 1.2) to investigate changes in resource processing with increased ecosystem deterioration, the number of individual pathways of resource interception and transformation was not identified. Species and functional diversity have been shown to enhance resource processing in models and in experimental situations, but the transfer of this knowledge to the landscape requires further investigation. The pathways investigated in this study could be broken down further. For example, the number of microbial pathways may be investigated through comparison of the activity of various enzymes that are used for microbial metabolism (Kirchman *et al.* 2004). In addition, the importance of hyporheic zones for phosphorus processing and stream metabolism could be investigated. Also, the importance of autotrophic and heterotrophic organisms for phosphorus processing and stream metabolism may be identified. This may be investigated by making the assumption that the demands of autotrophic respiration are met through internal carbon production and so heterotrophic respiration is related to the consumption of water dissolved organic carbon.

The conceptual model of Brookes *et al*. (In press) provides a basis for management priorities at the landscape scale, but it is not completely substantiated and does not have predictive power. Studies of ecosystems add weight to the conceptual model, but research should also focus on how ecosystem level changes provide pathways at the landscape scale. Models, such as the model for urban storm-water improvement conceptualisation (Cooperative Research Centre for Catchment Hydrology, Monash University, Melbourne, Australia), predict the benefits of management options for water quality. An understanding of resource interception and transformation at the landscape level and input into such models could also provide predictive power for the benefits of management to ecosystems. This may identify resource processing ‘hot spots’ that should be preserved and rehabilitated to maximise resource interception and transformation. It will also identify the level of preservation and rehabilitation that is required to provide the ecosystem services and what level of improvements can be achieved. Restoration ecology in general is underdeveloped in aquatic systems. This needs to be addressed, as it is essential that we extend our knowledge on how and what components of freshwater systems can be rehabilitated.

8.5 Conclusions

Much attention has been paid to anthropogenic impacts upon physical and chemical conditions in freshwater ecosystems, as well as the structure of particular functional groups (Boulton 1999). This project has demonstrated that two stream ecosystem functions were altered across a rural-urban gradient in ways that exemplified inefficient processing of nutrients; reduced phosphorus retention and increased dominance of autotrophic communities. It was also demonstrated that the rehabilitation of an attribute of stream ecosystems in a degraded stream altered these ecosystem functions in a way that reflected those of more pristine streams.

The efficiency of resource processing provides a sound basis for ecological restoration, particularly in freshwater ecosystems where the implications of 'channelling' of resources into fewer pathways have been observed with the occurrence of algal blooms (Brookes *et al.* In press). The efficiency of resource processing will reflect not only the physical and biological diversity, but also the complex interactions between physical, chemical and biological components that provide the integrity of the system. The multiple pathways concept provides a framework for management strategies, which should aim to restore pathways of resource processing, thereby restoring the resilience, resistance and stability of ecosystems. It is evident that successful rehabilitation requires numerous strategies, co-ordinated at the scale of the catchment to ensure that resources are shared between multiple pathways (Brookes *et al.* In press).

Our understanding of differences in resource processing in pristine and impacted ecosystems is limited and so predictions of the benefits of restoring pathways are not possible. An understanding will assist the rehabilitation and preservation of ecosystems, which will allow ecosystems to provide the many services that are essential for the existence of humans (Costanza *et al.* 1997). This will improve the aesthetic and recreational values of these ecosystems and have benefits for freshwater biota. One of the most important services that freshwater ecosystems provide is water treatment, which will only be provided if there is efficient resource processing. The importance of this service will be amplified as demand for water resources increases and freshwater ecosystems continue to be degraded.

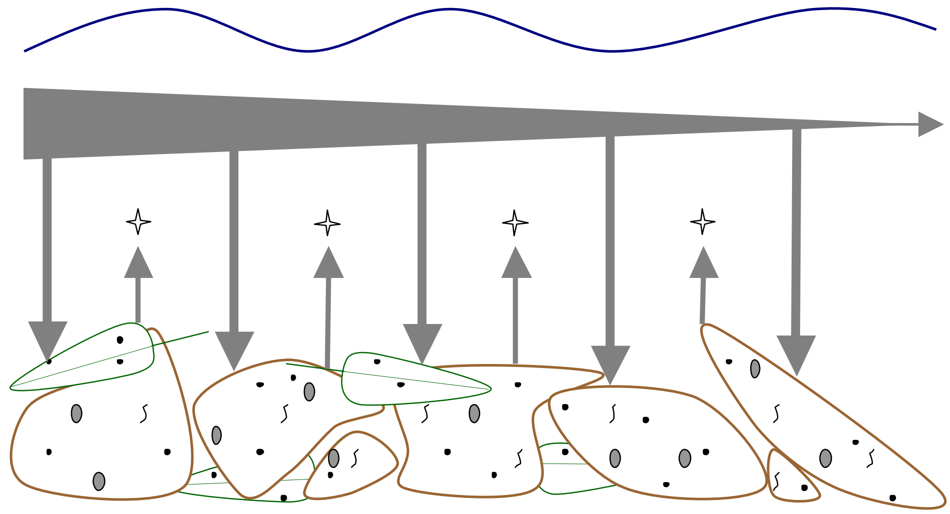


Figure 8.1. Conceptual diagram of resource processing in pristine streams. Arrows represent the transfer of resources, between rocks (brown shapes), leaves (green shapes), diatoms (grey ovals), filamentous algae (black lines), bacteria and fungi (black dots) and higher trophic levels (stars). The diversity of interception pathways, represented by the different functional groups, results in efficient resource interception. Higher trophic levels maintain low abundances and low metabolic rates of microbial organisms and resources are passed up the food chain, representing efficient resource processing.

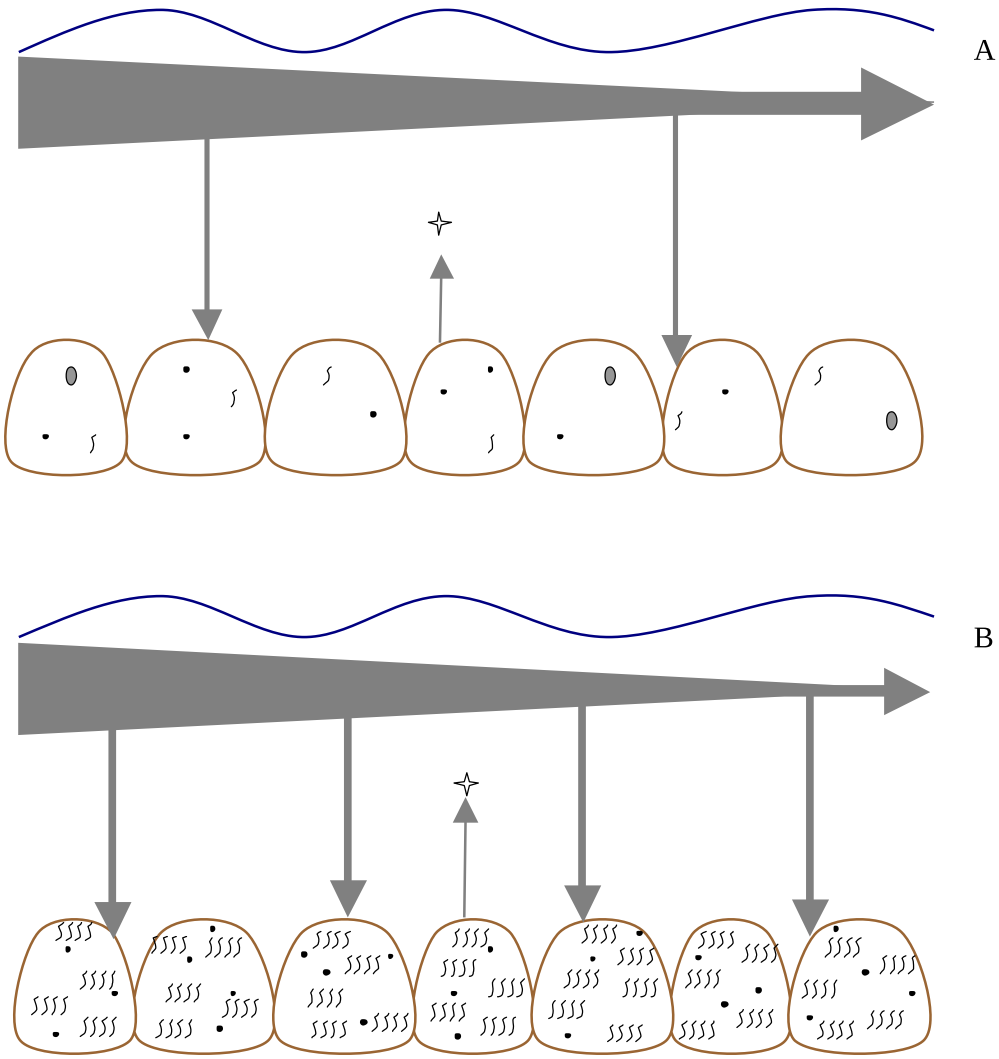


Figure 8.2. Conceptual diagram of two phases of resource processing in degraded streams. Arrows represent the transfer of resources, between rocks (brown shapes), diatoms (grey ovals), filamentous algae (black lines), bacteria and fungi (black dots) and higher trophic levels (stars). In A, there is low microbial biomass and metabolic rates and few pathways for resource interception. In addition, few resources are passed on to higher organisms, with a majority passing downstream, representing inefficient resource processing. In B, there is a dominance of filamentous algae, which results in high metabolic rates and restricts other pathways of resource interception. Although more resources are intercepted than in A, few of these are passed on to higher organisms, representing inefficient resource processing.

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