Composition and bioavailability of DOC across a rural-urban gradient

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Declaration

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

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Todd A. Wallace

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Summary

A great deal of attention has been focused on the effects of changes in land use on the physical and chemical conditions of streams and riparian zones. There is also currently substantial momentum and effort directed at restoring these areas. However, there is a distinct lack of understanding of not only the processes that occur in natural systems, but also the impact that changes in land use have actually had on those systems, and of how the "restored" system will function post intervention. The objective of this thesis was to examine the impact of urbanisation on the composition, and bioavailability and retention of organic carbon in streams.

Changes in composition, and bioavailability of organic carbon in stream water were investigated across rural-urban gradients in sub-catchments of the Torrens River, a mediterranean catchment in southern Australia. The influence of land use on the relative proportion of particulate and dissolved organic carbon, and the importance of different size fractions of the total organic carbon pool in driving biochemical oxygen demand (B.O.D.$_5$) was assessed under base flow and storm flow conditions. Despite an expectation that an increased proportion of oxygen demanding material would be comprised of particulate material in the urbanised catchments, the results demonstrate that dissolved organic carbon comprises a substantial component of the organic carbon pool in both the rural (83%) and urban (89%) sites. Furthermore, although particulate material actually represents a higher proportion of oxygen demanding material in the rural sites (23%) than in the urban sites (4%), the difference is not statistically significant.

Bioassays performed on stream water samples demonstrated that DOC from the urbanised streams was more bioavailable than in the rural streams; the DOC in the urban streams exerted an oxygen demand per unit organic carbon 2.75 times higher than the rural streams. Furthermore, the DOC in samples from the urban streams was depleted in an exponential manner. In contrast, DOC was depleted in a slow, linear manner in samples from the rural streams. Ion-exchange fractionation of the samples revealed significant differences in urban and rural stream water DOC that demonstrates that urbanisation induces a substantial shift away from the naturally occurring range of DOC compounds (e.g. humic and fulvic acids, carbohydrates, oligosaccharides, polysaccharides) towards synthetic compounds (e.g. synthetic detergents, hydrocarbons, pesticides) which is correlated with an increase in BOD:DOC ratios. However, an assessment of the impact of inflowing stormwater on

DOC dynamics and water quality in Torrens Lake (a shallow urban weir pool) demonstrated that the DOC fractions most readily depleted and therefore most likely to be the most problematic, oxygen demanding organic compounds were the aquatic humic substances (e.g. humic and fulvic acids), and hydrophilic acids (e.g. fatty acids, sugar acids, hydroxyl acids).

The shift from native tree species to introduced deciduous species that commonly occurs in urbanised areas may have a series of profound effects on ecosystem function and stability. Bioassays and ion-exchange fractionation revealed that DOC released from the introduced species (English elm, London plane tree, white poplar and introduced grasses) has a distinctly different composition than that leached from a common native species (river red gum). Observed imbalances in DOC:FRP ratios and DOC metabolism kinetics between the different species indicates that changes in dominant vegetation may have serious implications on biogeochemical cycles. Furthermore, the rapid release of DOC from all litter types tested indicates that if gross pollutant traps (designed and installed to protect streams from pollutants such as leaf litter) are not cleared for 48-72 hours after the onset of rain, the majority of water soluble, oxygen demanding material will still enter the receiving water.

Sediment core studies revealed that although undisturbed and resuspended sediments generate a substantial oxygen debt (0.8 and 1.4 g O_2 m^{-2} day^{-1} respectively), external loading of oxygen demanding organic material is responsible for the episodic deoxygenation of the water column that is often observed in Torrens Lake following rain events. Furthermore, although internal loading of filterable reactive phosphorus (FRP) from sediments (17mg FRP m^{-2} day^{-1}) represents a major source of bioavailable P that is potentially available to support algal blooms, external loading from inflowing stormwater (40μg FRP L^{-1}) continues to represent a major management concern and impediment to controlling the episodic nuisance and harmful algal blooms experienced in the Torrens Lake.

Urbanisation induced changes to the ability of a stream to retain DOC was assessed in three contrasting stream reaches; a reach that has retained a complex geophysical channel structure, a reach that has been converted to an open concrete channel, and a reach that has been converted to an underground concrete channel. DOC uptake kinetics in the degraded reach were characterised by long retention times, increased dilution, and comparatively short uptake lengths (79.9 ±7.4m). In comparison, the heavily engineered concrete channel was characterised by high water velocities and long uptake lengths (273.9±43.8m). In contrast to the engineered reaches, the degraded reach maintained a relatively stable expected peak DOC concentration, uptake length and percent uptake, indicating that restoring stream complexity in urbanised streams by removal of concrete channels and reconstruction of natural meandering flow paths has a major role for improving the buffering capacity of urban streams.

Chapter 1: General Introduction

1.1 Introduction

Natural Organic Matter (NOM) is central in the ecology of surface and groundwater, and originates either from terrestrial sources within the catchments of creeks, rivers and lakes (allochthonous organic matter), or from organisms within the aquatic ecosystem (autochthonous organic matter). Phytoplankton, periphyton, bacteria, and macrophytes represent the major sources of autochthonous NOM. The primary sources of allochthonous NOM in forested catchments are large woody debris (LWD; logs, branches), course particulate material (CPOM; leaf litter, bark, twigs), fine particulate material (FPOM; generated from processing of LWD, CPOM and the flocculation of dissolved organic matter), and dissolved organic matter (DOM) (Robertson *et al.*, 1999; Ward, 1986). It is generally considered that a substantial component of the allochthonous DOM entering streams via multiple pathways, including overland, sub-surface and downstream flow is leached from terrestrial plant material (Baldwin, 1999; McKnight *et al.*, 2003). However, soils (Nelson *et al.*, 1996), and grazed grasslands (McTiernan *et al.*, 2001) are also a key source of DOM in some catchments.

Our understanding of the relative role of allochthonous and autochthonous NOM is complicated by the inherent variability within and between rivers, and it is unlikely that any single model of ecosystem processes will have universal application (Robertson *et al.*, 1999). Conceptual ecological models such as the river continuum concept (RCC) (Vannote *et al.*, 1980) suggest that metabolism in low order (1-3) streams is typically dependent on the input of allochthonous organic matter, predominantly in the form of leaf litter. This model emphasises downstream transport of DOC as a key process. The Serial Discontinuity Concept (Ward and Stanford, 1983) continues the theme of downstream transport, but considers the disruptive effect of barriers to flow (e.g. dams, weirs) on transport of NOM and the subsequent impact on trophic functional groups. The Flood Pulse Concept (Junk *et al.*, 1989) retains the concept that the majority of allochthonous carbon input is from leaf litter, but extends the RCC model by incorporating lateral exchange of NOM via flood plain-river channel interactions associated with variation in river water levels.

The RCC model suggests the relative importance of fine particulate and dissolved organic material from upstream, and inputs of autochthonous organic material, increases as stream size increases. It has been demonstrated that in low order streams, up to 99% of total energy inputs are from allochthonous NOM (Fisher and Likens, 1973). Cole and Caraco (2001) estimated that for a hypothetical catchment in north-eastern USA/Canada that has ratio of terrestrial to aquatic area of 200:1, a total catchment water load to the aquatic zone of 100 m year^{-1}, and a typical in-river dissolved organic carbon concentration of 10mgL^{-1}, the input of allochthonous material is 1000 g C m^{-2}. Cole and Caraco (2001) suggest that aquatic systems would have to be exceptionally productive for autochthonous inputs to exceed allochthonous inputs. Despite this, the Riverine Productivity Model presented by Thorp and Delong (1994) suggests that the majority of allochthonous material is refractory, and that rivers are dependent on autochthonous sources and direct (local) inputs of allochthonous NOM. The relative role of allochthonous and autochthonous inputs in lakes will be dependent on multiple factors including external nutrient load and internal productivity (Cole *et al.*, 2002). Irrespective of the exact role of allochthonous and autochthonous material and the influence of flow regimes, the transfer of NOM from the terrestrial to the aquatic component of catchments represents a major source of carbon, nitrogen and phosphorus to the aquatic zones or ecosystems (Aitkenhead-Peterson *et al.*, 2003), and the NOM inputs are recognised as having a fundamental influence on food webs (Findlay and Sinsabaugh, 2003), and the optical properties of water (Kirk, 1980).

The average concentration of NOM in surface waters worldwide has been estimated to be 10mgL^{-1}, of which approximately 50% is organic carbon (Gjessing *et al.*, 1998), and it is common for the terms organic matter and organic carbon to be regularly interchanged throughout the literature. The majority of total organic carbon (TOC) in aquatic ecosystems is composed of particulate organic carbon (POC) and dissolved organic carbon (DOC) (Findlay and Sinsabaugh, 1999; Wetzel, 2001). Globally, the ratio of DOC to POC is typically in the order of 10:1 (Wetzel, 2001) in aquatic ecosystems. In undeveloped catchments, DOC concentrations (in freshwater) are typically in the range of 1-5mgL^{-1} (Findlay and Sinsabaugh, 1999), and it has been estimated that the majority (up to 75%) of energy inputs to streams is in the form of DOM (Fisher and Likens, 1973; McDowell and Fisher., 1976; Meyer *et al.*, 1981; Volk *et al.*, 1997).

The relative partitioning of NOM in particulate and dissolved phases remains poorly understood (Guo *et al.*, 2003; Robertson *et al.*, 1999), and is complicated by factors such as the substantial release (up to 25% of organic carbon) of water soluble compounds from leaf litter within short time periods (hours-days) following immersion (Baldwin, 1999; Duncan, 1997; Francis and Sheldon, 2002; Glazebrook and Robertson, 1999). It is however recognised that factors such as seasonal litter fall patterns, proximity to the river channel, and flood return periods are likely to have a substantial impact on the relative importance of POC and DOC from leaf litter, as it has been demonstrated that factors such as the age of leaf litter can impact the bioavailability of DOC leached from leaf litter (Baldwin *et al.*, 2003).

The organic carbon component of NOM takes part in effectively all biogeochemical cycles, yet our knowledge of NOM composition is limited, partially due to the complexity of NOM, and partly due to a lack of coordinated research (Egeberg *et al.*, 1999). Despite the lack of detailed knowledge the following key factors are recognised; the DOM in aquatic systems is fundamentally comprised of peptidic material, N-acetylamino sugars, polyphenolic material, and polysaccharides (Christy *et al.*, 1999); DOM is predominantly metabolised (oxidised) by bacteria and fungi (Findlay and Sinsabaugh, 1999; Robertson *et al.*, 1999); the relative concentrations of bioavailable carbon, nitrogen and phosphorus have a substantial influence on instream biogeochemical cycles (Bernhardt and Likens, 2002; Wetzel, 2001); and, that DOM represents a major proportion of the total organic carbon budget in streams and rivers (Findlay and Sinsabaugh, 1999).

Although our knowledge of DOC composition (Afcharian *et al.*, 1997) and utilisation by heterotrophs is poor (Arvola and Tulonena, 1998), the rate and extent of oxidisation is generally considered to be a reflection of the quality of the organic matter present (Westrich and Berner, 1984). Servais *et al.* (1989) define biodegradable DOC as the proportion of the total DOC that is oxidised by bacteria within the time scale of days-months. In comparison, DOC that is degraded within 1-2 weeks is considered labile (Søndergaard and Middelboe, 1995), and may be oxidised very rapidly (e.g. hours-days). Estimates of the proportion of total DOC that is actually labile, range from less than 1 to greater than 50% (Meyer, 1994), with a cross-system average estimated at 19% (Søndergaard and Middelboe, 1995).

Catchments can be classified into four primary zones; terrestrial, low order streams, rivers, and the terminal water-body (Brookes *et al.*, 2005). The terminal water body may be an aquifer, wetland, lake, coastal lagoon, estuary or the ocean (Walsh *et al.*, 2004). Within each of the four primary zones of any given catchment, a variety of physical and biogeochemical processes occur which have the potential to either increase or reduce the load of NOM flowing towards the receiving water. The inherent complexity present in natural ecosystems imparts resilience to major disturbances and therefore provides ecosystem integrity (Walker, 1995). Development of catchments often leads to large-scale landscape changes across each of these zones, and ecosystems often experience a shift in their composition.

The replacement of native tree species such as eucalypts (e.g. the river red gum, *Eucalyptus camaldulensis*), which have a peak litter fall period in summer (Attiwell *et al.*, 1978; Pressland, 1982), with introduced deciduous species (e.g. English elm (*Ulmus procera*), London plane (*Platanus acerifolia*), white poplar (*Populus alba*)) that have peak litter fall periods in autumn (Schulze and Walker, 1997), may have a series of profound effects on the timing of resource delivery, ecosystem function and stability. Furthermore, the removal of riparian vegetation, drainage of wetlands, and grazing pressures has altered the geomorphology of streams (Brierley *et al.*, 1999).

The ability of streams and rivers to retain nutrients as they are conveyed from one zone to another is a result of a complex range of physical and biogeochemical processes (Benoit, 1971). Changes to stream geomorphology may alter the residence time of water in streams (Robertson *et al.*, 1999). The potential for resources to interact with pathways capable of intercepting and retaining that resource (Butterini and Sabater, 1998; D'Angelo and Webster, 1991; Hall *et al.*, 2002; Triska *et al.*, 1989) may therefore be greatly reduced. Brookes *et al.* (2005) suggest that the development of catchments results in a reduced number of pathways for the interception and processing of resources flowing "downstream", and that this may result in resources overloading the receiving water. The concept that the size and frequency of landscape patches regulates the functional capacity of a landscape to intercept resources (water and nutrients) has been widely applied to pastoral lands and terrestrial landscape rehabilitation projects (Tongway and Hindley, 2004).

The most problematic case of catchment development is urbanisation. Landscape changes associated with catchment urbanisation typically include a reduction in vegetation density, the proliferation of impervious surfaces, and modification to streams (and rivers) to allow for flood protection. The proliferation of impervious surfaces reduces the surface area available for infiltration of rainfall into the soil, and the removal of topsoil during development reduces the infiltration capacity for the remaining surface area (Walsh *et al.*, 2004). The direct connection (via constructed stormwater infrastructure) that often occurs between impervious surfaces and receiving waters (Walsh, 2002) in urbanised catchments shifts the dominant flow path for rain falling in the catchment into streams, from subsurface and groundwater flow to overland flow (Walsh *et al.*, 2004), dramatically increases the velocity of surface run-off (Paul and Meyer, 2001), and applies significant hydraulic pressure on receiving water bodies (Hatt *et al.*, 2004).

In intact or relatively undisturbed ecosystems, the episodic input of allochthonous NOM is regarded as a fundamental ecological process, and the NOM inputs are considered to be an essential resource (e.g. Junk *et al.*, 1989; Vannote *et al.*, 1980). However, in highly disturbed systems such as urbanised catchments, episodic inputs of allochthonous NOM may function as critical pollutants (Lawrence and Breen, 1998) rather than essential resources. For example, the input of a large pool of readily bioavailable NOM may stimulate heterotrophic metabolism and generate a substantial oxygen debt and anoxic conditions. Oxygen-demanding organic material is considered one of the most significant pollutants in terms of ecological impacts contained in stormwater (Lawrence and Breen, 1998).

The rapid and marked decline in water quality following rain events has a substantial negative impact on the environmental and social amenity value of urban waterways. Ecological impacts of water column de-oxygenation include highly visible impacts such as fish kills (Erskine *et al.*, 2005), reduced growth rates, and less visible impacts such as disruption of endocrine systems (Wu *et al.*, 2003), embryonic development in fish (Shang and Wu, 2004), and degradation of aquatic macroinvertebrate communities (Feminella *et al.*, 2003; Walsh, 2002; Walsh *et al.*, 2001). Anoxic conditions may also impact the quality of water within the river/lake system via the release of sediment bound pollutants such as manganese, iron (Davison, 1993), phosphorus (Laws, 1993; Martinova, 1993; Mortimer, 1941) and ammonium (Boulton and Brock, 1999; Lawrence and Breen, 1998; Morin and Morse, 1999) potentially increasing the concentration of nutrients available to support nuisance and harmful algal blooms.

In catchments where water is harvested for potable supply, alterations to the composition and bioavailability of allochthonous DOC entering aquatic ecosystems may be highly problematic. DOC can function as the principal factor influencing treatment cost (Hine and Bursill, 1987). NOM fouls membrane filters used in potable water treatment (Cho *et al.*, 1999), and some DOC fractions (e.g.

those with neutral charge) are resistant to traditional pre-treatment techniques (Chow *et al.*, 2004; Chow *et al.*, 2000). These fractions react with chlorine during the disinfection phase, to generate potentially toxic or carcinogenic by-products, and contribute to bacterial regrowth in distribution systems (Prevost *et al.*, 1998; Simpson and Hayes, 1998). Furthermore, DOC complexes with metals (e.g. lead and zinc) and hydrophobic compounds such as hydrocarbons, herbicides and pesticides, and the transport of DOC and toxic pollutants from surface runoff into ground water via infiltration systems is of substantial environmental concern (Ellis and Hvitved-Jacobsen, 1996), particularly given the current and projected use of aquifer storage and recovery systems. Consequently there is strong interest from throughout the water science and technology community in the characterisation of DOC to further define our understanding on the composition and reactivity of DOC (Chow *et al.*, 2004; Weishaar *et al.*, 2003)

1.2 The Project

The literature reveals that organic carbon is a fundamental component of aquatic ecosystems. However, the lack of available information on relationships between land use and organic carbon indicates a substantial knowledge gap, particularly where urban sprawl encroaches into rural areas. This knowledge gap appears particularly evident in landscapes with mediterranean climates, where weather patterns are characterised by wet winters and hot dry summers that are often punctuated by sudden and intense rainstorms. The proliferation of impervious surfaces in urbanised landscapes leads to an increase in the volume of runoff generated by rain events. This has led to the widespread implementation of engineering solutions such as the modification of creeks to improve their capacity to rapidly convey large volumes of water to minimise the risk of flooding in urban areas. This process has typically involved the re-alignment and armouring of the beds and banks of creeks.

It is intuitive that the increased magnitude of human activities and density of pollutant sources (e.g. vehicle traffic, houses, commercial and industrial areas) in urbanised areas will lead to a substantial shift in the sources and types of organic carbon present between rural and urban catchments. For example, it is an unfortunate by-product of urbanisation that open spaces such as gardens, parklands, sports fields and streetscapes are often planted with exotic plant species that are functionally different to the indigenous vegetation of the area. In the Adelaide region, native trees are typically evergreen and shed leaves during summer and early autumn. In stark contrast, the exotic tree species that are widely planted in the Adelaide region are deciduous, exhibiting an autumn senescence, shedding their leaves as winter approaches. Furthermore, the concentration of compounds derived from incompletely combusted petroleum products is likely to be higher in urban than rural environments. Consequently, it is considered highly probable that the composition and bioavailability of organic carbon in a rural catchment would be substantially different to that in a rural catchment.

The Adelaide region in South Australia is an ideal place to test some of these assumptions about the composition and bioavailability of organic carbon between rural and urban environments. Adelaide has a population of approximately one million, and the catchment that encompasses the city (the Torrens Catchment) has a strong rural-urban gradient evident in five major sub-catchments. Each of the creeks in these sub-catchments has been subjected to varying levels of modification. The Torrens River itself passes through the centre of Adelaide and has been dammed near the central business district. The weir pool created (The Torrens Lake) has become a central feature and recreational area of the city, but is subject to numerous water quality problems. There is an ongoing debate as to whether these problems are a function of internal loading or whether they are generated from external loading by material carried into the lake via the creeks and constructed stormwater infrastructure that drain both rural and urban areas.

In recognition of the importance of carbon in aquatic systems, the focus of this project has been on organic carbon. The initial aim of the project was to test the hypothesis that there would be an increased proportion of oxygen demand driven by particulate organic material in urban than rural streams due to shifts in carbon sources and the degree of terrestrial and in-stream processing that occurs during transport from one environment to another. This also entailed an investigation to determine whether dissolved or particulate organic carbon was the dominant form of carbon in each land use type. These baseline data formed the basis for the next phase of the project, which was to identify the bioavailability of the organic carbon and to characterise its chemical composition via ion-exchange fractionation. This section tested the hypothesis that the organic carbon derived from the rural catchments would be of a different composition, and be less bioavailable than that in the urban streams.

Linking the information obtained on organic carbon in the tributary creeks to observed water quality problems in the Torrens Lake formed the next stage of the project. This section tested the hypothesis that the environmental problems evident in the lake are related to the concentration, composition and bioavailability of the organic carbon that is discharged into the lake. As the tributary streams are ephemeral, it was anticipated that summer rain events would mobilise large volumes of inorganic and organic material from the terrestrial component of the catchment, and transport that material into the lake. It was proposed that the organic material would act as a substrate for microbial activity and lead to acute water quality problems (e.g. anoxia). With the knowledge that the vegetation around the lake and in the vicinity of the Torrens River is dominated by exotic vegetation, a comparative study of the composition and bioavailability of carbon derived from native and exotic vegetation was undertaken to investigate their relative role in the water quality problems observed in the Lake.

Although it is well recognised that nutrients such as phosphorus are released from sediments under anoxic conditions (Martinova, 1993), the relative importance of internal and external phosphorus loads on the episodic algal blooms observed in the Torrens Lake has been an ongoing subject of debate. To inform this debate, an assessment of the relative role of external and internal loading formed the next stage of the project. The final stage of the project tested the hypothesis that initially stimulated this project: What evidence could be established to support the hypothesis that streams that had been highly modified would have a substantially reduced capacity to retain, store or transform potential pollutants than intact, or lightly modified streams? The following sections provide more detail on each respective chapter.

1.2.1 The relationship between particle size and biochemical oxygen demand

It is widely reported that a large proportion of the oxygen demanding material contained in urban stormwater is comprised of particulate material (Lawrence and Phillips, 2003; Mann and Hammerschmid, 1989; Sartor *et al.*, 1974). Furthermore, urban stormwater management guidelines often identify effective treatment of total suspended solids (TSS) as a minimum requirement for stormwater pollution control; yet it remains unclear what the relationship between particulate material and biochemical oxygen demand (BOD) actually is, as there is a distinct lack of published urban stormwater studies that report BOD across a range of size classes which includes dissolved (<0.45μm) material.

Preliminary research performed in the Torrens Catchment (Wallace *et al.*, 2002) demonstrated that in stream water samples, 85% of the organic carbon contained in particles less than 150μm in size is contained in the dissolved (DOC: <0.45μm) fraction (DOC = 0.174 + 0.853TOC; r^2 = 0.95, n = 32, P < 0.001). Because the onset of anoxic conditions following rain events is a major management concern in this catchment, accurately determining the relationship between organic material size classes and BOD is of great interest. This project investigates the relative importance of different size fractions of the organic carbon pool in driving biochemical oxygen demand across the rural-urban gradient of the Torrens Catchment (Chapter 3) by testing the hypothesis that there would be an increased proportion of BOD driven by particulate organic material in the urbanised catchments.

1.2.2 Impact of urbanisation on organic carbon composition and bioavailability

The chemical composition of the organic matter transported from the terrestrial component to the receiving water is dependent on the topography, vegetation and land use of the individual catchment. Changes in land use (forest-agriculture-urbanisation-industry) can change the nature, timing, and delivery of the organic matter inputs. Factors such as the replacement of native vegetation with introduced plant species, and the increased input of polycyclic aromatic hydrocarbons generated from incomplete combustion of petroleum fuels (Evans *et al.*, 1990), can be expected to have a major impact on the composition and bioavailability of organic carbon transported to receiving waters.

Changes in the composition and bioavailability of organic carbon may also be compounded by how well the terrestrial component is connected to the receiving water. For example, in rural or low-density urban catchments that have low percentages of impervious areas, differences in topography mean that some areas are less likely to drain into the creeks etc., and are therefore less likely to contribute organic carbon directly to the creek/river system (Robertson *et al.*, 1999). In contrast, the direct connection (via constructed stormwater infrastructure) that often occurs between impervious surfaces and receiving waters (Walsh, 2002) in urbanised catchments rapidly transports stormwater away from the localised catchment and into receiving waters (Wong *et al.*, 1999) such that the vast majority of the catchment is artificially drained into creeks and rivers (Robertson *et al.*, 1999).The increased level of connectivity between rural and urban catchments (Walsh, 2002) reduces the potential for interception and processing of resources via multiple-interception pathways (Brookes *et al.*, 2005) that would normally occur during transfer of water from the terrestrial component of the catchment into the receiving water.

Although a limited number of urban stormwater studies have demonstrated significant differences in the relative proportion of specific groups of organic compounds from rural and developed catchments (e.g. Fam *et al.*, 1987), and numerous studies have investigated the bioavailability of NOM in potable water supplies, measurements of the bioavailability of organic content in urban runoff are scarce, and there is a distinct lack of studies that have assessed the bulk composition and bioavailability of NOM across rural-urban gradients.

Recognising that the bioavailability of NOM may be affected by toxic compounds (e.g. zinc, copper) in runoff from road surfaces (Zhao *et al.*, 1999), it is considered highly likely that there will be fundamental changes in DOC composition and subsequent bioavailability associated with changes in land use due to the introduction of compounds that simply are not present, or are only present at trace levels (Walsh *et al.*, 2004) in rural catchments. The project tested the hypothesis that there would be distinct differences in the concentration, composition, BOD and degradation of DOC across the rural-urban gradient of multiple sub-catchments (Chapter 4). Measurements of the concentration, composition and bioavailability of DOC were also combined with measurements of biochemical oxygen demand and in-situ dissolved oxygen concentrations to quantify the impact of a rain event inflow on the composition and processing of the DOC pool, and water quality in the Torrens Lake, an urban weir pool on the main river channel (Chapter 5).

1.2.3 Effect of replacing native vegetation with introduced species on NOM processes

The impacts of replacing native vegetation with introduced species may be wide ranging. For example, it is considered that leaves from deciduous species such as the weeping willow (*Salix baylonica*), chestnut (*Castanea* sp.), oak (*Quercus* sp.) and alder (*Alnus* sp.) decay more rapidly than evergreen species such as eucalypts (e.g. *Eucalyptus camaldulensis*) (Barlocher and Graca, 2002; Canhoto and Graca, 1996; Janssen and Walker, 1999). Furthermore, the replacement of native tree species such as eucalypts with introduced deciduous species can shift peak litter fall period from summer (Attiwell *et al.*, 1978; Pressland, 1982) to autumn (Schulze and Walker, 1997). This change in timing may have a series of profound effects on ecosystem function and stability (e.g. impacts on invertebrate shredder communities). The influence of differences in the composition and subsequent bioavailability of NOM leached from native and introduced species is not well understood. However, McArthur and Richardson (2002) demonstrated substantial differences in leaching rates, DOC composition (e.g. molecular weight and polyphenolic content) and bioavailability for deciduous and coniferous trees in forests in British Columbia.

This project tested the hypothesis that leaf litter from introduced species would leach nutrients at a faster rate than a representative native species, and that the DOC released from the introduced species would have a distinctly different composition due to differences in structural content (e.g. lower humic acid and lignin content), and would subsequently be more bioavailable than that leached from the native species (Chapter 6).

1.2.4 Internal and external loading of critical pollutants

Oxygen demanding organic material and phosphorus have been identified as critical pollutants in stormwater (Lawrence and Breen, 1998). Consequently, identification of the relative role of internal and external loading of these pollutants is critical to effective management of water bodies. Despite internal oxygen demand from sediments having been shown to be a dominant oxygen demanding process in several rivers (Kelly, 1997; Matlock *et al.*, 2003), sediment oxygen demand (SOD) is generally overlooked in water quality monitoring programs, while the BOD of inflowing water is routinely measured. Determining the relative role of oxygen demand from external loading (inflowing surface water) and internal sources is however essential to the effective management of constructed water bodies, particularly when considering the maximum sustainable load of oxygen demand from inflowing waters, and the potential effectiveness of management actions such as artificial mixing. Furthermore, targeting management actions on reductions in external loading of phosphorus may not deliver a reduction in the occurrence of algal blooms (Oliver and Ganf, 2000) if internal loading is high (Jensen and Anderson, 1992; Søndergaard *et al.*, 1993).

Despite deoxygenation of the water column and episodic toxic algal blooms being a regular management concern for the Torrens Lake, the relative role of external (stormwater inflows) and internal loading (from the lake sediments) on (a) in-lake oxygen demand and (b) peak phosphorus concentrations have not been rigorously investigated. The thesis tested the hypothesis that external loading of oxygen demanding organic material is responsible for the episodic deoxygenation of the water column following rain events (Chapter 7). This component of the thesis was also used to provide an assessment of the relative role of external and internal loading on water column phosphorus concentrations.

1.2.5 The impact of urbanisation on the ability of stream reaches to intercept organic carbon

In many urbanised catchments streams have been engineered to manage flooding with a subsequent simplification of in-stream structure and complexity. However, there is currently a substantial global interest in restoring riparian habitat and in-stream channel complexity in urbanised streams (e.g. Cutler, 1999; Frost, 2000; Kelly, 2001; Suren *et al.*, 2002; Wong *et al.*, 1999). Despite improvements in water quality being a stated aim of many urban stream restoration projects (e.g. Frost, 2000; Kelly, 2001), improvements in downstream water quality have been largely ignored, and there appears to be no published literature that provides a direct comparison of DOC uptake capacity between intact, degraded and engineered creeks.

This component of the project tested the hypothesis that an urban stream reach that has retained a complex geophysical channel structure has a higher capacity to buffer downstream ecosystems from DOC inputs than an urban stream reach that has been converted to a concrete channel. The hypothesis was tested by comparing the ability of a degraded reach, an open concrete channel reach, and an underground concrete channel reach in an urban stream to process a point source input of concentrated DOC at a range of discharges (Chapter 8).

1.3 Summary

Our knowledge of the impact of landscape changes on the composition of organic matter inputs, and of the effects of those changes on organic carbon dynamics and ecosystem function is limited. If these landscape changes alter the composition and timing of organic matter inputs, there may be a fundamental shift in ecological function and stability, because the biogeochemical cycles of organic carbon, nitrogen and phosphorus are intrinsically linked (Harris, 1999; Wetzel, 2001). Furthermore, despite being an essential resource, natural organic matter is problematic in the treatment and quality management of water for potable supply. It is also becoming increasingly recognised that organic compounds in urban runoff have detrimental effects on aquatic ecosystem health including toxicity, eutrophication and de-oxygenation, and that management measures must be implemented to protect aquatic ecosystems from those effects (Lloyd *et al.*, 2001). Reducing the pollutant loads transported to receiving waters in urban runoff is widely recognised as the next màjor issue requiring action to improve water quality in our urban and coastal waterways (Wong, 2000). Consequently there is strong interest from throughout the water science community (both ecological and technical) to further define our knowledge of the impacts of catchment development on the composition, transport and bioavailability of NOM.

The objective of this thesis was to investigate the impact of urbanisation on NOM composition, metabolism, and transport within the conceptual framework proposed by Brookes *et al.* (2005) "that degradative processes associated with changes in land use lead to a reduction in resource processing during transport between the terrestrial component of the catchment and the receiving water".
The specific aims of the project were to investigate (i) the impact of urbanisation on the relative role of particulate and dissolved organic matter in generating oxygen demand in stream waters; (ii) the impact of urbanisation on concentration, composition, bioavailability and oxygen demand of DOC in stream waters; (iii) the impact of urban stormwater inflows on the composition and processing of the DOC pool in a shallow weir pool; (iv) the influence of replacement of native vegetation with exotic species on DOC quality and quantity; (v) the relative role of internal and external loading of oxygen demanding organic material in deoxygenation of the water column in a shallow weir pool; and (vi) the impact of engineering for flood management on the ability of a stream reach to buffer downstream ecosystems from DOC inputs.

This project not only contributes to the general pool of knowledge on the impact of urbanisation on NOM transport and metabolism, but also represents the first in-depth study of its kind that is specific to this catchment. The distinct change in land use across multiple sub-catchments provides a unique opportunity to assess the impact of urbanisation on the composition and bioavailability of organic carbon.

Chapter 2. General Methods.

2.1 Catchment Description

The Torrens catchment is the largest catchment within the Adelaide region, and is located between latitudes 35°45' and 35°00'. Approximately 500,000 people live in (156,000 residences) the catchment, and the region has a mediterranean climate. Other locations considered to have similar, mediterranean climates are California (USA) Chile, South Africa, and Spain (Marti and Sabater, 1996). The Torrens catchment has a relatively consistent rainfall with the majority (approximately 70%) occurring throughout a 6-month period. In the upper catchment average annual rainfall is in the range 680-820 mm. In the lower catchment, average annual rainfall is more location specific, and ranges from 420-725mm. Rainfall is largely confined to the winter-spring period, and many of the streams in the catchment cease to flow over summer (Hassell, 1997; TCWMB, 2002).

The catchment is divided into three distinct regions (Figure 2.1), with topography and hydrology influencing the predominant land use in each region. The upper catchment (approximately 342 km^2) has been extensively cleared, with less than 12% of native vegetation remaining, much of which is confined to a narrow strip along the top of the Mount Lofty Ranges. Land use is predominantly rural (pasture 66%, native vegetation and conservation 19%, plantations 3.4%, horticulture 5.7%, residential and urban 0.6%). The catchment also functions as a watershed region, providing approximately 20% (35,700 ML) of Adelaide's water supply (TCWMB, 2002). The Kangaroo Creek reservoir effectively separates the watershed region from the urban-rural region. Water is released from Kangaroo Creek Reservoir and diverted to Hope Valley Reservoir via Gorge Weir (downstream of 6th Creek). A large number of the approximately 1200 farm dams in the catchment are on-stream, and impact stream flow patterns. Subsequently, the upper catchment typically contributes little flow to the river below Gorge Weir, and in summer flows in the lower catchment are generally only associated with rain events (Hassell, 1997; TCWMB, 2002).

Land use in the upper section of the urban-rural region (approximately 162 km^2) is predominantly rural. The tributaries streams (First to Fifth Creeks) arise in rural areas of the catchment, dissect the hills scarp and have narrow, steep sided V shape profiles. The demarcation between rural and urban land use is distinct, and is generated by the steep topography of the hills face zone. There are a number of conservation parks on the steep hills face zone of the catchment, including Cleland (994 ha; First Creek sub-catchment), Horsnell Gully (Third Creek sub-catchment), Morialta (536 ha; Fourth Creek sub-catchment), and Black Hill (701 ha; Fifth Creek sub-catchment). These parks combine to form a continuous band of vegetation across the Mount Lofty Ranges. The dominant vegetation in these parks is eucalyptus woodlands, including messmate stringybark *Eucalyptus obliqua,* long-leaved box *E. goniocalyx,* pink gum *E. fasciculosa,* river red gum *E. camaldulensis* and South Australian blue gum *E. leucoxylon* (TCWMB, 2002). The creeks emerge from the foothills of the hills face zone and flow across the eastern Adelaide Plains (Hassell, 1997; TCWMB, 2002).

The lower (urban) component of the urban-rural region (approximately 100 km^2) is located on the Adelaide Plains. In this zone, the terrain is gently sloping, and the catchment is heavily urbanised. The only major open spaces are Linear Park (the river corridor), and the Adelaide City Parklands (Hassell, 1997). Private land ownership typically extends to the mid line of the tributary creeks, with no riparian buffer zone or easement rights. The majority of the Adelaide Central Business District is located within this section of the lower catchment (TCWMB, 2002). The proliferation of impervious surfaces (roads, pavement, roofs etc) has dramatically increased run-off, with an estimated 18,900ML of stormwater generated in the urban catchment annually (TCWMB, 2002). This stormwater is directed into the tributary streams and the Torrens River via constructed stormwater infrastructure, and is recognised as being significant in terms of flood flows in the tributary creeks (Hassell, 1997). Extensive reaches of the tributary creeks have been engineered into concrete channels to manage flooding. In sections, the creek channels have been fully enclosed and diverted underground, and the flood capacity of many of the creeks does not meet accepted standards for developed urban areas (TCWMB, 2002).

In the Central Business District, a major weir constructed on the river in the 1880's forms Torrens Lake, a shallow weir pool with an estimated standing volume of 420 ML (bank full capacity ~ 478ML), a surface area of 0.16km^2, and a mean depth of 2.6m (Regel, 2003). Approximately 8% of the urban catchment enters the River below the City Weir. Consequently, the majority of stormwater from the catchment flows through the lake, causing the lake to function as a stormwater detention basin for the catchment. The lake suffers numerous water quality problems including anoxia and blooms of toxic cyanobacteria. The Torrens River discharges an estimated 40,000ML of water annually to Gulf St Vincent at Henley Beach via a 3.5km long artificial outlet cut through the sand dunes known as Breakout Creek. This acts as a major urban stormwater outlet, with associated environmental and aesthetic impacts on the beach and near-shore environment (TCWMB, 2002).

2.2 Locations of sampling sites

Samples for analysis of parameters such as biochemical oxygen demand (BOD), total suspended solids, (TSS) dissolved organic carbon (DOC) and ion-exchange fractionation of DOC were collected from seven sites above the rural-urban gradient (rural sites: 1st, 2nd, 3rd, 4th, 5th and 6th creek and from Torrens River) and 7 sites below the rural-urban gradient (urban sites 1st, 2nd, 3rd, 4th, 5th creeks, and from the inlet and outlet end of Torrens Lake (see Fig 2.1).

2.3 Sample Containers

Samples for analysis (e.g. BOD, TSS, DOC and DOC fractionation) were collected in PTFE containers. Prior to use, the PTFE containers were washed (24 hours in a 5% solution) with 7X detergent (ICN Biomedicals Australasia), rinsed with reverse osmosis (RO) water then acid washed (24 hours in 10% HCl), and rinsed with RO water. The PTFE containers were subsequently filled to capacity with deionised RO water and left to stand for 48 hours, rinsed and allowed to dry. This procedure was performed to minimise leaching of compounds from the containers into the samples.

2.4 Preparation of GF/C filters

The Whatman GF/C filters used to pre-filter the samples were individually washed with 3 x 100mL rinses of deionised RO water, and oven dried at 103°C. Preliminary laboratory trials demonstrated that the washing procedures for both the PTFE containers and the GF/C filters were sufficient to ensure that DOC contamination from the containers and filters was below detectable limits.

2.5 Five-day Biochemical Oxygen Demand

Five-day Biochemical Oxygen Demand (B.O.D.$_5$) was performed in accordance with APHA Standard Method 5210B (Eaton *et al.*, 1995). Samples were diluted sufficiently to ensure the maintenance of oxic conditions throughout the bioassay periods. On all occasions, blank controls were established to allow for correction for oxygen demand generated by the dilution water. The dilution water utilised was reverse osmosis purified water that had been filtered (0.45μm), aerated for 3 hours, and stabilised for 24 hours. The dilution water was seeded with 20mL L^{-1} of 37μm filtered Torrens Lake water to ensure a sufficient biomass of microorganisms to metabolise the biodegradable organic matter present in the samples. Control checks were performed utilising glucose-glutamic acid checks as defined in Eaton *et al.* (1995).

2.6 Dissolved Oxygen

Dissolved oxygen for measurements of biochemical oxygen were obtained using a WTW (Wissenschaftlich-Technische Werkstätten GMBH & Co. KG) CellOx 325 oxygen sensor attached to a WTW Oxi 330i dissolved oxygen meter. The unit was calibrated via titration checks in accordance with Standard Method 4500-O C (Eaton *et al.*, 1995).

2.7 Dissolved Organic Carbon

Filtered (0.45μm) samples for analysis of DOC were acidified to pH 2 with 1M perchloric acid and stored in the dark at <4°C until analysis. Prior to analysis, samples were allowed to equilibrate to standard room temperature (20°C) and adjusted to pH 2.8 with 0.5M and 0.1M sodium hydroxide (NaOH), and 0.1M perchloric acid. DOC concentrations were determined utilising an SGE ANATOC II total organic carbon analyser. DOC analysis was performed in non-purgeable organic carbon (NPOC) mode (to remove DIC from analysis per Buffam *et al.*, 2001; Tranvik, 1988) using titanium dioxide as a catalyst in the presence of near-UV light. Benzoic Acid was utilised as a DOC standard for calibration of the analyser. Three replicate measurements of DOC were made for each sample, with the DOC concentration determined as the average of the three measurements. Variation between replicate measurements was typically less than 2% RSD (residual standard deviation).

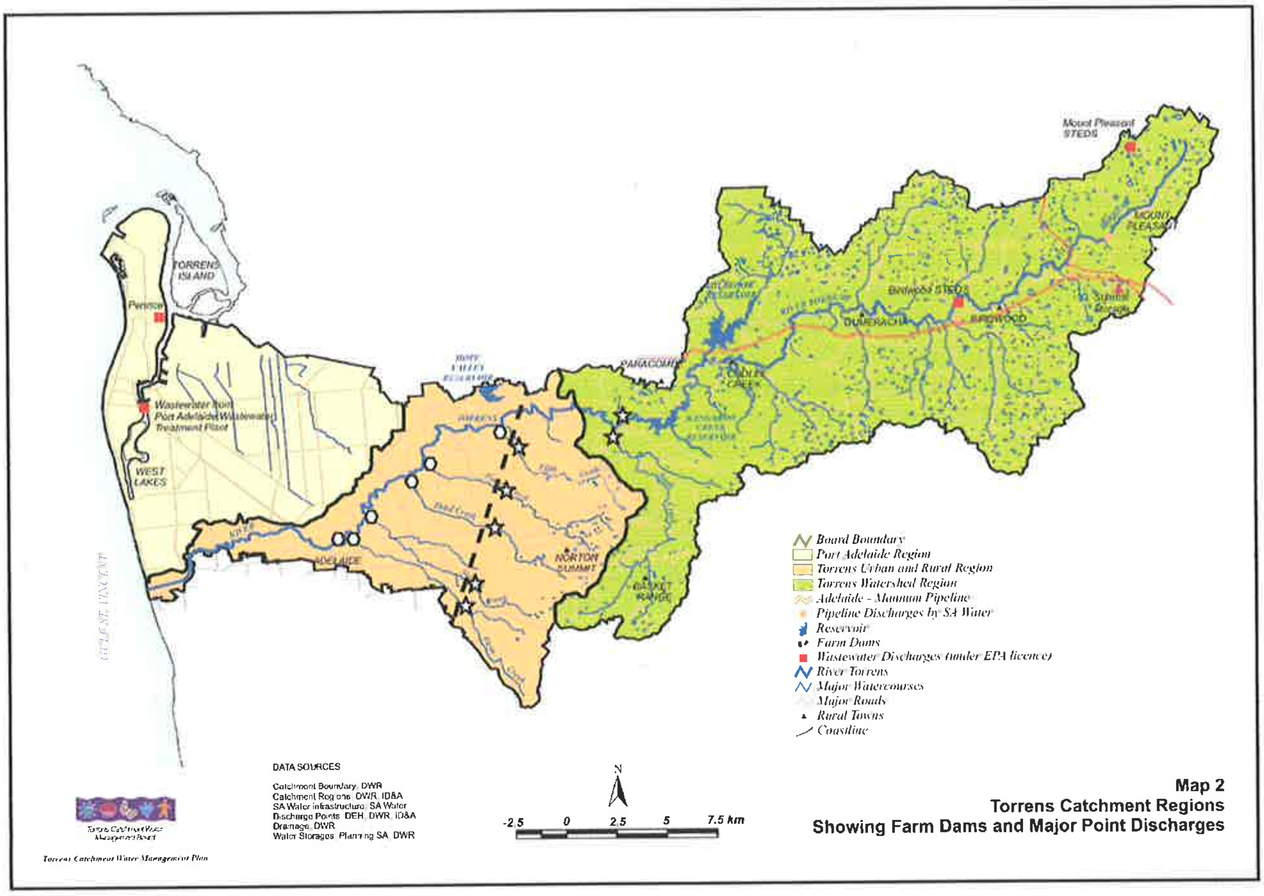

Figure 2.1. Map of Torrens Catchment showing upper (watershed region) and lower (urban-rural) region. Dotted line in urban-rural catchment denotes demarcation between urban and rural regions. White triangles designate location of rural (1st, 2nd, 3rd, 4th, 5th and 6th creek and Torrens River) sampling sites. White hexagons designate locations of urban (1st, 2nd, 3rd, 4th, 5th creeks, and from the inlet and outlet end of Torrens Lake) sampling sites (map reproduced courtesy of Torrens Catchment Water Management Board)

2.8 Time series assessment of BOD and DOC biodegradability

Time series assessments of BOD and DOC biodegradability were performed via a modification of the APHA standard method (5210B) for biochemical oxygen demand (Eaton *et al.*, 1995). A schematic of the protocol is provided in Figure 2.2. The process is described below. The measurements of dissolved oxygen and DOC on consecutive samples provide biochemical oxygen demand and DOC biodegradability (*b*DOC) curves respectively.

A) Upon return to the laboratory the samples were homogenised by inversion mixing, pre-filtered through (pre-washed) Whatman GF/C filters and subsequently filtered through Whatman PVDF 0.45μm membrane filters.

B) 155mL sub-samples of the filtered sample were transferred to eight (8) individual BOD bottles (Wheaton, USA) for analysis of dissolved oxygen and DOC at time steps of 0, 1, 2, 3, 4, 5, 7 and 10 days.

C) The bottles were filled to capacity (310mL) with dilution water (see below for description of dilution water), sealed and inverted to mix the water.

D) Eight blank controls (dilution water only) were established to allow for correction for oxygen demand generated by the dilution water at each time step.

E) Each BOD bottle was subsequently incubated for the respective time period (e.g. time step 0 = zero hours, 2 days = 48 hours etc.) at 20°C in the dark.

F) At the respective time, the sample was removed from the controlled temperature room, and dissolved oxygen concentration in the sample was measured in the bottle.

G) A 50mL aliquot of the water in the bottle was subsequently filtered (0.45μm), acidified to pH 2.8

H) The sample was analysed for DOC.

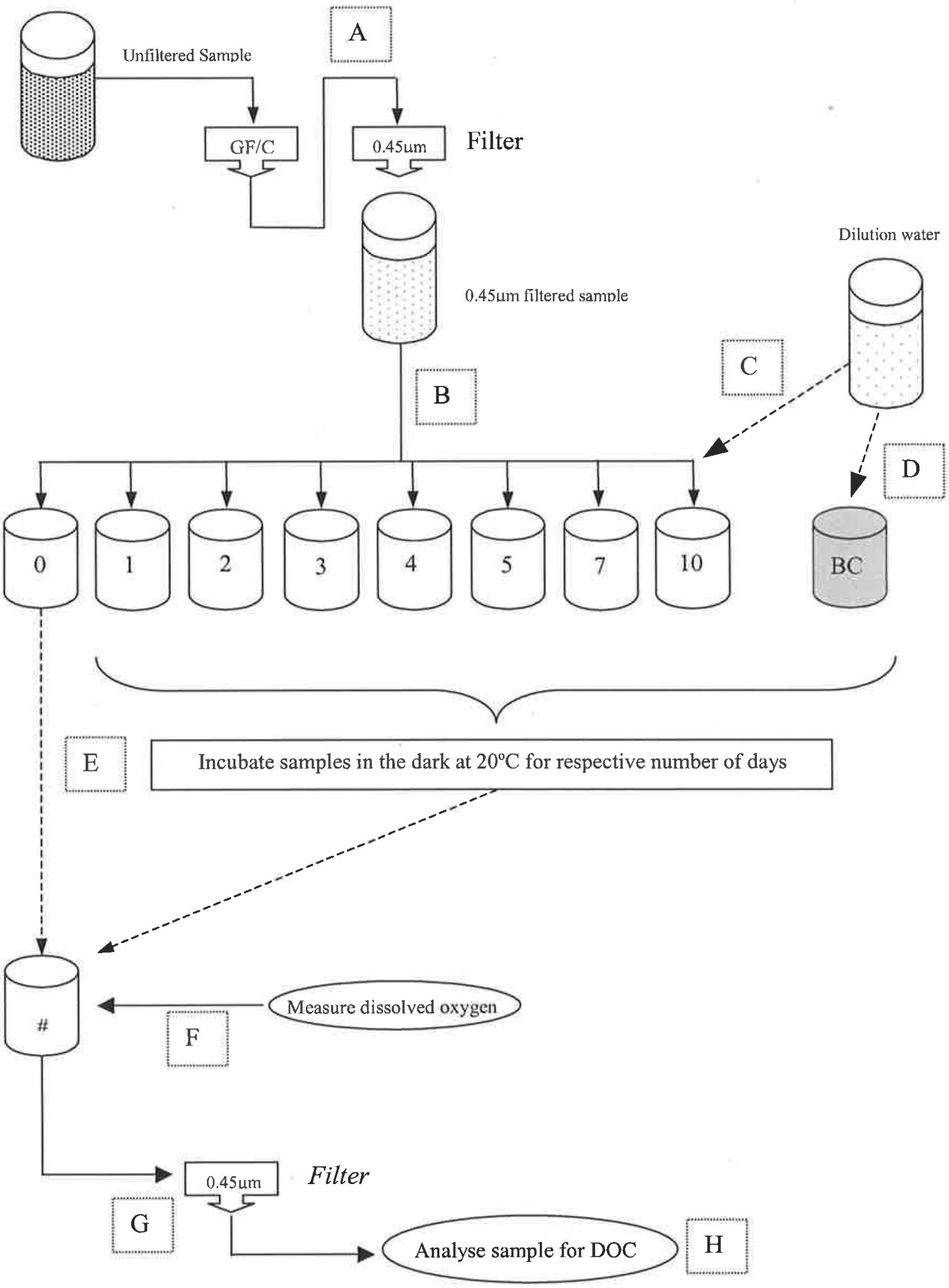

Figure 2.2. Schematic of protocol for analysis of biodegradability of DOC. Steps: [A] filter sample through GF/C and 0.45µm filter, [B] transfer 155mL of sample to 8 BOD bottles, [C] Fill bottles with dilution water and [D] establish 8 blank controls, [E] incubate samples for respective number of days, [F] measure dissolved oxygen in BOD bottle, [G] refilter a 50mL aliqout of the water from the bottle, [H] analyse for DOC.

2.9 Ion-exchange fractionation

The DOC present in the samples was characterised via ion exchange fractionation into five distinct macro-fractions (Table 2.1) utilising minor modifications to a technique described by Imai *et al.* (2001) which is based on the technique developed by Leenheer (1981). The samples were fractionated utilising three ion-exchange resins: Supelite™ DAX-8, Biorad AG®MP50, and Biorad AG®MP1. The relative composition of the five fractions generates a physicochemical signature for the water sample.

Table 2.1 Classification of organic solutes for dissolved organic matter [reproduced from Imai *et al*, 2001]

Fraction	Solute Compound Classes
Hydrophobic acids (AHS)	Aquatic humic substances (humic and fulvic acids)
Hydrophobic neutrals (HoN)	Hydrocarbons, pesticides, carbonyl compounds, linear alkylbenzene sulfonate
Hydrophilic Acids (HiA)	Sugar acids, fatty acids, hydroxyl acids
Bases (BaS)	Aromatic amines, protein, amino acids, aminosugars
Hydrophilic neutrals (HiN)	Carbohydrates: oligosaccharides, polysaccharides

2.9.1 Resin Cleaning Procedure

- *Supelite™ DAX-8*
  1. Immerse 50g of resin in 0.1M NaOH, stir and allow to stand overnight.
  2. Decant NaOH, and repeat process six times (decant fines at each step).
  3. Immerse resin in 300mL of methanol, stir for 24 hours.
  4. Decant methanol, and repeat process.
  5. Allow to stand for 24 hours then decant methanol.
  6. Rinse resin with 3L of hot (~60°C) deionised water to drive off methanol
  7. Rinse resin with six 250mL washes of 0.1M NaOH
  8. Rinse resin with eight 250mL washes of hot (~60°C) deionised water
  9. Rinse resin with eight 250mL washes of room temperature (~20°C) deionised water
  10. Analyse water from final rinse to ensure that DOC bleed from resin is $<1 mgL^{-1}$.

- Biorad AG®MP50

1. Immerse 50g of resin in deionised water, stir and allow to stand overnight. Decant water (decant fines at each step).
2. Immerse resin in 300mL of methanol, stir for 24 hours.
3. Decant methanol, and repeat process.
4. Allow to stand for 24 hours then decant methanol.
5. Rinse resin with 6L of room temperature (~20°C) deionised water
6. Rinse resin with 6L of hot (~60°C) deionised water to drive off methanol
7. Rinse resin with 6L of room temperature (~20°C) deionised water
8. Analyse water from final rinse to ensure that DOC bleed from resin is <0.5mgL^{-1}.
9. Rinse resin with 50mL 0.1M NaOH
10. Immerse resin in 500mL of 2N HCl, stir for 24 hours to hydrogen saturate resin.
11. Condition resin with 1L deionised water.

- *Biorad AG®MP1*

Follow steps 1-8 as for Biorad AG®MP50

9. Rinse resin with 50mL 0.1M NaOH.
10. Immerse resin in 500mL of 1M NaOH stir for 24 hours to convert resin to free base form.
11. Condition resin with 1L deionised water.

2.9.2 Loading Resin Columns

50mL glass burettes (acid washed) were used for the columns. A plug of glass wool was inserted above the tap of the burette to retain the resins, and a second glass wool plug was inserted on top of the resin bed to minimise disturbance to the bed during application of the samples. Minimum volumes of each resin required were determined using Equation 1.

$$\text{Volume} = V_o / \text{resin porosity} \qquad \textbf{Equation 2.1}$$

Where $V_o = [\text{sample volume} / (k' + 1)] / 2$

and the column capacity $k' = 50$

- *Supelite^{TM} DAX-8*

3.5mL (wet volume) of the pre-washed Supelite^{TM} DAX-8 resin was poured (as a slurry) into a glass burette. Immediately before applying the sample, the column was rinsed, alternating between 50mL of 0.1M NaOH and 50mL of 0.1M HCl three times, followed by 50mL of deionised water. The deionised water was retained as a blank sample (B_1).

- *Biorad AG®MP50 and Biorad AG®MP1*

6mL of the cation (AG®MP50) and 12mL of the anion (AG®MP1) exchange resins were poured (as a slurry) into individual glass burettes. The columns were conditioned by rinsing each column with approximately 500mL of deionised water. Blank samples were collected from each AG®MP50 and AG®MP1 column after conditioning (B_2 and B_3 respectively).

A schematic of the DOM fractionation protocol used is provided in Figure 2.3. The process is described below.

A) Upon return to the laboratory the samples were homogenised by inversion mixing, pre-filtered through (pre-washed) Whatman GF/C filters and subsequently filtered through Whatman PVDF 0.45μm membrane filters. A 250mL sample was then adjusted to pH 2 with 5M HCl.
B) A 50mL sub-sample was retained for DOC analysis (DOC_1 = AHS, HoN, HiA, BaS, HiN)
C) The remaining 200mL of sample was applied to the column containing the Supelite^{TM} DAX-8 non-ionic resin at a rate of 1-1.5mLmin^{-1}.
D) The AHS and HoN fractions are retained on the non-ionic resin.
E) Sample is collected and a 40mL sub-sample collected for DOC analysis (DOC_2 = HiA, BaS, HiN).
F) 50mL of 0.1M NaOH is applied to column containing the Supelite^{TM} DAX-8 non-ionic resin at a rate of 1-1.5mLmin^{-1} to elute AHS from the non-ionic resin.
G) Sample containing AHS is collected and analysed for DOC (DOC_3 = AHS)

H) The remaining sample is applied to the column containing the Biorad AG®MP50 cation exchange resin at a rate of 1-1.5mLmin^{-1}.

I) The BaS fraction is retained on the cation exchange resin

J) Sample is collected and a 40mL sub-sample collected for DOC analysis (DOC_4 = HiA and HiN).

K) The remaining sample is applied to the column containing the Biorad AG®MP1 anion exchange resin at a rate of 1-1.5mLmin^{-1}.

L) The HiA fraction is retained on the anion exchange resin

M) Sample is collected and a 40mL sub-sample collected for DOC analysis (DOC_5 = HiN).

The samples collected for DOC analysis at the various steps were adjusted to pH 2.8 with 0.1M NaOH and 0.1M perchloric acid for analysis. The concentration of DOC in each fraction was determined using Equation 2 (Imai *et al.*, 2001).

$$AHS = DOC_2 * (\text{eluted volume} / \text{sample volume}) \qquad \textbf{Equation 2.2}$$

$$HoN = DOC_1 - AHS - (DOC_3 - B_1)$$

$$BaS = (DOC_3 - B_1) - (DOC_4 - B_2)$$

$$HiA = (DOC4 - B_2) - (DOC_5 - B_3)$$

$$HiN = DOC_5 - B_3$$

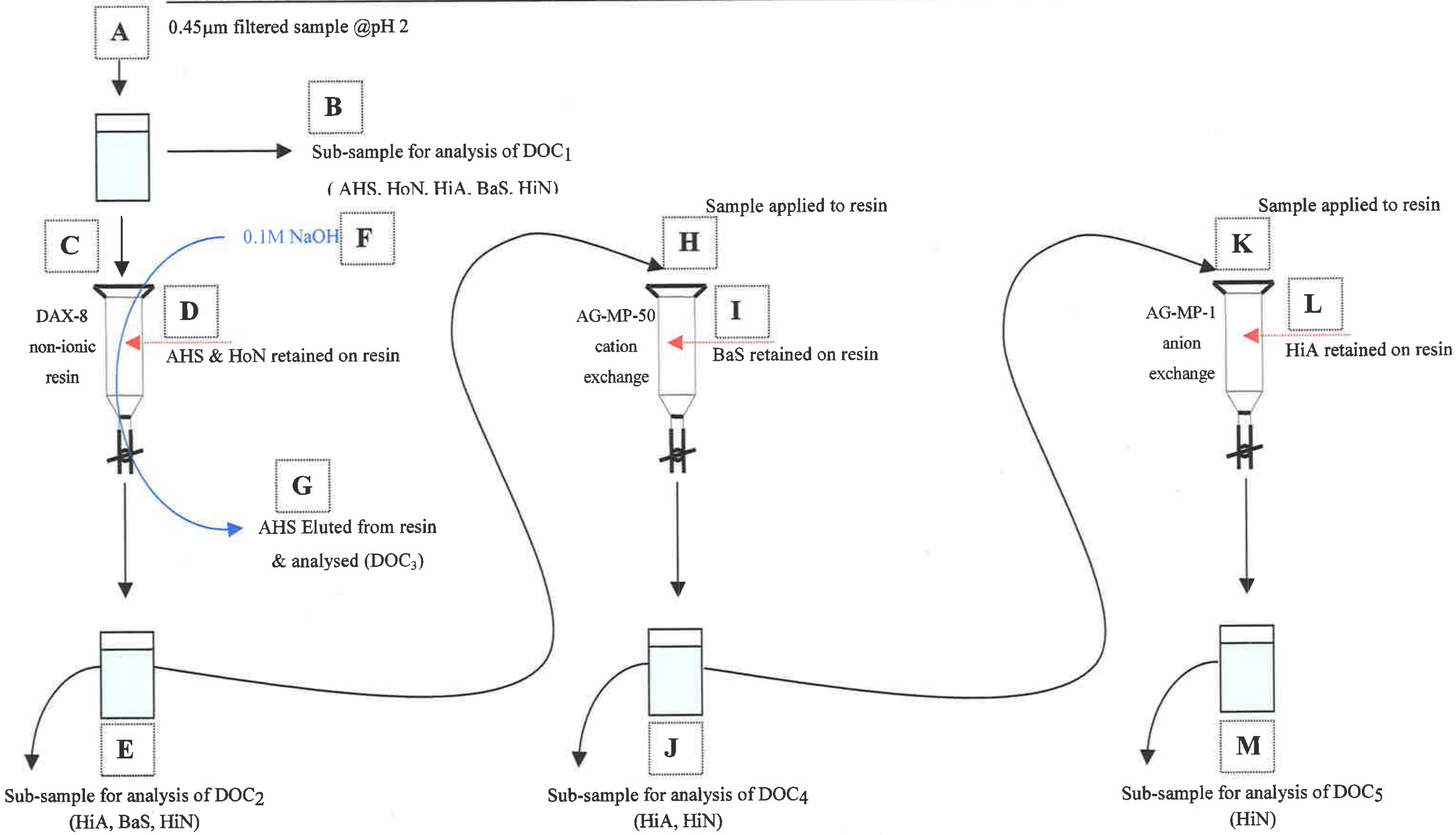

Figure 2.3. Schematic of protocol for ion-exchange fractionation of DOC. Steps: {A} filter sample and adjust to pH2, {B} analsyse for DOC_1, {C} apply sample to resin, {D} AHS & HoN retained on resin, {E} subsample for analysis of DOC_2, {F} elute AHS from resin, {G} sample for analysis of DOC_3, {H} apply sample to resin, {I} BaS retained on resin, {J} sample for analysis of DOC_4, {K} apply sample to resin, {L} HiA retained on resin, {M} sample for analysis of DOC_5

Chapter 3: Relative importance of particulate and dissolved organic carbon across the rural-urban gradient of the Torrens Catchment

3.1. Introduction

Organic matter inputs are considered an essential resource for biogeochemical cycles, and the majority of total organic carbon (TOC) in aquatic ecosystems is composed of particulate organic carbon (POC) and dissolved organic carbon (DOC) (Findlay and Sinsabaugh, 1999; Wetzel, 2001). Globally, the ratio of DOC to POC is typically in the order of 10:1 (Wetzel, 2001) in aquatic ecosystems. However, the relative partitioning of NOM in particulate and dissolved phases remains poorly understood (Guo *et al.*, 2003; Robertson *et al.*, 1999), is likely to vary spatially and temporally both within and between systems, and the influence of landscape changes associated with urbanisation on partitioning of the total organic pool in particulate and dissolved phases is unclear.

It has been estimated that dissolved organic matter constitutes the majority (up to 75%) of energy inputs to streams (Fisher and Likens, 1973; McDowell and Fisher., 1976; Meyer *et al.*, 1981; Volk *et al.*, 1997). Studies in Australian catchments have also demonstrated that a substantial proportion of organic material in urban stormwater is contained in the dissolved (Goonetilleke *et al.*, 2005) or fine particulate phase (Mann and Hammerschmid, 1989). However, it is widely reported (Lawrence and Phillips, 2003; Sartor *et al.*, 1974) that a large proportion of the oxygen demanding material contained in urban stormwater is comprised of particulate material.

Oxygen-demanding organic material is considered one of the most significant pollutants in terms of ecological impacts contained in stormwater (Lawrence and Breen, 1998). There is a strong focus on total suspended solids (TSS) in stormwater modelling, monitoring and treatment programs (Duncan, 1997; Lloyd *et al.*, 2001; McAlister *et al.*, 1995). The reason for its prominence is that it is well recognised that a significant proportion of inorganic and organic stormwater-borne pollutants are associated with particulate material (Ellis, 1979; Latimer *et al.*, 1990; Leeming and Maher, 1992; Rinella and McKenzie, 1982; Walker and Wong, 1999). Understanding the relative importance of dissolved and particulate material in driving biochemical oxygen demand within individual systems is critical in furthering our understanding of ecosystem function, and our ability to manage the system effectively. For example, management strategies (e.g. detention basins, infiltration basins) for reducing the biochemical oxygen demand in receiving waters need to be developed that are able to effectively intercept and treat the oxygen demanding organic material in the stormwater.

A preliminary project (Wallace *et al.*, 2002) performed in the Torrens Catchment, demonstrated that stormwater flowing from the urbanised sub-catchments to the main river channel contains a substantial biochemical oxygen demand (~60mgL^{-1}) and has been linked to complete water column deoxygenation of the Torrens Lake within 24 hours (Wallace *et al.*, 2002). If it can be demonstrated that treatment systems for managing suspended solids have the potential to reduce the biochemical oxygen demand in inflowing stormwater, there is an increased likelihood of funding being directed to structural management techniques capable of delivering multiple water quality benefits in the Torrens Catchment.

This component of the project tested the hypothesis that there would be an increased proportion of oxygen demand driven by particulate organic material in urban than rural streams. This also entailed an investigation to determine whether dissolved or particulate organic carbon was the dominant form of carbon in each land use type. Measurements of POC, DOC and biochemical oxygen demand were assessed across the rural-urban gradient of the Torrens Catchment in both dry weather (baseflow) and wet weather (stormflow) conditions. It is proposed that any differences in organic carbon size distribution and oxygen demand would be attributable to shifts in carbon sources and the degree of terrestrial and in-stream processing that occurs during transport from one environment to another.

3.2. Materials and methods

3.2.1 Catchment Description

A detailed description of the Torrens Catchment is provided in Chapter 2. Samples were collected from sites above and below the rural-urban demarcation. The rural sampling sites were located in areas at which the streams emerge from conservation parks. The samples from the urbanised reaches of the tributary streams sites were collected at sites located above the confluence (typically < 25 m) of the tributary streams with the Torrens River. Samples collected from the Torrens River upstream and downstream of the confluence of tributary streams were collected from sites at least 50 m up, and downstream of the confluence.

It is recognised that the location of the rural and urban sites on a downstream gradient potentially complicates the assessment of changes in land use (rural-urban) on organic carbon size distribution and oxygen demand, however, the aim of the research was to assess the impacts of urbanisation on these parameters within the tributary streams of the Torrens Catchment, and the nature of the Torrens Catchment is that the headwater-mid reach stream sections are dominated by rural land use, and the downstream reaches are heavily urbanised.

3.2.2 Relationship between TOC, POC and DOC

The relationship between TOC, POC and DOC throughout the lower catchment of the Torrens Catchment was examined by collecting samples during dry weather flows (DWF) and wet weather flows (WWF). A total of 67 samples (48 urban and 19 rural samples) were collected between 27 March 2002 and 11 November 2002 from 23 sites throughout the urban-rural zone (see Table 3.1). Samples were collected at gauging weirs or similar hard structures that confined flow, and allowed the samples to be collected from the central portion of the flow. Samples were collected using a 2L PTFE beaker fitted to a 2.5m sampling pole. Three (3) 1.5L grab samples were obtained at 5-minute intervals and were pooled together in a single 5L PTFE container to produce a 4.5L composite sample. The containers containing the composite samples were stored in the dark in an ice filled, insulated container prior to return to the laboratory. The 5L PTFE containers and 2L PTFE beakers used for sample collection had been pre-cleaned according to the protocol described in Chapter 2. Upon return to the laboratory the composite stream water samples were homogenised by inversion mixing immediately prior to sub-samples being collected for analysis of TSS, B.O.D_5, TOC, POC, and DOC.

Analysis of B.O.D_5 was performed according to APHA Standard Method 5210B (Eaton *et al.*, 1995). Organic carbon analysis was performed on an SGE ANATOC I (SGE, Melbourne, Australia). Total organic carbon concentration was measured on samples that had been passed through a 150μm nylon screen (this step was performed to exclude particles larger than the internal diameter of tubing associated with the carbon analyser). The second sub-sample was filtered through pre-washed Whatman GF/C filters and subsequently through Whatman PVDF 0.45μm membrane filters for analysis of organic carbon contained in the dissolved fraction (DOC) (see Chapter 2 for further details on $B.O.D_5$ and organic carbon analysis).

3.2.3 Relationship Between TSS and B.O.D.₅

The relationship between total suspended solids and biochemical oxygen demand throughout the lower catchment of the Torrens Catchment was examined in the 67 samples collected during dry weather flows (DWF) and wet weather flows (WWF) throughout 2002. A sub-sample of the composite stream water samples collected were analysed for TSS and $B.O.D._5$. TSS analysis was performed according to APHA Standard Method 2540D (Eaton *et al.*, 1995).

Table 3.1. Locations of sampling sites throughout the urban-rural zone of the Torrens Catchment (see Fig 2.1 for map of approximate locations).

River-Tributary	Rural Sampling Site	Urban Sampling Site
Torrens River	(1) Playford Bridge	N/A
Torrens River	(2-3) u/s and d/s of the confluence of 6th creek	N/A
Torrens River	(4-5) u/s and d/s of the confluence of 5th creek	N/A
Torrens River	N/A	(12-13) u/s and d/s of the confluence of 4th creek
Torrens River	N/A	(14-15) u/s and d/s of the confluence of 3rd creek
Torrens River	N/A	(16-17) u/s and d/s of the confluence of 2nd creek
Torrens River	N/A	(18) City Weir-Torrens Lake
6th Creek	(6) Castambul-Terminal end of Creek	N/A
5th Creek	(7) Blackhill Conservation Park	(19) Terminal end of Creek
4th Creek	(8) Morialta Conservation Park	(20) Terminal end of Creek
3rd Creek	(9) Horsnell Gully Conservation Park	(21) Terminal end of Creek
2nd Creek	(10) Michael Perry Botanic Reserve	(22) Terminal end of Creek
1st Creek	(11) Cleland Conservation Park	(23) Terminal end of Creek

3.2.4 Relationship between total B.O.D.$_5$ and filtered B.O.D.$_5$

A total of 87 samples were collected during wet weather flows during 2003 from sites 1,6, 8-11 (rural land use), and sites 19-23 (urban land use). Stream water samples were collected as 4.5 L composite samples (consisting of 3 x 1.5 litre grab samples obtained at 5 minute intervals). The samples were sub-sampled upon return to the laboratory. One sub-sample was retained for analysis of total (unfiltered) B.O.D.$_5$. The second sub-sample was filtered through pre-washed Whatman GF/C filters and subsequently through Whatman PVDF 0.45μm membrane filters for analysis of B.O.D.$_5$ contained in the dissolved fraction (f B.O.D.$_5$).

3.2.5 Particle size distribution of oxygen demanding substances

High-resolution analysis of particle size distribution and oxygen demand (B.O.D.$_5$) was performed on samples collected during wet weather flows from rural sites 6,8,10,11 on 5th June 2003, and urban sites 20-23 on 12 June 2003 (see Table 3.1 for site locations). Stream water samples were collected as 4.5 L composite samples (consisting of 3 x 1.5 litre grab samples obtained at 5 minute intervals). Samples were successively passed through a series of 5000, 150, 80, 37, 10, 5, 1, 0.45 and 0.22μm filters. 400mL of filtrate was collected for B.O.D.$_5$ analysis at each filter step. This provided a quantitative measure of the amount of oxygen demanding organic material contained in size fractions larger than those that could be analysed on the SGE organic carbon analyser.

3.2.6 Data Analysis

Regression curves displayed in graphs are fitted to means; error bars are ± 1 standard error (SE). All univariate statistical tests were performed using the package JMP In version 3.2.6 (SAS Institute Inc. 1996). Normality was tested using the Shapiro-Wilk W Test, and the equality of variances with the Levene test. For all statistical tests $\alpha = 0.05$.

3.3. Results

3.3.1 Relationship between TOC and DOC

There was a strong linear relationship (Fig. 3.1) between TOC and DOC in the samples collected during dry weather and wet weather flows from both the rural (DOC = 0.542 + 0.829*TOC, r^2 = 0.948, P= <0.0001, n = 19) and urban sites (DOC= -0.171 + 0.890*TOC, r^2 = 0.950, P= <0.0001, n = 48). These results suggest that at the rural sites, 83% of the organic carbon <150μm is in the dissolved form, and that at the urban sites, 89% is in the dissolved form. Despite the indication of a slight (~6%) increase in the relative proportion of DOC in the urbanised sub-catchments, the slopes of the regression lines are not significantly different (ANCOVA {$F_{1,130}$ = 0.349, P = 0.556}). When all samples are compared together, the relationship between DOC and TOC was DOC = 0.0515 + 0.881*TOC (r^2 = 0.967, P= <0.0001, n= 67).

3.3.2 Relationship Between TSS and B.O.D.$_5$

A linear relationship was observed between TSS and B.O.D.$_5$ in the samples from the rural sites (B.O.D.$_5$ = 1.552+0.134*TSS, r^2 = 0.383, P = 0.005, n = 19), and an exponential relationship was observed for the urban sites (B.O.D.$_5$ =34.73(1-$e^{-0.045*TSS}$), r^2 = 0.468, P= <0.0001, n = 48). For all samples across the rural-urban gradient, there was an exponential relationship between TSS and B.O.D.$_5$ (B.O.D.$_5$ = (35 .09(1-$e^{-0.034*TSS}$)), r^2 = 0.568, P= <0.0001, n = 67) which asymptotes at TSS >150mgL^{-1} (Fig. 3.2). Although the relationship between TSS and B.O.D.$_5$ appears to be near linear at TSS concentrations below 150mgL^{-1}, regression analysis on the TSS data between 0-150mgL^{-1} (B.O.D.$_5$ = 5.032+0.473*TSS, r^2 = 0.366, P= <0.0001, n=56) indicates that variation in TSS concentration explains only 36% of the variation in B.O.D.$_5$.

3.3.3 Relationship between total B.O.D.$_5$ and filtered B.O.D.$_5$

Strong linear relationships were observed between B.O.D.$_5$ and 0.45 μm filtered B.O.D.$_5$ in the samples collected from both the rural (fB.O.D.$_5$= 0.140 + 0.772*B.O.D.$_5$, r^2 = 0.986, P = <0.0001, n = 39) and urban (fB.O.D.$_5$= 0.808 + 0.957*B.O.D.$_5$, r^2 = 0.959, P = <0.0001, n = 48) sites (Fig. 3.3). These results suggest that in the rural areas, 23% of the oxygen demanding material is comprised of particulate material, and that in the urban areas the proportion decreases to 4%. Although this difference appears substantial, statistical comparison of the slopes reveals that the difference is not significant (ANCOVA $\{F_{1,170} = 0.526, P = 0.470\}$). When the relationship was compared for all samples across the rural-urban gradient, fB.O.D.$_5$ = -0.045 +0.995*B.O.D.$_5$ ($r^2 = 0.959$, P = <0.0001, n = 87).

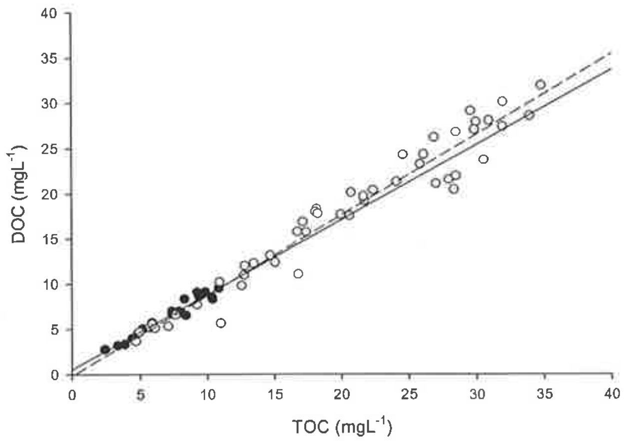

Figure 3.1. Relationship between Dissolved Organic Carbon and Total Organic Carbon. Closed Circles represent Rural Samples: (dotted regression line: (DOC = 0.542 + 0.829*TOC, $r^2 = 0.948$, P= <0.0001, n = 19). Open Circles represent Urban Samples: (solid regression line: DOC= -0.171 + 0.890*TOC, $r^2 = 0.950$, P= <0.0001, n = 48).). [For all samples: DOC = 0.051+0.881*TOC, $r^2 = 0.967$, n= 67; regression line not shown].

3.3.4 Particle size distribution of oxygen demanding substances

Samples collected from the rural streams exhibited a consistent B.O.D.$_5$ (2.63 ± 0.52 mgL^{-1}) that was independent of the progressive, step-wise removal of particulate material (ANOVA: F=0.6525 , df 8, P=0.7273). Samples collected from the urban sites, exhibited a similar response (Fig. 3.4), in that stepwise removal of particulate material did not significantly reduce the B.O.D.$_5$ exerted (ANOVA: F=0.4647, df_8, P=0.8700). This was despite the observation that the B.O.D.$_5$ in the urban sites was 3.5 times greater than that observed at the rural sites (Two way ANOVA: F=21.16, df_1, P=<0.0001).

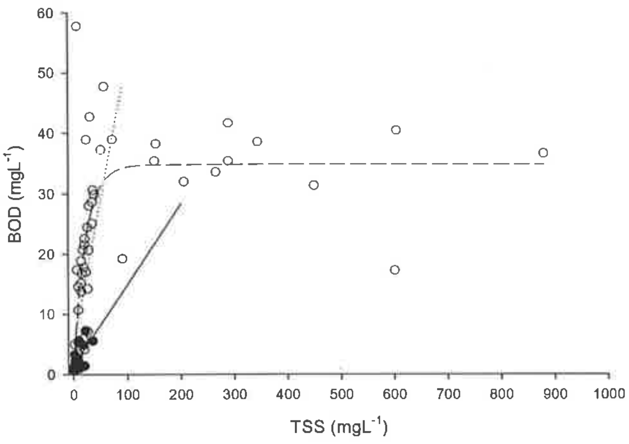

Figure 3.2. Relationship between Total Suspended Solids (TSS) and Biochemical Oxygen Demand (B.O.D.$_5$): Solid Circles = rural samples (y = 1.552+0.134x, r^2 = 0.383, P = 0.005, n = 19), Open circles = urban samples (y=34.73(1-$e^{-0.0452x}$), r^2 = 0.468, P= <0.0001, n = 48)., for all samples with TSS <150 mgL^{-1}, (y= 5.032+0.473x, r^2 = 0.366, P= <0.0001, n=67) (dotted regression line).

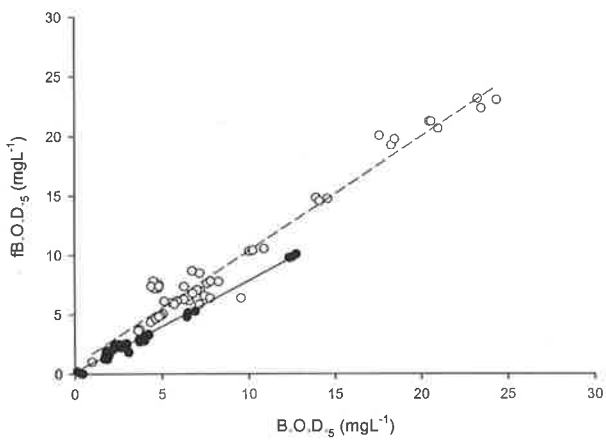

Figure 3.3. Relationship between B.O.D.$_5$ and 0.45 µm filtered B.O.D.$_5$: Closed Circles = Rural samples (fB.O.D.$_5$ = 0.140 + 0.772*B.O.D.$_5$, r^2 = 0.986, P = <0.0001, n = 39) Open Circles = Urban samples (fB.O.D.$_5$ = 0.808 + 0.957*B.O.D.$_5$, r^2 = 0.959, P = <0.0001, n = 48). [For all samples y = (-0.045+0.995x) r^2 = 0.959, P = <0.0001, n = 87) regression line not shown]

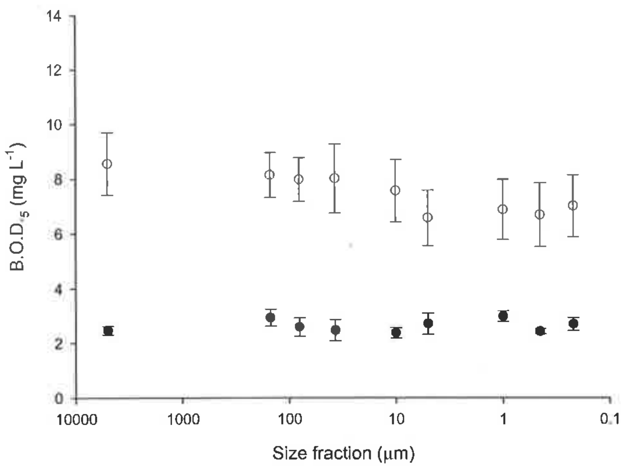

Figure 3.4. B.O.D.$_5$ contained in relative size fractions of stream water collected from the 4 rural sites on 5th June 2003 (closed circles) and the 4 urban sites on 12th June 2003 (open circles). Error bars are ± 1 S.E.

3.4. Discussion

Comparison of the data across the rural-urban gradient suggests a shift in the relative importance of particulate and dissolved material with changes in land use. Regression analysis of the data collected between March and November 2002 indicates that particulate material represents a slightly higher proportion of the TOC in the rural sites (17%) than in the urban sites (11%), but the difference is not statistically significant. Furthermore, there was no significant response to the progressive removal of particulate material on reducing B.O.D.$_5$ at the rural and urban sites (Fig. 3.4). Regression analysis of the B.O.D.$_5$ vs fB.O.D.$_5$ data (Fig. 3.3) indicates that particulate material represents a slightly higher proportion of oxygen demanding material in the rural (23%) sites than in the urban sites (4%), however statistical comparison of the slopes revealed that the difference is not significant. Although it is unlikely that rural samples would exert higher oxygen demands than those observed, it is considered that if higher B.O.D.$_5$ values were recorded in the rural samples, they may have weighted the top end of the regression sufficiently to statistically separate the slopes.

Analysis of the water quality data throughout the rural-urban sub-catchment demonstrates that the majority of the organic carbon <150µm is contained in the dissolved fraction (DOC), and that there was not a strong, causative relationship between particulate material and biochemical oxygen demand. The relationships that were observed between TSS and B.O.D.$_5$ (Fig. 3.2) are considered to be an artifact of a concurrent increase in both TSS and B.O.D.$_5$ during wet weather, rather than evidence of a strong correlation between TSS and B.O.D.$_5$. Evidence supporting this conclusion is (i) the observation that for all samples throughout the rural-urban sub-catchment, 88% of the organic carbon <150μm is contained in the dissolved fraction; (ii) the observation that throughout the rural-urban sub-catchment, 96% of the total B.O.D.$_5$ is driven by dissolved organic material; and (iii) the failure to demonstrate a substantial impact of the progressive removal of particulate material on reducing B.O.D.$_5$ at both urban and rural sites.

Other studies in Australian catchments support the findings of this study; that in urbanised catchments, a high proportion of the oxygen demanding organic material is in the dissolved (or very-fine particulate) phase. Goonetilleke *et al.* (2005) concluded from a study of 3 primary and 3 sub-catchments in Queensland, Australia, that in the urbanised sub-catchments studied, the majority of the TOC is in the form of dissolved material. In addition, Mann and Hammerschmid (1989) demonstrated that in a developing residential catchment in New South Wales, Australia, 42% of chemical oxygen demand (COD) was associated with material <2μm. In contrast, Sartor *et al.* (1974) reported that in urbanised catchments in North America, only 24.3% of total B.O.D.$_5$ is associated with material smaller than 43μm, and default values presented by Lawrence and Phillips (2003) for use in calculating sustainable stormwater loads to Australian waterways, are set at 6% of the total B.O.D.$_5$ being contained in the <0.7μm range. In comparison, the results of this study indicate that 82% of the total B.O.D.$_5$ is contained in material <0.22μm. The particle size-B.O.D.$_5$ distribution results from this study are compared to those of Sartor *et al.* (1974) and Lawrence and Phillips (2003) in Fig. 3.5.

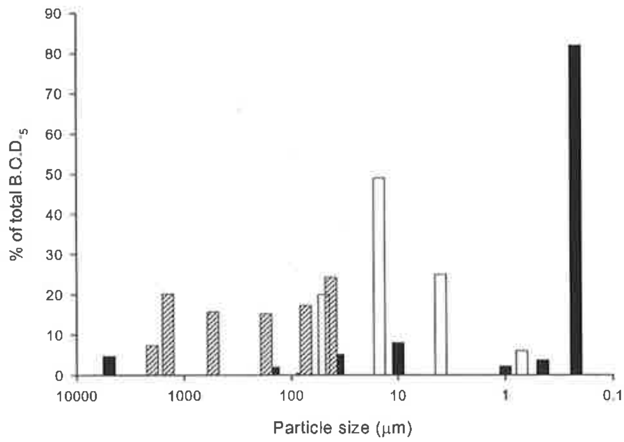

Figure 3.5. Comparison of results of size fractionation-biochemical oxygen demand distribution: Solid bars represent urban stormwater data from this study [size ranges tested: <5000μm, <150μm, <80μm, <37μm, <10μm, <5μm, <1μm, <0.45μm, <0.22μm] Shaded bars represent data from Sartor *et al.* (1974) [size ranges reported: >2000μm, 2000-840μm, 840-246μm, 246-140μm, 104-43μm, <43μm]. Open bars represent data from Lawrence and Phillips (2003) [size ranges reported: 50μm, 15μm, 4μm, 0.7μm].

There are a number of potential explanations for the variation in studies that demonstrate that the majority of the oxygen demanding organic material is in the dissolved phase (Goonetilleke *et al.*, 2005; Mann and Hammerschmid, 1989), and those that demonstrate that the majority of the oxygen demanding organic material in the particulate phase (Lawrence and Phillips, 2003; Sartor *et al.*, 1974). These include variation in the development stage of the catchment (Mann and Hammerschmid, 1989), and catchment specific variation in the size distribution and mineral composition of particulate material. Oxygen demand per gram of particulate material increases as particle size decreases (Lawrence and Phillips, 2003), and it is recognised that the average particle size from Australian streets is smaller than that from overseas catchments (Walker and Wong, 1999). In addition, particulate material from road surfaces would be mostly comprised of inorganic material (Goonetilleke *et al.*, 2005). Depending on the specific mineral characteristics of the particulate material, and the physico-chemical characteristics (e.g. hydrophobic-hydrophilic nature) of the oxygen demanding, organic material itself, there may not be strong binding between the particulate material and DOC (McKnight *et al.*, 2003).

On impervious surfaces, the rainfall that mobilises accumulated pollutants produces large volumes of water moving at relatively high velocities, which may release DOC from leaf material or inorganic particulate material (Hillman *et al.*, 2004). It is well recognised that a large proportion of allochthonous organic carbon is derived from leaf litter, and significant concentrations of DOC have been shown to be rapidly leached from leaf litter following inundation (Baldwin, 1999; Francis and Sheldon, 2002; Glazebrook and Robertson, 1999), therefore a substantial pool of DOC may become available even if particulate leaf litter is not transported into the stormwater system. Additional factors such as plant species, season (Hongve, 1999) terrestrial ageing of the leaf litter (Baldwin, 1999), and the extent of physical damage to leaf material (Cowen and Lee, 1973) affect the rates of nutrient leaching following immersion, potentially adding to variation in POC:DOC ratio's within and between catchments.

There are substantial limitations and obstacles to the effective catchment management and reduction of the impacts of runoff. These limitations include a lack of understanding of runoff characteristics from catchments with varying land use (Fletcher *et al.*, 2001). Although the research hypothesis that there would be an increased proportion of oxygen demand driven by particulate organic material in urban than rural streams could not be supported, this study does provide strong evidence that it is critical to consider the particle size distribution of oxygen demanding organic material from individual catchments in order to ensure that management decisions are appropriate for the catchment in question. The observation that throughout the urban region of the Torrens Catchment the majority of the organic carbon and B.O.D.$_5$ is contained in the dissolved fraction has implications in stormwater management, water sensitive urban design and the effectiveness of structural treatment measures (e.g. gross pollutant traps, swales, detention basins, treatment wetlands, bio-retention systems).

For the Torrens Catchment, where 95% of the total B.O.D.$_5$ is driven by material <0.45μm, predictions of sustainable B.O.D.$_5$ loads to receiving waters based on the particle grading values presented by Lawrence and Phillips (2003) would be incorrect with potentially catastrophic impacts on receiving waters. Furthermore, stormwater treatment systems that are designed such that the predominant treatment pathway is via sedimentation of particulate material (e.g. detention/sedimentation basins/wetlands) will have little impact on reducing a B.O.D.$_5$ predominantly driven by DOC unless the retention time of water in the system is long enough for the B.O.D.$_5$ to be exhausted via biological degradation of the organic material.

Based on the results of this study, it is considered that directing funding solely to structural management techniques and treatment trains primarily designed to intercept TSS, with an expectation of delivering a substantial reduction in B.O.D.$_5$ would deliver a poor return in the Torrens Catchment. At-source measures such as pervious pavements, and percolation trenches-infiltration basins may be more efficient (Lawrence and Breen, 1998). Implementation of structural best management practices will also need to be backed up with a reduction in drainage connection (proportion of impervious surface area connected directly to streams by pipes or drains (Walsh, 2002), and increases in non-structural best management practices (e.g. use and disposal of household chemicals, land use management, on-site runoff management, and management of pollutant buildup (Lawrence *et al.*, 1996; Taylor, 2002).

The baseline data obtained in this component of the project forms the basis for the next phase of the project, which was to identify the bioavailability of the organic carbon present and to characterise its chemical composition via ion-exchange fractionation. The small but statistically non-significant increase in the proportion of DOC in the urban areas observed in the current chapter is probably not a concern in itself. However, the bioassay results obtained in the following chapter (Chapter 4) indicate that the DOC from the urban areas is substantially more bioavailable than that from the rural streams. The slight increase in the relative proportion of dissolved DOC, combined with an increase in bioavailability may alter biogeochemical cycling rates and destabilize the ecosystem (Wetzel, 2001) in the urban areas.

Chapter 4: Characterisation of the composition and bioavailability of dissolved organic carbon across the rural-urban gradient in the Torrens Catchment.

4.1 Introduction.

A wide range of catchment specific attributes (Aitkenhead-Peterson *et al.*, 2003; Walsh *et al.*, 2004) including stream order, geology, vegetation, and land use influence the concentration and composition of autochthonous and allochthonous organic carbon compounds present in aquatic ecosystems. Characterising the influence of changes in land use on shifts in the composition and bioavailability of organic matter transferred from the terrestrial to the aquatic component of catchments is of significant interest to the water science and technology community, as NOM is recognised as having a fundamental influence on nutrient cycles, food webs (Findlay and Sinsabaugh, 2003), and the optical properties of water (Kirk, 1980).

The concentration and chemical composition of dissolved organic material plays a critical role in increasing the absorption and attenuation of ultraviolet radiation (Morris *et al.*, 1995; Weishaar *et al.*, 2003; Wetzel *et al.*, 1995) thus imparting a substantial influence on the depth of the euphotic zone in surface waters (Weishaar *et al.*, 2003). Water samples with an increased proportion of humic material compounds may exert higher rates of UV absorption/attenuation than streams with comparatively low proportions of humic material. Shifts in the composition of NOM inputs associated with changes in land use may alter rates of absorption/attenuation of UV, and subsequently impact on ecosystem function by altering the underwater light field and the amount of photosynthetically active radiation available to planktonic and benthic communities (Morris *et al.*, 1995; Wetzel *et al.*, 1995). Furthermore, the relative concentrations of bioavailable carbon, nitrogen and phosphorus have a substantial influence on biogeochemical cycles (Wetzel, 2001). For example, while the proportion of labile DOC within individual streams has been shown to change between dry and wet weather flows in some streams (Volk *et al.*, 1997), and to remain constant in others (Buffam *et al.*, 2001), the availability of labile carbon has been demonstrated to have a substantial impact on nitrogen cycling in streams (Bernhardt and Likens, 2002; Butturini *et al.*, 2000; Strauss and Lamberti, 2002). A consequence of shifts in the ratio of labile-recalcitrant DOC during rain events is that when high concentrations of readily bioavailable DOC are present, what would normally be considered an essential resource can become a contaminant, particularly if the oxidisation of the DOC generates a substantial oxygen debt.

It is intuitive that there would be an observable shift in the range of organic compounds present in developed and undeveloped catchments. However, the potential impacts of urbanisation on dissolved organic carbon (DOC) composition and quality are unclear and not easily defined, as there is a distinct lack of comparable studies on DOC bioavailability and stream metabolism between rural and urban streams. Although a limited number of urban stormwater studies have demonstrated significant differences in the relative proportion of specific groups of organic compounds from rural and developed catchments (e.g. Fam *et al.*, 1987), there is a distinct lack of studies that have assessed the bulk composition and bioavailability of NOM across rural-urban gradients.

The previous chapter investigated the hypothesis that there would be an increased proportion of oxygen demand driven by particulate organic material in urban than rural streams. The current chapter extends the work of the previous chapter by testing the hypothesis that there would be distinct differences in the composition and bioavailability of dissolved organic carbon across the rural-urban gradient. It was proposed that urbanisation would induce changes to the composition of the bulk DOC pool via shifts in both the composition of inputs, and the degree of terrestrial and in-stream processing that occurs during transport from one environment to another. Furthermore, it was proposed that the urbanisation-induced shifts in composition would be correlated with an increase in DOC biodegradability. This was investigated by comparing the relative concentration, composition and biodegradation of DOC in stream water samples collected from above and below the rural-urban gradient of the Torrens Catchment.

4.2 Methodology

4.2.1 Catchment Description and Sampling Sites

A detailed description of the Torrens Catchment is provided in Chapter 2. Samples were collected from a total of seven sites above (rural: 1^{st}, 2^{nd}, 3^{rd}, 4^{th}, 5^{th} and 6^{th} creek and from Torrens River) and 7 sites below the rural-urban demarcation (urban: 1^{st}, 2^{nd}, 3^{rd}, 4^{th}, 5^{th} creeks, and from the inlet and outlet end of Torrens Lake) see Fig 2.1 (Chapter 2) for relative locations. The rural sampling sites were located in areas at which the streams emerge from conservation parks. The urban sites were located above the confluence (typically < 25 m) of the tributary streams with the Torrens River. It is recognised that the location of the rural and urban sites on a downstream gradient potentially complicates the assessment of changes in land use (rural-urban) on DOC composition and bioavailability (it is generally accepted that the ratio of autochthonous: allochthonous DOC generally increases as stream order increases). However, the aim of the research was to assess the impacts of urbanisation on DOC bioavailability within the tributary streams of the Torrens Catchment, and the nature of the Torrens Catchment is that the headwater-mid reach stream sections are dominated by rural land use, and the downstream reaches are heavily urbanised.

4.2.2 Sample Collection

Samples were collected at gauging weirs or similar hard structures that confined flow, and allowed the samples to be collected from the central portion of the flow. Samples were collected using a 2L PTFE beaker fitted to a 2.5m sampling pole. Three 1.5L grab samples were obtained at 5-minute intervals and were pooled together in a single 5L PTFE container to produce a 4.5L composite sample. The containers containing the composite samples were stored in the dark in an ice filled, insulated container prior to return to the laboratory. The 5L PTFE containers and 2L PTFE beakers used for sample collection had been pre-cleaned according to the protocol described in Chapter 2 (General Methods).

4.2.3 Biochemical Oxygen Demand – Dissolved Organic Carbon ratios: Baseline Data

The relationship between BOD and DOC throughout the lower catchment of the Torrens Catchment was examined on the baseline data collected during 2002. BOD and DOC results were compiled to produce a data set of BOD:DOC ratios for a total of 67 samples collected during base-flow and storm-flow conditions from 14 sites throughout the urban-rural zone between 27 March 2002 and 11 November 2002. The BOD values were obtained according to Standard Method 5210B (Eaton *et al.*, 1995) without inhibition of nitrification (see Chapter 2 for details).

4.2.4 Carbonaceous biochemical oxygen demand, SUVA, and DOC depletion.

Samples were collected on 30th January 2003 from the urban sites on 1st, 2nd, 3rd and 4th Creeks, and from the rural zones on 1st, 2nd and 6th Creeks, as there was no surface water present in the rural sites on 3rd, 4th and 5th creeks at the time of sampling. The rural sample from 6th Creek was collected above the confluence (< 20 m) of the tributary stream with the Torrens River, as unlike 1st to 5th creek, there is no substantial urbanisation present in the catchment of 6th Creek. Five (5) day carbonaceous (nitrification inhibited) biochemical oxygen demand (CBOD), DOC and specific ultraviolet absorbance ($SUVA_{254}$) was measured on these samples.

Samples for time series analysis of carbonaceous biochemical oxygen demand and DOC depletion were collected from the rural sites on 1st, 4th, 5th and 6th Creeks, and from the urban sites on 1st, 3rd and 4th Creeks during base-flow conditions on 27th June. There was no surface water present in either the rural zones of 2nd, 3rd Creeks, or the urban zone of 2nd Creek at the time of sampling. Samples were also collected from the rural and urban sites on 1st, 2nd, 3rd and 4th Creeks during storm-flow conditions on 24th July 2003.

Although a number of methods (Hammes and Egli, in press; Servais *et al.*, 1989; Servais *et al.*, 1987) have been developed for the characterisation of the bioavailability of dissolved organic carbon for the water industry, in this research, simple bioassays using a modification of the standard test for biochemical oxygen demand (Eaton *et al.*, 1995) were utilised. In the biodegradability tests used in the time series analysis of CBOD and DOC depletion for this research, the bioassay period was extended from the standard 5 days used in BOD analysis, to 10 days, and dissolved oxygen and DOC measurements were made on independent samples at times 0, 1, 2, 3, 4, 5, 7 and 10 days. The consecutive measurements provide time series curves for CBOD and DOC biodegradability. A detailed description and schematic of the protocol used is presented in Chapter 2.

4.2.5 Characterisation of DOC – relationship to bioavailability

The relationship between the composition of the DOC pool and its relative bioavailability was assessed on samples collected during storm-flows generated by a summer and a winter rain event. The samples collected on 20th February 2003 (summer rain event) were obtained from the urban sites on 1st, 2nd, 3rd and 4th Creeks, and from the rural zones on 1st, 2nd, 3rd and 6th Creeks. 6th Creek was utilised as a substitute site, as there was no surface water present in the rural zones of 4th or 5th creek. The samples collected on 24th July 2003 (winter rain event) were collected from the urban and rural zones of 1st, 2nd, 3rd and 4th Creeks. Five day CBOD and initial DOC concentration was measured on the summer rain event samples. Time series measurements of CBOD and DOC depletion were performed on the winter rain event samples.

The complexity and variability in DOC precludes the use of most high resolution analytical techniques (e.g. pyrolysis GC-MS) in characterising DOC in water samples into a easily interpretable format (Servais *et al.*, 1989). The potential for the use of extracellular enzymes in characterizing the effects of urbanisation on DOC bioavailability, is currently being assessed in Melbourne, Australia (Harbott, 2003). Ion exchange fractionation is currently one of the most commonly utilised techniques for isolating DOC fractions (Afcharian *et al.*, 1997), and in the research reported here, the DOC present in the samples was characterised via ion exchange fractionation into 5 distinct macro-fractions utilising minor modifications to a technique described by Imai *et al.* (2001) which is based on the classic technique developed by Leenheer (1981).

A detailed description of the ion exchange technique utilised is provided in Chapter 2 of this thesis. The samples were fractionated utilising 3 ion-exchange resins: Supelite™ DAX-8, Biorad AG®MP50, and Biorad AG®MP1. The five fractions produced were hydrophobic acids (AHS; e.g. humic and fulvic acids), hydrophobic neutrals (HoN; e.g. large cellulose polymers, hydrocarbons, pesticides, LAS (linear alkylbenzene sulfonate) and carbonyl compounds), hydrophilic acids (HiA; e.g. fatty acids, sugar acids, hydroxyl acids), bases (BaS; e.g. aromatic amines, proteins, amino acids, aminosugars), and hydrophilic neutrals (HiN; e.g. carbohydrates, oligosaccharides, polysaccharides, alcohols, ketones). The relative composition of these fractions generates a physicochemical signature for the water sample. The DOC composition was compared to the CBOD and CBOD:DOC results to assess if there was a correlation between shifts in DOC composition and oxygen demand and bioavailability.

4.3 General methods

4.3.1 Sample preparation

Upon return to the laboratory, the samples for analysis of DOC and oxygen demand driven by dissolved organic material (<0.45μm) were homogenised by inversion mixing, pre-filtered through pre-washed (see Chapter 2) Whatman GF/C filters and subsequently filtered through Whatman PVDF 0.45μm membrane filters.

4.3.2 Carbonaceous Biochemical Oxygen Demand

Measurements of biochemical oxygen demand samples were analysed for carbonaceous biochemical oxygen demand (CBOD) utilising Standard Method 5210B (Eaton *et al.*, 1995). Nitrification was inhibited via the addition of 3mg 2-chloro-6-(trichloro methyl) pyridine (TCMP) to each individual BOD bottle. Details of dilution water etc. are provided in Chapter 2. As measurements of BOD are generally interpreted as reflecting the degradation of easily biodegradable DOC (Imai *et al.*, 2001), BOD:DOC ratios can be considered to provide a relative measure of DOC biodegradability. Eaton (1995) states that measurements of BOD that include nitrogenous oxygen demand may have limited value assessing the oxygen demand associated with organic material. Consequently, the inclusion of a chemical inhibitor (TCMP) to inhibit nitrification is considered to have increased the reliability of BOD:DOC ratios as a method for assessing the relative difference in DOC bioavailability across the rural-urban gradient.

4.3.3 Bioassays – supplementary nutrients

Although the concentration of bioavailable carbon has long been considered to limit heterotrophic metabolism in aquatic ecosystems, it is well established that both phosphorus and nitrogen may limit planktonic heterotrophic metabolism, and result in an accumulation of biodegradable DOC (Arvola and Tulonena, 1998; Vadstein *et al.*, 2003). Subsequently, additional nitrogen (N) and phosphorus (P) was added to the bioassays to ensure that measurements of CBOD and DOC biodegradation were representative of the biodegradability of the DOC pool, and that microbial metabolism was not limited by ambient concentrations of N or P (Elser *et al.*, 2000; Søndergaard and Middelboe, 1995). Sodium Nitrate ($NaNO_3$) was utilised as the supplementary nitrogen compound. Di-potassium hydrogen orthophosphate (K_2HPO_4) was utilised as the supplementary phosphorus compound. The amount of $NaNO_3$ and K_2HPO_4 added was calculated to provide minimum initial concentrations of 1000µg N L^{-1} and 100µg P L^{-1} respectively.

4.3.4 Dissolved Oxygen

Dissolved oxygen was measured using a WTW (Wissenschaftlich-Technische Werkstätten GMBH & Co. KG) CellOx 325 oxygen sensor attached to a WTW Oxi 330i dissolved oxygen meter.

4.3.5 Dissolved Organic Carbon

DOC concentrations were determined utilising an SGE ANATOC II total organic carbon analyser. DOC analysis was performed in non-purgeable organic carbon mode, according to the protocol described in Chapter 2.

4.3.6 Specific Ultra Violet Absorbance ($SUVA_{254}$)

Specific UV absorbance (SUVA) provides a method of characterising the DOC in a water sample by measuring the absorbance (usually at 254 nm) of a given water sample, and normalising the detected absorbance to the concentration of DOC in the sample. $SUVA_{254}$ is generally considered to provide information about the general characteristics of DOC, and is considered effective for estimating the aromatic carbon content of DOC. $SUVA_{254}$ was calculated via the equation: $SUVA = (UV_{abs254} / DOC_{mgL^{-1}}) * 100$ (Weishaar *et al.*, 2003). UV absorbance at 254nm was measured on 0.45µm filtered samples utilising a Hitachi U-2000 UV-Vis spectrophotometer fitted with an auto-sampler and a 1cm path length quartz cuvette.

4.3.7 Data Analysis

Regression curves displayed in graphs are fitted to means; error bars are ± 1 standard error (SE). All univariate statistical tests were performed using the package JMP In version 3.2.6 (SAS Institute Inc. 1996). Normality was tested using the Shapiro-Wilk W Test, and the equality of variances with the Levene test. Square root and log transformations were applied (unsuccessfully) to data sets exhibiting non-normal distribution and unequal variances. Those data sets were subsequently analysed using non-parametric (Wilcoxon/Kruskal-Wallis) analysis. Differences in DOC composition between the sites were analysed using indicator species analysis (Dufrene and Legendre, 1997) and non-metric scaling (NMS) ordination. Single factor NPMANOVA was used to compare the composition of DOC across the rural-urban gradient in the tributary streams. Indicator species analysis and NMS ordinations were performed using PCOrd; version 4.28 (McCune and Mefford, 1999). NPMANOVA was undertaken using the procedure described by Anderson (2001). Bray-Curtis distances were used to calculate the similarity matrix for all multivariate statistical analyses (Bray and Curtis, 1957) and two-dimensional ordination solutions with stress lower than 20% were deemed acceptable (sensu (Clarke, 1993). For all statistical tests $\alpha = 0.05$.

4.4 Results

4.4.1 Biochemical Oxygen Demand – Dissolved Organic Carbon ratios: Baseline Data

There was a significant difference (ANOVA: df = 65, F = 25.035, P = <0.0001) in the BOD:DOC ratios between the rural and urban sites (Fig. 4.1 A and B). At the rural sites, the mean BOD:DOC ratio was 0.46 (± 0.14), in the urban streams, the mean BOD:DOC ratio was 1.30 (±0.09).

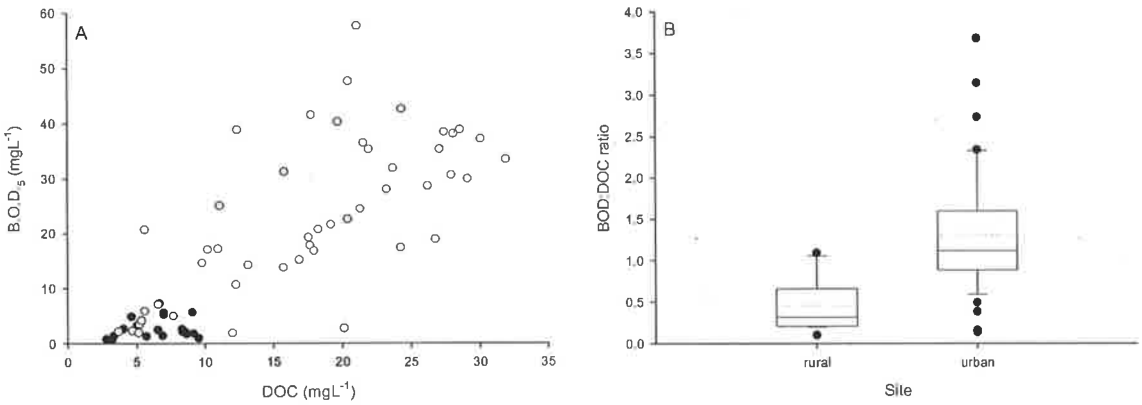

Figure 4.1. [A] Relationship between DOC (mgL^{-1}) and B.O.D.$_5$ (mgL^{-1}) in rural (solid circles) and urban (open circles) streams during dry and wet weather flows in 2002. [B] B.O.D.$_5$:DOC ratio in rural and urban streams during dry and wet weather flows in 2002. Upper and lower boundaries of the box represent the 25th and 75th percentiles respectively. Error bars on whisker plots denote the 10th and 90th percentiles. Solid and broken horizontal lines within box represent the median and mean respectively. Solid circles represent outliers.

4.4.2 Carbonaceous biochemical oxygen demand, SUVA, and DOC depletion

The CBOD (Figure 4.2[A]) exerted by the 0.45µm filtered storm-flow samples collected from the urban sites on 30th January 2003 (19.4 mgL^{-1} ±1.8) was an order of magnitude higher than that observed in the samples collected from the rural sites (1.9 mgL^{-1} ±0.1). The elevated CBOD:DOC ratio (Figure 4.2[B]) observed in the urban sites (0.99 ±0.07) compared to the rural sites (0.36 ±0.05) demonstrates that there is a significant (Wilcoxon/Kruskal Wallis: df = 1, ChiSq = 4.5, P = 0.040) difference in DOC bioavailability in the urban streams during summer storm-flows. Although the $SUVA_{254}$ do not indicate a difference in the percent aromaticity of the DOC between the rural and urban sites, a consequence of the differences in CBOD between the rural and urban sites, is that there are substantial differences in the $SUVA_{254}$:CBOD ratios between the rural and urban sites.

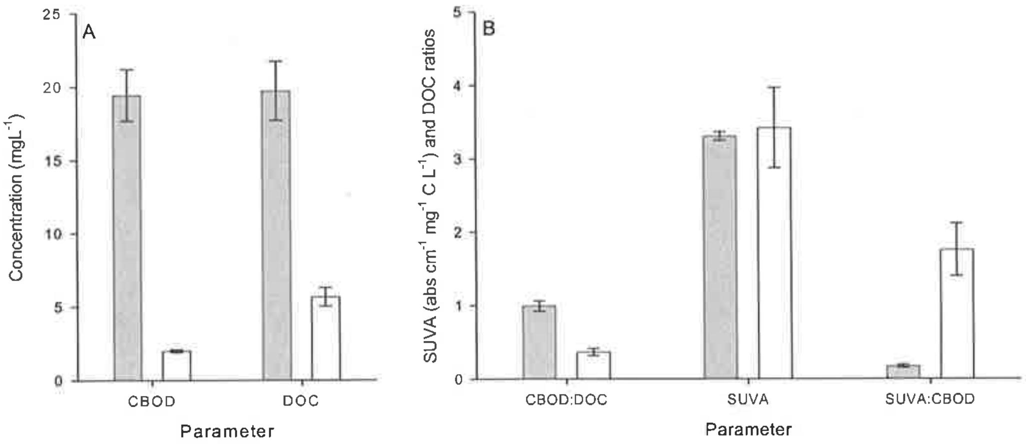

Figure 4.2. [A] CBOD and DOC; and [B] CBOD:DOC ratio, SUVA and SUVA:CBOD ratio in urban (shaded bars) and rural (open bars) streams during wet weather flows on 30.1.2003.

The time series measurements of CBOD for the baseflow samples collected on 27th June 2003 (Figure 4.3) indicate that there was not a substantial difference in oxygen demand between the rural and urban streams. Due to a technical fault with the carbon analyser, time series DOC results are not available for these samples. The initial DOC concentration in the base-flow samples from the rural and urban streams was 7.00 (±1.37) mgL^{-1} and 5.43 (±0.47) mgL^{-1} respectively. The relative bioavailability of the DOC as measured by CBOD:DOC ratios was not found to be significantly different (Wilcoxon/Kruskal Wallis: df =1, ChiSq =1.125, $P = 0.289$) between the rural (0.24 ±0.03) and urban streams (0.36 ±0.04).

In comparison to the samples collected under base-flow conditions, the time series measurements of CBOD and DOC depletion on the samples collected on 24th July 2003 (Figure 4.4) demonstrate that during storm-flow conditions, the bioavailability of DOC in the samples from the urban streams is higher than the rural samples. There was a significant difference (Wilcoxon/Kruskal Wallis: df =1, ChiSq = 4.5, $P = 0.034$) in relative bioavailability of the DOC as measured by CBOD:DOC ratios between the urban (0.42 ±0.07) and rural (0.15 ±0.02) streams. Furthermore, the DOC in the urban samples (Figure 4.4[A]) was depleted in an exponential manner (see figure legend for regression equations). In contrast, the DOC in the rural samples (Figure 4.4[B]) was depleted in a slow, linear manner. Although the CBOD curves display an exponential function in both the rural and urban stream samples, there is a significant difference (Wilcoxon/Kruskal Wallis: df =1, ChiSq = 5.3333, P = 0.021) between the CBOD values observed at day 10 in the rural (1.1 mgL^{-1}) and urban (3.4 mgL^{-1}) streams.

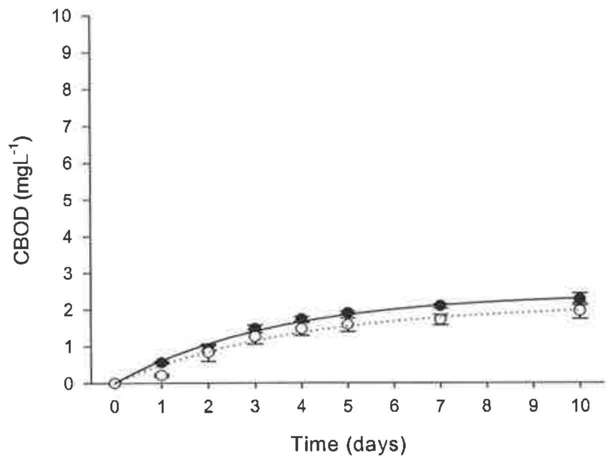

Figure 4.3. Carbonaceous biochemical oxygen demand (mgL^{-1}) in samples collected during base-flow conditions on 27.6.2003. Solid circles = rural streams ($y = 2.143(1-e^{-0.257x})$, $r^2= 0.971$, F = 200.04, P = <0.0001); Open Circles = urban streams ($y = 2.442(1-e^{-0.288x})$, $r^2= 0.993$, F =852.16, P = <0.0001).

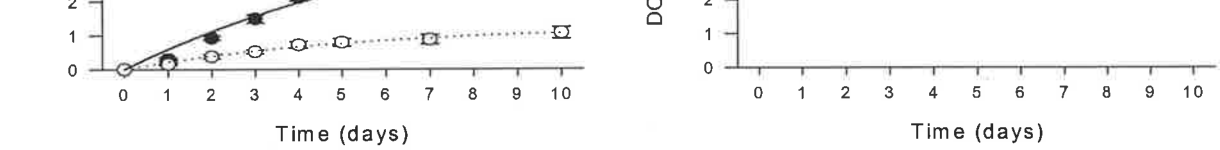

Figure 4.4. Ten day time series of [A] oxygen demand and [B] DOC metabolism in streamwater collected during storm-flow on 24.7.2003. Open circles = rural sites, Solid circles = urban sites. Oxygen demand: urban streams ($y = 4.76(1-e^{-0.133x})$, $r^2= 0.979$, F = 274.57 , P = <0.0001); rural streams ($y = 1.26(1-e^{-0.185x})$, r^2 =0.988, F = 506.94 , P = <0.0001). DOC metabolism: urban streams ($y=3.16+3.33e^{-0.545x}$, $r^2= 0.947$, F = 44.93, P = 0.0006); rural streams ($y = 5.53 - 0.060x$, $r^2= 0.918$, F = 66.99, P = 0.0002).

4.4.3 Carbonaceous oxygen demand and ion exchange fractionation of DOC

The comparatively high CBOD:DOC ratio observed in the urban stream (1.11 ±0.07) samples collected during summer storm-flows on 20th February 2003 (Figure 4.5[A]) indicates that the DOC in the urban streams is substantially more bioavailable than that from the rural streams (0.55 ±0.12). Fractionation of the DOC in the samples (Figure 4.5[B]) revealed significant differences (NPMANOVA, $df = 1$, $F = 35.74$, $P = 0.028$) in the composition of the DOC between the rural and urban samples. Indicator species analysis (Table 4.1) reveals that although the only significant indicator for the DOC from the urban stream water samples is a high proportion of hydrophobic neutrals (HoN), an additional characteristic of urban DOC is an elevated proportion of base compounds (BaS). In comparison, rural stream water samples are characterised by an elevated proportion of hydrophobic acids (AHS) and to a lesser extent hydrophilic acids (HiA), but neither of the indicators are significant at $\alpha = 0.05$.

The pattern of comparatively high bioavailability (measured via CBOD:DOC ratios) in the urban stream samples is also evident in the winter storm-flow samples (Figure 4.6[A]), despite the relatively similar DOC concentrations in both the rural and urban samples collected on 24th July 2003. The CBOD:DOC ratios in the urban and rural streams were 0.42 (±0.07) and 0.15 (±0.02) respectively. The increase in bioavailability was also evident in the DOC depletion curve (Figure 4.4[B]). Ion-exchange fractionation of the DOC pool (Figure 4.6[B]) reveals that there are significant differences (NPMANOVA, $df = 1$, $F = 144.12$, $P = 0.028$) in the composition of the DOC between the rural and urban samples. Indicator species analysis (Table 4.2) reveals that the DOC from the urban streams is characterised by a high proportion of both hydrophobic neutrals and hydrophilic acids. In comparison, the DOC from the rural streams is characterised ($P = 0.054$) by a high proportion of hydrophilic neutrals, and to a lesser extent, hydrophobic acids.

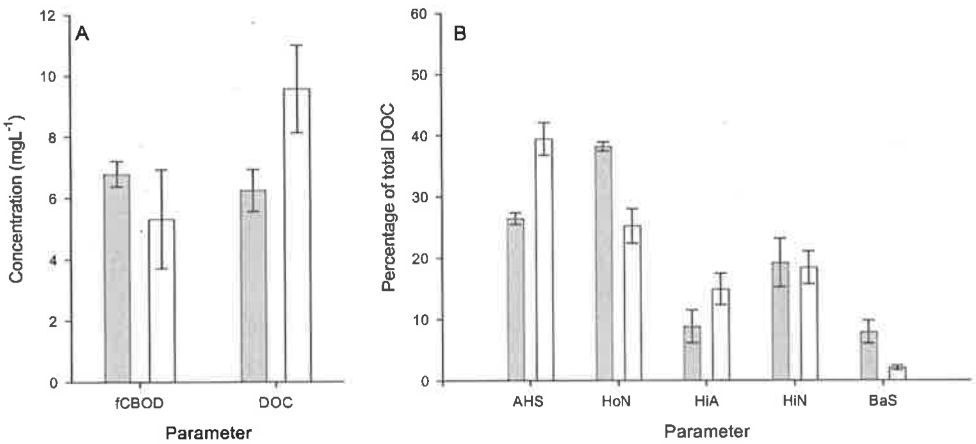

Figure 4.5. [A] 0.45μm filtered CBOD (fCBOD) and DOC; and [B] Ion-exchange fractionated DOC in summer storm-flow samples collected on 20.2.2003. Shaded bars = urban sites, Open bars = rural sites. AHS (aquatic humic substances), HoN (hydrophobic neutrals), HiA (hydrophilic acids), HiN (hydrophilic neutrals), BaS (bases). CBOD:DOC ratios: urban sites 1.11 (±0.07), rural sites 0.55 (±0.12).

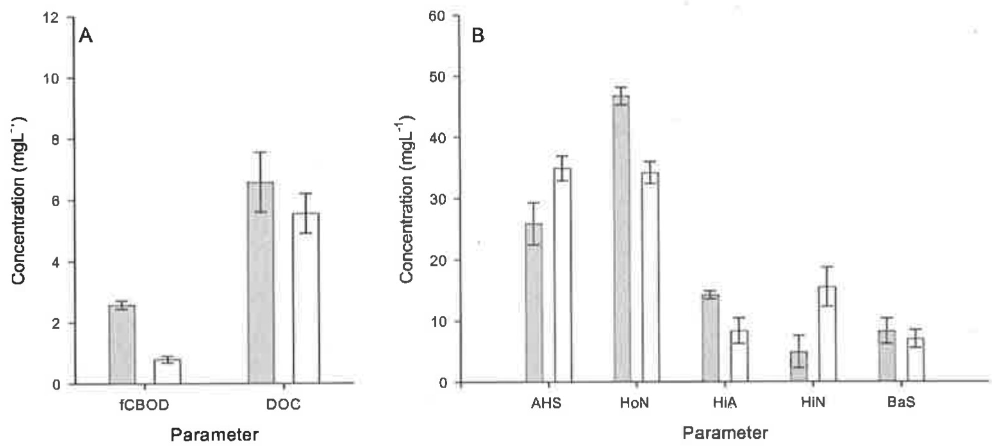

Figure 4.6. [A] 0.45μm filtered CBOD (fCBOD) and DOC; and [B] Ion-exchange fractionated DOC in winter storm-flow samples collected on 24.7.2003. Shaded bars = urban sites, Open bars = rural sites. AHS (aquatic humic substances), HoN (hydrophobic neutrals), HiA (hydrophilic acids), HiN (hydrophilic neutrals), BaS (bases). CBOD:DOC ratios: urban sites 0.42. (±0.07), rural sites 0.15 (±0.02).

Table 4.1. Indicator Species Analysis for summer storm-flow samples collected from the rural and urban streams on 20.2.2003. Indicator fractions with P values < 0.05 are exclusive indicators for DOC from the respective site (rural-urban).

Site	Indicator Fraction		P*
Rural	Hydrophobic Acids	AHS	0.0860
Rural	Hydrophilic Acids	HiA	0.3780
Urban	Hydrophobic neutrals	HoN	0.0300
Urban	Hydrophilic neutrals	HiN	0.9060
Urban	Bases	BaS	0.3050

Table 4.2. Indicator Species Analysis for winter storm-flow samples collected from the rural and urban streams on 24.7.2003. Indicator fractions with P values < 0.05 are exclusive indicators for DOC from the respective site (rural-urban).

Site	Indicator Fraction		P*
Rural	Hydrophobic Acids	AHS	0.1350
Rural	Hydrophilic Neutrals	HiN	0.0540
Urban	Hydrophobic Neutrals	HoN	0.0300
Urban	Hydrophilic Acids	HiA	0.0300
Urban	Bases	Bas	0.6730

Hierarchical Cluster Analysis (Figure 4.7) and NMS ordination (Figure 4.8) of the summer storm-flow DOC fractionation results reveal that there are substantial differences in the composition of the DOC from the different sites within and between the rural-urban groups. The composition of the DOC from 6th creek is distinctly different from the DOC from all other sites. The closest match is is the DOC from the rural site on 3rd creek, (~40% similarity). Furthermore, the composition of the DOC from the rural site on 2nd creek and the urban site on 4th creek are indistinguishable, as is the composition of the DOC from the rural site on 3rd creek and the urban site on 2nd creek.
Analysis of the DOC fractionation data from the winter storm-flow samples using Hierarchical Cluster Analysis (Figure 4.9) and NMS ordination (Figure 4.10) reveals that there are substantial

differences in the composition of the DOC both within and between the rural-urban groups. The level of similarity within the four rural creeks is ~38%, and is ~56% within the four urban creeks. The difference between the rural and urban creeks is approximately 50%.

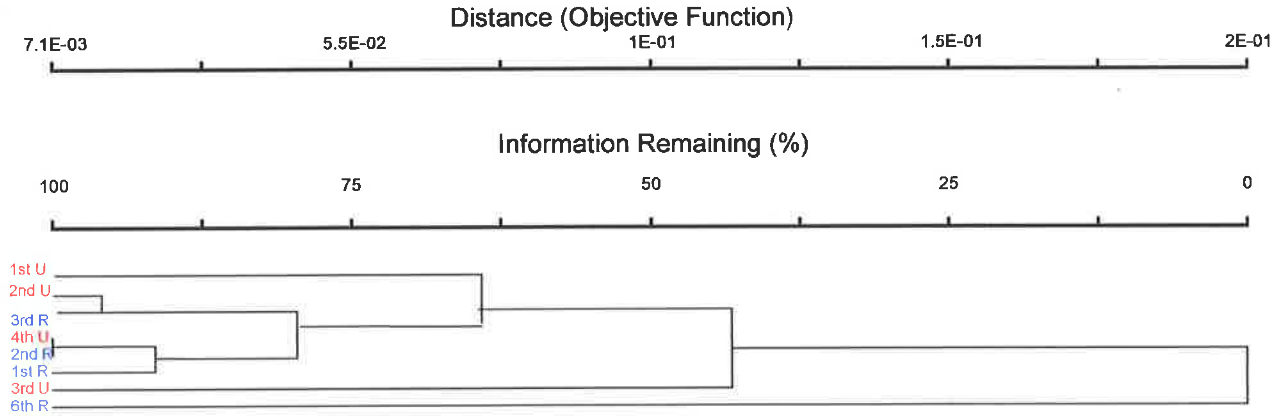

Figure 4.7. Hierarchical Cluster Analysis depicting separation between DOC in samples collected during summer storm flows from the rural and urban streams on 20.2.2003. 1st = 1st creek, 2nd = 2nd Creek, 3rd = 3rd Creek, U = urban sites, R = rural sites.

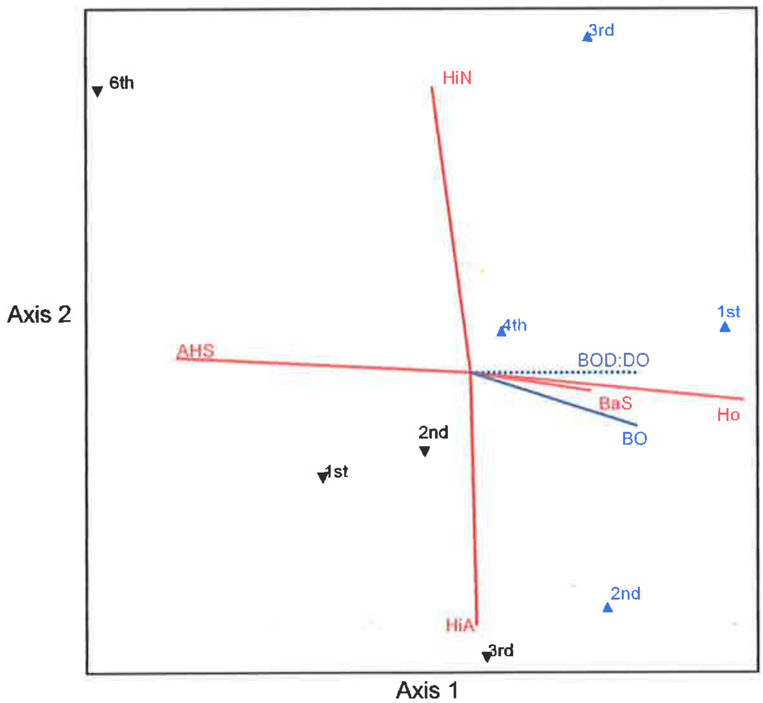

Figure 4.8. NMS ordinations depicting separation between DOC in samples collected during summer storm flows from the rural and urban streams on 20.2.2003. Stress = 4.44%. Blue upright triangles = urban sites. Black inverted triangles = rural sites.

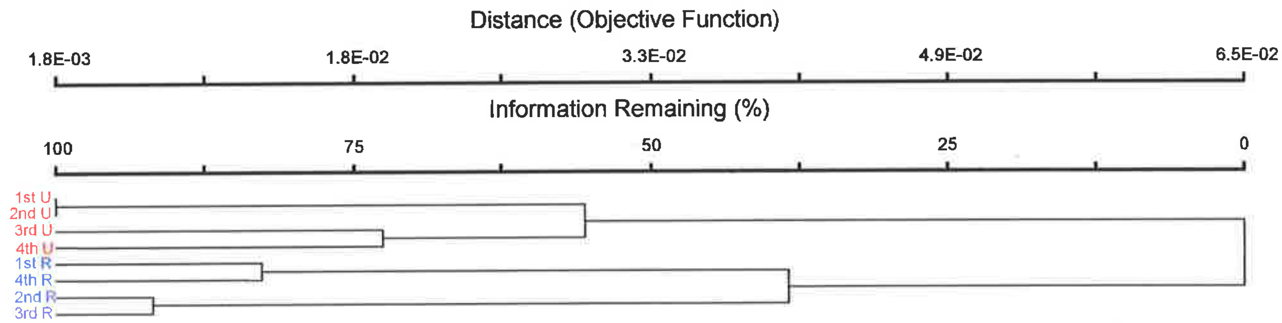

Figure 4.9. Hierarchical Cluster Analysis depicting separation between DOC in samples collected during winter storm flows from the rural and urban streams on 24.7.2003. 1st = 1st creek, 2nd = 2nd Creek, 3rd = 3rd Creek, U = urban sites, R = rural sites.

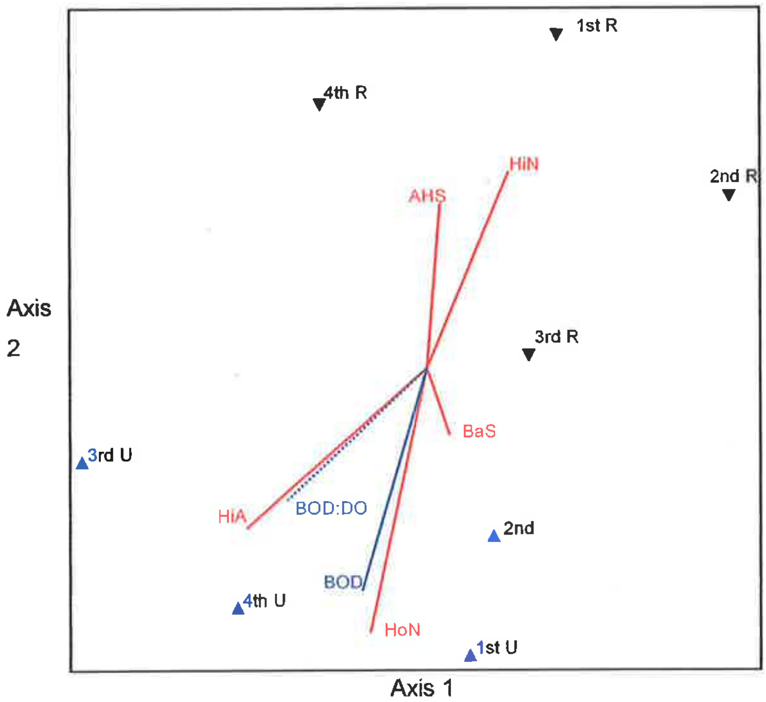

Figure 4.10. NMS ordinations depicting separation between DOC in samples collected during winter storm flows from the rural and urban streams on 24.7.2003. Stress = 4.19%. Blue upright triangles = urban sites. Black inverted triangles = rural sites.

4.5. Discussion

4.5.1 Biochemical Oxygen Demand – Dissolved Organic Carbon ratios: Baseline Data

The baseline data provides a strong indication that there are notable differences in the magnitude of oxygen demand exerted relative to DOC concentration between the urban and rural samples: at the rural sites, the mean BOD:DOC ratio was significantly lower (0.46), than the BOD:DOC ratios observed at the urban sites (1.30). It is difficult to compare the BOD:DOC results of this study with others, as published studies that have assessed the bioavailability of NOM and provide measurements of BOD and DOC across rural-urban gradients are scarce. It is also important to note that the use of BOD:DOC ratios for assessment of DOC bioavailability needs to be viewed with caution, as nitrification may represent a substantial proportion of the oxygen demand observed in the bioassays. The inclusion of a nitrification inhibitor increases the reliability of CBOD:DOC ratios as a method for assessing relative differences in DOC bioavailability.

4.5.2 Carbonaceous biochemical oxygen demand, SUVA, and DOC depletion

The CBOD observed in the storm-flow samples collected on 30th January 2003, was an order of magnitude higher in the urban sites than in the rural sites (19.4 mgL^{-1} cf 1.9 mgL^{-1}). In the winter base-flow samples, there was not a significant difference in CBOD:DOC ratios across the rural-urban gradient. However, in both the summer and winter storm-flow samples, there is a substantial shift in apparent bioavailability across the rural-urban gradient, with the CBOD:DOC ratios observed in the urban sites significantly higher than those observed in the rural sites. The apparent decrease in CBOD:DOC ratios in the rural sites between winter baseflow and stormflow samples (0.24 cf 0.15) may reflect DOC being transported from different sources and through different soil horizons (Buffam *et al.*, 2001).

The interpretation of elevated CBOD:DOC ratios as indicative of increased DOC bioavailability is supported by the measurements of DOC depletion in the winter storm-flow samples. The samples from the urban sites had relatively high CBOD:DOC ratios, and the DOC was depleted in an exponential manner. In comparison, in the rural samples (which had relatively low CBOD:DOC ratios) the DOC was depleted in a slow, linear manner. The CBOD observed in the summer storm-flow samples was an order of magnitude higher, and the CBOD:DOC ratios was 2.75 times higher in the urban sites than in the rural sites. Even in winter, where the difference in DOC concentrations between the rural and urban samples (5.6 mgL^{-1} cf 6.6 mgL^{-1}) was much lower than the difference observed in summer (5.7 mgL^{-1} cf 19.7 mgL^{-1}), the magnitude and rate of the CBOD exerted demonstrates that the DOC in the urban streams during storm-flows could be considered a pollutant rather than a resource. Due to the ephemeral nature of the creeks in the Torrens Catchment, the impacts of this shift in DOC bioavailability would be most pronounced during rain events in summer, when there is typically no dry weather base-flow in the streams, and little or no rural stream flow generated from small rain events to dilute runoff from impervious surfaces.

The bioassays also demonstrate that although the oxygen demand curves tend to asymptote by day 5, the standard 5-day biochemical oxygen demand test would underestimate the oxygen demand exerted over a 10-day period. For the winter base-flow samples the 10-day oxygen demand would be underestimated for the rural and urban sites by 19% and 16% respectively. For the winter storm-flow samples, the 10-day oxygen demand would be underestimated by approximately 25% for both rural and urban sites. The suggestion that a 5-day incubation period underestimates BOD is supported by Hufschmid *et al.* (2003), who demonstrated that in samples containing inhibitory compounds (e.g. copper), a bioassay period of 5 days underestimates BOD, and suggested that 10 or even 15 days may be required to obtain a representative result.

Søndergaard and Middleboe (1995) consider DOC that is degraded within 1-2 weeks as labile. The DOC depletion observed in the samples collected on 24th July 2003 suggests that the DOC from the rural streams is relatively recalcitrant as very little is depleted within the ten-day bioassay period. In contrast a substantial proportion of DOC from the urban streams would be classified as labile. The proportion of DOC that could be considered labile (depleted within 10 days) in the rural samples (10.8%), and in the urban samples (53.9%) fits within the lower and upper end respectively of the proportion of total DOC that is reported by Meyer (1994) as being labile (less than 1 to greater than 50%). Consequently, the results from this study demonstrate that urbanisation induces a substantial shift in the bioavailability of DOC in stream water.

The results of the $SUVA_{254}$ analysis did not reveal any substantial difference that could be considered to define DOC between the rural and urban sites. Additional absorbance data performed as scans on samples collected in the generation of baseline data, measuring absorbance at 10nm increments between 190-750 nm, failed to demonstrate a substantial difference between urban and rural stormwater samples (Wallace *et al.*, 2002). This indicates that $SUVA_{254}$ was insensitive to the shift in DOC composition observed in the ion-exchange fractionation. Fukushima *et al.* (1996) also observed that $SUVA_{260}$ measured on lake, river and pond samples did not change substantially with DOC biodegradation. The results from these separate studies support the conclusion of Weishaar *et al.* (2003), that generalized properties such as UV absorbance may not be effective for determining the chemical composition and reactivity of DOC, particularly when considering samples from a wide range of environments.

4.5.3 Relationship between BOD, bDOC and DOC composition: Tributary streams

DOC in rivers is typically comprised of humic compounds, polysaccharide carbohydrates and amino acids (Volk *et al.*, 1997), compounds classified in the groups AHS, HiN and BaS respectively with the ion-exchange fractionation technique used in this research. These compounds are primarily produced from leaching of DOC from leaf litter and from subsurface and groundwater inflows through organic rich soils (Boulton *et al.*, 1998). Thurman (1985) reports that AHS is the dominant component of DOC in rivers. Imai *et al.* (2001) report that the DOC in a forest stream (in Japan) is dominated by AHS, and in a mixed land use catchment, riverine DOC is dominated by AHS and HiA. Rain falling on impervious surfaces generates large volumes of water moving at relatively high velocities, and may remobilise compounds such as herbicides, pesticides, and surfactants (e.g. HoN compounds) that have been sprayed onto paved and concrete areas to control weeds (Williamson, 2003).

The DOC in the rural streams in this study is characterised by an elevated proportion of AHS and HiA in summer, and HiN and AHS in winter. In contrast to the rural streams, the DOC from the urbanised streams was characterised by HoN (hydrocarbons, pesticides, carbonyl compounds, LAS, large cellulose polymers) in summer, and by HoN and HiA (fatty acids, sugar acids, hydroxyl acids) in winter. The significant difference in DOC composition between the rural and urban sites in both the summer and winter storm-flow samples demonstrates that urbanisation induces a substantial shift away from the naturally occurring range of DOC compounds, towards synthetic compounds (e.g. synthetic detergents (LAS) and pesticides). The observation that in addition to significant variation in DOC composition between the rural and urban creeks, there is substantial variation in

DOC composition within the rural and urban streams, combined with the observation that the level of variation changes between seasons (winter-summer) demonstrates the significance of catchment specific attributes (e.g. land use, rainfall, vegetation, antecedent dry period, overland/subsurface flow paths, drainage connection) in regulating the composition of DOC within any given stream reach.

The elevated proportion of HoN in the urban samples in both seasons provides a strong indication that variation in percent composition of HoN compounds may be responsible for the variation in CBOD:DOC ratio's. When the values for CBOD and CBOD:DOC are overlaid on the NMS ordinations, it is evident that in summer, there is a strong correlation between the proportion of HoN and BaS, and both CBOD and CBOD:DOC ratios. In winter, there is a strong correlation between the proportion of HoN and BOD, and a strong correlation between CBOD:DOC and HiA. The indication that HoN and BaS compounds are responsible for the increased bioavailability of DOC from the urban streams is supported by Sonnenberg and Holmes (1998), who found a decrease in the proportion of hydrophobic neutral/base compounds during treatment of paper mill wastewaters in aerobic ponds. This indication that HoN compounds are easily biodegraded is also supported by the results of Imai *et al.* (2001), who observed a substantial decline in the proportion of HoN compounds between the influent and effluent from a domestic sewage treatment plant.

4.5.4 General Discussion

In forested catchment streams of southeastern Australia, baseflow is primarily driven by either sub-surface or ground water flows. Overland flow into streams occurs infrequently e.g. during storms that either saturate or exceed the infiltration capacity of the soil (Walsh *et al.*, 2004). In contrast, the proliferation of impervious surfaces in urbanised catchments reduces the surface area available for infiltration of rainfall into the soil, and the removal of topsoil during development reduces the infiltration capacity for the remaining surface area (Walsh *et al.*, 2004). The increased velocity of surface run-off (Paul and Meyer, 2001), and the direct connection (via constructed stormwater infrastructure) that often occurs between impervious surfaces and receiving waters (Walsh, 2002) in urbanised catchments shifts the dominant flow path for rain falling in the catchment into streams, from subsurface and groundwater flow to overland flow (Walsh *et al.*, 2004).

The shift in dominant flow paths in urbanised catchments from subsurface and groundwater flows to overland flow reduces the potential for interception and processing of resources via multiple-interception pathways (Brookes *et al.*, 2005) that would normally occur during transfer of water from the terrestrial component of the catchment into the receiving water. Consequently, in addition to changes in DOC composition associated with changes in land use due to the introduction of compounds that simply are not present, or are only present at trace levels (Walsh *et al.*, 2004) in rural catchments, the relatively high CBOD:DOC ratios observed in the urban streams may be a reflection of a higher proportion of unprocessed DOC reaching the creeks. If HoN is, as indicated by the results of Imai *et al.* (2001) and Sonnenberg and Holmes (1998), readily bioavailable and subsequently susceptible to interception and processing during sub-surface and groundwater flows, improving non-structural best management practices (e.g. use and disposal of chemicals), and reducing the direct connection between impervious surfaces and receiving waters must, as suggested by Walsh (2003), be addressed as a first priority for restoring water quality in urban streams.

The current chapter assesses the composition of the initial DOC pool in relation to the utilisation of the bulk DOC pool, but does not investigate the utilisation of individual fractions. The following chapter (Chapter 5) extends the current work, and provides an assessment of the microbial utilisation of the various DOC fractions in an urban weir pool.

Chapter 5: Characterisation of dissolved organic carbon bioavailability in an urban weir pool

5.1. Introduction

Highly disturbed urban ecosystems such as small, shallow lakes are prone to recurrent deoxygenation (Douglas and O'Brien, 1987) via episodic inputs of oxygen demanding organic material. The Torrens Lake (a shallow urban weir pool on the main river channel) is an example of such a system, where the episodic input of stormwater containing high concentrations of DOC has been linked to complete water column deoxygenation within 24 hours (Wallace *et al.*, 2002). Previous work (Chapter 4) has demonstrated that urbanisation induces a substantial shift in the composition and bioavailability of DOC in stream water. For example, in streams with predominantly rural catchments, 11% of the DOC is depleted within 10 days. In contrast, 54% of the DOC in streams from the heavily urbanised zones of the Torrens catchment is depleted within the same time span.

The DOC bioavailability values reported (Chapter 4) for opposing land uses fit within the lower and upper end respectively of the proportion of total DOC that is reported by Meyer (1994) as being labile (less than 1 to greater than 50%), and demonstrate that urbanisation induces a substantial shift in the composition and bioavailability of DOC in stream water. Although it is intuitive that urban stormwater inflows would induce an observable shift in the range of organic compounds present in receiving waters such as weir pools, the impacts of stormwater inflows on DOC composition and quality in receiving waters are unclear and not easily defined. Despite some notable exceptions which compare the composition of DOC flowing into receiving waters from contrasting land use areas (e.g. Imai *et al.*, 2001), there is a distinct lack of studies on the impact of stormwater inflows on DOC composition and bioavailability. However, evaluation and understanding of changes to the ambient DOM pool induced by recurrent disturbances such as rain events is essential to the efficient management of waterways.

This project extends the work of the previous chapter (Chapter 4), by investigating the influence of a stormwater inflow on carbon processing in a weir pool on the main river channel. The project tests the hypothesis that the inflow of stormwater would induce a significant shift in the concentration, composition and bioavailability of DOC in the Torrens Lake. It is anticipated that the inflow would not only increase the total concentration of DOC, but also alter the composition, and subsequently increase the proportion of readily bioavailable material in the bulk DOC pool. Furthermore, it is proposed that the increased availability of labile organic material would stimulate heterotrophic metabolism and generate a substantial oxygen debt in Torrens Lake. The hypothesis was tested via time series measurements of biochemical oxygen demand, DOC concentration, composition, and *in-situ* dissolved oxygen concentration, prior to, and in the days following a rain event inflow.

5.2. Methodology

5.2.1 Site Description

A detailed description of the Torrens Catchment is provided in Chapter 2. The Torrens Lake is a shallow weir pool in the Adelaide Central Business District. The lake is formed by a weir constructed on the Torrens River in the 1880's, and has a capacity of 420 ML, a surface area of 0.16km^2, and a mean depth of 2.6m (Regel, 2003). Urban stormwater is directed into the tributary streams, the river and the lake via constructed stormwater infrastructure. These inflows cause the lake to function as a stormwater detention basin for the catchment. The lake suffers numerous water quality problems including anoxia and recurrent blooms of toxic cyanobacteria.

The rain event that was sampled occurred on 28th March 2004, with a total rainfall of 16 mm being recorded by the Bureau of Meteorology at Kent Town (~ 2km from the lake). The antecedent dry period was 20 days when 8mm of rain was recorded. Prior to the rain event there was no substantial flow in the main river channel, and no inflow into the lake via the tributary streams (water from the rural catchment is harvested in a series of reservoirs for potable supply, and in addition to the river being highly regulated in the urban zone, the tributary streams are highly ephemeral and typically do not flow during the summer months). Consequently, due to the proliferation of impervious surfaces in the urbanised sub-catchments, the rain event inflow to the lake was dominated by runoff from impervious surfaces in the urbanised components of the catchment.

5.2.2 Sample Collection

Samples were collected from the inlet (east) and outlet (west) end of the Torrens Lake as depth integrated samples, using a 25mm internal diameter column sampler lowered to within 100-200mm of the lake sediments. Sufficient column sampler shots were transferred to a single 5L PTFE container to produce a 4.5L composite sample. Three spatially separated (>10 m) and independent 4.5L composite samples were collected from each end of the lake. The samples were immediately stored in the dark in an ice filled, insulated box, prior to return to the laboratory.

The PTFE containers used for sample collection had been pre-cleaned according to the protocol described in Chapter 2. Upon return to the laboratory the samples for analysis of DOC and oxygen demand driven by dissolved organic material (<0.45µm) were homogenised by inversion mixing, pre-filtered through pre-washed (see Chapter 2) Whatman GF/C filters and subsequently filtered through Whatman PVDF 0.45µm membrane filters.

5.2.3 Carbonaceous Biochemical Oxygen Demand & Dissolved Organic Carbon Metabolism – Laboratory Study

Samples for analysis of Carbonaceous Biochemical Oxygen Demand (CBOD) and DOC metabolism were collected during dry weather (DW) prior to, and during the wet weather (WW) induced stormwater inflow on 28 March 2004. Analysis was performed on 0.45µm filtered samples, as previous research (Chapter 3) had demonstrated that the majority of the oxygen demanding organic material in urban stormwater from the catchment was contained in the size fraction <0.45µm. Analysis for CBOD and DOC metabolism was performed using a time series bioassay based on the standard test (Standard Method 5210B) for biochemical oxygen demand (Eaton *et al.*, 1995). Dissolved oxygen and DOC measurements were made on independent samples at times 0, 1, 2, 3, 4, 5, 7 and 10 days. The consecutive measurements provide time series curves for CBOD and DOC biodegradability. Measurements of CBOD were obtained by inhibiting nitrification via the addition of 3mg 2-chloro-6-(trichloro methyl) pyridine (TCMP) to each individual BOD bottle. Dissolved oxygen was measured using a WTW (Wissenschaftlich-Technische Werkstätten GMBH & Co. KG) CellOx 325 oxygen sensor attached to a WTW Oxi 330i dissolved oxygen meter. A detailed description and schematic of the protocol used is presented in Chapter 2.

Supplementary levels of nitrogen (N) and phosphorus (P) were added to the bioassays to ensure that measurements of CBOD and DOC biodegradation were representative of the biodegradability of the DOC pool, and that microbial metabolism was not limited by ambient concentrations of N or P (Elser *et al.*, 2000; Søndergaard and Middelboe, 1995). Sodium Nitrate ($NaNO_3$) was utilised as the supplementary nitrogen compound. Di-potassium hydrogen orthophosphate (K_2HPO_4) was utilised as the supplementary phosphorus compound. The amount of $NaNO_3$ and K_2HPO_4 added was calculated to provide minimum initial concentrations of 1000µg N L^{-1} and 100µg P L^{-1} respectively.

5.2.4 In-situ study of dissolved oxygen and DOC concentrations

In-situ dissolved oxygen concentration was measured using a YSI (Yellow Springs Instrument Co. Inc) 5739 oxygen sensor attached to a TPS Pty Ltd Model WP-82Y Dissolved Oxygen-Temperature meter. Vertical dissolved oxygen profiles were measured at each site by lowering the probe through the water column, and recording the dissolved oxygen concentration at 0.5 m intervals between the water surface and the lake sediments.

Samples were collected pre-rain during dry weather (DW), during the wet weather (WW) stormwater inflow, and post-rain at time steps of 1,2,3,4,5,8 and 10 days. These samples were analysed for bulk DOC concentration, and fractionated using ion-exchange resins to provide a time series assessment of the metabolism of both bulk DOC and individual DOC fractions. Due to logistical constraints, ion-exchange fractionation was only performed on the DW, WW and the 1, 3, 5 and 10-day post rain samples. The DOC present in the samples was characterised via ion exchange fractionation into 5 distinct macro-fractions utilising minor modifications to a technique described by Imai *et al.* (2001) which is based on the classic technique developed by Leenheer (1981). A detailed description of the ion exchange technique utilised is provided in Chapter 2.

The samples were fractionated utilising three ion-exchange resins: Supelite™ DAX-8, Biorad AG®MP50, and Biorad AG®MP1. The five fractions produced were hydrophobic acids (AHS; e.g. humic and fulvic acids), hydrophobic neutrals (HoN; e.g. large cellulose polymers, hydrocarbons, pesticides, LAS (linear alkylbenzene sulfonate) and carbonyl compounds), hydrophilic acids (HiA; e.g. fatty acids, sugar acids, hydroxyl acids), bases (e.g. aromatic amines, proteins, amino acids, aminosugars), and hydrophilic neutrals (HiN e.g. carbohydrates, oligosaccharides, polysaccharides, alcohols, ketones). The relative composition of these fractions generates a physicochemical signature for the water sample. The DOC composition was compared to the CBOD results to assess if there was a correlation between shifts in DOC composition and oxygen demand.

5.2.5 Dissolved Organic Carbon

DOC concentrations were determined utilising an SGE ANATOC II total organic carbon analyser. DOC analysis was performed in non-purgeable organic carbon mode, according to the protocol described in Chapter 2.

5.2.6 Data Analysis

Regression curves displayed in graphs are fitted to means; error bars are ± 1 standard error (SE). All univariate statistical tests were performed using the package JMP In version 3.2.6 (SAS Institute Inc. 1996). Normality was tested using the Shapiro-Wilk W Test, and the equality of variances with the Levene test. Square root and log transformations were applied (unsuccessfully) to all data sets exhibiting non-normal distribution and unequal variances. Those data sets were subsequently analysed using non-parametric (Wilcoxon/Kruskal-Wallis) analysis. Statisitical values (df, Chisq and P values) reported are for Wilcoxon/Kruskal-Wallis unless stated otherwise. Differences in DOC composition between the sites were analysed using indicator species analysis (Dufrene and Legendre, 1997) and non-metric scaling (NMS) ordination. Single factor NPMANOVA was used to compare the composition of DOC between samples. Indicator species analysis and NMS ordinations were performed using PCOrd; version 4.28 (McCune and Mefford, 1999). NPMANOVA was undertaken using the procedure described by Anderson (2001). Bray-Curtis distances were used to calculate the similarity matrix for all multivariate statistical analyses (Bray and Curtis, 1957) and two-dimensional ordination solutions with stress lower than 20% were deemed acceptable (sensu (Clarke, 1993). For all statistical tests $\alpha = 0.05$.

5.3. Results

5.3.1 Carbonaceous Biochemical Oxygen Demand & DOC depletion – Laboratory Study

The CBOD exerted by the dry-weather (DW) and wet weather (WW) samples is shown in Fig 5.1. In all samples, the CBOD is exerted in an exponential manner, and had reached an asymptote at day

10. However, the oxygen demand observed in the samples collected at the inlet during DW (Fig. 5.1B) was exerted at a substantially higher rate than in any of the other samples. In keeping with standard methods, CBOD results will be compared as measured at day 5, and referred to as $CBOD_5$. The DW samples collected from the outlet end of the lake exerted the lowest $CBOD_5$ (0.9 mgL^{-1}±0.04), followed by the WW samples from the outlet (1.1mgL^{-1}±0.3), the DW samples from the inlet (1.6 mgL^{-1} ±0.3), and the WW samples from the inlet (17.6 mgL^{-1}±0.6). Although there was an order of magnitude increase in $CBOD_5$ between the DW and WW samples collected from the inlet, the $CBOD_5$ exerted by the samples collected from the outlet zone did not change markedly (df_1, ChiSq = 0.196, P = 0.658) between the DW and WW sampling periods.

Inflowing stormwater increased the concentration of DOC at the inlet from a DW concentration of 8.6mgL^{-1}, to a WW concentration of 18.8 mgL^{-1}. At the outlet however, there was no discernable difference in DOC concentration between the DW and WW sampling period (9.4 mgL^{-1} cf 9.2mgL^{-1}). The bioassay curves (Fig. 5.2) demonstrate that at day 5, the DOC in the samples collected from the inlet zone during DW was not depleted (df_1, ChiSq =2.333, P = 0.127). In contrast, the DOC in the WW samples from the inlet was significantly depleted (df_1, ChiSq =3.86, P = 0.050), and the depletion of the DOC occurred in an exponential manner. In comparison, the DOC in the samples collected from the outlet zone was not depleted in either the DW (df_1, ChiSq = 2.333, P = 0.127) or the WW samples (df_1, ChiSq =0.048, P = 0.827).

5.3.2 In-situ study of dissolved oxygen and DOC concentrations

At the lake inlet, DO concentrations (Fig. 5.3A) decreased from DW levels of 10.4 mgL^{-1} to 8.5 mgL^{-1} at the time of the WW inflow. By day 1 (19 hours post inflow) DO had decreased to 6 mgL^{-1}, and concentrations less than 3 mgL^{-1} were recorded from day 2-5 inclusive. At day 8, water column DO concentrations (7.1 mgL^{-1}) at the inlet had increased, but were still below saturation (9.3 mgL^{-1}) at the recorded water temperature (18.6°C). At the lake outlet, although DO decreased from 6.2 mgL^{-1} during DW, to a minimum of 2.4 mgL^{-1}on day 3, a decrease in DO was not observed until day 2. DO concentrations at the outlet began to recover quicker than at the inlet. The time series analysis of DOC concentrations in the lake is depicted in Fig 5.3B. At the inlet, *in-situ* DOC concentrations increased from 6.7 mgL^{-1} during DW, to 18.2 mgL^{-1} during WW. Concentrations of DOC at the inlet zone subsequently decreased in an exponential manner, and by day 4, had stabilised at pre-rain concentrations. At the outlet, an increase in DOC concentration was not evident between the DW and WW samples. However, an increase in DOC was evident in the samples collected on day 1, when DOC concentrations increased from a pre-rain concentration of 7.7 mgL^{-1}, to 9.5 mgL^{-1}. By day 2, DOC concentrations at the outlet (7.9 mgL^{-1}) had returned to pre-rain levels.

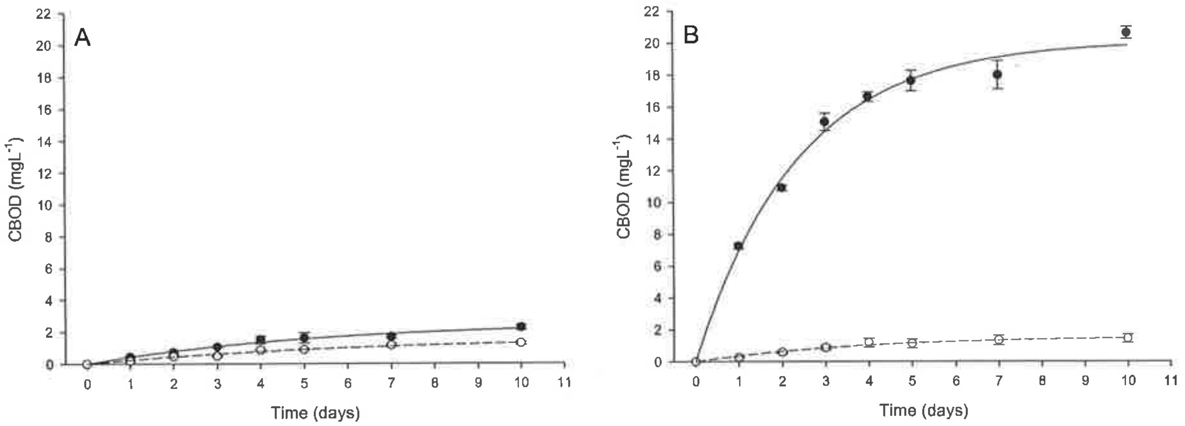

Figure 5.1. Ten day time series of CBOD in samples collected [A] during DW, and [B] during the WW inflow of stormwater on 28.3.2004. Solid circles = inlet end of lake. Open Circles = outlet end of lake. Oxygen demand curves: Inlet end of lake ($y = 4.76(1-e^{-0.133\,x})$, $r^2 = 0.979$, $F = 274.57$, $P = <0.0001$); outlet end of lake ($y = 1.26(1-e^{-0.185\,x})$, $r^2 = 0.988$, $F = 506.94$, $P = <0.0001$). Error bars are 1 ±S.E.

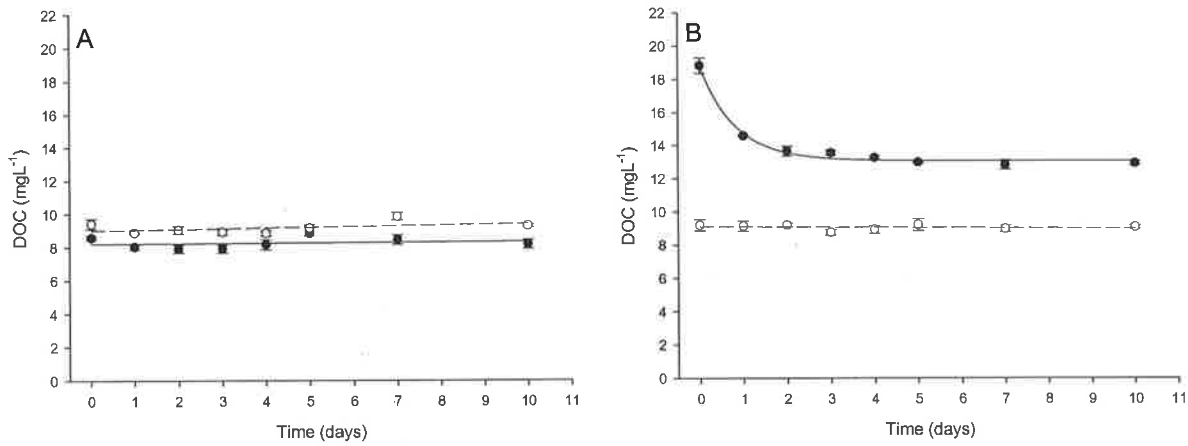

Figure 5.2. Ten day time series of DOC depletion in samples collected [A] immediately before, and [B] during the inflow of stormwater on 28.3.2004. Solid circles = inlet end of lake inlet. Open circles = outlet end of lake. DOC metabolism: Inlet end - DW ($y = 9.004 + 0.042\,x$, $r^2 = 0.163$, $F = 1.1704$, $P = 0.321$); Outlet end - DW ($y = 8.198 + 0.014\,x$, $r^2 = 0.020$, $F = 0.1204$, $P = 0.741$). Inlet end – WW ($y = 13.06 + 5.736e^{-1.224x}$, $r^2 = 0.991$, $F = 260.64$, $P = <0.0001$), Outlet end – WW ($y = 9.099 - 0.011\,x$, $r^2 = 0.0472$, $F = 0.297$, $P = 0.606$).

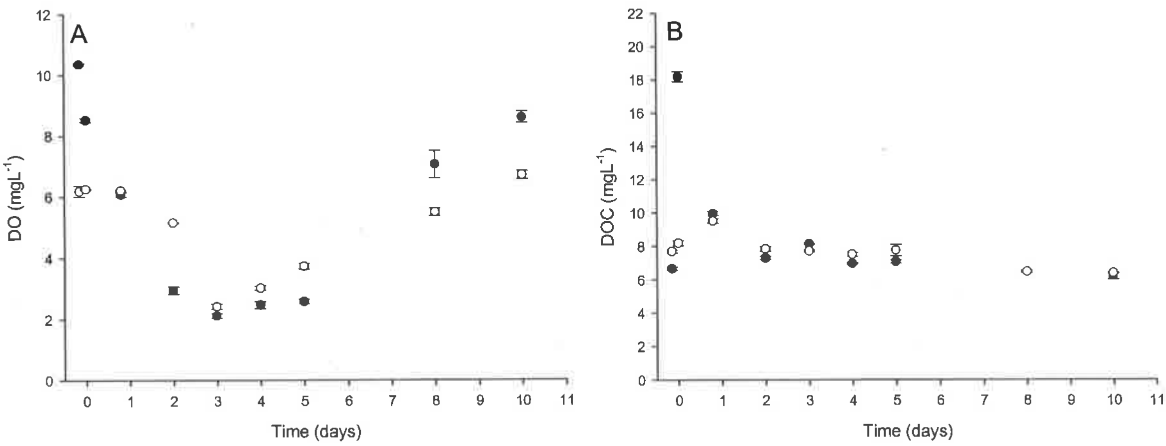

Figure 5.3. Ten day time series of [A] dissolved oxygen and [B] DOC in Torrens Lake immediately prior to (time = -0.15 days), at (time = 0 days) and subsequent to (time > 0 days) the inflow of stormwater on 28.3.2004. Solid circles = lake inlet. Open Circles = outlet end of lake. Values of in-situ dissolved oxygen concentrations are means of depth-integrated readings taken at 3 sites. Error bars are 1 ±S.E.

Ion exchange fractionation of the DOC in the samples into five distinct macro-fractions reveals that there were significant differences (NPMANOVA, df =11, F = 60.8689, P = 0.0001) in the composition of the DOC over the 10-day sampling period. Prior to the inflow of stormwater, the differences in the DOC pool between the inlet and outlet end of the lake were confined to slightly higher concentrations of AHS (0.3 mgL^{-1}), HoN (0.5 mgL^{-1}) and HiA (0.3 mgL^{-1}) at the outlet (Fig. 5.4). In the WW samples, the concentration of HiA at the inlet increased from 0.2 to 5.9 mgL^{-1} (a factor of 34.9), AHS increased from 3.6 to 8.5 mgL^{-1}, and HiN slightly from 1.9 to 3.2 mgL^{-1}. A slight increase in BaS (0.2 to 0.4 mgL-1) and decrease in HoN (0.7 to 0.3 mgL^{-1}) was also evident (Fig. 5.4). In contrast, the changes observed between DW and WW at the outlet were of a substantially lower magnitude; HiA increased from 0.5 to 0.8 mgL^{-1}, AHS increased from 3.9 to 4.1 mgL^{-1}, BaS increased from 0.2 to 0.3 mgL^{-1}. HiN decreased from 1.9 to 1.7 mgL^{-1}, and HoN increased from 1.2 to 1.4 mgL^{-1}.

The concentration of the three fractions that increased markedly (AHS, HiA and HiN) between DW and WW, decreased in the subsequent days. HoN decreased from a pre-rain concentration of 0.7 mgL^{-1} to a WW concentration of 0.3 mgL^{-1}, and then increased to a maximum of 2.4 mgL^{-1} over the subsequent days. BaS concentrations were stable (df = 5, ChiSq = , P = 0.0495) over the 10 days.

Indicator species analysis (Table 5.1) reveals that the samples collected from the inlet end of the lake during WW inflows are characterised by a high proportion of AHS, HiA, and HiN. There are no significant indicator fractions for the DW samples from either the inlet or outlet; however, HoN is a significant indicator for the DOC at the outlet on day 5.

Hierarchical cluster analysis (Fig. 5.5) indicates that the differences in DOC composition between the inlet and outlet during DW equate to a variation of less than 20%. In comparison, the composition of DOC in samples collected from the inlet zone during WW is distinctly different (~80%) from that at the inlet during DW, and that at the outlet during both DW and WW. The composition in the inlet WW samples is also substantially different from that at both ends of the lake at all other times. The NMS ordination (Fig. 5.6) depicts the shift in DOC composition at the inlet during WW away from that present during DW, and that observed at the outlet during both DW and WW. The differences between the DW and WW samples at the outlet are relatively small (<20%), indicating that the composition of DOC at the outlet did not change markedly between the DW and WW sampling periods. By day 1, the DOC composition at both ends of the lake had merged substantially (Fig 5.6), and the differences were confined to ~16%. The composition of the samples at the inlet and outlet separated slightly at day 3 (Fig. 5.5, 5.6). DOC composition at the inlet on days 5 and 10 and the outlet on days 3, 5, and 10 merge, and are separated by differences of ~30% (Fig. 5.5). On day 10, DOC composition from the inlet and outlet form a distinct group (Fig. 5.6), with differences of <15% (Fig. 5.5).

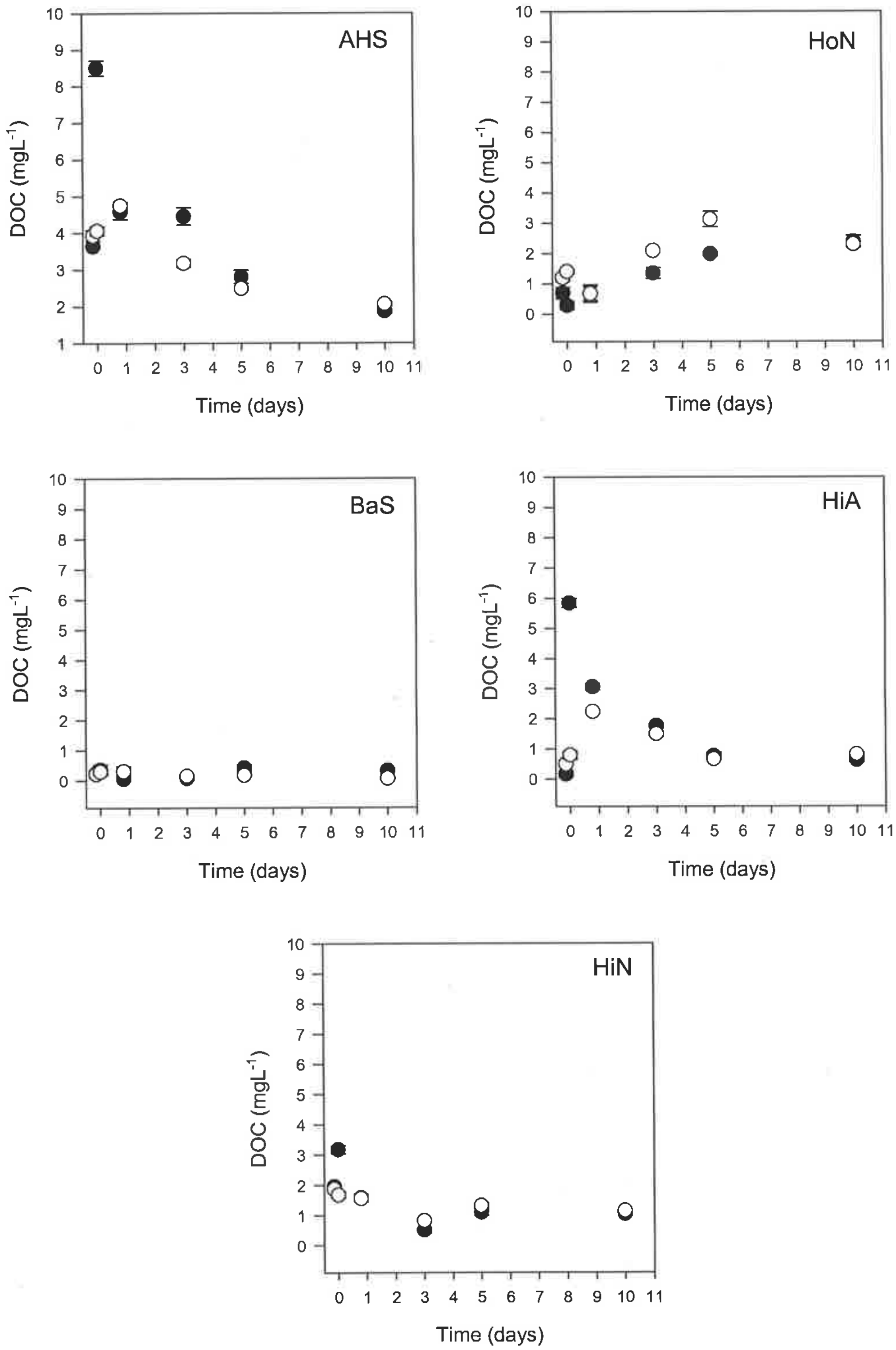

Figure 5.4. Ten-day time series of DOC fractions in samples collected from the Torrens Lake immediately prior to (time = -0.15 days), at (time = 0 days) and subsequent to (time > 0 days) the inflow of stormwater on 28.3.2004. Solid circles = lake inlet. Open Circles = outlet end of lake. AHS = aquatic humic substances, HoN = hydrophobic neutrals, BaS = bases, HiA = hydrophilic Acids, HiN = hydrophilic neutrals. Error bars are 1 ±S.E.

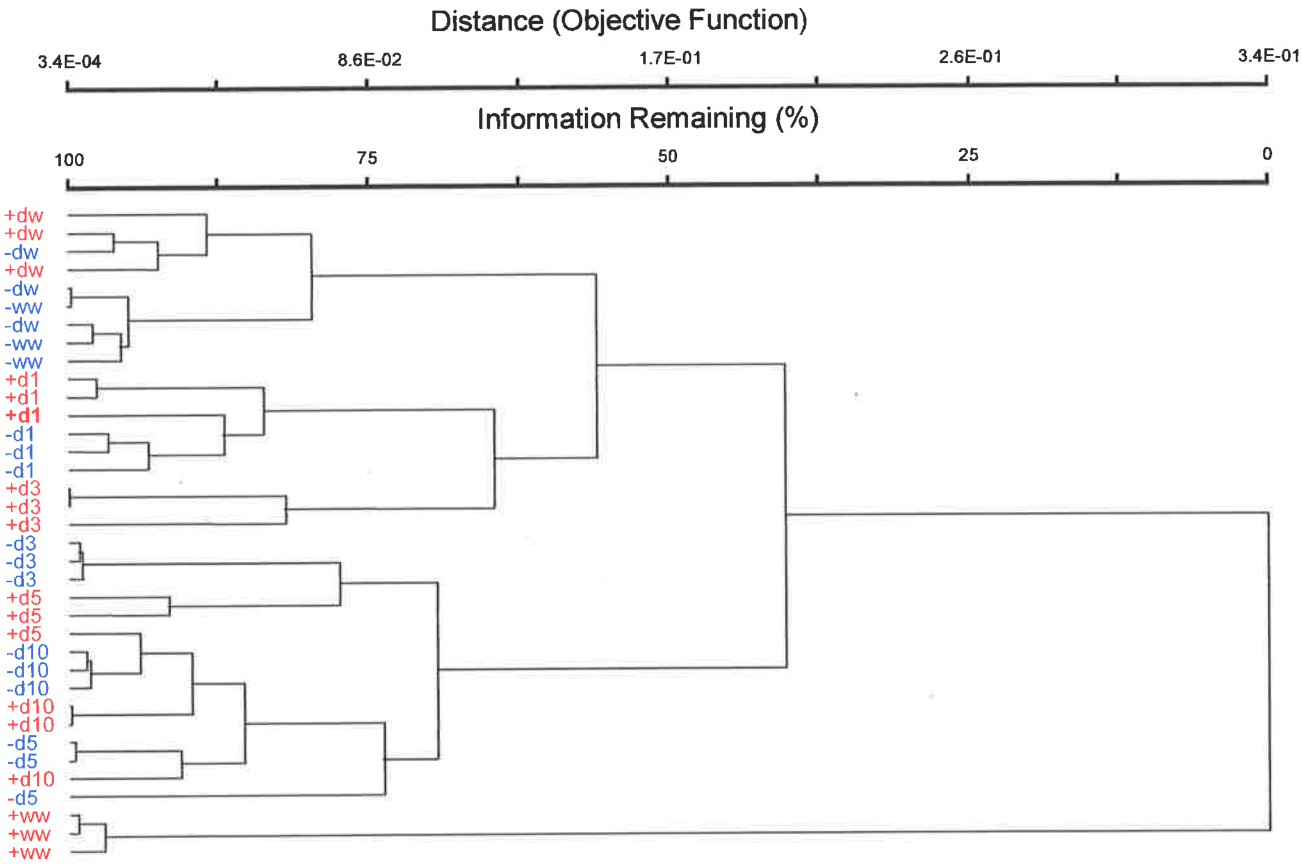

Figure 5.5. Hierarchical Cluster Analysis depicting separation between DOC in samples from inlet end of lake and outlet end of Torrens Lake throughout the 10 day sampling period. Red text prefixed with a (+) represent inlet samples, blue text prefixed with a (-) represent outlet samples. dw = dry weather, ww = wet weather, d1 = day 1, d3 = day 3, d5 = day 5, d10 = day 10.

Table 5.1. Indicator Species Analysis for water samples collected from Torrens Lake over the 10-day sampling period. Indicator fractions with P values < 0.05 are exclusive indicators for DOC from the respective sites.

Site	Indicator Fraction		P*
Inlet WW	Hydrophobic acids	AHS	0.0030
Inlet WW	Hydrophilic acids	HiA	0.0030
Inlet WW	Hydrophilic neutrals	HiN	0.0030
Inlet Day 5	Bases	BaS	0.3330
Outlet Day 5	Hydrophobic neutral	HoN	0.0040

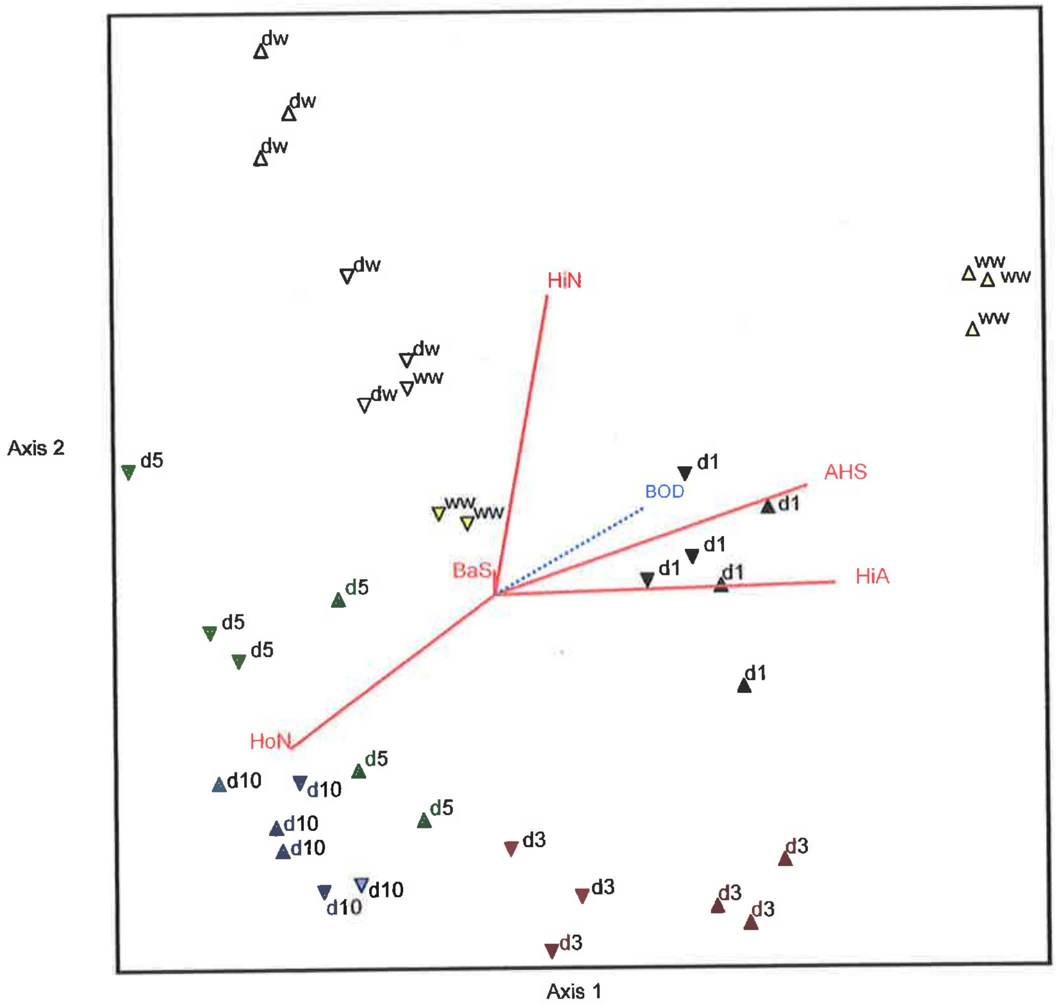

Figure 5.6. NMS ordination depicting separation between DOC in samples from inlet end of lake (upright triangles) and outlet end of lake (inverted triangles). Stress = 5.02%. Open Triangles = dry weather (dw), yellow triangles = wet weather (ww), solid triangles = day 1, red triangles = day 3, green triangles = day 5, blue triangles = day 10. Vectors: AHS = aquatic humic substances, HoN = hydrophobic neutrals, BaS = bases, HiA = hydrophilic Acids, HiN = hydrophilic neutrals. BOD = biochemical oxygen demand.

5.4. Discussion

5.4.1 Integrated discussion on laboratory and in-situ studies of DOC dynamics

Prior to the rain event, DOC concentrations, biodegradability and oxygen demand were not substantially different between the inlet and outlet zones of the lake. Hierarchical cluster analysis (HCA) and indicator species analysis (ISA) indicates that differences in the DOC pool between the inlet and outlet during DW were less than 20%. It is suggested that these differences are not substantial enough to be indicative of a major difference in the composition of the DOC pool between the two ends of the lake. Dissolved oxygen concentrations (10.4 and 6.2mgL^{-1}) were above the environmental trigger value (6.2-6.8mgL^{-1}) presented in the ANZECC/ARMCANZ guidelines (2000) for urban lakes at the water temperature range recorded during the sampling period (17-21°C). The failure to observe a substantial difference between the pre-rain samples collected from the two ends of the lake is considered to be a reflection of the hydrology of the lake. The ephemeral nature of the tributary creeks, and the high level of regulation on the main river channel generate long residence times in the lake, particularly during summer. During periods of little inflow to the lake, wind driven or density driven currents generated by differential heating are potentially more influential on water movement and mixing in the weir pool than downstream flow.

The inflowing stormwater had an immediate, major impact on the concentration, bioavailability and composition of organic matter at the inlet. DOC concentrations increased by a factor of 2.7 (from 6.7 mgL^{-1} to 18.2 mgL^{-1}) and the laboratory bioassays (Fig. 5.2) demonstrate that the biodegradability of the bulk DOC pool increased substantially, with more than 27% of the DOC present in the WW samples being oxidised within 24 hours. The degradation of the DOC increased the $CBOD_5$ exerted by the samples at the inlet, from 1.6 to 17.6 mgL^{-1}, with CBOD:DOC ratios increasing from 0.19 (±0.03) to 0.94 (±0.06). Between the DW and WW sampling periods, dissolved oxygen at the inlet zone decreased from 10.4 mgL^{-1} to 8.5 mgL^{-1}.

The composition of the DOC at the inlet was distinctly different from that observed prior to the rain event (Fig. 5.4). The abundance of the macro-fractions AHS and HiA increased substantially (along with a moderate increase in HiN), and function as significant indicators for the DOC at the outlet during WW. The NMS ordination (Fig. 5.6) demonstrates the magnitude and direction of the shift in composition between the samples collected at the inlet and outlet under DW and WW. In stark contrast to the major changes observed at the inlet, substantial changes in the concentration, bioavailability and composition of organic matter were not observed at the outlet, and dissolved oxygen concentrations in the outlet zone remained stable. It is proposed that the lack of observable change in the DOC pool at the outlet at this time is attributable to the plume of inflowing water not having reached the outlet end of the lake at the time of sampling.

Within <24 hours (19 hours post WW sampling; day 1), the concentration of DOC at both the inlet (10.0 mgL^{-1}) and outlet (9.5 mgL^{-1}) had effectively equilibrated, indicating that the plume of stormwater had dispersed through the lake. The composition of the DOC at both ends of the lake had also merged, with the HCA (Fig. 5.4) depicting the low level (~16%) of separation between the inlet and outlet. This is confirmed by the collective grouping of day 1 samples in the NMS ordination (Fig. 5.6), which demonstrates that AHS and HiA dominate the composition of these samples. Although the decrease in DOC concentration at the inlet (Fig. 5.3B) is considered to reflect dispersion of the plume throughout the lake, the results of the laboratory bioassay on the samples collected from the inlet (Fig. 5.2B) demonstrate a substantial depletion of DOC within the same time period, indicating that a considerable degree of microbial uptake of DOC would also have also occurred during this period. The composition of the DOC pool in the lake (Fig. 5.4) indicates that this uptake is confined largely to depletion of the AHS, HiA and HiN fractions. Dissolved oxygen concentrations at the inlet decreased from the 10.4mgL^{-1} recorded during DW, to 6.1mgL^{-1}. The observed *in-situ* decrease (4.3mgL^{-1}) in DO is reflected in the oxygen demand (7.3 mgL^{-1}) exerted in the first 24 hours of the laboratory bioassays (Fig. 5.1B). Dissolved oxygen concentrations in the outlet zone remained stable within this time period.

At day 2, DOC concentrations were equivalent at the inlet and outlet (7.3 and 7.9 mgL^{-1} respectively), and were decreasing towards the concentrations observed in the DW sampling period. The decreased rate of depletion of DOC observed *in-situ* reflects the asymptote observed in the laboratory bioassays performed on the WW inlet samples. CBOD measured in the bioassays within the first 48 hours was 10.9 mgL^{-1}, while *in-situ* dissolved oxygen concentrations decreased to 2.9 mgL^{-1} at the inlet, and 5.2mgL^{-1} at the outlet.

DOC concentrations had effectively stabilised at the inlet outlet on day 3. However, the composition of the DOC at the two ends of the lake had separated slightly (Fig. 5.4 and Fig. 5.6). Visual inspection of the time series fractionation data (Fig. 5.4) indicates that the separation is due to the relative abundance of AHS at the inlet, and HoN at the outlet. The stabilisation of *in-situ* and bioassay DOC concentrations indicates that depletion of the bulk DOC pool has stalled, yet the *in-situ* fractionation time series demonstrates that the DOC pool is being selectively utilised. The position of the samples in the NMS ordination demonstrate the decreasing abundance of AHS and HiA, and the increasing dominance of HoN. Dissolved oxygen concentrations at the inlet and outlet reached the minima recorded on day 3 (2.1 and 2.4 mgL^{-1} at the inlet and outlet respectively), with DO beginning to recover at both ends of the lake on day 4. The recovery is reflected in the substantial decrease in oxygen demand observed in the bioassays between days 3 and 4.

At day 5, *in-situ* DOC concentrations at the opposing ends of the lake remained stable, indicating minimal depletion of the DOC pool. This slowing of DOC utilisation is reflected in the laboratory bioassay of the WW samples collected from the inlet. However, the time series fractionation data continues to demonstrate selective utilisation of the AHS and HiA fractions. Although the composition of the DOC at the outlet and inlet begin to merge (Fig. 5.4, 5.6, 5.7), the relative abundance of HoN present at the outlet functions as a significant indicator for the DOC pool at the outlet, maintaining a level of separation in DOC composition between the inlet and outlet. Dissolved oxygen concentrations begin to improve at both the inlet and outlet, however, there is a observable lag in recovery at the inlet, and at both ends of the lake, DO concentrations are depressed below the environmental ANZECC/ARMCANZ (2000) trigger value, indicating a period of prolonged environmental stress.

DOC concentrations at the inlet and outlet decreased marginally by day 8, and DOC depletion in the laboratory bioassay had also reached an asymptote. It is suggested that this observation indicates that the majority of the bioavailable allochthonous DOC had been utilised, but that some selective utilisation of DOC was occurring. The exhaustion of the pool of oxygen demanding organic material and the associated oxygen debt are reflected in the *in-situ* DO concentrations increasing; however, DO concentrations remain below the environmental trigger value. By day 10, DOC concentrations had effectively stabilised, and the composition of the DOC pool at the inlet and outlet had merged (Fig. 5.4, 5.6, 5.7). It is interesting to note that the composition of the DOC pool had not returned to that observed in DW samples, with the most substantial change being an increase in the abundance of HoN, and a decrease in AHS (and to a lesser extent HiN).

5.4.2. General Discussion

The increased $CBOD_5$ in the samples from the inlet is associated not only with an increase in the magnitude of the DOC pool, but also a substantial shift in the apparent bioavailability and composition of the DOC pool. Connell (1981) states that under most circumstances, clean river water should have a BOD_5 of approximately 1mgL^{-1}, and that a BOD_5 greater than 10mgL^{-1} indicates that the water is seriously polluted. Based on that benchmark, the recorded $CBOD_5$ at the inlet (1.6mgL^{-1}) and outlet (0.9 mgL^{-1}) during DW indicates a relatively low level of organic pollution during periods of no, or little inflow. In comparison, the $CBOD_5$ measured in samples collected from the inlet zone during WW (17.6 mgL^{-1}) was an order of magnitude higher than that observed in the DW samples, and is well above the 10mgL^{-1} threshold for indicating significant organic pollution proposed by Connell (1981). Although the in-lake $CBOD_5$ is not as high as peak values recorded in the tributary streams (e.g. 57mgL^{-1} in second creek), the value is comparable to both the average B.O.D.$_5$ recorded in the urban streams (23.1 mgL^{-1}) and that recorded in the Torrens Lake (20.7 mgL^{-1}) during a similar sized (~20mm) rain event on 28th March 2002 (Wallace *et al.*, 2002).

The oxygen demand exerted by the organic material in the stormwater flowing into Torrens Lake had a major impact on DO concentrations in the lake, and indicates that the NOM inputs functioned as a critical pollutant which had a substantial and sustained impact on the water quality of the lake. At the inlet, DO was rapidly depleted to a minimum of 2.1 mgL^{-1}, and DO concentrations less than 3 mgL^{-1} were recorded from day 2-5 inclusive. The ANZECC/ARMCANZ guidelines (2000) presents an environmental trigger value of 70% saturation for urban lakes, equivalent to 6.2-6.8mgL^{-1} at the water temperature range recorded during the sampling period (17-21°C). Hart (1974) recommended similar minimum dissolved oxygen levels (6.2-6.5 mgL^{-1}) for freshwaters at this temperature range. Consequently, the depletion of DO to levels of less than 3 mgL^{-1} is of major concern for the ecology of the lake.

BaS concentrations were stable at both the inlet and outlet over the 10-day sampling period. Although this may indicate that BaS is a relatively inactive fraction, Imai *et al.* (2001) suggest that the compounds that comprise the BaS fraction (amino acids, proteins, aromatic amines, aminosugars), would not be expected to be found in high levels in lake water. At the inlet, the concentration of the HoN fraction decreased from a DW concentration of 0.7 mgL^{-1} to a WW concentration of 0.3 mgL^{-1}, and then increased to a maximum of 2.4 mgL^{-1} over the subsequent days. Based on the composition of compounds in the HoN fraction (hydrocarbons, pesticides, carbonyl compounds, LAS, large cellulose polymers) it is believed that the increase in HoN may be caused by compounds leaching from particulate material transported into the lake by the stormwater inflow.

The concentration of the AHS and HiA fractions increased substantially during WW (along with a moderate increase in HiN at the inlet), and then decreased rapidly at both the inlet and outlet in the subsequent days, suggesting that a substantial component of each of these fractions is readily bioavailable. When the CBOD values from the laboratory bioassays of the DW and WW samples are overlaid on the NMS ordination, it is evident that there is a strong correlation between CBOD and AHS, and to a lesser extent HiA and HiN. It is therefore proposed that the observed increase in oxygen demand is due to the importation, and subsequent rapid microbial utilisation of the AHS and HiA fractions. This suggestion is supported by the results of Sonnenberg and Holmes (1998), who reported that AHS and HiA fractions were significantly reduced in the treatment of pulp and paper mill extracts, and concluded that this reflected microbial uptake of wastewater DOC.

DOC in rivers is typically comprised of humic compounds, polysaccharide carbohydrates and amino acids (Volk *et al.*, 1997), compounds classified in the groups AHS, HiN and BaS respectively with the ion-exchange fractionation technique used in this research. Leachate from leaf litter and from subsurface and groundwater inflows through organic rich soils is the primary source of these compounds (Boulton *et al.*, 1998). Thurman (1985) reports that AHS is the dominant component of DOC in rivers. Imai *et al.* (2001) report that the DOC in a forest stream (in Japan) is dominated by AHS, and in a mixed land use catchment, riverine DOC is dominated by AHS and HIA. Humic compounds (AHS) are often considered to be relatively recalcitrant (Mogren *et al.*, 1990). However, although a large proportion of humic material may not be biodegradable, it has been demonstrated that humic substances may comprise as much as 75% of the total pool of biodegradable DOC in stream water samples (Volk *et al.*, 1997). Volk *et al.* (1997) propose that carbohydrates and amino acids bound to humic compounds may represent ~30% of the biodegradable AHS. It is also recognised that photolysis of humic compounds by UV radiation can increase the abundance of small fatty acid compounds that are readily bioavailable (Wetzel *et al.*, 1995). Consequently, the general assumption that AHS are not readily bioavailable should be interpreted with caution.

The correlation between CBOD and AHS, and to a lesser extent HiA and HiN observed in this current work is different from that obtained in Chapter 4. In Chapter 4, stream water samples were collected across a rural-urban gradient, and a strong correlation was observed between CBOD and both HoN and BaS during summer, and between CBOD and HoN in winter. Other authors have shown that HoN is readily biodegraded in paper mill wastewaters (Sonnenberg and Holmes, 1998), and sewage effluent (Imai *et al.*, 2001), and it was subsequently proposed (in Chapter 4) that the correlation between CBOD and HoN provided a strong indication that variation in percent composition of HoN compounds may be responsible for the increased oxygen demand and apparent bioavailability of DOC from the urban streams. However, the actual biodegradation of the individual fractions was not assessed in that work (DOC fractionation was only performed on the samples as collected from the rural and urban streams), and this current work appears to provide additional insight.

It is anticipated that the correlation obtained in the previous work (Chapter 4) may simply reflect a substantial concomitant increase in both CBOD and the proportion of HoN (hydrocarbons, pesticides, carbonyl compounds, LAS, and large cellulose polymers) in urban stormwater. The actual increase in DOC bioavailability and subsequent biochemical oxygen demand observed in the urban samples may have been driven by comparatively small increases in the abundance of other bioavailable fractions. Although Sonnenberg and Holmes (1998) report that HoN compounds were effectively removed from wastewater, they suggest that this reduction is probably a combined result of adsorption and microbial uptake, as hydrophobic compounds will typically bind to particulate material (e.g. suspended sediments and colloidal material).

The HiN (e.g. carbohydrates) fraction is generally considered to be readily bioavailable, and the rapid depletion of HiN following the rain event inflow observed in this study supports this. However, Volk *et al.* (1997) have demonstrated that 40% of carbohydrates in stream water are not utilised. Although the HiN fraction has been shown in this and other research (Chow *et al.*, 2004) to be present in comparatively low concentrations, the HiN fraction represents a major challenge to the treatment of water for potable supply. The neutral DOC fraction is resistant to traditional pre-chlorination treatment techniques (Chow *et al.*, 2004; Chow *et al.*, 2000). Treatment recalcitrant DOC is highly problematic as it reacts with chlorine during the disinfection phase, to generate potentially toxic or carcinogenic by-products, and contribute to bacterial regrowth in distribution systems (Prevost *et al.*, 1998; Simpson and Hayes, 1998). It is therefore interesting to note that while the rain event did increase the concentration of this potentially problematic fraction, the impact of the inflow was primarily observed at the inlet zone, and was short lived (1 day). In a reservoir utilised for potable supply, selective withdrawal of water may have provided a management option to mitigate impacts on treatment processes.

The depletion of DOC observed in the laboratory bioassays during DW (~5%) and WW (31%) falls within the lower, and mid-upper range respectively of the proportion of DOC that is reported to be labile (1-50%) by Meyer (1994). DOC concentrations in both the *in-situ* and the laboratory bioassays indicate that depletion of the DOC pool had stalled by day three. However, the *in-situ* fractionation time series demonstrated that the DOC pool is being selectively utilised. This observation demonstrates the usefulness of the ion-exchange fractionation technique for investigating DOC metabolism and the inherent weakness of bulk DOC measurements in studies of DOC dynamics.

This work provides a clear demonstration that stormwater inflows to the lake generate a substantial shift in the composition and bioavailability of DOC, and that the increased availability of labile organic material stimulates heterotrophic metabolism and generates a substantial oxygen debt. Although dilution and dispersion must be taken into account, the observation that DOC concentrations at the outlet did not reach those at the inlet, and the difference in DOC composition evident between the two ends of the lake even when DOC concentrations had equilibrated, suggests that there is a considerable level of DOC processing by the microbial community in the lake. For example, it is of note that the concentration of AHS and HiA (the two fractions considered to be primarily responsible for the oxygen debt) do not increase to the same levels as those observed at the inlet, and the extent of the oxygen debt at the outlet was not as severe as that at the inlet. Therefore, it can be considered that the lake functions as a treatment system for the downstream ecosystem. The lake appears to maintain this role even during inter-rain event periods, by significantly reducing $CBOD_5$ levels between the inlet and outlet zone.

Chapter 6: Relative composition and bioavailability of nutrients leached from leaf litter and garden waste

6.1 Introduction

Primary ecological models such as the river continuum concept (RCC) (Vannote *et al.*, 1980) suggest that metabolism in low order (1-3) streams is typically dependent on the input of allochthonous organic matter, predominantly in the form of leaf litter. The Flood Pulse Concept (Junk *et al.*, 1989) extends the RCC model to include floodplain-river channel interactions, yet retains the concept that the majority of allochthonous carbon input is from leaf litter. Recognition of the importance of leaf litter inputs has led to extensive study on the three primary phases in organic matter processing; leaching, conditioning and fragmentation, and there is a large body of work investigating these phases. It has been demonstrated that there is a substantial release of water-soluble compounds from leaf litter within a short period of time (hours-days) following immersion (Baldwin, 1999; Francis and Sheldon, 2002; Glazebrook and Robertson, 1999). Duncan (1997) estimates that 5-20% of nutrient content (carbon, nitrogen, phosphorus) can leach from submerged plant material. Furthermore, it is recognised that leachate from freshly fallen leaves contributes to the labile (readily bioavailable) component of the bulk NOM pool (Boulton and Brock, 1999).

In intact catchments with predominantly native vegetation, the ecosystem will have adapted to the quality and timing of leaf litter inputs. However, the shift from native tree species to introduced deciduous species that commonly occurs in urbanised areas, may impact ecosystem function and stability. For example, the replacement of native tree species such as eucalypts (e.g. river red gum, *Eucalyptus camaldulensis*), which have a peak litter fall period in summer (Attiwell *et al.*, 1978; Barlocher and Graca, 2002; Boulton, 1991; Pozo *et al.*, 1997; Pressland, 1982), with introduced deciduous species (e.g. London plane, *Platanus acerifolia*) that have peak litter fall periods in autumn (Murphy and Giller, 2000; Schulze and Walker, 1997), shifts the seasonality of resource delivery. This shift in timing, quantity, and potentially quality (bioavailability) of the NOM inputs may have a substantial impact on biogeochemical cycles.

The magnitude of any impacts on biogeochemical cycling are likely to be particularly important in urbanised catchments where substantial vegetation changes occur in conjunction with major changes to catchment hydrology. For example, the direct connection (via constructed stormwater infrastructure) that often occurs between impervious surfaces and receiving waters (Walsh, 2002) and the increased velocity of surface run-off (Paul and Meyer, 2001), increases the potential of leaf litter to be transported directly into streams. Consequently, material that is leached from the leaves will be released directly into the water body; short circuiting interception and processing that would normally occur during transport via overland and subsurface flow paths.

In addition to being a major source of organic carbon, leaf litter represents a major source of phosphorus (Cowen and Lee, 1973). Phosphorus has long been considered to be central in limiting primary production of many aquatic systems (Vollenweider, 1968), and in freshwater ecosystems, phosphorus has traditionally been considered to be the nutrient limiting phytoplankton metabolism (Hecky and Kilham, 1988). Toxic algal blooms are a major management concern for many water management authorities, and it is well established that phytoplankton blooms are often generated by observable changes in factors such as nutrient loading (Reynolds, 1997). The remobilisation of sediment bound phosphorus through development of anoxic conditions, combined with phosphorus released from leaf litter may generate excessively high concentrations of bioavailable phosphorus. Consequently, periods of high leaf litter input may be problematic in systems susceptible to eutrophication.

Despite being a fundamental issue in catchment management, the existing knowledge on the impacts of changes in vegetation diversity, density, and seasonal litter fall patterns associated with changes in land use on organic carbon dynamics and ecosystem function is limited. McArthur and Richardson (2002) demonstrated substantial differences in leaching rates, DOC composition (e.g. molecular weight and polyphenolic content) and bioavailability for deciduous and coniferous trees from forests in British Columbia. This project tested the hypothesis that leaf litter from introduced species would leach a higher concentration of nutrients per gram of leaf litter than a representative native species. Furthermore, it was proposed that the bulk DOC pool released from the introduced species would have a distinctly different composition, and be more bioavailable than that leached from the native species. This was investigated by comparing the rates of leaching of DOC and phosphorus, and the relative oxygen demand, composition and bioavailability of DOC leached from introduced and native plant material. Potential differences in factors such as leaf structural content, (e.g. higher lignin and humic acid content in the representative native), and re-absorption of nutrients from leaves prior to abscission were anticipated to be primary drivers of differences in the quantity and quality of leachate from introduced and native leaf litter.

The information generated from this research is expected to have implications in the design of stormwater infrastructure and structural best management practices, and may provide valuable insights into the suitability of wide spread plantings of introduced, deciduous species in urban catchments.

6.2 Materials and Methods

6.2.1 Leaf litter (plant material) collection

The plant species chosen for this study were selected on the basis that they are heavily represented in the standing stock of autumn leaf litter in the urbanised sub-catchment of the Torrens River, Adelaide, South Australia. Release of filterable reactive phosphorus (FRP) and dissolved organic carbon (DOC) was compared between leaf litter from English elm (*Ulmus procera*), London plane (*Platanus acerifolia*), white poplar (*Populus alba*), river red gum (*Eucalyptus camaldulensis*), and grass cuttings (mixed species). The English elm, London plane, and white poplar are introduced, deciduous species. Grass cuttings were selected as being representative of garden waste.

Leaf litter and grass cuttings that would have been susceptible to being transported into the Torrens River during the next rain event were collected from within linear park, a recreational park along the banks of the Torrens River. Leaf litter was collected from under three spatially separated (>50 m) trees for each tree species, and grass cuttings were collected from three separate stream side bank areas. No attempt was made to determine how much time had elapsed since the leaf litter had fallen from the trees, or in the case of grass cuttings, how long since the grass had been cut. However, all of the leaves collected were intact.

6.2.2 Preparation of leachate- FRP and DOC release

After collection the leaf litter and grass cuttings were air dried at 20°C for 48 hours. Approximately 4 g (accurately weighed and recorded) of each litter type was added to individual 2L Erlynmeyer flasks. The leaf litter was flooded with 1 L of 0.45μm filtered reverse osmosis (RO) water, and the flasks were stored at 20°C, in the dark. After 6 hours, the water was drained from the leaf litter, and the leaf litter in each flask was subsequently re-flooded with 1 L of 0.45μm filtered RO water. The water removed from the leaf litter was filtered through pre-washed Whatman GF/C filters and subsequently through Whatman PVDF 0.45μm membrane filters. Two 50mL, and two 250mL sub-samples were collected from the filtered water from each flask. One 50mL sub-sample and one 250mL sub-sample were acidified to pH 2 for analysis of DOC and ion exchange fractionation of the DOC pool respectively. The second 50mL sub-sample was retained for analysis of FRP. The remaining 250mL sample was utilised for analysis of biochemical oxygen demand and biodegradability of the DOC released from the plant material. All samples were stored at <4°C in the dark pending analysis.

The overlying water was exchanged on days 1, 2, 3, 5, 7 and 10. Fifty (50) mL sub-samples were collected at each time step for analysis of DOC and FRP release. No clearly visible biofilms were evident on the leaf material. The FRP and DOC released from the plant material was calculated by correcting for mass, and summing consecutive values to produce cumulative FRP and DOC curves for the 10 day period.

6.2.3 Oxygen demand and biodegradability of DOC released from plant material

The biochemical oxygen demand (BOD) and biodegradability of the DOC released from the plant material was assessed on the sample collected at t = 6 h. BOD was assessed using a modification of APHA Standard Method 5210B (Eaton *et al.*, 1995). Individual BOD (310mL) bottles were established for analysis of dissolved oxygen and DOC at time steps of 0, 1, 3, 5, 7 and 10 days. In order to initiate the bioassays as rapidly as possible post collection of the leachate (<2 hours), no attempt was made to standardise the concentration of DOC in the bioassays. Samples were diluted sufficiently to ensure the maintenance of oxic conditions throughout the 10-day bioassay period. The dilution water used was a 50/50 mixture of 0.45μm filtered RO water and 0.45μm filtered Torrens Lake water that had been aerated for 3 hours, and stabilised for 24 hours. The dilution water was seeded with 20mLL^{-1} of 37μm filtered Torrens Lake water to ensure a sufficient biomass of microorganisms to metabolise the biodegradable organic matter present in the samples.

Additional nitrogen (Sodium Nitrate, $NaNO_3$) and phosphorus (di-potassium hydrogen orthophosphate, K_2HPO_4) were added to supplement nutrient concentrations released from the plant material, and to ensure that nitrogen or phosphorus did not limit DOC degradation. The amount of $NaNO_3$ and K_2HPO_4 added was calculated to provide minimum initial concentrations of 1000μg N L^{-1} and 100μg P L^{-1} respectively. The samples were incubated at 20°C in the dark. At each time step, dissolved oxygen in the respective bottle was measured, 50mL of sample was withdrawn from the bottle, re-filtered through Whatman PVDF 0.45μm membrane filters, preserved to pH 2 and subsequently analysed for DOC (providing a measure of biodegradable dissolved organic carbon: BDOC). Blank controls were established to allow for correction for oxygen demand generated by the dilution water at each time step.

6.2.4 Fractionation of the DOC pool

Ion-exchange resins were utilised to characterise the DOC released from the plant material by its distribution in functional categories. The samples were fractionated using minor modifications to the technique described by Imai *et al.* (2001), which is based on that developed by Leenheer (1981). A detailed description of the technique utilised is provided in Chapter 2. The 0.45μm filtered sub-samples collected at t = 6 h were fractionated utilising 3 ion-exchange resins: Supelite™ DAX-8, Biorad AG®MP50, and Biorad AG®MP1 to produce five distinct DOC fractions. The five fractions produced were hydrophobic acids (AHS: e.g. humic and fulvic acids), hydrophobic neutrals (HoN: e.g. large cellulose polymers, hydrocarbons, pesticides, carbonyl compounds, linear alkylbenzene sulfonate), hydrophilic acids (HiA: e.g. fatty acids, sugar acids, hydroxyl acids), bases (BaS: e.g. aromatic amines, proteins, amino acids, aminosugars), and hydrophilic neutrals (HiN: e.g. carbohydrates, oligosaccharides, polysaccharides, alcohols, ketones). The relative composition of these fractions generates a physicochemical signature for the water sampled.

6.2.5 Analytical methods

The FRP concentration in collected sub-samples was determined utilising APHA method 4500-P E (Eaton *et al.*, 1995) using a Hitachi U-2000 double beam spectrophotometer (Hitachi Ltd, Tokyo, Japan). The DOC concentration in each sub-sample was determined utilising an SGE ANATOC II total organic carbon analyser. DOC analysis was performed in non-purgeable organic carbon (NPOC) mode utilising titanium dioxide as a catalyst in the presence of near-UV light. Three replicate measurements of DOC were made for each sample, with the DOC concentration determined as the average of the three measurements. Variation between replicate measurements was typically less than 2% RSD. Samples for direct analysis of DOC on the ANATOC II were adjusted to pH 2.8 with 0.1M perchloric acid. The samples for ion-exchange fractionation were adjusted to pH 2 with 5 M HCl for the fractionation procedure. Post-fractionation the pH was adjusted to 2.8 with 0.1M NaOH and 0.1M perchloric acid for DOC analysis. Benzoic Acid was utilised as a standard for calibration of the analyser. Dissolved oxygen was measured using a WTW Oxi 330i dissolved oxygen probe.

6.2.6 Data Analysis

Regression curves displayed in graphs are fitted to means; error bars are ± 1 standard error (SE). Regression equations for all curves are contained in Table 6.1. Differences in DOC composition between the leaf leachates were analysed using indicator species analysis (Dufrene and Legendre, 1997), non-metric scaling (NMS) ordination, and one-way NPMANOVA . Indicator species analysis and NMS ordinations were performed using PCOrd; version 4.28 (McCune and Mefford, 1999). NPMANOVA was undertaken using the procedure described by Anderson (2001). Bray-Curtis distances were used to calculate the similarity matrix for all multivariate statistical analyses (Bray and Curtis, 1957) and two-dimensional ordination solutions with stress lower than 20% were deemed acceptable (sensu (Clarke, 1993). For all statistical tests $\alpha = 0.05$.

6.3 Results

6.3.1 FRP release

The release of FRP from plant material is shown in Figure 6.1. The release of FRP from the English elm occurred in a linear manner. In contrast the release of FRP from the other plant materials occurred in a hyperbolic manner. Grass cuttings released the highest concentration of FRP per gram of leaf material (806.5 ±70.1μg g^{-1}), followed by London plane (733.4 ±186.1μg g^{-1}), river red gum (241.4 ±16.2μg g^{-1}), white poplar (144.2 ±25.6 μg g^{-1}), and English elm (110.7 ±23.4 μg g^{-1}).

6.3.2 DOC release

The release of DOC from all types of leaf litter occurred in a hyperbolic manner, and is shown in Figure 6.2. The white poplar (150.4 ±4.6μg g^{-1}) released the highest amount of DOC, followed by river red gum (110.4 ±3.9μg g^{-1}), English elm (72.5 ±6.7 μg g^{-1}), London plane (24.4 ±1.2μg g^{-1}), and grass cuttings (23.7 ±2.6μg g^{-1}).

There is a correlation between DOC and FRP release (Fig. 6.3). Species that released relatively high concentrations of DOC (white poplar, English elm, river red gum), released relatively low concentrations of FRP. Conversely, species that released relatively low concentrations of DOC (grass cuttings and London plane), released relatively high concentrations of FRP. This variability is evident in the DOC:FRP ratios, with grass cuttings and London plane exhibiting comparatively low ratios (29.3 ±0.8 and 39.9 ± 13.3 respectively), river red gum and English elm exhibiting moderate ratios (459.4 ± 14.9 and 693.2 ± 103.4 respectively), and white poplar exhibiting relatively high (1136.2 ±261.9) DOC:FRP ratios.

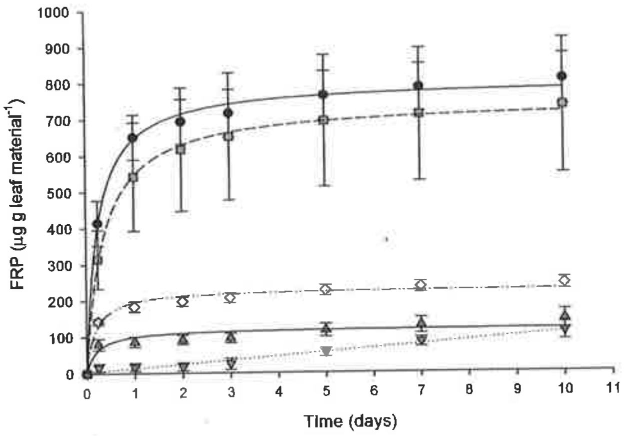

Figure 6.1. Cumulative filterable reactive phosphorus (FRP) release over 10 day period for: grass cuttings (solid circles), English elm (red triangles & dotted regression line), London plane (green squares & broken regression line), river red gum (yellow diamonds), and white poplar (blue triangles). See Table 6.1 for regression equations.

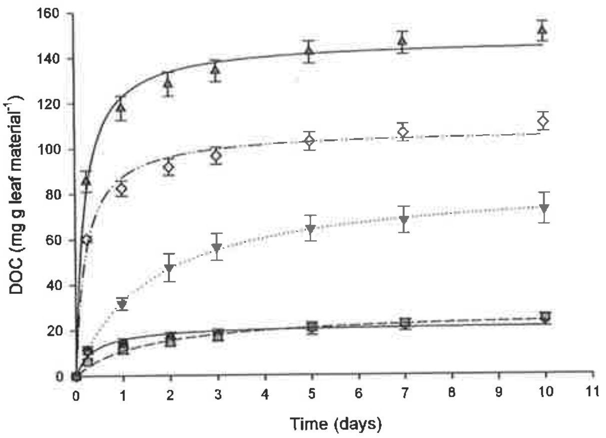

Figure 6.2. Cumulative dissolved organic carbon (DOC) release over 10 day period. grass cuttings (solid circles), English elm (red triangles & dotted regression line), London plane (green squares & broken regression line), river red gum (yellow diamonds), and white poplar (blue triangles). See Table 6.1 for regression equations.

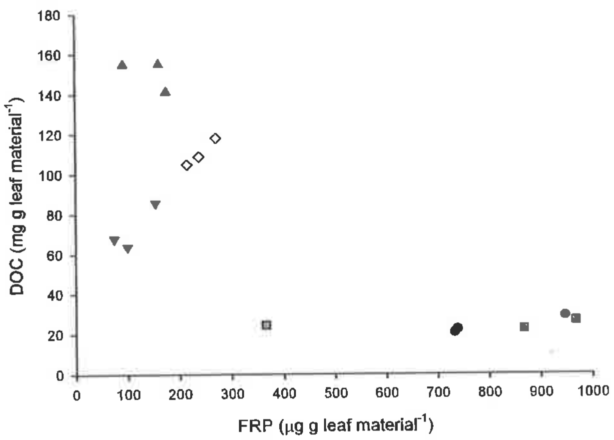

Figure 6.3. Correlation between peak DOC and FRP release from grass cuttings (solid circles), English elm (red triangles), London plane (green squares), river red gum (yellow diamonds), and white poplar (blue triangles).

6.3.3 Oxygen demand and biodegradability of DOC released from plant material

The oxygen demand (mg O_2 per g leaf material) exerted by leachate collected at t = 6 h over the 10-day period occurred in an hyperbolic manner, and is depicted in Figure 6.4. The white poplar exerted the highest oxygen demand per gram of leaf material (50.0 ±2.8 mg O_2 g^{-1}), followed by river red gum (39.8 ±2.2 mg O_2 g^{-1}), English elm (25.4 ±1.4 mg O_2 g^{-1}), grass cuttings (24.4 ±0.7 mg O_2 g^{-1}) and London plane (18.2 ±1.6 mg O_2 g^{-1}).

When the oxygen demand exerted by leachate collected at t = 6 h is expressed as mg O_2 per mg DOC, the oxygen demand is still exerted in a hyperbolic manner, but there is a reversal in the plant species exerting the highest oxygen demands (Fig. 6.5). The London plane exerts the highest oxygen demand per mg DOC released (3.1 ±0.3 mg O_2 mg DOC $^{-1}$), followed by the English elm (2.4 ±0.2 mg O_2 mg DOC^{-1}), grass cuttings (2.2 ±0.3 mg O_2 mgDOC^{-1}), river red gum (0.7 ±0.02 mg O_2 mg DOC^{-1}), and white poplar (0.6 ±0.04 mg O_2 mgDOC^{-1}).

The biodegradability of the DOC contained in the leachate is depicted in Figure 6.6. Depletion of the DOC leached from the white poplar (78%) and river red gum (72%) occurred in an exponential manner. In contrast, depletion of the DOC leached from the English elm (50%), grass cuttings (37%), and London plane (21%) occurred in a linear fashion.

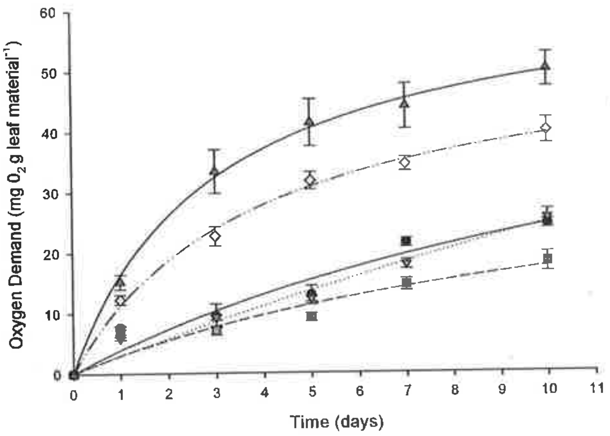

Figure 6.4. Oxygen demand (expressed in mg oxygen per g leaf material) exerted by leachate collected at t = 6 h over 10 day period: grass cuttings (solid circles), English elm (red triangles & dotted regression line), London plane (green squares & broken regression line), river red gum (yellow diamonds), and white poplar (blue triangles). See Table 6.1 for regression equations.

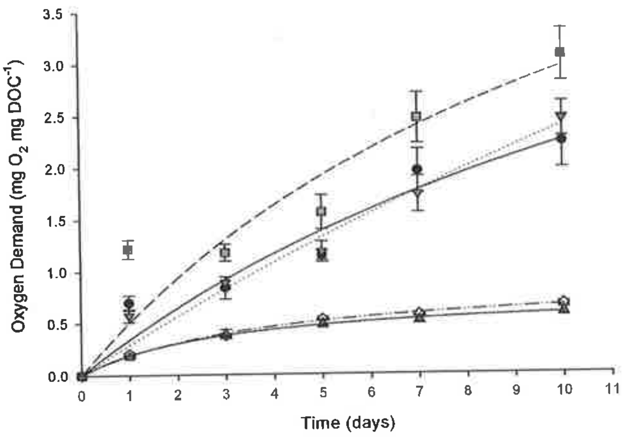

Figure 6.5. Oxygen demand (expressed in mg O_2 per mg DOC) exerted by leachate collected at t = 6 h over 10-day period: grass cuttings (solid circles), English elm (red triangles & dotted regression line), London plane (green squares & broken regression line), river red gum (yellow diamonds), and white poplar (blue triangles). See Table 6.1 for regression equations.

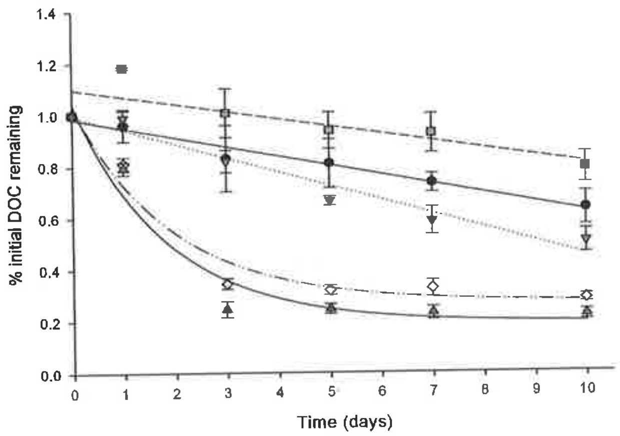

Figure 6.6. Biodegradability of DOC leached from plant material under oxic conditions: grass cuttings (solid circles), English elm (red triangles & dotted regression line), London plane (green squares & broken regression line), river red gum (yellow diamonds), and white poplar (blue triangles). See Table 6.1 for regression equations.

6.3.4 Fractionation of the DOC pool

Ion exchange fractionation of the DOC pool into five distinct macro-fractions (Fig. 6.7) revealed significant differences (NPMANOVA: df = 4, F = 389.3162, P = 0.0002) in the composition of the DOC leached from the different plant species. Hierarchical Cluster Analysis (Fig. 6.8) demonstrates that there is a major separation between river red gum, white poplar, and the other species. The composition of all species is substantially different, however the DOC leached from the river red gum is distinctly different to that leached from all other species. The most similar are English elm and London Plane, with differences of ~35%.

The respective ratios of the five DOC macrofractions (e.g. AHS:HoN, HiN:BaS) are also significantly different (NPMANOVA: df_{14}, F = 3.460, P = 0.002) between the five vegetation species. NMS ordination (Fig. 6.9) and indicator species analysis indicates that DOC leached from grass cuttings is characterised by a high proportion of hydrophobic neutrals and bases (Table 6.2), and that the relatively high ratios (Table 6.3) of HoN:AHS (0.53 ±0.1), HoN:HiN (1.25 ±0.1), BaS:AHS (0.27 ±0.03), BaS:HiA (0.28 ±0.01) and BaS:HiA (0.66 ±0.1) are significant indicators for the DOC leached from grass cuttings. DOC leached from river red gum leaf litter is characterised by a high proportion of hydrophobic acids (Table 6.2), with the relatively high ratios of AHS:BaS (62.95 ±27.9), AHS:HiA (1.58 ±0.1) and AHS:HiN (3.93 ±0.4) functioning as significant indicators (Table 6.3) for river red gum leaf leachate.

The DOC leached from white poplar is characterised by a high proportion of hydrophilic acids (Table 6.2). This is translated in high ratios of HiA:AHS (1.62 ±0.1), HiA:HoN (52.08 ±33.4) and HiA:HiN (3.15 ±0.2), in addition to a high ratio for BaS:HoN (6.98 ±4.9) functioning as significant indicators (Table 6.3) for DOC leached from White Poplar. Although a high proportion of hydrophilic neutrals are an indicator for London plane (Table 6.2), the relationship is not significant because English elm and London plane both exhibit a high proportion of hydrophilic neutrals. There is no indicator for English elm. There also no significant indicators for the ratios of DOC macrofractions for either English elm or London Plane (Table 6.3).

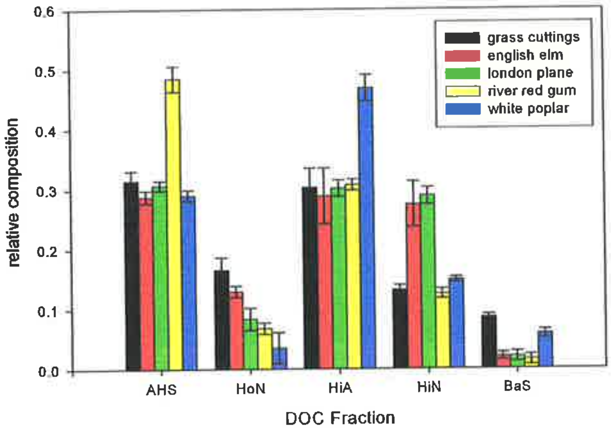

Figure 6.7. Macro-fractions of DOC leached from plant material. AHS = hydrophobic acids, HON = hydrophobic neutrals, HiA = hydrophilic acids, HiN = hydrophilic neutrals, BaS = bases.

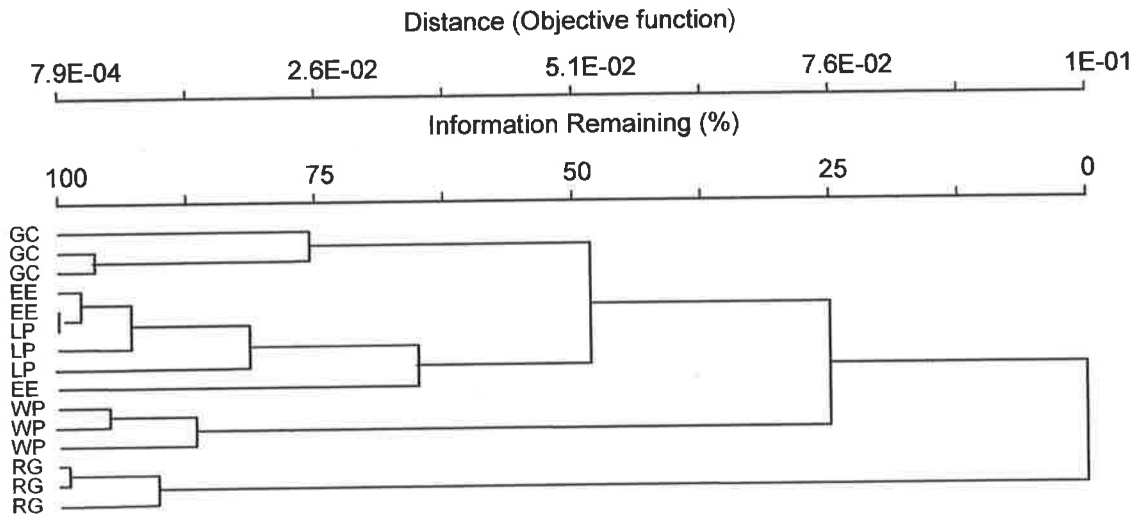

Figure 6.8. Hierarchical Cluster Analysis depicting separation between species based on ion exchange fractionation of DOC leached from plant material. GC= grass cuttings, EE = English elm, LP = London plane, WP = white poplar, RG = river red gum.

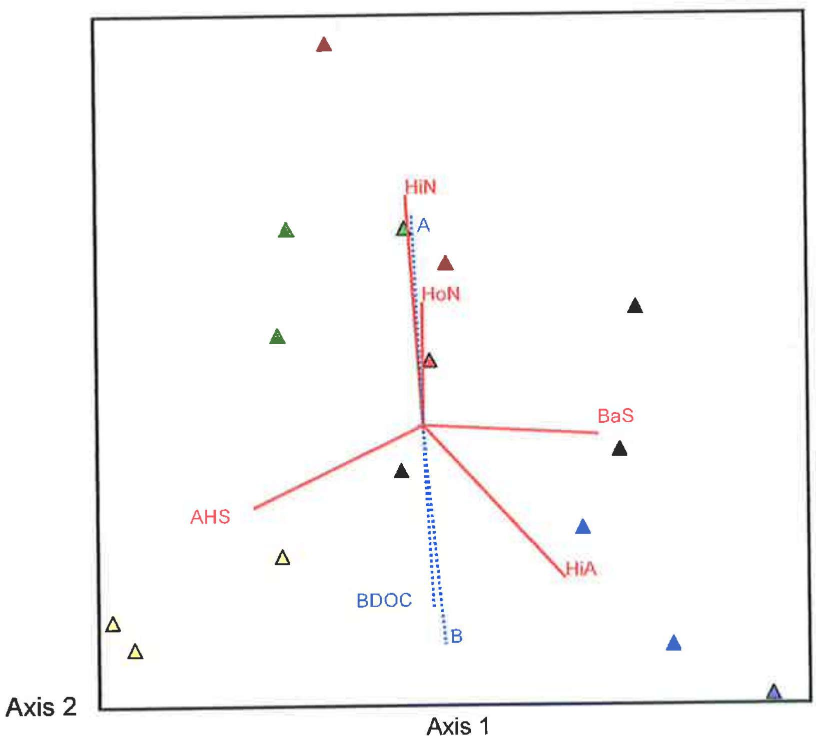

Figure 6.9. NMS ordinations depicting separation between species based on ion-exchange fractionation of DOC leached from plant material; and the relationship between DOC composition, biodegradability and oxygen demand. Stress = 13.3%. Grass cuttings = black triangles, English elm = red triangles, London plane = green triangles, river red gum = yellow triangles, and white poplar blue triangles. Vectors: AHS = hydrophobic acids; HoN = hydrophobic neutrals; HiA = hydrophilic acids; HiN = hydrophilic neutrals; BaS = bases; BDOC = biodegradable DOC; A = mg O_2 mg DOC^{-1}; B = mg O_2 mg leaf material^{-1}.

Table 6.1. Regression equations for FRP and DOC release, oxygen demand and biodegradability of DOC.

Factor	Species	Relationship	Equation	r^2	DF	P
FRP release (µg FRP per g leaf)	grass cuttings	hyperbolic	FRP = (801.418*day)/(0.242+day)	0.996	7	<0.0001
FRP release (µg FRP per g leaf)	English elm	linear	FRP = 2.180 + (10.76*day)	0.970	7	<0.0001
FRP release (µg FRP per g leaf)	London plane	hyperbolic	FRP = (743.699*day)/(0.364+day)	0.999	7	<0.0001
FRP release (µg FRP per g leaf)	river red gum	hyperbolic	FRP = (230.820*day)/(0.190+day)	0.979	7	<0.0001
FRP release (µg FRP per g leaf)	white poplar	hyperbolic	FRP = (121.466*day)/(0.227+day)	0.865	7	0.0008
DOC release (mg DOC per g leaf)	grass cuttings	hyperbolic	DOC = (21.896*day)/(0.390+day)	0.935	7	<0.0001
DOC release (mg DOC per g leaf)	English elm	hyperbolic	DOC = (84.379*day)/(1.597+day)	0.999	7	<0.0001
DOC release (mg DOC per g leaf)	London plane	hyperbolic	DOC = (27.120*day)/(1.521+day)	0.983	7	<0.0001
DOC release (mg DOC per g leaf)	river red gum	hyperbolic	DOC = (107.210*day)/(0.230+day)	0.989	7	<0.0001
DOC release (mg DOC per g leaf)	white poplar	hyperbolic	DOC = (147.046*day)/(0.201+day)	0.993	7	<0.0001
BOD (mg O_2 per g leaf)	grass cuttings	hyperbolic	BOD = (60.041*day)/(14.483+day)	0.939	5	0.0014
BOD (mg O_2 per g leaf)	English elm	hyperbolic	BOD = (138.70*day)/(45.890+day)	0.971	5	0.0003
BOD (mg O_2 per g leaf)	London plane	hyperbolic	BOD = (38.909*day)/(12.193+day)	0.883	5	0.0053
BOD (mg O_2 per g leaf)	river red gum	hyperbolic	BOD = (54.647*day)/(3.868+day)	0.996	5	<0.0001
BOD (mg O_2 per g leaf)	white poplar	hyperbolic	BOD = (64.508*day)/(2.968+day)	0.998	5	<0.0001
BOD (mg O_2 per mg DOC)	grass cuttings	hyperbolic	BOD = (5.963*day)/(16.547+day)	0.935	5	0.0016
BOD (mg O_2 per mg DOC)	English elm	hyperbolic	BOD = (12.763*day)/(43.369+day)	0.971	5	0.0003
BOD (mg O_2 per mg DOC)	London plane	hyperbolic	BOD = (6.520*day)/(12.033+day)	0.885	5	0.0052
BOD (mg O_2 per mg DOC)	river red gum	hyperbolic	BOD = (0.906*day)/(3.859+day)	0.996	5	<0.0001
BOD (mg O_2 per mg DOC)	white poplar	hyperbolic	BOD = [(0.755*day)/(0.298+day)	0.997	5	<0.0001
DOC depletion (% intial DOC)	grass cuttings	linear decay	DOC = 0.983 – (0.361*day)	0.973	5	0.0003
DOC depletion (% intial DOC)	English elm	linear decay	DOC = 0.995- (0.054*day)	0.956	5	0.0007
DOC depletion (% intial DOC)	London plane	linear decay	DOC = 1.098 - 0.029*day)	0.713	5	0.0344
DOC depletion (% intial DOC)	river red gum	exponential decay	$DOC = 0.269+0.765e^{-0.5173*day}$	0.964	5	0.0068
DOC depletion (% intial DOC)	white poplar	exponential decay	$DOC = 0.188+0.858e^{-0.5386*day}$	0.956	5	0.0093

Table 6.2. Indicator Species Analysis comparing the composition of DOC leached from leaf litter and grass cuttings. Indicator fractions with P values < 0.05 are exclusive indicators for DOC from the respective leaf litter types.

Plant Species	Indicator Fraction		P*
River red gum	Hydrophobic acids	AHS	0.0310
Grass cuttings	Bases	BaS	0.0100
Grass cuttings	Hydrophobic neutrals	HoN	0.0260
White Poplar	Hydrophilic acids	HiA	0.0120
London Plane	hydrophilic neutrals	HiN	0.0990

Table 6.3. Indicator Species Analysis comparing the ratios of the respective DOC macrofractions leached from leaf litter and grass cuttings. Indicator fractions with P values < 0.05 are exclusive indicators for DOC ratios from the respective leaf litter types. P values marked with * denote significant indicators.

Plant Species	Ratios of macrofractions	P*
Grass cuttings	HoN:AHS	0.0490 *
	HoN:HiA	0.1580
	HoN:HiN	0.0010 *
	BaS:AHS	0.0270 *
	BaS:HiA	0.0100 *
	BaS:HiN	0.0100 *
English Elm	HoN:BaS	0.4830
	HiN:AHS	0.1090
	HiN:HiA	0.2240
London Plane	HiN:BaS	0.3770
River Red Gum	AHS/BaS	0.0460 *
	AHS/HiA	0.0200 *
	AHS/HiN	0.0100 *
	HiA/BaS	0.2830
White Poplar	AHS/HoN	0.0760
	BaS/HoN	0.0380 *
	HiA/AHS	0.0110 *
	HiA/HoN	0.0220 *
	HiA/HiN	0.0290 *
	HiN/HoN	0.0990

6.4 Discussion

6.4.1 FRP and DOC release

For all species except English elm, the majority of FRP and DOC release occurred within the first 48 hours, after this time, the rate of release declined markedly. After 24 hours, 14% of the DOC had leached from the English Elm, 25% from the London plane, 48% from the grass cuttings, 55% from river red gum, and 57% from the white poplar leaf litter. In comparison, Francis and Sheldon (2002) demonstrated that approximately 50% of the DOC leaches from river red gum leaf litter within the first 24 hours. McArthur and Richardson (2002), demonstrated leaching rates of 74%, 30%, and

14% from red alder (*Alnus rubra* (Bong.)), western red cedar (*Thuja plicata* Donn), and western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) respectively, within the first 24 hours of a 7 day inundation period.

For English elm, FRP release occurs in a linear manner as opposed to a hyperbolic manner, which is in contrast to all other species tested. Furthermore, DOC does not asymptote until 120 h compared to 48 h for the other species, suggesting that the mechanisms controlling FRP and DOC release in the English elm may be different than in the other species.

6.4.2 Biochemical Oxygen Demand

When the oxygen demand exerted by the leaf leachates is expressed as mg O_2 per g leaf material, the white poplar exerted the highest oxygen demand per gram of leaf material, followed by river red gum, English elm, grass cuttings and London plane. In distinct contrast, when the oxygen demand is expressed as mg O_2 per mg DOC, there is a reversal in the plant species exerting the highest oxygen demands. The London plane exerts the highest oxygen demand per mg DOC released, followed by the English elm, grass cuttings, river red gum, and white poplar. In addition to delivering the lowest peak oxygen demands (expressed as mg O_2 per mg DOC) of the five species studied, the majority of the biochemical oxygen demand exerted by the leachate from the river gum and white poplar leaf litter is effectively exhausted at day 3. This infers that in addition to exerting less O_2 demand on the system, the stress is exerted for a shorter period of time, allowing the ecosystem to recover quicker. In contrast, the leachate from the London Plane, English elm, and grass cuttings, exerts a higher O_2 demand, and continues to exert that stress even at day 10. Consequently, it is considered that DOC leached from leaf litter of these species would have a greater impact on the receiving water.

Respiration quotients (mg O_2 mg DOC^{-1}) at day 5 for river red gum (0.53 ±0.02) and white poplar (0.48 ±0.04) are similar to those observed in the rural streams (0.46 ±0.07) of the Torrens Catchment (Chapter 4). In contrast, the respiration quotients at day 5 for DOC leached from London Plane (1.56 ±0.17), English Elm (1.18 ±0.10), and grass cuttings (1.14 ±0.04) are similar to those observed in the urbanised streams (1.30 ±0.10) of the Torrens Catchment (Chapter 3). At day 10, the respiration quotient for river red gum (0.66 ±0.02) and white poplar (0.58 ±0.04) are substantially lower than those exhibited by grass cuttings (2.23 ±0.25), English elm (2.45 ±0.17) and London Plane (3.07

±0.25), which could be considered to be relatively high, as the standardised respiration quotient for carbohydrates is 1.00. However, when NH_3 is the sole nitrogen source, the respiration quotient increases to 1.62. In addition, the respiration quotient for nitrification is 4.3 mg O_2 per mg NH_3-N converted to NO_3^-. As nitrification was not inhibited in the biochemical oxygen demand assays, nitrification appears to exert a substantial non-carbonaceous oxygen demand in the leachate from London Plane, English Elm, and grass cuttings.

6.4.3 DOC metabolism

The depletion of DOC from river red gum (72%) and white poplar (78%) leaf material is comparable to that observed in other studies. For example, in a study on the metabolism of the DOC in leachate obtained from 18 different tree species, Strauss and Lamberti (2002) demonstrated that on average, 75% of the DOC was metabolised within a 24 day period, and that the majority of the DOC degradation occurred within the first six days. Baldwin (1999) demonstrated that at low DOC leaf biomass (consequently low DOC concentrations), 98% of the DOC leached from freshly fallen river red gum leaves was degraded over a period of 30 days.

In contrast to studies showing high biodegradability, O'Connell *et al.* (2000) demonstrated that only 34-49%, of DOC released from river red gum leaf litter was metabolised. There is however a number of substantial differences between the techniques used by O'Connell *et al.* (2000) and those used in this study, which offer potential explanations for the variation. As discussed by Francis and Sheldon (2002) oven drying has been demonstrated to have a substantial impact on processing rates. O'Connell *et al.* (2000) dried the leaf samples at 105°C to constant weight, prior to submersing the leaf material; in the current experiment, the leaf material was air dried at 20°C for 48 hours.

In a series of leachate metabolism studies, Baldwin (1999) demonstrated that as DOC concentrations increase, degradation decreases, and proposed that as DOC concentration increases, either a chemical in the leaf leachate suppresses microbial activity, or that the microbial community become nutrient limited. Elevated DOC concentrations may have contributed to the low biodegradability observed in O'Connell *et al.* (2000) experiments. Based on leaf mass, water volume, and concentrations of DOC released per gram of leaf material, the DOC concentrations in the

experiments of O'Connell *et al.* (2000) are estimated to be two orders of magnitude higher (>1000mgL^{-1}) than those used in the current experiments (<10 mgL^{-1}).
High DOC concentrations can be ruled out as a cause for the relatively low biodegradability observed in the English elm, London plane and grass cuttings, as these species had the lowest (~5mg L^{-1}) initial DOC concentrations.

The degradability of the DOC leached from the English elm (50%), is similar to that observed by (Hongve, 1999) for deciduous trees (45%). The high variability in FRP released, and the relatively low amount, and biodegradability (21%) of the DOC leached from London Plane leaf litter may reflect a longer period of terrestrial ageing, which may have included a wetting period, resulting in a substantial component of the bioavailable DOC and FRP being already leached. Baldwin (1999) utilised weak-anion-exchange chromatography to demonstrate that DOC released from fresh River Red Gum (*Eucalyptus camaldulensis* Denh) is comprised of different compounds and is more bioavailable than DOC released from terrestrially aged material. 98% of the DOC leached from freshly fallen river red gum leaves was degraded over a period of 30 days. In contrast, only 30% of the DOC leached from red gum leaves that had been aged on a flood plain for 5 months was degraded. This may also offer an explanation for the lower bioavailability of river red gum leachate observed by O'Connell *et al.* (2000), who utilised leaf litter comprised of varying ages and degrees of breakdown, compared to recently fallen leaf material.

6.4.4 Characterisation of DOC via ion-exchange fractionation

Multivariate analysis combined with the distinctly different shapes of both the oxygen demand and the bioavailability curves demonstrates that there are significant differences in the quality of the DOC leached from the leaf litter from the different species. NMS ordination of the BOD and BDOC data with the DOC fractions contained in the leachate collected at 6 h, demonstrates that both the oxygen demand exerted per mg leaf material, and the biodegradability of the DOC (BDOC) from all species is strongly correlated with the proportion of hydrophilic acids (HiA) and hydrophobic acids (AHS) present. Conversely, the oxygen demand exerted per mg DOC is strongly correlated with the proportion of hydrophilic neutrals (HiN) and hydrophobic neutrals (HoN) present.

It is of particular note that BDOC and oxygen demand exerted per mg leaf material are correlated with AHS and HiA, as this observation matches the rapid microbial utilisation of AHS and HiA in lake water observed in Chapter 5. Humic compounds (AHS) are often considered to be relatively recalcitrant (Mogren *et al.*, 1990). However, although a large proportion of humic material may not be biodegradable, it has been demonstrated that humic substances may comprise as much as 75% of the total pool of biodegradable DOC in stream water samples (Volk *et al.*, 1997).

6.4.5 General Discussion

The London plane and to a lesser extent, the English elm are popular street trees, and are widely planted in urban areas. Leaf fall from the deciduous species occurs primarily in late autumn (Murphy and Giller, 2000), resulting in a large standing biomass of autumn leaf litter, which is susceptible to being transported into urban waterways. A substantial proportion (60-90%) of gross pollutants in urban stormwater (Allison and Chiew, 1995; Hassell, 1997; Sim and Webster, 1992) is leaf litter and garden waste. Recognition that leaf litter from exotic trees functions as a pollutant within urban landscapes has prompted initiatives by catchment water management authorities to reduce leaf litter loads. The scale of the issue is such that the Adelaide City Council allocates approximately $125,000 to clean up the leaf litter annually (Golding, 2002).

The installation of gross pollutant traps (GPT's) is commonly utilised as a structural management technique to protect aquatic ecosystems from pollutants in urbanised catchments. When gross pollutants are intercepted by traditional rack or net style GPT's, the material is held in the flow path of the water. Consequently, the rapid nutrient leaching rates observed in this and other studies have important implications in water sensitive urban design and stormwater infrastructure. Despite the installation of GPT's to reduce nutrient inputs from leaf litter and garden waste, the rapid release of nutrients observed, suggests that a substantial component of the soluble nutrients will be leached out of the leaf litter and garden waste, and subsequently flow into the receiving water.

In streams where there is base flow, if the GPT's are not cleared for 48-72 hours post the onset of rain, the majority of water soluble, oxygen demanding organic material will still enter the receiving water. Consequently, the ability of GPT's to protect downstream ecosystems from nutrient inputs (carbon, nitrogen and phosphorus) leached from leaf litter and garden waste would appear to be tightly coupled to the response time required for trash racks to be cleared post rain events. The suggestion that GPT's may not be effective in reducing oxygen demand in urbanised catchments is supported by the observation that there is no significant impact of the progressive removal of particulate material on reducing biochemical oxygen demand at both urban and rural sites throughout the Torrens Catchment (Chapter 3).

The shift in quality, quantity and timing of leaf litter can be anticipated to have a series of substantial impacts on biogeochemical cycles. The London plane and English elm produced a relatively low total mass of DOC, and the oxygen demand per gram of leaf litter was also relatively low. However, the oxygen demand per mg of DOC from both English elm and London plane was relatively high, and the London plane leached a relatively high mass of FRP. Consequently, the large standing biomass of leaf litter from these species on impervious surfaces and within stormwater infrastructure during autumn may generate substantial water quality problems in receiving waters following rain events. The shift from exponential depletion of the river red gum leachate (high proportion of AHS) and white poplar (high proportion of HiA) to linear depletion of the leachate from English elm, London plane and grass cuttings, indicates a substantial shift in the quality (considered as bioavailability or microbial utilisation) of the DOC between these species associated with the shift in DOC composition.

It is suggested that shifts in the mass balance of leaf litter from native and exotic plant species may substantially influence biogeochemical cycling within receiving waters such as the Torrens Lake. For example, the observed DOC:FRP ratio of the leachate from the river red gum was 459:1. In comparison, the DOC:FRP ratios of the grass cuttings, London plane tree, English elm and white poplar were 29.3:1, 39.9:1, 693:1, and 1136:1 respectively. This indicates that the stoichiometric food quality (Elser *et al.*, 2000) of the exotic species is substantially different to that of the native river red gum. In comparison to the river red gum (and to a lesser extent the English elm), the grass cuttings and London plane are P-rich, and the white poplar is P-deficient. These data suggest that in catchments that have historically been P-limited, the wide spread replacement of native vegetation with exotic species such as the London plane tree, and poor management of grass cuttings may be important factors in eutrophication processes. In addition to impacts on microbial food webs and water quality, the composition of macroinvertebrate communities in streams may be affected by the change from native to exotic trees. For example, freshwater shrimps (*Paratya australiensis*) have been shown (Schulze and Walker, 1997) to prefer leaves from the native river red gum (*Eucalyptus camaldulensis*) over leaves from the deciduous exotic willow *Salix babylonica*.

Major changes in the chemical properties (hydrophobic-hydrophilic) of DOC may have a substantial impact on the fate of DOC in both surface and groundwater systems. Changes to the surface properties of DOC may influence the partitioning of compounds such as metals (e.g. lead and zinc), hydrocarbons, herbicides and pesticides which complex with DOC. Strongly hydrophobic DOC compounds may partition with colloidal and fine particulate material and subsequently settle out of the water column. In contrast, hydrophilic compounds are more likely to remain suspended in the water column (Sonnenberg and Holmes, 1998). The transport of DOC and toxic pollutants from surface runoff into ground water via infiltration systems is of substantial environmental concern (Ellis and Hvitved-Jacobsen, 1996), particularly given the current and projected use of aquifer storage and recovery systems throughout South Australia. Although the HiN fraction has been shown to be both present in comparatively low concentrations, and readily bioavailable (Chapter 5), the increased proportion of HiN observed in the leachate from the English elm and London plane indicates that these species are unsuitable for wide spread planting in catchments utilised for potable supply as the hydrophilic neutral (HiN) fraction represents a major challenge to the treatment of water for potable supply (Chow *et al.*, 2004; Chow *et al.*, 2000).

This work provides a clear demonstration that the DOC released from the exotic species tested has a distinctly different composition from the representative native species. The replacement of native species such as the river red gum, which has a peak litter fall period in summer, a DOC which is distinctly different from the other species tested, and a moderate DOC:FRP ratio, with introduced deciduous species that have peak litter fall periods in autumn, and either low or high DOC:FRP ratios may have a series of profound effect on ecosystem function and stability. Consequently, the widespread planting of introduced deciduous species should be avoided. Management should focus on the use of trees that are indigenous to the region and offer biodiversity conservation values. It is interesting to note that there is concern over the ecological impacts of the broad scale replacement of native deciduous riparian forest with eucalyptus plantations in Europe (Pozo *et al.*, 1997).

Chapter 7: A comparison of pelagic and sediment oxygen demand and phosphorus dynamics in an urban weir pool.

7.1 Introduction

In urbanised catchments, stormwater is typically directed into streams, rivers, estuaries and coastal embayments via constructed stormwater infrastructure (Walsh, 2002). The organic material transported to receiving waters via urban stormwater is recognised as a critical pollutant (Lawrence and Breen, 1998) because stimulation of heterotrophic metabolism via episodic inputs of labile material in stormwater may generate substantial oxygen demands in both the water column and sediments. The combined oxygen demands from the water column and sediments may generate a large oxygen debt, with small shallow lakes particularly at risk of deoxygenation (Douglas and O'Brien, 1987).

While the biochemical oxygen demand (BOD) of surface waters is routinely measured, sediment oxygen demand (SOD) is generally overlooked in water quality monitoring programs. Although SOD is often assumed to represent the degradation of relatively recalcitrant material that has accumulated in the sediments (Lawrence, 2001), SOD has been shown to be a dominant oxygen demanding process in several rivers (Kelly, 1997; Matlock *et al.*, 2003). Consequently, the ability to determine the relative role of BOD from external loading (inflowing surface water) and internal sources (SOD) is essential to the effective management of a constructed water body, particularly when considering the maximum sustainable load of oxygen demand from inflowing waters.

The Torrens Lake is a shallow urban weir pool that suffers numerous water quality problems including anoxia and recurrent blooms of toxic cyanobacteria. Previous work (Chapter 5) has shown that the episodic input of urban stormwater that is directed into the river channel via constructed stormwater infrastructure and the tributary streams, stimulates heterotrophic metabolism in the water column, and generates a substantial oxygen debt in the lake. Despite this previous work, sediment oxygen demands have not yet been rigorously assessed, and the role of SOD in generating the anoxic conditions observed in Torrens Lake is currently unknown. Consequently, determining the role of sediment oxygen demand in deoxygenation of the water column is the focus of the current chapter.

In addition to the ecological problems associated with anoxia, nuisance and toxic phytoplankton (algal) blooms present a major management issue in the Torrens Lake. It is well established that phytoplankton blooms are often generated by observable changes in factors such as nutrient loading (Reynolds, 1997). Internal loading from potential release of phosphorus from lake sediments under anoxic conditions is therefore a substantial issue for management of the lake. Although it has been suggested that internal loading is the major contributor of bioavailable phosphorus (AWQC, 2000; Stokes, 1999; TCWMB, 2002) there remains a substantial level of uncertainty over the relative role of internal and external loading as the primary source of phosphorus supporting the episodic blooms of toxic cyanobacteria observed.

This project was utilised to test two hypotheses. Firstly, that external loading of oxygen demanding material is the primary stressor responsible for the episodic deoxygenation of the water column following rain events; and secondly, that external loading of phosphorus during rain event inflows represents a larger, primary source of FRP than release of FRP from sediments under anoxic conditions (internal loading). The first hypothesis was tested by comparing BOD in samples collected from the lake water column, and SOD in sediment cores collected from the lake. The second hypothesis was tested via measurements of the release of filterable reactive phosphorus (FRP) from the sediment cores used in the oxygen demand experiments.

The Torrens Lake functions as a sedimentation basin, and it has been estimated that the lake retains 34 percent of inflowing suspended solids (Tonkin Consulting, 2000). Consequently, it was anticipated that higher levels of SOD and FRP release would be recorded in samples collected from the inlet than at the outlet end of the lake. Furthermore, it was anticipated that there would be a marked increase in BOD and SOD in the samples collected during wet weather due to the influx of bioavailable organic material from the ephemeral tributary streams. Consequently, water column and sediment samples were collected for analysis from the inlet and outlet end of the lake in both dry weather (when there was no inflow) and wet weather (when there was stormwater inflow).

7.2 Methodology

7.2.1 Site Description

A detailed description of the Torrens Catchment is provided in Chapter 2. The Torrens Lake is a shallow weir pool in the Adelaide Central Business District. A weir constructed on the Torrens River in the 1880's forms the lake, and the depth of the lake varies from approximately 1m at the inlet to a maximum of 6m at the weir. Average depth is 2.6m, and water levels are maintained via operation of the weir (AWQC, 2000). The bank full volume of the lake is 478ML (standing volume is estimated at 420ML), with the surface are of the lake estimated at 0.16km^2 (Regel, 2003). Urban stormwater is directed into the tributary streams, the river and the lake via constructed stormwater infrastructure. These inflows cause the lake to function as a stormwater detention basin for the majority of the catchment (only around 8% of the urban catchment enters the river below the weir) and approximately 60% of the pollutants entering the lake originate from the urbanised sub-catchments (TCWMB, 2002).

7.2.2 Sample Collection

Sediment cores were collected from the inlet and the outlet end of the lake on 3 occasions during May 2004: during wet weather conditions on (urban stormwater inflow to lake) on 5th May 2004, during dry weather conditions (no inflow to lake) on 13th May 2004, and during wet weather conditions (urban stormwater inflow to lake) on 20th May 2004. Sediment cores were collected from a boat, using 320mm x 57mm (ID) clear Plexiglas tubes attached to a remote coring device. The depth of sediment obtained in each core was approximately 100mm, with an average water volume of 560mL overlying the cores. Individual cores were examined to ensure that the profile of the sediment core was intact. Cores that were not intact were subsequently discarded. Intact cores were kept vertical, and immediately stored in the dark in an ice filled, insulated box, and were subsequently returned to the laboratory within 1 hour of collection.

At the same time as the sediment cores were collected, lake water was collected from the inlet end of the lake for use in the bioassays. The water was collected as depth integrated samples, using a 25mm internal diameter column sampler lowered to within 100-200mm of the lake sediments. Sufficient column sampler shots were transferred to two pre-washed (see Chapter 2) 5L PTFE containers to obtain 10L of lake water. The water was immediately stored in the dark in an ice filled, insulated box, and subsequently returned to the laboratory within 1 hour of collection. This water was homogenized by inversion mixing; pre filtered through pre-washed (see Chapter 2) Whatman GF/C filters and subsequently filtered through Whatman PVDF 0.45μm membrane filters. The filtered water was transferred to an acid-washed, 10L glass carboy. This water was seeded with 20mL L^{-1} of 37μm filtered lake water (to ensure that an active pelagic microbial community would be present in the core systems) prior to use. The water samples were filtered in order to maintain consistency in the approach to BOD analysis performed throughout this thesis. It is important to note that the filtering process is not believed to have substantially reduced the BOD exerted by the water samples, as previous work (Chapter 3) demonstrated that 96% of the total BOD is exerted by dissolved (<0.45μm) material.

7.2.3 Sediment Oxygen Demand

In inlet zones or areas with high velocity or turbulent flows, the re-suspension of sedimentary material may increase the rate of sediment oxygen demand (e.g. Doyle and Rounds, 2003). Therefore a comparison of oxygen demand from benthic and resuspended sediment material was also undertaken to ensure that sediment oxygen demand was not underestimated. Eight intact cores were collected from each end of the lake on 5th May 2004. Twelve intact cores were collected from each end of the lake on both 13th and 20th May 2004. Four cores were utilised for analysis of benthic sediment oxygen demand. The additional cores collected on both the 13th and 20th May 2004 were utilised for analysis of re-suspended sediment oxygen demand. Four cores were utilised for analysis of sediment composition (see section on Sediment Composition below for details).

Analysis of sediment oxygen demand included a comparison of (a) pelagic oxygen demand (controls - water only in core systems), (b) benthic sediment oxygen demand, and (c) re-suspended sediment oxygen demand. Four (4) replicate cores were established for each condition. The water contained in the cores was carefully siphoned off. This water was replaced with the water that had been collected from the lake (care was taken to ensure minimal disturbance of the sediment).

Cores were sealed with a PTFE lid fitted with a sampling port, and a 20mm x 3mm Teflon stir bar. The Teflon stir bars were fitted in order to maintain a water velocity in the cores sufficient to ensure that SOD was not limited by the rate of transport of oxygen into the sediment. In cores being utilised for analysis of re-suspended sediment oxygen demand (RSOD), the stir bars were suspended 5mm above the sediment surface. In the cores being utilised for analysis of benthic sediment oxygen demand (BSOD), the stir bars were suspended approximately 200mm from the sediment surface. Sets of eight cores were evenly distributed around a magnetic stirrer, with the height of the stirrer adjusted to correspond with the height of the Teflon stir bars. The variation in the spacing between the stir bars and the sediment-water interface allowed a single stirring velocity to be established that was sufficient to re-suspend sediment in the cores for analysis RSOD, but was below the threshold for re-suspension of the sediment in the cores for analysis of BSOD.

Cores were incubated for 5 days at 20°C in the dark. The decision to incubate the cores at standard rather than ambient conditions was based on the temperature dependency of sediment oxygen demand (Douglas and O'Brien, 1987), observations that P release from sediments is temperature dependent (Jensen and Anderson, 1992), and the desire to generate an estimate of sediment oxygen demand comparable to standard biochemical oxygen demands. Dissolved oxygen concentrations were measured at time steps of 0, 1, 3, 6, 24, 48, 72, 96, and 120 hours, via the sampling port using a WTW (Wissenschaftlich-Technische Werkstätten GMBH & Co. KG) CellOx 325 oxygen sensor attached to a WTW Oxi 330i dissolved oxygen meter.

Sediment oxygen demand was calculated Equation 7.1 (Ferguson *et al.*, 2003):

$$SOD = ([C_{t1} - C_{t0}]) \times V/SA)/T \qquad \text{Equation 7.1}$$

where SOD is the sediment oxygen demand in grams of $O_2\ m^{-2}day^{-1}$, C_{t0} = oxygen concentration at time zero, C_{t1} = oxygen concentration at the end of the specified time period (e.g. one day), V = volume of water (in litres) overlying the sediments in the core system, and SA = the surface area of sediments in the incubation chamber. Calculated SOD values were subsequently corrected for pelagic oxygen demand to provide a comparison of the relative oxygen demand of the pelagic zone, benthic and re-suspended sediments.

To provide a comparison of the relative oxygen demand of sediments and the pelagic zone, a benthal demand index (BDI) was calculated according to Equation 7.2 (adapted from Douglas and O'Brien, 1987).

$$\mathrm{BDI} = a / (1 - a) \qquad \text{Equation 7.2}$$

where a = pelagic oxygen demand ($\mathrm{mgL^{-1}\ O_2\ day^{-1}}$) / SOD ($\mathrm{mgL^{-1}\ O_2\ day^{-1}}$))

BDI values greater than 1 indicate that oxygen demand is dominated by pelagic processes, values less than 1 indicate that oxygen demand is dominated by benthic processes.

An additional comparison is provided via the technique used by Burns *et al.* (1996) to compare the water column depth at which the SOD consumes the same amount of oxygen as a BOD, and therefore determine if SOD or BOD was the dominant oxygen demanding process in any given depth of water. The value (water column demand potential = pSOD) is calculated according to Equation 7.3.

$$\mathrm{pSOD} = \mathrm{SOD}[\mathrm{gO_2m^{-2}day^{-1}}] / \mathrm{BOD}\ [\mathrm{gO_2m^{-3}day^{-1}}] \qquad \text{Equation 7.3}$$

7.2.4 Sediment Composition

Sediments were carefully removed from the four Plexiglas cores set aside for analysis of sediment composition. From each core, the top 5cm of sediment was recovered, transferred to an aluminium tray and oven dried at 50°C for 72 hours. The sediment was then homogenized, and sub-samples were collected for analysis of total volatile solids and total phosphorus content. Total volatile solids were measured (in triplicate) on 1g sub-samples from the top 5 cm of the core, according to APHA method 2540 E (Eaton *et al.*, 1995). These results were interpreted as a surrogate measurement for sediment organic matter (OM) content. Total phosphorus (TP) content of the lake sediments was analysed using a Lachat flow injection analyser (FIA). Analysis was performed in duplicate, according to the NATA approved methodology and QA/QC system of Diagnostic Services Pty Ltd.

7.2.5 Benthic flux of filterable reactive phosphorus

Benthic flux of filterable reactive phosphorus (FRP) out of the sediments and into the overlying water column was assessed at time steps of 0, 1, 3, 6, 24, 48, 72, 96, and 120 hours. 20mL of water was withdrawn, and filtered through a Whatman 0.45µm syringe filter for analysis of FRP. An equal amount of water was replaced from a reservoir (stored in the temperature-controlled room in which the bioassays were performed) containing the remainder of the 10L of lake water initially used to fill the cores. The extraction and replacement of 20mL resulted in a dilution of the water overlying the cores of <4%.

Analysis for FRP was performed according to APHA method 4500-P E (Eaton *et al.*, 1995) using a Hitachi U-2000 double beam spectrophotometer (Hitachi Ltd, Tokyo, Japan). Due to a series of technical errors, time series results of FRP release are only available for the samples collected on 20th May 2005. Measurements of final FRP concentration (concentration of FRP in water samples collected from cores at day 5) were only performed on the samples collected from the BSOD cores. Phosphorus flux was calculated using the Equation 7.4 (Ferguson *et al.*, 2003):

$$\text{FRP flux} = ([C_{t1} - C_{t0}) \times V/SA)/T \qquad \text{Equation 7.4}$$

Where FRP flux is in $\mu g\, m^{-2} day^{-1}$, C_{t0} = FRP concentration at time zero, C_{t1} = FRP concentration at the end of the specified time period (e.g. one day), V = volume of water (in litres) overlying the sediments in the core system, and SA = the surface area of sediments in the incubation chamber.

7.2.6 Data Analysis

Raw data were plotted as means ± 1 standard error (SE), and curves were fitted to the means using Sigma Plot (Version 8.0, SPSS Inc). Remaining statistical tests (e.g. ANOVA) were performed using the package JMP In version 3.2.6 (SAS Institute Inc. 1996). Normality was tested using the Shapiro-Wilk W Test, and the equality of variances with the Levene test. Square root and log transformations were applied to all data sets exhibiting non-normal distribution and/or unequal variances. Data sets that did not respond to the transformations were subsequently analysed using non-parametric (Wilcoxon/Kruskal-Wallis) analysis. For all statistical tests $\alpha = 0.05$.

7.3 Results

7.3.1 Oxygen Demand Curves

Measurements of 5-day biochemical oxygen demand ranged from 2.6mgL^{-1} in the samples collected during dry weather (13th May 2004), to 6.1mgL^{-1} (5th May 2004) and 7.3mgL^{-1} (20th May 2004) in the samples collected during wet weather. The time series measurements of dissolved oxygen (DO) concentrations in the core systems (Fig. 7.1) reveals substantial shifts in the rates of oxygen depletion from BOD and SOD between the sampling dates. The depletion of DO in the control cores (water only - oxygen demand due to pelagic metabolism) occurred at a relatively slow linear rate (see Table 7.1 for regression equations) in the dry weather (Fig. 7.1 [A]) samples, and at a faster yet still linear rate, in the first set of wet weather (Fig. 7.1 [B]) samples. In contrast, the depletion of DO due to BOD occurred in an exponential manner in the second set (Fig. 7.1 [C]) of wet weather samples. This result suggests that there may have been a substantial difference in the quality (and subsequently bioavailability) of the organic matter transported in the inflowing stormwater, which was more bioavailable and therefore more readily oxidized in the second rain event.

The time series analysis of oxygen demand in water overlying the sediment cores reveals that DO depletion in these systems occurs at a substantially faster rate than that occurring in the control cores. The exponential curves fitted in the figures (see Table 7.1 for regression equations) are presented for clarity. However, it is apparent that O_2 depletion occurs in a linear fashion in the early stages (day 0-1) of the bioassay, and shifts towards an exponential function as oxygen concentrations approach zero. In general, depletion of DO due to BSOD occurs at a faster rate at the inlet than outlet, and depletion of DO due to RSOD is greater than depletion due to BSOD. This is investigated further in the following sections. It is likely that the increased rate of DO depletion between BOD and SOD is attributable to factors such as differences in microbial populations (e.g. density, species and activity), and these differences are accounted for in the benthal demand index (discussed in the following sections).

7.3.2 Sediment Oxygen Demand

Throughout the literature there is a trend to utilise DO depletion values obtained in the first 24 hours of incubation for comparison of sediment oxygen demand in core systems (Barcelona, 1983; Douglas and O'Brien, 1987; Grenz *et al.*, 2000). This convention of using the oxygen demand values obtained between 0 and 24 hours is subsequently adopted for analysis of the present data. Values for BSOD and RSOD were corrected for pelagic oxygen demand, sediment surface area, and water volume. The oxygen demand values presented in Figure 7.2 provide an assessment of the relative level of oxygen demand in the water column (BOD) and sediments (BSOD and RSOD). There is a significant difference in BOD (ChiSq = 9.846, df_2, P = 0.007) between the three sampling dates (Fig. 7.2) that is due to the increase in BOD in the sample collected on 20th May 2004 (Fig. 7.1). Subsequent analysis of the SOD data shows that neither BSOD (ANOVA {F = 2.3857, $df_{2,11}$ P = 0.148}) or RSOD (ANOVA {F = 1.717, $df_{2,11}$ P = 0.236}) change significantly between the sampling dates despite the increase in pelagic oxygen demand.

Comparison of the pooled SOD data indicates that there is no difference in BSOD (ANOVA {F = 0.635, $df_{1,23}$ P = 0.434}) between the inlet and weir end of the lake, but that RSOD is higher at the inlet end of the lake (ANOVA {F = 6.460, $df_{1,15}$ P = 0.024}). Furthermore, oxygen demand from resuspended sediments (RSOD) is higher (ANOVA {F=34.942, $df_{1,39}$, P = <0.0001}) than oxygen demand from undisturbed sediments (BSOD).

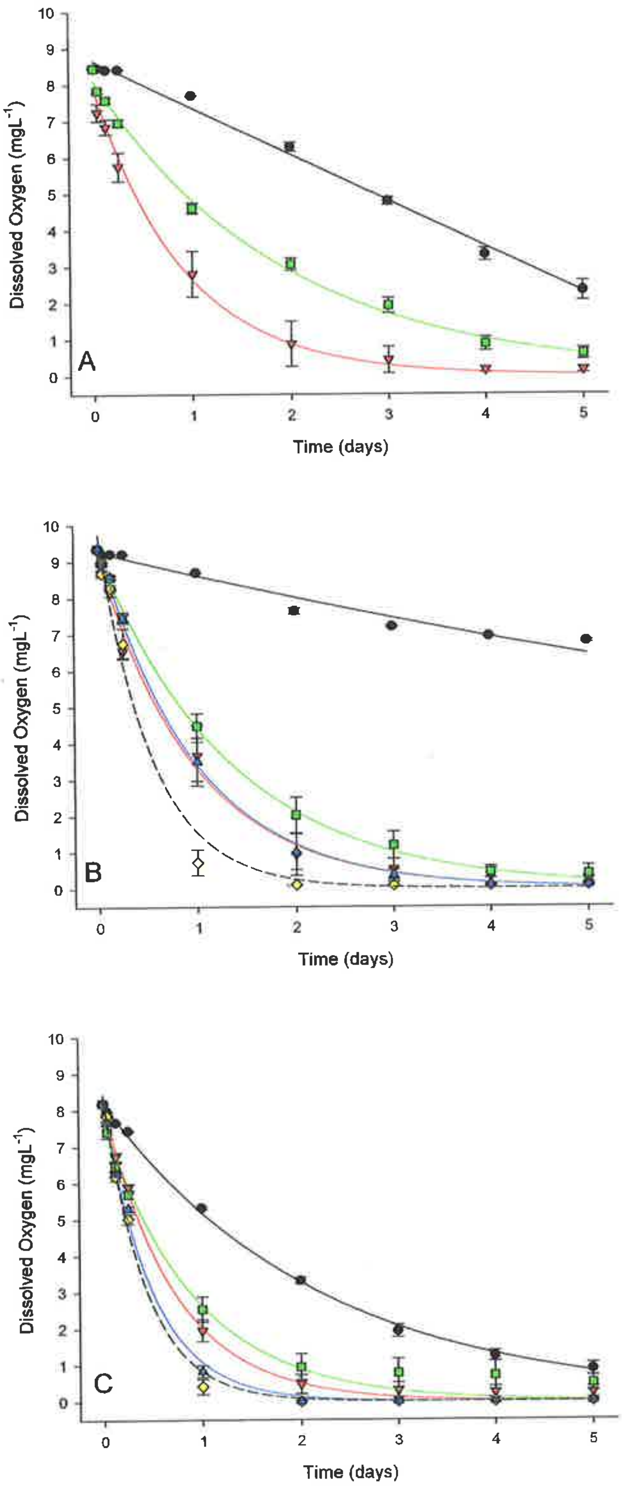

Figure 7.1. Comparison of dissolved oxygen in water overlying cores in samples collected [A] during wet weather 5th May 2004, [B] dry weather 13th May 2004, and [C] during wet weather 20th May 2004. Closed circles (and solid line) represent pelagic oxygen demand, Red inverted triangles (and red line) represent BSOD cores from the inlet, Green squares (and green line) represent BSOD cores from the outlet (weir), Yellow diamonds (and broken line) represent RSOD cores from the inlet, Blue triangles (and blue line) represent RSOD cores from the outlet. Error bars are ±1 SE (n = 4). SeeTable 7.1 for regression equations.

Table 7.1. Regression equations for BOD in the control cores, and BSOD and RSOD in the sediment cores collected from the inlet and outlet end of the Torrens Lake on the 5th, 13th and 20th of May 2004. Degrees of freedom for all equations = df_8. All values for oxygen demands (y) are in mgL-1, and all values for times (x) are in days.

Date	Site	Parameter	Equation	r^2	F	P
5.5.2004	Control	BOD	$y = 9.210 - 0.561x$	0.947	123.9174	<0.0001
13.5.2004	Control	BOD	$y = 8.651 - 1.258x$	0.994	1223.56	<0.0001
20.5.2004	Control	BOD	$y = -0.147 + 8.332e^{-0.441x}$	0.999	3408.05	<0.0001
5.5.2004	Inlet	BSOD	$y = 0.153 + 7.821e^{-1.167x}$	0.995	575.46	<0.0001
13.5.2004	Inlet	BSOD	$y = 0.155 + 9.046e^{-1.077x}$	0.996	662.57	<0.0001
20.5.2004	Inlet	BSOD	$y = 0.188 + 8.043e^{-1.499x}$	0.999	4340.15	<0.0001
5.5.2004	Outlet	BSOD	$y = 0.058 + 8.076e^{-0.528x}$	0.996	796.82	<0.0001
13.5.2004	Outlet	BSOD	$y = 0.152 + 9.143e^{-0.773x}$	0.999	2809.57	<0.0001
20.5.2004	Outlet	BSOD	$y = 0.606 + 7.306e^{-1.427x}$	0.997	1123.47	<0.0001
13.5.2004	Inlet	RSOD	$y = -0.090 + 9.814e^{-1.801x}$	0.989	270.91	<0.0001
20.5.2004	Inlet	RSOD	$y = -0.080 + 8.493e^{-2.283x}$	0.997	891.19	<0.0001
13.5.2004	Outlet	RSOD	$y = -0.114 + 9.597e^{-0.991x}$	0.999	2589.39	<0.0001
20.5.2004	Outlet	RSOD	$y = -0.071 + 8.343e^{-1.997x}$	0.998	1571.69	<0.0001

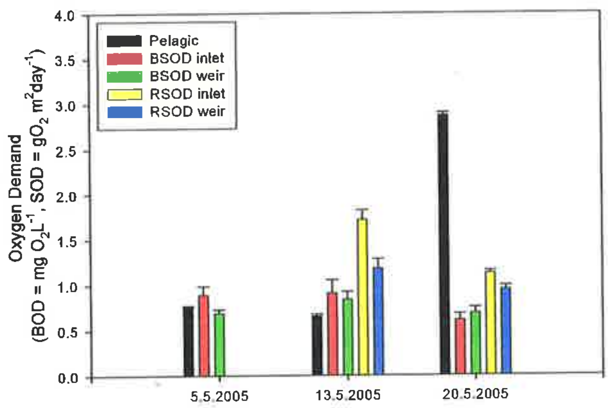

Figure 7.2. Comparison of the relative oxygen demand generated in the water column in the first 24 hours of incubation by pelagic metabolism, benthic sediments (BSOD) and resuspended sediments (RSOD) at the inlet and outlet zone of Torrens Lake on 5.5.2005, 13.5.2005, and 20.5.2005. Pelagic oxygen demand values are as per standard biochemical oxygen demand (calculated from control cores). Sediment oxygen demand values are corrected for pelagic oxygen demand, sediment surface area, and water volume. Error bars are ±1 SE (n = 4).

7.3.3 Benthal Demand Index

A direct comparison of the relative importance of BOD, BSOD, and RSOD in de-oxygenation water column is provided by the benthal demand index (Douglas and O'Brien, 1987). The results (Table 7.2) indicate that during periods when the daily rate of BOD is relatively low (<0.8 $mgL^{-1}day^{-1}$), BSOD and RSOD dominate oxygen demand at both the inlet and outlet end of the lake. In comparison, when the daily rate of BOD is relatively high (2.9 $mgL^{-1}day^{-1}$), BOD dominates over BSOD at both the inlet and outlet, and dominates over RSOD at the outlet. RSOD does however continue to be the dominant oxygen demanding process at the outlet end of the lake.

The water column demand potential at the inlet (calculated from Equation 7.3, see Table 7.3 for results) demonstrates that when BOD is low (< 0.8 mgL^{-1} day^{-1}), pBSOD and pRSOD consume the same amount of oxygen as pelagic metabolism (BOD) in water columns 1.4m and 2.6m deep respectively. Because the water column at the inlet is <1m deep, SOD functions as the dominant oxygen demanding processes when BOD is low (e.g. <0.8mgL^{-1}). In contrast, at the outlet, pBSOD and pRSOD are 1.3m and 1.8m. As the water column at the outlet is ~3m deep, SOD retains an important role, but BOD is the dominant oxygen demanding process. In comparison, when BOD increases to 2.9 $mgL^{-1}day^{-1}$, pBSOD and pRSOD at the inlet decreases to 0.2m and 0.4m respectively, and at the outlet, pBSOD and pRSOD are also <0.4m. Consequently, at both the inlet and the outlet, BOD is the dominant oxygen demanding process under relatively high rates of BOD.

Table 7.2. Benthal demand index (BDI). BDI values greater than 1 (shown in bold) indicate cores in which oxygen demand is dominated by pelagic processes (Calculated using Equation 7.2: adapted from Douglas and O'Brien, 1987).

Date	BDI (BSOD inlet)	BDI (BSOD outlet)	BDI (RSOD inlet)	BDI (RSOD outlet)
5.5.04	0.21	0.41	n/a	n/a
5.5.04	0.36	0.36	n/a	n/a
5.5.04	0.28	0.39	n/a	n/a
5.5.04	0.34	0.31	n/a	n/a
13.5.04	0.17	0.28	0.09	0.17
13.5.04	0.49	0.20	0.13	0.23
13.5.04	0.24	0.29	0.14	0.17
13.5.04	0.20	0.30	0.12	0.15
20.5.04	**1.40**	**2.58**	0.91	**1.37**
20.5.04	**2.01**	**2.28**	0.97	**1.36**
20.5.04	**3.05**	**1.78**	0.99	**1.08**
20.5.04	**1.84**	**4.26**	0.85	**1.15**

Table 7.3. Potential water column oxygen demanding potential of BSOD and RSOD in Torrens Lake. pBSOD (and pRSOD) represents the equivalent depth of water column required to consume the same amount of oxygen as SOD based on the BOD recorded in the water column. (Calculated using Equation 7.3: adapted from Burns *et al.* 1996).

Date	Inlet pBSOD (m)	Outlet pBSOD (m)	Inlet pRSOD (m)	Outlet pRSOD (m)
5.5.2005	1.17	0.91	n/a	n/a
13.5.2005	1.38	1.27	2.61	1.79
20.5.2005	0.21	0.24	0.39	0.33

7.3.4 Sediment Composition

The results of the organic matter (OM) and total phosphorus (TP) analysis are summarised in Table 7.4. As anticipated, sediment OM content is higher (ANOVA, {$F_{1,22} = 13.252$, $P = 0.002$}) at the inlet end of the lake. However, there is no difference in the TP content (ANOVA, {$F_{1,22} = 0.166$, $P = 0.688$}) between the inlet and outlet end of the lake. Although there was no apparent relationship between sediment OM content and sediment oxygen demand (Fig. 7.3 [A]), there is a relationship between sediment OM content and sediment TP content ([$y = -105.51 + 66.703x$], $r^2 = 0.497$, df_9, $F = 7.897$, $P = 0.023$) at the outlet end of the lake (Fig. 7.3 [B]).

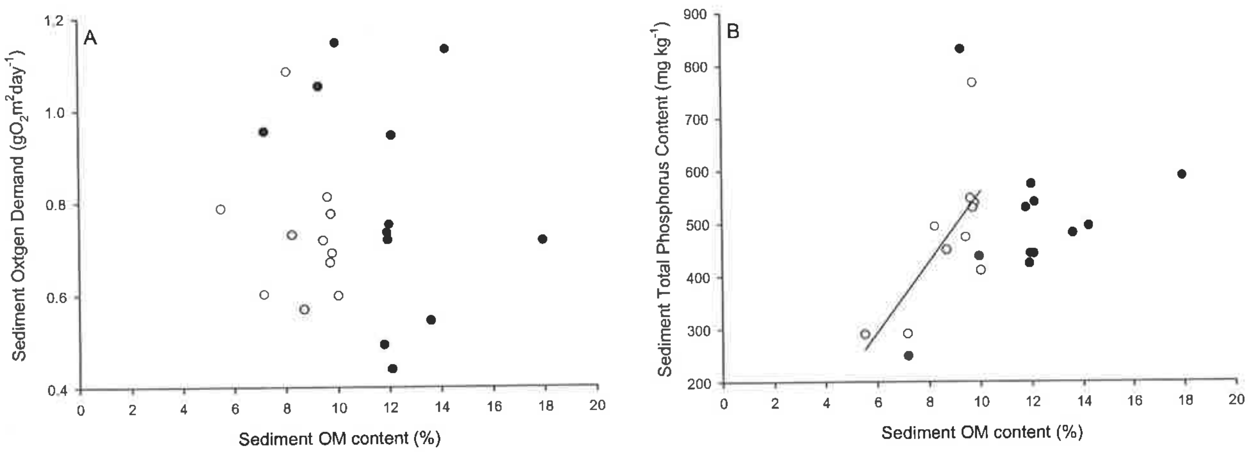

Figure 7.3. [A] Relationship between sediment OM content and benthic sediment oxygen demand (BSOD); and [B] relationship between sediment OM content and sediment total phosphorus (TP) content at the inlet (solid circles) and outlet (open circles) ends of Torrens Lake (solid regression line represents relationship between OM and TP at the outlet only, see text for regression equation).

Table 7.4. Summary of sediment oxygen demand and sediment composition in cores collected from the inlet and outlet end of Torrens Lake. Mean values are shown in bold. Values in brackets are ±1SE (n=4).

Site	Date	BSOD $gO_2m^{-2}day^{-1}$		RSOD $gO_2m^{-2}day^{-1}$		OM %		TP (mg kg^{-1})	
Inlet	5.5.2004	0.89	(0.10)			14.08	(1.39)	549.3	(20.9)
	13.5.2004	0.91	(0.15)	1.72	(0.11)	9.57	(0.95)	511.9	(121.2)
	20.5.2004	0.61	(0.07)	1.13	(0.03)	12.39	(0.41)	447.5	(12.2)
	Mean	**0.80**	**(0.10)**	**1.43**	**(0.30)**	**12.01**	**(1.32)**	**502.9**	**(29.7)**
Outlet	5.5.2004	0.69	(0.04)			8.05	(1.04)	412.3	(70.2)
	13.5.2004	0.84	(0.09)	1.18	(0.11)	8.87	(0.40)	378.7	(127.2)
	20.5.2004	0.69	(0.06)	0.95	(0.04)	9.50	(0.35)	542.3	(97.5)
	Mean	**0.74**	**(0.05)**	**1.07**	**(0.12)**	**8.81**	**(0.42)**	**444.4**	**(49.9)**

7.3.5 Benthic flux of filterable reactive phosphorus

The time series analysis of FRP flux (Fig. 7.4) obtained from the sediment cores collected on 20th May 2005 indicates that substantial accumulation of FRP (released from the sediments) in the overlying water does not occur until DO concentrations in the water column fall below 2 mgL^{-1}. Furthermore, despite the similarity in rates of oxygen depletion, accumulation of FRP occurs in a sigmoidal function ($[y = 416.849 / (1 + e^{-(x-2.423 / 0.679)}]$, $r^2 = 0.999$, df_8, $F = 8389.16$, $P = <0.0001$) in the cores from the inlet end of the lake. In comparison FRP accumulation occurs in a linear manner ($[y = 6.894 + 29.684x]$ $r^2 = 0.992$, df_8, $F = 878.344$, $P = <0.0001$) in the cores collected from the outlet end of the lake. Rates of accumulation at the inlet and outlet are approximately equivalent when DO levels are greater than 2 mgL^{-1}. However, rates of accumulation change markedly at the inlet when DO falls below 2 mgL^{-1}. This shift indicates that there is a difference in the sediment composition and or FRP release mechanisms between the two ends of the lake.

Peak FRP flux does not occur until DO concentrations in the overlying water fall below 0.1mgL^{-1} (Fig. 7.5 [A]). Comparison of the accumulated FRP released over 5 days reveals that FRP flux was higher (ChiSq =8.333, df_1, $P = 0.004$) at the inlet (85.1mg $FRPm^{-2}$) than at the weir end of the lake (18.2 mg $FRPm^{-2}$). Accepting the suggestion that there is a difference in the sediment composition and or FRP release mechanisms between the two ends of the lake, it is interesting to note that there was a difference in sediment OM content, but no difference in TP between the inlet and outlet end of the lake, and that there are no apparent relationships between sediment TP content and FRP flux at either end of the lake (Fig. 7.5 [B]).

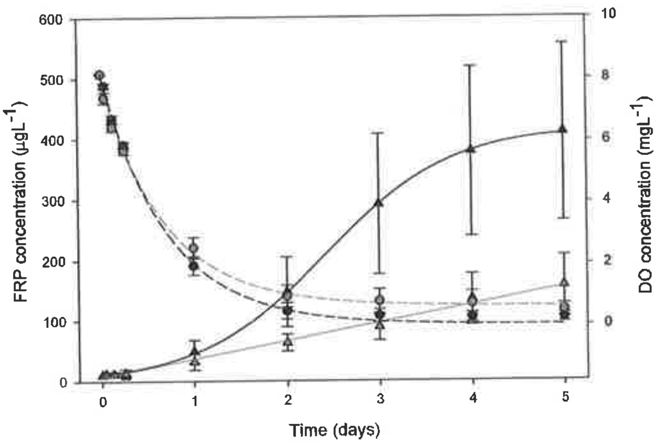

Figure 7.4. Dissolved Oxygen (DO) and FRP dynamics in water overlying sediment cores collected 20.5.2005.Red circles = DO in cores from outlet end of lake; Red triangles = FRP in cores from outlet end of lake; Black circles = DO in cores from inlet of lake; Black triangle = FRP in cores from inlet end of lake. Error Bars are +/- 1 S.E. (n = 4).

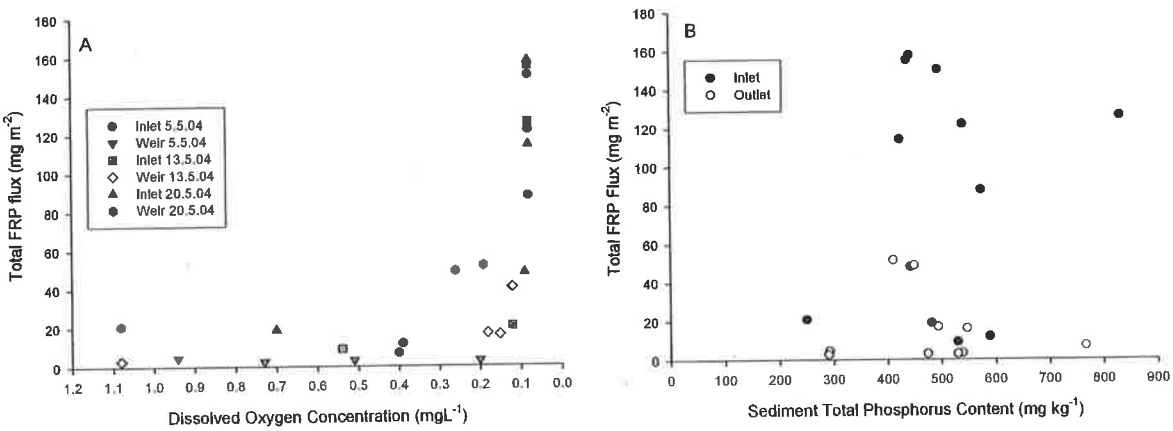

Figure 7.5. [A] Relationship between final dissolved oxygen concentration and FRP concentration in water overlying sediment cores and [B] Relationship between sediment total phosphorus content and FRP flux. Cores collected from the inlet and outlet end of Torrens Lake on 5.5.2004, 13.5.2004 and 20.5.2004.

7.4 Discussion

7.4.1 Sediment oxygen demand

The average BSOD values obtained in this study (~0.8g $O_2\,m^{-2}day^{-1}$) are in the same range as those obtained in other studies on agricultural and stormwater-impacted rivers. For example, Matlock *et al.* (2003) report average SOD values of 0.62g $O_2\,m^{-2}day^{-1}$ (range 0.13-1.2) from the Arroya Colorado River. Lawrence (2001) states that for sediments in areas prone to urban stormwater discharges, SOD values are typically around 0.2g $O_2m^{-2}day^{-1}$, and that values may increase to 0.5 - 0.8g $O_2m^{-2}day^{-1}$ in sediments with relatively high OM content. The USEPA (1994) benchmark ranks SOD values less than 1.0g $O_2\,m^{-2}\,day^{-1}$ as low, and SOD values greater than 1.0g $O_2\,m^{-2}\,day^{-1}$ as high. Chapra (1997) suggests that SOD values in the range 1-10g $O_2\,m^{-2}\,day^{-1}$ indicate that the sediments are highly enriched in organic matter. Based on these SOD values from the literature, the sediment oxygen demand in the Torrens Lake is at the top end of the range expected for areas heavily impacted by urban stormwater (Lawrence, 2001), but would not be considered high by the USEPA (1994). Furthermore, the results suggest that the sediments would be classified as having a "relatively" high OM content by Lawrence (2001), but would not be classified as heavily enriched with OM by Chapra (1997).

It was anticipated that oxygen demand from resuspended sediments would be greater than oxygen demand from undisturbed, or benthic sediments. This expectation was based on the results of other studies. For example, in a study on the Tualatin River Basin (Oregon), Doyle and Rounds (2003) observed average SOD values of 1.9g $O_2\,m^{-2}\,day^{-1}$ at mixing velocities below the threshold for sediment re-suspension, and 3.1g $O_2\,m^{-2}\,day^{-1}$ at mixing velocities above the threshold for sediment re-suspension. The results of the current research indicate that in the Torrens Lake, RSOD is approximately 44% higher than BSOD at the inlet, and approximately 31% higher than BSOD at the outlet. Although there was no difference in BSOD between the two ends of the lake, the observation that sediment OM content and the RSOD of sediments were higher at the inlet end of the lake than at the weir end of the lake is not unexpected, as the inlet zone would be a depositional zone for stormwater borne sediments. In addition, the OM in the cores from the inlet may be more readily bioavailable, and the surface sediments may be comprised of relatively fine material that is easily disturbed by turbulence.

The BDI, pBSOD and pRSOD results of this study indicate that when the rate of BOD is relatively low (<0.8 mgL^{-1}day^{-1}), SOD represents the dominant oxygen demanding process in the lake; BSOD and RSOD at the inlet consumes more oxygen than BOD in the available depth of water column and SOD is the governing process. Under these conditions, oxygen demand from benthic sediments and any resuspended sediment (e.g. sediments disturbed by turbulence generated from boat traffic) potentially contribute to the low dissolved oxygen levels often observed Torrens Lake. However, when the rate of BOD increases to relatively high levels (2.9 mgL^{-1}day^{-1}), pBSOD and pRSOD values decrease to below the standing water depth, and BOD becomes the governing oxygen demanding process.

With in-lake BOD rates of 7.26 (±0.17) mgL^{-1}day^{-1} recorded following summer rain events (Chapter 5), BSOD and RSOD are not considered a primary pathway in de-oxygenation of the water column in Torrens Lake. The justification for this statement is that BDI values at the inlet approached unity (0.93 ±0.03) when BOD values were at 2.9 mgL^{-1}day^{-1}. When estimated using a BOD rate of 5mgL^{-1}day^{-1}, a BSOD of 0.8 g O_2 m^{-2} day^{-1}and a RSOD of 1.43 g O_2 m^{-2} day^{-1}, pBSOD and pRSOD values decrease to 0.16m and 0.29m respectively; substantially less than the standing water column depth. The suggestion that BOD is the dominant oxygen depleting process in the Torrens Lake is supported by the results of other studies. For example, in a study of three lakes in New Zealand, including a shallow (<6m) eutrophic urban lake (Hamilton Lake), Burns *et al.* (1996) observed that SOD played a significant role in oxygen depletion of hypolimnetic waters, but that the role of pelagic oxygen demand was more important in terms of the deoxygenation of the entire water column.

7.4.2 FRP release

FRP release over the 5-day incubation period was higher at the inlet than at the weir end of the lake (85.1 cf 18.2 mg FRP m^{-2}), and the time series analysis reveals that FRP release occurs in a different manner at the inlet than at the outlet. As there was no difference in sediment TP content between the two ends of the lake, and the pattern of DO depletion was similar, the difference in FRP flux is potentially attributable to differences in sediment chemistry. The binding of phosphorus to sediments is controlled by ferric iron (Fe^{3+}) in most urban catchments (Lawrence, 2001), and factors such as the P:Fe ratio are recognised as having a substantial impact on P release (Phillips *et al.*, 1994; van der Molen and Boers, 1994). The mechanisms of FRP flux were not studied in this project, however Jenkins (2000) utilised chemical analysis to determine the reductant-soluble phosphorus content (a measure of how much P can potentially be released under anoxic conditions) of the Torrens Lake sediments. The results of that analysis reveal that the pool of P potentially mobile under anoxic conditions at the inlet was double that at the weir end of the lake (13% cf 6.5%), and this change in reductant-soluble phosphorus content may be responsible for the shift from linear to sigmoidal FRP release observed.

The potential water column concentration of FRP generated from sediment release can be estimated for the lake. As the Torrens Lake has sheer sides for most of its length, it can be assumed that the surface area of the sediments is approximately equivalent to the water surface area (0.15 km^2). Based on the average FRP flux obtained from sediments collected at the inlet end of the lake (85.1mg FRP m^{-2}), the potential flux into the water column is 12.8kg FRP over 5 days. At the standing volume (420ML), this would generate a water column FRP concentration of 30.4μgL^{-1}. Although this technique underestimates the total sediment surface area, and assumes even mixing of the water column, this estimate can be taken as a worst-case scenario, as the average FRP release is substantially lower at the weir end of the lake (18.2mg FRP m^{-2}) than at the inlet end.

Due to the large size of the lower catchment (~230km^2) stormwater volumes sufficient to completely replace the volume of water in the lake are readily generated. The estimated FRP concentration of 30.4μgL^{-1} potentially generated by anoxic conditions in the lake is of serious concern, as it is well above ANZECC/ARMCANZ trigger value of 5μgL^{-1}. However, stormwater from the heavily urbanised sub-catchments that enters the lake has average FRP concentrations of 40μgL^{-1} (TCWMB *unpublished data*), and the estimated maximum potential concentration of FRP resulting from sediment remobilisation is 76% of that which would be generated in the lake if inflowing stormwater from the heavily urbanised sub-catchments completely replaced the water in the lake.

TCWMB (2002) concluded from the reports of AWQC (2000) and Arup Stokes (1999) that the recent toxic algal blooms in the lake were caused primarily by nutrient remobilisation from anoxic sediments. This assertion was based on an estimated sediment P release of 90 mg FRP m^{-2} (TCWMB 2002). This value is higher than the maximum recorded in both the current study (85 mg FRP m^{-2}) and that recorded by Jenkins (2000) in Torrens Lake (60.0 mg FRP m^{-2}). It should also be noted that in the current study, peak release of FRP into the overlying water (flux >50 mg FRP m^{-2}) only occurred when dissolved oxygen concentrations measured within the core systems (at approximately 120mm from the water-sediment interface) fell below $0.1 mgL^{-1}$. Rain events do not deliver a sufficient volume of oxygen demanding material to depress dissolved oxygen concentrations to this level (Chapter 5; Wallace *et al.*, unpublished data). Therefore under most circumstances, actual FRP release is likely to be significantly lower than potential release, and the estimated value of 90 mg FRP m^{-2} is considered to be a substantial overestimate. It is also of note that AWQC (2000) commented that while the concentrations of FRP in lake water samples were potentially attributable to internal loading, the relatively high concentrations of TP and TKN also present in the samples was not consistent with sediment release of FRP.

7.4.3 General Discussion

The total FRP (combined external and internal) load is a major concern for the management of Torrens Lake. However, the results of this project support the hypothesis that external loading is the primary driver of the poor water quality regularly observed in the Torrens Lake. As previously discussed, concentrations of FRP in inflowing stormwater exceed the potential internal load, and rain events do not depress oxygen concentrations low enough for peak FRP release to occur. The relative importance of FRP release from sediments may increase during hot, calm weather when external loads are absent and the water column is subject to stratification. However, ambient water column FRP levels (5-10 μgL^{-1}) in the lake are more than sufficient to support a bloom given the right environmental conditions. This suggestion is supported by Ganf *et al.* (1999). Consequently internal loading from FRP remobilisation associated with rain events is not considered to be a primary trigger for the episodic algal blooms observed in Torrens Lake.

Attempts by the Torrens Catchment Water Management Board to manage internal loading by artificial aeration and mixing to prevent deoxygenation of the water column, are not likely to be sufficient to prevent the re-occurrence of toxic and nuisance algal blooms. Reductions in internal loading are highly dependent on reductions of external loading (Jensen and Anderson, 1992; Kleeberg *et al.*, 2000; Søndergaard *et al.*, 1993), and therefore substantial reductions in external loading of P and oxygen demanding organic matter from inflowing stormwater will be also be required.

Chapter 8: The role of stream condition in DOC retention in an urbanised stream.

8.1 Introduction

Streams and rivers are a critical link between the terrestrial zone and the terminal water body of a catchment, as they convey the majority of the water and nutrients from the terrestrial zone to the terminal waterbody (Hall *et al.*, 2002; Peterson *et al.*, 2001). The ability of streams and rivers to retain nutrients as they are conveyed from one zone to another is the result of a complex range of physical and biogeochemical processes (Benoit, 1971). McColl (1974) stated that the role of the stream reach in buffering downstream ecosystems from eutrophication, by reducing and dispersing nutrient loads, may be substantially reduced by factors such as the condition of riparian vegetation, previous nutrient loading, the type of stream bed, and the degree of human disturbance. It is therefore of note that concentrations of nutrients are often elevated in urban streams (Hatt *et al.*, 2004; Paul and Meyer, 2001).

Natural streams and rivers exhibit extensive spatial (and temporal) variability (e.g. meandering channels with pool and riffle zones), that provide a diverse range of habitats for physical and biogeochemical processes, including transfer between surface water, sediments, and the hyporheic zone (Baker *et al.*, 1999; Findlay, 1995; Findlay *et al.*, 1993; Vervier *et al.*, 1993). In urbanised catchments, it is common for streams and rivers to have suffered severe bank and channel erosion, with a subsequent simplification of the physical structure of the streambed. It is also common for urban streams to have been engineered to manage flooding (Walsh *et al.*, 2004). This has typically involved the realignment of creek flow paths, and the conversion of creek beds into excavated and concrete channels (Wong *et al.*, 1999) which in some cases, have been diverted underground. The conversion of streambed to concrete channel in urbanised streams eliminates interaction between surface, hyporheic and ground water zones, removes the habitat required for emergent vegetation to establish, and reduces the surface area available for colonisation by microbial biofilms.

Brookes *et al.* (2005) propose that a primary consequence of simplification of stream geomorphology would be a reduction in the capacity of a stream reach to process nutrients, due to a reduction in the number of available/efficient pathways for nutrient interception and subsequent utilisation and or transformation. There is currently a substantial global interest in restoring riparian habitat and in-stream channel complexity in urbanised streams (e.g. Cutler, 1999; Frost, 2000; Kelly, 2001; Suren *et al.*, 2002; Wong *et al.*, 1999). Although improvements in water quality are a stated aim of many urban stream restoration projects (e.g. Frost, 2000; Kelly, 2001), assessment of project performance has typically focused on community perceptions and macro-invertebrate diversity and abundance. Improvements in downstream water quality have been largely ignored.

Despite being an important issue, the knowledge base on in-stream nutrient dynamics is patchy, and it is generally considered to be a research area requiring more attention. Numerous studies have investigated the uptake of phosphorus and nitrogen (e.g. Marti and Sabater, 1996; Meals *et al.*, 1999; Mulholland *et al.*, 1997; Peterson *et al.*, 2001; Sabater *et al.*, 2000; Triska *et al.*, 1989) in streams. Although there are some notable works (Baker *et al.*, 1999; Bernhardt and Likens, 2002; Lock and Hynes, 1976; Lush and Hynes, 1978; McDowell, 1985; Munn and Meyer, 1990), there are comparatively few such studies that have investigated dissolved organic carbon (DOC) uptake in streams. Furthermore, there appears to be no published literature that provides a direct comparison of DOC uptake capacity between intact, degraded and engineered creeks.

The aim of this study was investigate the influence of channel morphology and complexity on DOC retention within a given stream reach. The project tested the hypothesis that an urban stream reach that has retained a complex geophysical channel structure has a higher capacity to buffer downstream ecosystems from DOC inputs than an urban stream reach that has been converted to a concrete channel. Buffering capacity is not a well-defined concept. However, in this project, buffering capacity is considered as a combination of factors, including the proportion of the total DOC load intercepted, dilution and dispersion of the inputs, in-stream retention time, and uptake length. It was anticipated that when exposed to a short term nutrient addition, the stream reach with the most complex geophysical channel structure would intercept a higher proportion of DOC, dilute and disperse the DOC more effectively, retain the nutrient solution the longest, and require the shortest longitudinal distance to intercept the DOC.

8.2 Methodology

8.2.1 Site Description

A detailed description of the Torrens Catchment is provided in Chapter 2. The sites selected for this research project were located in the Third Creek sub-catchment. The upper catchment of Third creek is influenced by agriculture, with urbanisation throughout the lower catchment. This particular stream was chosen as it has a representative example of a degraded creek section, an open engineered concrete channel, and an underground, engineered concrete channel, all within a 2km reach in the urbanised section of the catchment.

The degraded reach (Fig. 8.1) has extensive channel and bank erosion but has retained coarse woody debris, a meandering channel with a series of deep pools (~1m), and shallow (<10cm) runs over sand and gravel beds, and variable stream width (1-3m). The open-engineered reach (Fig. 8.2) has a flat, concrete base, with a series of three "stairstep" sequences with runs of 30-40m between each step. Rocks embedded in the concrete channel have accumulated debris (primarily gravels). The stream width is consistent (~2m) throughout the reach. The underground-engineered reach (Fig. 8.3) is a v-shaped concrete channel, with no steps. Maximum width is approximately 3m. In both engineered reaches, the water depth during the experiments was less than 20cm, however during periods of peak storm-flow during rain events, bank full capacity within the vertical walls of the channels can exceed 1m.

The experiments presented here are un-replicated, and this potentially confounds interpretation of the results. However, it must be noted that the intent was to investigate the influence of channel morphology and complexity on DOC retention within a given stream reach, and to utilise the knowledge generated to assess the potential improvement in buffering capacity of the given stream reach, if stream complexity could be improved. The nutrient addition experiments were performed within each reach (degraded, open engineered and underground engineered) on four (4) occasions between August and October 2004. On each occasion, the experiments were performed sequentially, starting at the most downstream reach (open-engineered) and working upstream to the most upstream reach (underground-engineered), with all three reaches assessed within a 4 hour time period.

Figure 8.1. Degraded study reach in Third Creek. The meandering nature of the channel, variable stream width and the series of deep pools over cobble and gravel is evident.

Figure 8.2. Open-engineered study reach in Third Creek. The channel straightening, consistent width and flat concrete base is evident. The rocks embedded in the base trap gravel and generate some spatial heterogeneity.

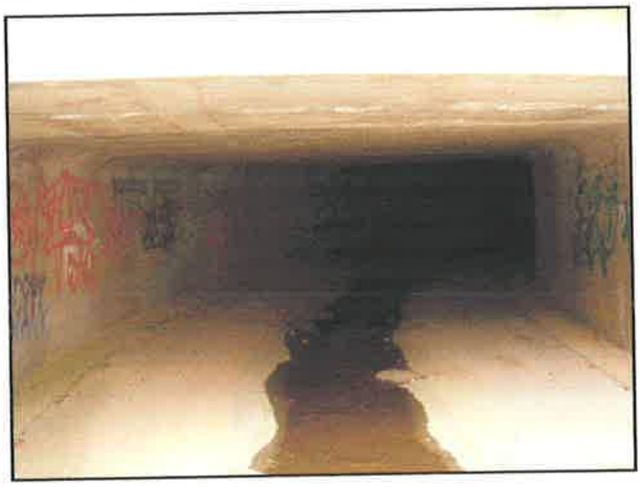

Figure 8.3. Underground-engineered study reach in Third Creek. The v-shaped concrete base, confined channel, consistent width and lack of channel complexity is evident.

8.2.2 Short-term DOC addition experiments

Short-term organic DOC addition experiments were utilised to assess the removal of dissolved organic carbon from stream water within the three contrasting stream reaches. The DOC used for the experiments was a combination of leaf leachate and D-Glucose. Leaf leachate was used as a primary source of DOC to provide a naturally occurring, and ecologically relevant (Junk *et al.*, 1989; Vannote *et al.*, 1980) source of DOC. The plant species chosen for generation of the leachate used in this study (White poplar; *Populus alba*, English elm; *Ulmus procera*, river red gum; *Eucalyptus camaldulensis*, and London plane tree; *Platanus acerifolia*) were selected as being heavily represented in the standing stock of autumn leaf litter in the urbanised sub-catchment of the Torrens River, Adelaide Australia.

Approximately 1.5kg of freshly fallen leaf litter was placed in a 200L drum filled with laboratory grade (0.45μm filtered reverse osmosis) water, and left to stand for 72 hours. After 72 hours the water was pumped out of the drum and stored in a clean 200L drum. The leaf litter in the drum was subsequently rinsed with a further 60L of laboratory grade water. This water was also pumped off. The leachate and rinse water were combined, and subsequently pumped through a series of cartridge filters (150, 10, 5, 1, and 0.45μm) and stored in the dark at <3°C for the duration of the experiments (10 weeks). The leachate derived a DOC concentration of $580 mgL^{-1}$. It was initially intended to utilise leaf leachate as the sole source of DOC for the experiments, but logistical problems associated with the generation, storage and transport of a sufficient volume (minimum total volume required =1200 L) of leaf leachate of a high enough concentration precluded this. Subsequently, the filtered leachate was split into twelve 20L aliquots that would be used as the base DOC, and D-Glucose was utilised to supplement the DOC concentration in the spike solution used in the experiments (described in detail below).

Sodium Chloride (NaCl) was utilised as a conservative tracer. Changes in the concentration of NaCl (measured as conductivity) as the solution passes downstream provide a direct measure of dilution and dispersion of the spike solution. Because the ratio of conservative tracer to reactive solute (DOC) is known, the expected DOC concentration can be calculated based on the conductivity recorded for each sample (Marti and Sabater, 1996). If no uptake of DOC occurs, the observed DOC concentration would reflect the expected DOC concentration. If the observed DOC concentration is different from the expected concentration, the stream reach can be considered to be acting as either a sink or source of DOC.

Prior to each experiment at the selected sites, 75L of stream water was removed from the stream and temporally stored in a 110L tank. This water was subsequently enriched with 20L of the 0.45μm filtered leaf leachate. D-Glucose (pre-dissolved in 5L of laboratory grade water) was utilised to boost the concentration of DOC to the target level of $650mgL^{-1}$. Sufficient NaCl was dissolved in the collected water to attain a target level conductivity of $750mScm^{-1}$. Target levels for both DOC and conductivity were determined through preliminary trials to ensure that after dilution and dispersion along the 100m reach, an increase in DOC and conductivity would be detectable above ambient levels.

Once the NaCl was dissolved and the solution had stabilised, three measurements of conductivity were recorded using a TPS WP-84 Conductivity-Salinity-Temperature meter (TPS Pty. Ltd., Brisbane, Australia). Three 50mL samples were also collected from the spike solution for analysis of DOC concentration. The spike solution was then pumped back into the stream (Johnson Cartridge Submersible Bilge Pump L450 12V) at a rate of 36 litres per minute. Sampling stations were established at 100m downstream of the input site, where conductivity and time were logged, and stream water samples (50mL) were manually collected at regular intervals from the time the pump was switched on until conductivity returned to background levels. Conductivity measurements and samples were taken at the mid-point of the stream. Collected samples were stored on ice, and returned to the laboratory. All samples were filtered through Whatman 0.45μm syringe filters, and preserved to pH 2 with 0.1M perchloric acid within 24 hours. DOC analysis was performed on an SGE ANATOC II (SGE, Melbourne, Australia).

8.2.3 Calculation of in-stream parameters and Solute Transport Modelling

8.2.3.1 Stream Discharge

Discharge through the creek sections was calculated according to Equation 8.1 (from Triska *et al.* 1989).

$$Q_0 = [(C_1 - C_b)/(C_p - C_b)]Q_1 \qquad \textbf{Equation 8.1}$$

Where Q_0 = Discharge (Ls^{-1}), Q_1 = Pumping rate (36 $Lmin^{-1}$), C_1 = Concentration of conservative tracer in the 100L spike solution (e.g. 750$mScm^{-1}$), C_b = Background concentration of conservative tracer in stream (e.g. 833 μScm^{-1}), and C_p = Peak concentration of conservative tracer recorded at the downstream sampling station (e.g. 1362 μScm^{-1}).

8.2.3.2 Dilution of the spike solution

Equation 8.1 was used to compare the effect of the contrasting stream morphology on spike dilution in the three contrasting reaches; Q_0 was altered from representing discharge, to representing dilution.

8.2.3.3 In-stream retention time

In-stream retention time of the spike solution was calculated as the elapsed time from the pump transferring the spike solution to the stream being switched on, to time at which conductivity, measured at 100m downstream, returned to ambient levels.

8.2.3.4 Interception of DOC – percent uptake.

Expected and observed DOC concentrations were plotted against elapsed time, and the area under each respective curve was calculated. Comparison of area under the respective curves provided a relative measure of percent retention of DOC.

8.2.3.5 Solute Transport Modelling

Solute transport modelling (Stream Solute Workshop, 1990) was used to determine coefficients for dilution, dispersion, velocity, decay, production, retardation, and to determine uptake lengths for each contrasting stream reach. These key hydrological and DOC retention properties were calculated using Matlab (Version 5.0.0.4073, The Mathworks Inc, Natwick, USA) and the governing equation for solute transport (equation 8.2).

$$R\frac{\delta c}{\delta t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\delta c}{\delta x} - \mu c + \gamma$$ **Equation 8.2**

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

Values for dispersion coefficient (D) and stream velocity (v) were modelled from the measurements of conductivity obtained at 100m using the analytical solution (equation 8.3) of the governing equation of solute transport without decay or production (van Genuchten and Alves, 1982).

$$c(x,t) = C_i + (C_o - C_i)A(x,t) \qquad 0 < t </= t_o \qquad \textbf{Equation 8.3}$$

$$c(x,t) = C_i + (C_o - C_i)A(x,t) - C_oA(x,t-t_o) \qquad t > t_o$$

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

and C_o is conductivity at the point of addition during the addition of the tracer solution, C_i is background conductivity, t_o is the time over which the tracer solution is added, exp is the exponential function and erfc is the complementary error function. The final values obtained for v and D were calculated by adjusting the in-stream conductivity (C_o) at the input site during addition of the tracer solution, and the values for v and D until the least sum of squares difference was attained between observed and modelled data.

The decay coefficient (μ), production rate (γ) and retardation factor (R) were subsequently modelled from the observed-DOC concentrations using the analytical solution (equation 8.4) of the governing equation of solute transport with decay and production (van Genuchten and Alves, 1982). The final values obtained for μ, γ and R were calculated by adjusting each respective value until the least sum of squares difference was attained between observed and modelled data.

Equation 8.4

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

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

Where

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

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

and

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

Uptake length (S_w) is effectively the distance travelled by a resource (or pollutant) molecule before being removed from the water column and is considered a useful index of how rapidly an element is removed from the stream water (Marti and Sabater, 1996; Munn and Meyer, 1990; Stream Solute Workshop 1990). DOC uptake length (S_w) was calculated using equation 8.5 (Stream Solute Workshop, 1990).

$$S_w = \frac{v}{\mu} \qquad \textbf{Equation 8.5}$$

Uptake length is widely utilised in the literature for comparing stream reaches (e.g. Bernhardt and Likens, 2002; Butterini and Sabater, 1998; Munn and Meyer, 1990). Consequently, uptake length was considered a suitable, comparative measure for this study to determine how three contrasting stream reaches within a short, contiguous section of creek process a point source pollutant input. It is important to note that for comparison of nutrient uptake in streams of different size, the mass transfer coefficient (which corrects for the effects of discharge on depth and velocity) should be utilised (Bernhardt and Likens, 2002; Davis and Minshall, 1999; Stream Solute Workshop 1990).

8.2.4 Data Analysis

Due to the nature of the data collected there are no spatially independent replicates for each stream reach type. Consequently, analysis of individual parameters (e.g. dilution of the spike solution, in-stream retention time, percent uptake, in-stream velocity) is confined to descriptive analysis. Relationships between environmental parameters and DOC retention parameters were assessed by regression analysis. Differences in the ability of the contrasting stream reaches to process the point source input (considered as a combination of in-stream retention time, interception/percent uptake, discharge, dilution, dispersion, velocity, decay, production, retardation, and uptake length) were analysed using single factor NPMANOVA, indicator species analysis (Dufrene and Legendre, 1997) and non-metric scaling (NMS) ordination. NPMANOVA was undertaken using the procedure described by Anderson (2001). Indicator species analysis and NMS ordinations were performed using PCOrd; version 4.28 (McCune and Mefford, 1999). Bray-Curtis distances were used to calculate the similarity matrix for all multivariate statistical analyses (Bray and Curtis, 1957). The two-dimensional ordination solution obtained had a final stress lower than 20% (ordination stress = 2.87%), and was subsequently deemed acceptable (sensu Clarke (1993)). Variability between experimental observations in each reach are reported as standard errors (S.E.). For all statistical tests $\alpha = 0.05$.

8.3 Results

8.3.1 Stream Discharge

The experiments were timed to provide a comparison of the ability of a degraded stream reach, an open concrete channel reach, and an underground concrete channel reach in an urban stream to intercept DOC at a range of discharges. Recognising inherent variability due to in-stream gains and losses, discharge through the entire study reach was assumed to be equivalent to that measured in the underground-engineered section based on principles of mass balance. The discharges calculated using Equation 8.1 are presented in Table 8.1. The plots of elapsed (retention) time versus expected/observed DOC are presented in Figure 8.4. The data were plotted on consistent axis to provide a clear demonstration of how the behaviour of the spike solution varied with discharge between the three contrasting reaches. The various factors (dilution, retention time, velocity etc.) evident in these curves are reported in the following sections.

Table 8.1. Discharge recorded in the underground-engineered reach at the time of the experiments.

Date	Discharge (Ls^{-1})
12.8.2004	139.6
19.8.2004	92.5
30.9.2004	39.4
6.10.2004	11.8

8.3.2 Dilution of the spike solution

Peak expected DOC concentrations were substantially higher in the underground-engineered reach compared to the degraded reach particularly in the experiments conducted at the lower discharges (Fig. 8.4). This was particularly evident in that dilution (*d'*)of the spike solution (Fig. 8.5) was markedly higher in the degraded reach (*d'* = 162.7 ±29.7), than in the open-engineered (*d'* = 72.43 ±24.5) and the underground-engineered reaches (*d'* = 70.8 ±28.4). Furthermore, the expected concentrations of DOC rise and fall sharply in the underground-engineered reach (Fig. 8.4). In contrast, expected concentrations of DOC rise and fall gently in the degraded reach. The observation that the rising and vertical limbs of the hydrographs in the underground-engineered reach are nearly vertical (and therefore approaching plug flow) provides evidence that this reach has no effective transient storage volume. In contrast, the hydrographs measured in the degraded creek section display substantial variation in retention time associated with variation in discharge, and the gentle rise and fall of the hydrograph demonstrate that the meandering channel section has retained a relatively high transient storage volume.

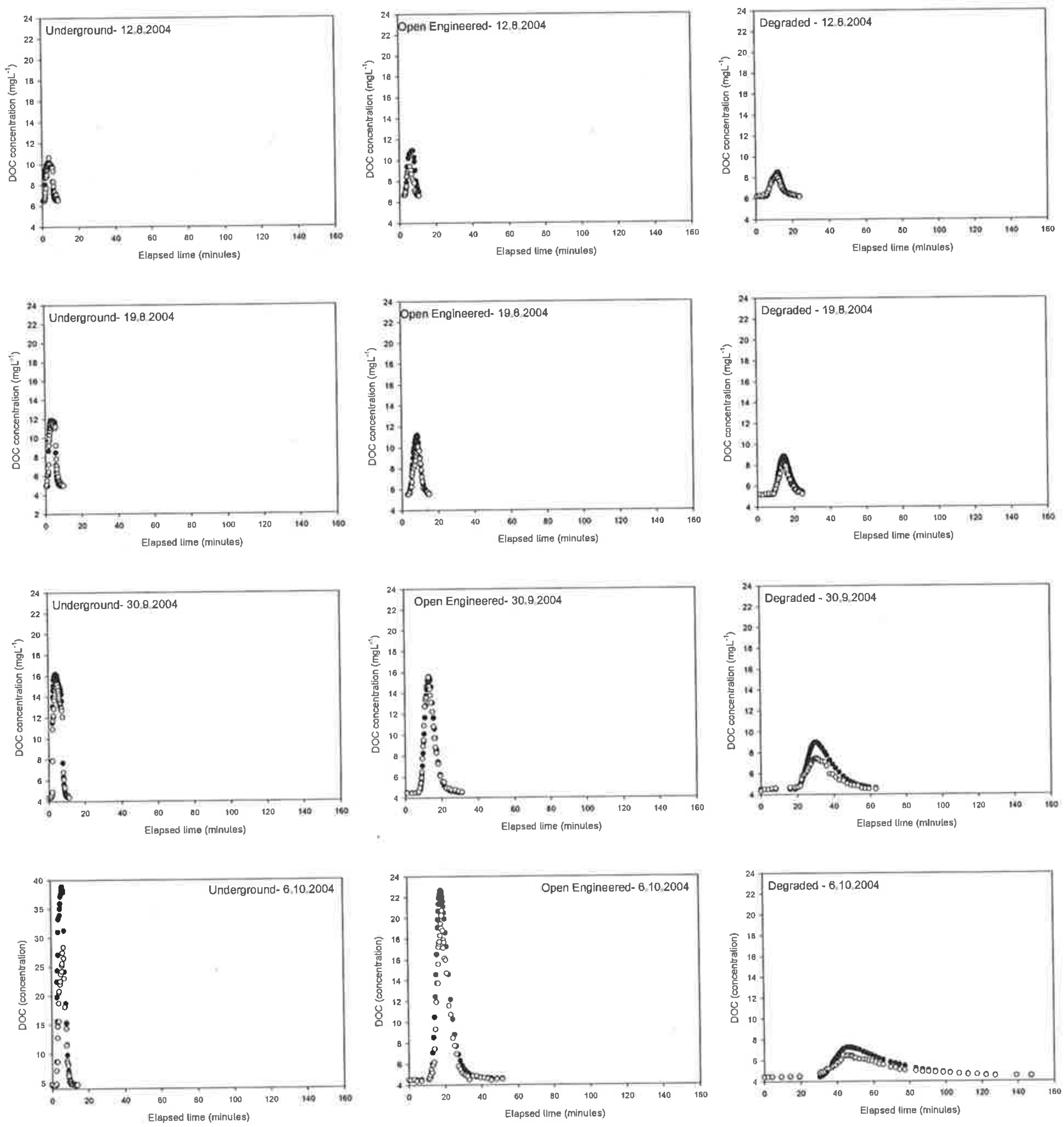

Figure 8.4. Expected and observed DOC concentrations for the 3 stream reaches (underground-engineered, open-engineered and degraded) over the 4 occasions. Discharge as measured in v shaped underground-engineered reach: 12.8.2004 = 139.6Ls^{-1}; 19.8.2004 = 92.5Ls^{-1}; 30.9.2004 = 39.4 Ls^{-1}; and 6.10.2004 = 11.8 Ls^{-1}. Note difference in range of DOC concentration values for the underground-engineered reach on 6.10.2004. Closed circles = expected DOC, Open circles represent observed DOC concentrations. Refer to text for detail on how expected DOC concentration was calculated.

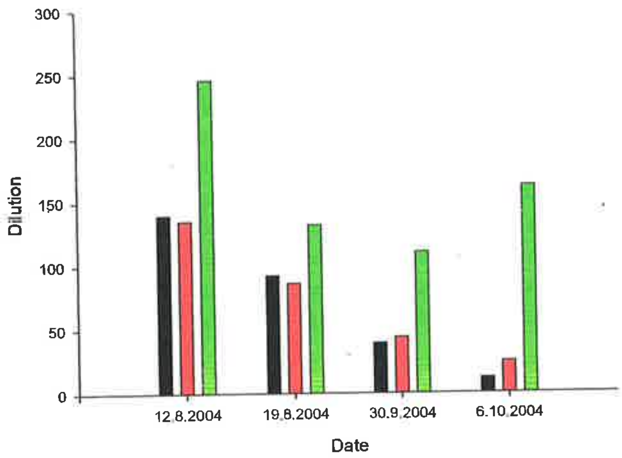

Figure 8.5. Dilution of the stream spike (calculated from peak expected DOC) in the three contrasting stream reaches on the four dates on which the experiments were conducted. Black columns = underground-engineered, red columns = open-engineered, green columns represent degraded reach.

8.3.3 In-stream retention time

On all occasions, the spike solution was retained in the degraded reach for an extended period relative to the engineered reaches (Fig. 8.4 and 8.6 [A]). At the highest discharge (139.6 Ls^{-1}) the spike was retained for 23 minutes and 45 seconds in the degraded reach compared to 10 minutes and 38 seconds in the open-engineered reach, and 7 minutes and 49 seconds in the underground-engineered reach. In comparison, at the lowest discharge, (11.8 Ls^{-1}), a retention time of 147 minutes and 40 seconds was recorded in the degraded reach, and the spike was retained for 48 minutes and 9 seconds and 13 minutes and 49 seconds in the open-engineered and underground-engineered reaches, respectively. In addition to the variability in in-stream retention time, there was also an important shift in the relationship between discharge and in-stream retention (Fig 8.6 [B]). In the degraded and open engineered reach the relationship was exponential [($y = 23.706 + 191.962e^{-0.038x}$), $r^2 = 0.999$, df_3, $F = 995.025$, $P = 0.022$] and [($y = 8.514 + 52.223^{e-0.024x}$), $r^2 = 0.999$. df_3, $F = 22167.42$, $P = 0.005$] respectively. In contrast, in the open-engineered reach the relationship was linear [($y = 13.351 - 0.047x$) $r^2 = 0.920$, df_3, $F = 22.901$, $P = 0.041$].

8.3.4 In-stream Velocity

There was substantial variation in in-stream velocity (Fig. 8.7 [A]) within and between the contrasting stream reaches. In the degraded reach, where in-stream velocity was lowest, velocity ranged from 9.7 m min^{-1} during the period of highest discharge, to 1.9 m min^{-1} at the period of lowest discharge. In comparison, in the open-engineered reach, in-stream velocity ranged from 19.5 m min^{-1} to 5.6 m min^{-1} at the highest and lowest discharges, respectively. In-stream velocity was highest in the underground-engineered reach, and ranged from 66.6 m min^{-1} to 20.6 m min^{-1} at the highest and lowest discharges, respectively.

Discharge had a significant influence on in-stream velocity in all of the reaches (Fig 8.7 [B]), however the influence of increasing discharge on in-stream velocity was markedly greater in the underground-engineered reach [(y = 13.731+0.388x), r^2 = 0.970, df_3, F = 65.201, P = 0.015] than in either the open-engineered [(y = 4.033+0.111x), r^2 = 0.998, df_3, F = 987.36, P = 0.001] or the degraded reach [(y = 1.031+0.063x), r^2 = 0.994, df_3, F + 315.16, P = 0.003].

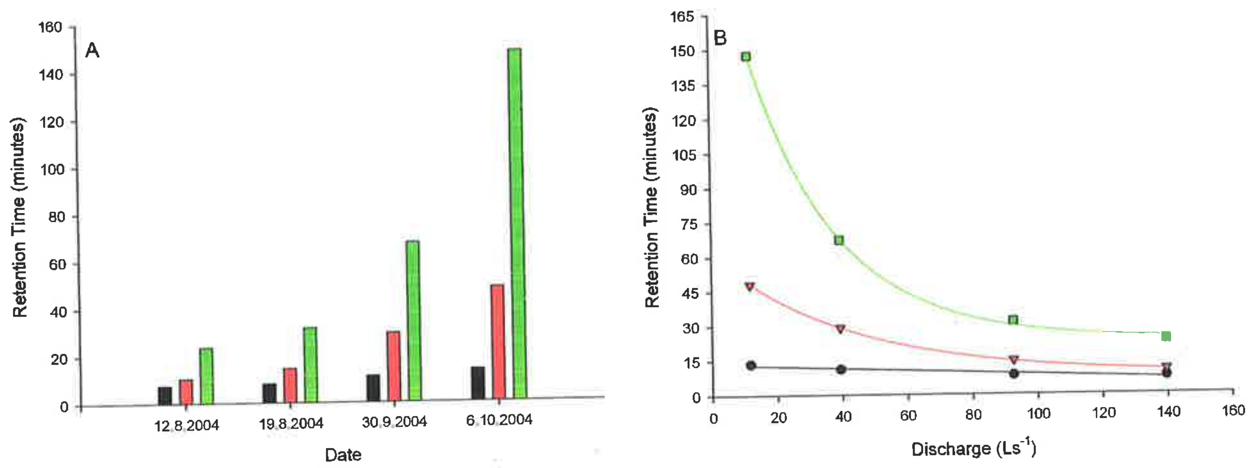

Figure 8.6. [A] In-stream retention time and [B] relationship between discharge and in-stream retention time in the 3 contrasting stream reaches. Black columns/circles = underground-engineered, red columns/triangles = open-engineered, green columns/squares represent degraded reach.

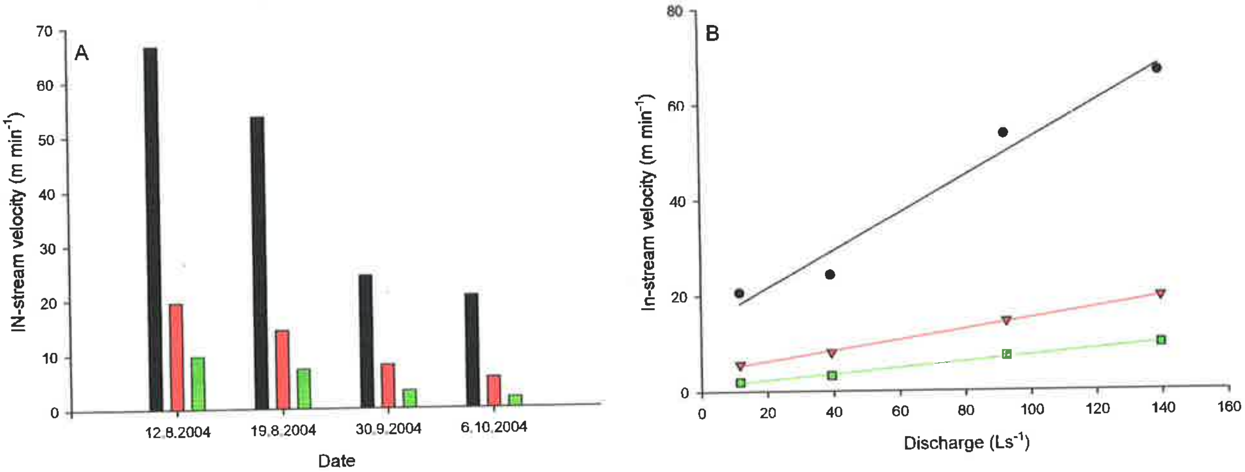

Figure 8.7 [A]. In-stream velocity (determined from solute modelling of the stream spike), and [B] relationship between discharge and in-stream velocity (see text for regression equations) in the three contrasting stream reaches. Black columns/circles = underground-engineered, red columns/triangles = open-engineered, green columns/squares represent degraded reach.

8.3.5 Interception of DOC – percent uptake

The highest interception of DOC (measured as percent uptake) was observed in the underground-engineered reach (9.53 ±6.73), the open-engineered (8.60 ±2.90) and then the degraded (4.61 ±1.30) stream reaches (Fig. 8.8 [A]). Substantial variability in percent uptake is evident within and between the individual reach types. Despite an expectation that this variability would be a function of retention time, no significant relationships between retention time and percent uptake (e.g. degraded stream: [($y = 3.879 + 0.011\ x$), $r^2 = 0.056$,, df_3, $F = 0.118$, $P = 0.764$) were observed (Fig. 8.8 [B]).

In-stream nutrient concentration is recognised as having an influence on nutrient uptake (Marti and Sabater, 1996). It is therefore of note that percent uptake in the underground-engineered reach was significantly influenced by peak DOC concentration (Fig. 8.9 [A] {$y = -9.881+1.008x$}, $r^2 = 0.987$, $F = 152.710$, df_3, $P = 0.007$). However, it must be noted that the elevated uptake in the underground reach only occurred when DOC was at a relatively high peak DOC concentration (38mgL^{-1}). During the remainder of the experiments, when peak DOC concentrations were comparable to those in the open-engineered and degraded reach, uptake was of a similar magnitude to that observed in the comparison reaches. Despite the variation in ambient water temperature throughout the duration of the experiments there is no apparent relationship between water temperature and percent uptake of DOC (Fig. 8.9 [B]).

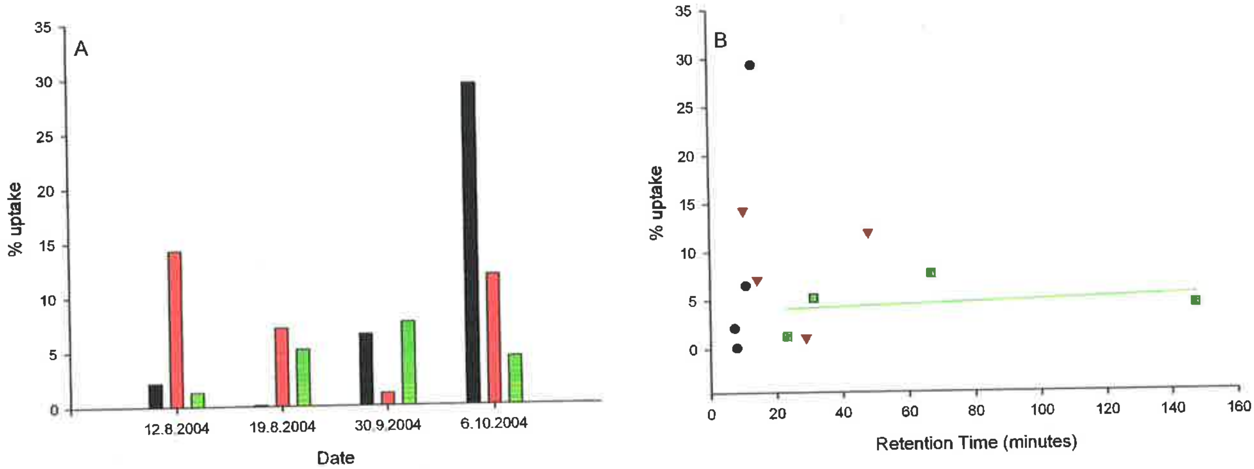

Figure 8.8 [A] Interception of DOC (measured as percent uptake), and [B] relationship between retention time and percent uptake in the three contrasting stream reaches. Black columns/circles = underground-engineered, red columns/triangles = open-engineered, green columns/squares represent degraded reach (Green regression line represents relationship between retention time and percent uptake for degraded reach only, see text for regression equation).

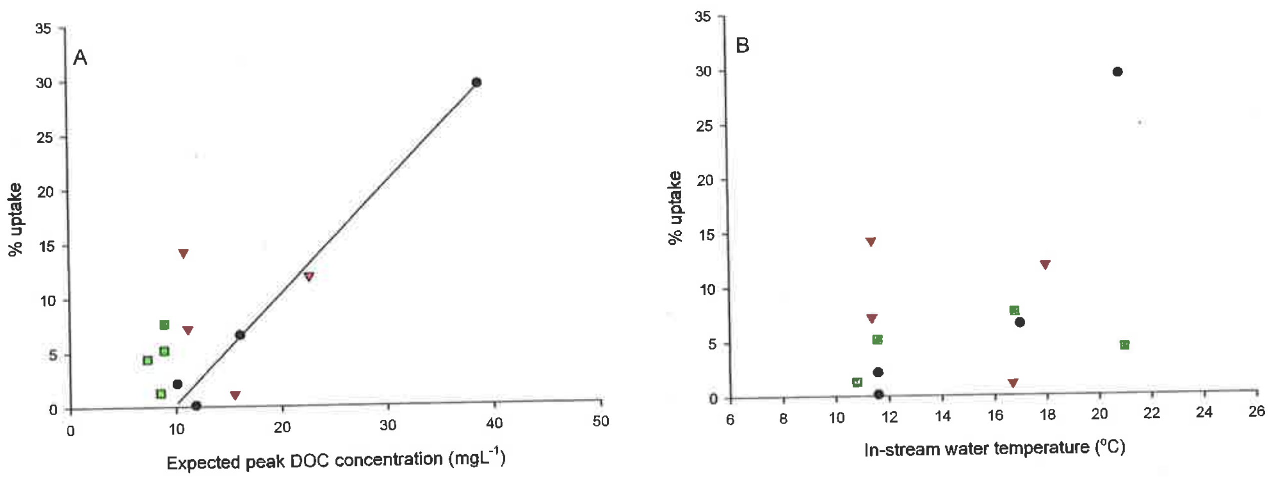

Figure 8.9. [A] Relationship between expected peak DOC concentration and percent uptake of DOC (Black regression line represents relationship between expected peak DOC concentration and percent uptake for underground-engineered reach only, see text for regression equation). [B] Relationship between in-stream water temperature and percent uptake. Black circles represent underground-engineered, red triangles represent open-engineered, green squares represent degraded reach.

8.3.6 Uptake length

Uptake length remained relatively consistent in the degraded reach compared to the engineered reaches (Fig. 8.10 [A]). The average uptake length was shortest (79.91m), and least variable in the degraded reach, ranging from 97.98m at high discharge, to 61.67m at low discharge. In comparison, the average uptake length in the open-engineered reach was 167.4m, and ranged from 234.9 m to 132.14m at the highest and lowest periods of discharge respectively. The underground-engineered reach displayed the longest average uptake length (273.9m), and the widest range; 384.9m and 187.3m at the highest and lowest periods of discharge respectively.

When the three contrasting steam reaches are considered in unison, there is a significant exponential relationship [($y = 88.612+662.789e^{-0.135x}$), $r^2 = 0.828$, df_{11}, $F = 21.604$, $P = 0.0004$] between increasing retention time and decreasing uptake length. However, there is not a significant relationship between retention time and uptake length within the degraded [($y = 95.694-0.234x$), $r^2 = 0.802$, df_3, $F = 8.118$, $P = 0.104$], open-engineered [($y = 128.658+886.918e^{-0.204x}$, $r^2 = 0.996$, df_3, $F = 128.949$, $P = 0.062$], or the underground-engineered reach [($y = 477.379-20.244x$), $r^2 = 0.406$, df_3, $F = 1.365$, $P = 0.363$].

Regression analysis (Fig. 8.11 [A]) indicated that uptake length was significantly related to discharge only in the open engineered reach [($y = 10.76 + 0.8445x$) $r^2 = 0.920$, $F = 23.097$, df_3, $P = 0.041$]; the relationship in the degraded reach is not significant [($y = 62.94 + 0.240x$) $r^2 = 0.082$, $F = 10.742$, df_3, $P = 0.082$]. Within the ranges observed in these experiments, peak DOC does not appear to have a substantial influence on uptake length in any of the reaches (Fig. 8.11 [B]). Furthermore, despite the variation in ambient water temperature, and the apparent trends (Fig. 8.12) in the degraded [($y = 120.705-2.711x$), $r^2 = 0.763$, df_3, $F = 6.425$, $P = 0.127$] and open-engineered reach [($y = 344.676-12.332x$), $r^2 = 0.735$, df_3, $F = 5.545$, $P = 0.143$], there are no significant relationships between water temperature and uptake length.

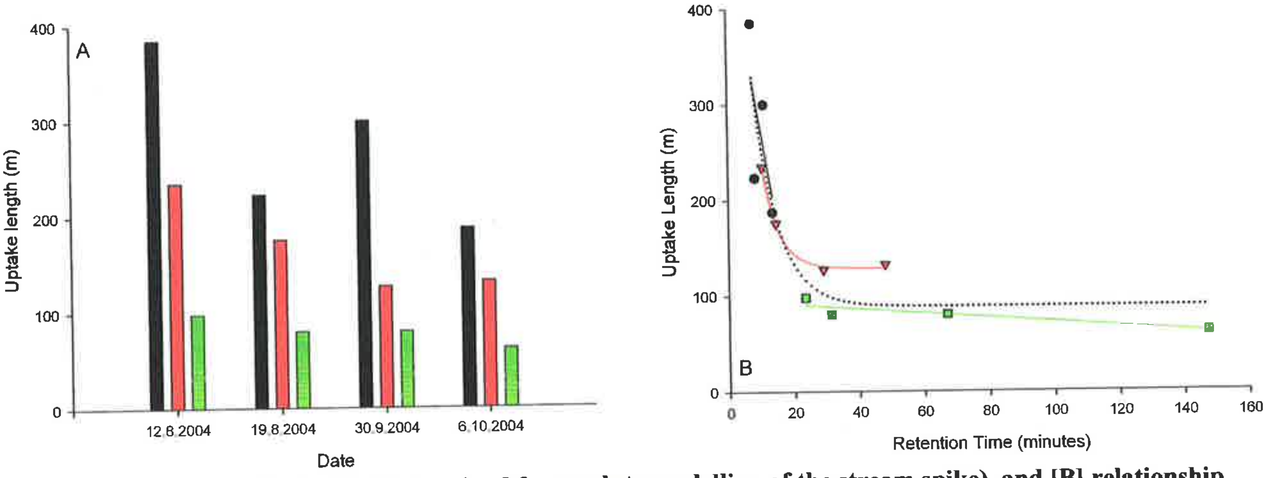

Figure 8.10. [A] Uptake length (determined from solute modelling of the stream spike), and [B] relationship between retention time and uptake length in the three contrasting stream reaches. Black columns/circles = underground-engineered, red columns/triangles = open-engineered, green columns/squares represent degraded reach. Broken regression line represents exponential relationship between retention time and uptake length when all three contrasting stream reaches are considered in unison (see text for regression equations).

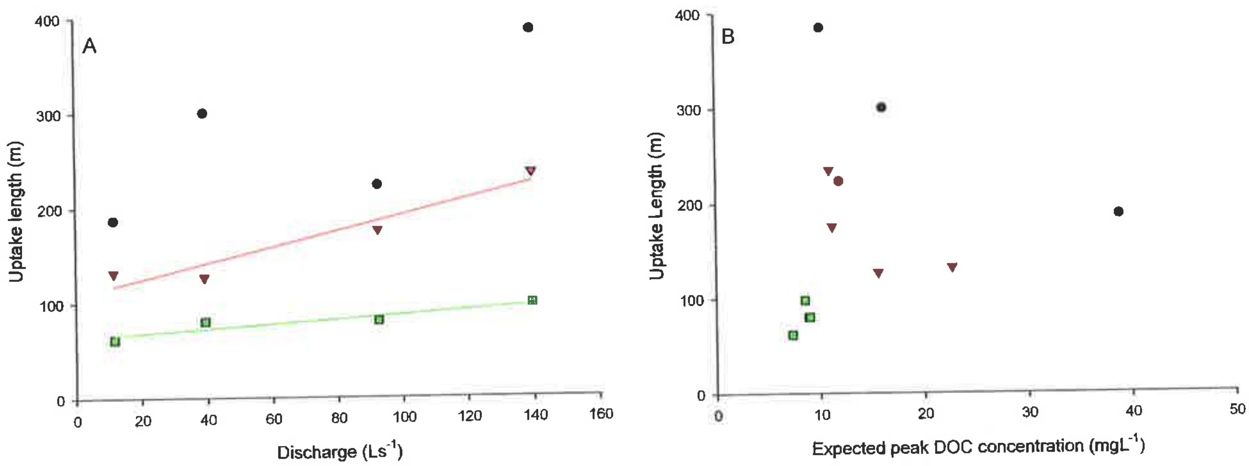

Figure 8.11. [A] Relationship between discharge and uptake length, and [B] expected peak DOC concentration and uptake length. Black circles = underground-engineered reach, red triangles = open-engineered reach, green squares = degraded reach. See text for regression equations.

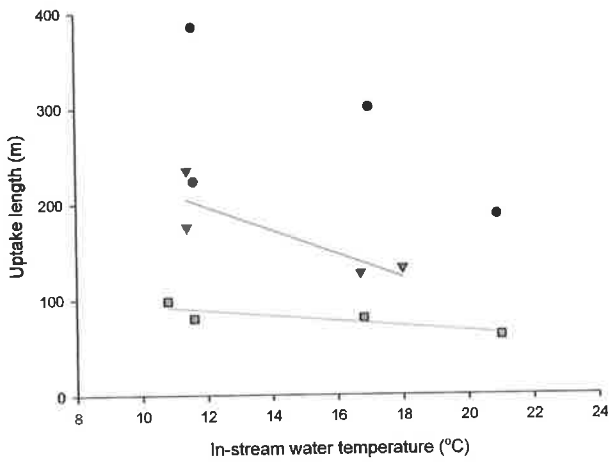

Figure 8.12. Relationship between in-stream water temperature and uptake length in the contrasting stream reaches. Black circles = underground-engineered reach, red triangles = open-engineered reach, green squares = degraded reach. See text for regression equations.

8.3.7 Solute Transport Modelling: dispersion, retardation factor, decay and production coefficients

The modelled coefficients for dispersion, retardation factor, decay and production are presented in Table 8.2. It is apparent that there is an elevated dispersion coefficient in the underground-engineered section (680.7 ±276.2) compared to the open-engineered (37.1 ±16.2) and degraded (15.9± 6.7) stream reaches. There is also an elevated retardation coefficient in the underground-engineered section. The modelled decay coefficient in the underground-engineered (0.15 ±0.03) reach is also markedly lower than obtained in the open-engineered (0.68 ±0.01) and degraded (0.65 ±0.02) reaches.

8.3.8 Assessment of the ability of the contrasting stream reaches to process the point source input

Differences in the ability of the contrasting stream reaches to process the point source input of concentrated DOC (considered as a combination of in-stream retention time, interception/percent uptake, discharge, dilution, dispersion, velocity, decay, production, retardation, and uptake length) was assessed using multivariate analysis.

Single factor NPMANOVA revealed that there are significant differences (NPMANOVA, df_{11}, F = 5.916, P = 0.0008) in the ability of the contrasting stream reaches to process the point source input. Hierarchical cluster analysis (Fig. 8.13) shows that at 100% resolution, behaviour of the spike solution is distinctly different in the underground-engineered reach than in the open-engineered and degraded reaches. At approximately 60% resolution, the behaviour of the spike solution in the open-engineered reach on 30.9.2004, and 6.10.2004, was distinctly different from that in (a) the degraded reach, and (b) that in the open-engineered reach on 12.8.2004 and 19.8.2004.

Table 8.2. Modelled coefficients for dispersion, retardation factor, decay and production for the three contrasting stream reaches.

Coefficient	Site/Date	Underground Engineered	Open Engineered	Degraded
Dispersion	12.8.2004	1400	80.7	34.5
	19.8.2004	810	42.1	16.5
	30.9.2004	360	15.5	6.4
	6.10.2004	153	10.1	6.2
Decay	12.8.2004	0.173	0.083	0.099
	19.8.2004	0.240	0.082	0.090
	30.9.2004	0.081	0.063	0.040
	6.10.2004	0.110	0.042	0.030
Production	12.8.2004	3.64	0.85	0.890
	19.8.2004	3.55	0.78	0.680
	30.9.2004	0.95	0.74	0.270
	6.10.2004	0.58	0.55	0.185
Retardation	12.8.2004	2.99	1.03	1.20
	19.8.2004	1.83	1.30	1.13
	30.9.2004	1.21	1.05	1.12
	6.10.2004	1.08	1.08	0.95

Indicator species analysis (ISA) reveals that the degraded creek reach is significantly characterised by the dilution of the spike solution that the reach provides (Table 8.3). In comparison, the underground-engineered reach is characterised by high velocity, long uptake lengths, and high coefficients for dispersion and decay. There are no significant indicators for the open-engineered reach. The NMS ordination (Fig. 8.14) supports the results of the ISA; (a) in the underground-engineered reach, solute behaviour is characterised by high velocity, long uptake lengths, and high coefficients for dispersion and decay, and (b) solute behaviour in the degraded reach is correlated with increasing dilution and retention time. The ordination also reveals that there is a minor correlation with % uptake in the open-engineered reach.

Table 8.3. Indicator Species Analysis for processing of the spike solution in the underground-engineered, open-engineered, and degraded stream reach in Third Creek. Indicator fractions with P values < 0.05 are exclusive indicators for solute behaviour from the respective sites.

Site	Indicator Fraction	P*
Degraded Creek	Retention Time	0.071
Degraded Creek	Dilution	0.046
Underground-engineered	Velocity	0.005
Underground-engineered	Dispersion coefficient (D)	0.005
Underground-engineered	Decay coefficient (h)	0.023
Underground-engineered	Production coefficient (G)	0.083
Underground-engineered	Retardation coefficient (R)	0.084
Underground-engineered	Uptake Length	0.023

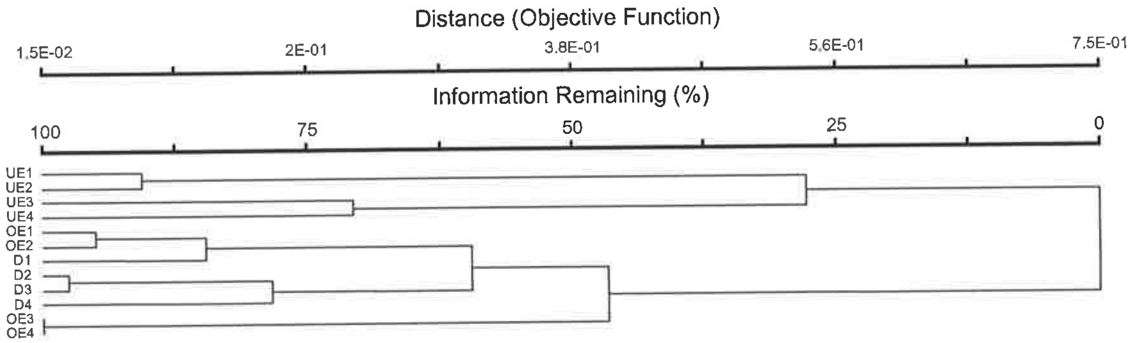

Figure 8.13. Hierarchical Cluster Analysis depicting the variation in processing of the spike solution in the contrasting stream reaches. UE = underground-engineered; OE = open-engineered; and D = degraded stream reaches in Third Creek. Postscipts represent dates: 1 = 12.8.2004, 2 = 19.8.2004, 3 = 30.9.2004, 4 = 6.10.2004 (e.g. UE1 = underground engineered reach on 12.8.2004).

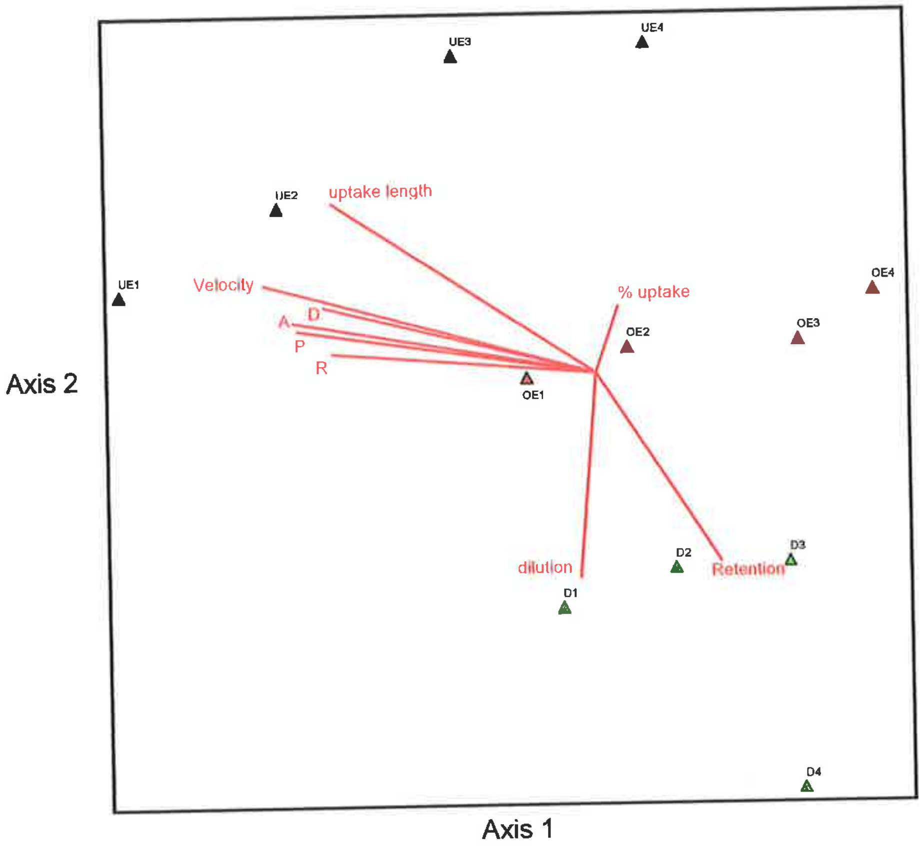

Figure 8.14. NMS ordination depicting the separation in processing of the spike solution in the contrasting stream reaches in Third Creek. Stress = 2.87%. Black Triangles (UE) = underground-engineered reach, Red triangles (OE) = open-engineered reach, Green Triangles (D) = degraded reach. Postscripts represent dates: 1 = 12.8.2004, 2 = 19.8.2004, 3 = 30.9.2004, 4 = 6.10.2004 (e.g. D4 = degraded reach on 6.10.2004). Vectors: D = decay coefficient; P = production coefficient; R = retardation coefficient; A = dispersion coefficient; velocity; uptake length; percent uptake; dilution; and retention time.

8.4. Discussion

8.4.1 Discharge

Discharge can be anticipated to have a strong influence on numerous hydrodynamic and biogeochemical factors in any system; however, there was a large degree of variation in the influence of discharge associated with the contrasting morphology of the reaches. The influence of discharge on retention time between the contrasting reaches was marked, from an exponential relationship with a wide range (6-fold) in the degraded reach, to a linear relationship with a narrow range (1.8-fold) in the underground-engineered reach. This shift away from a strong exponential relationship to a linear relationship, with little retentive capacity in the underground-engineered reach is a reflection of the apparent loss of transient storage volume in the engineered reaches. This change in stream-function is considered important, as decreased retention time within a reach reduces the potential for a resource/pollutant to come in contact with biotic or abiotic pathways capable of intercepting and retaining that resource/pollutant (Butterini and Sabater, 1998; D'Angelo and Webster, 1991; Hall *et al.*, 2002; Triska *et al.*, 1989), and studies (e.g. Mulholland *et al.*, 1997) have indicated that streams with relatively large transient storage zones display elevated rates of nutrient uptake.

Discharge had a stronger influence on in-stream velocity in the underground-engineered reach than in the two other reaches. Furthermore, discharge had a significant influence on uptake length in the open-engineered reach, and a trend towards increasing uptake length with increasing discharge was also evident in the underground-engineered reach. In contrast, discharge does not appear to affect uptake length in the degraded reach, as uptake length remained relatively stable (uptake length did not increase markedly with increasing discharge) across the range of discharges assessed.

8.4.2. Dilution

On each occasion, dilution of the spike solution was markedly (1.5-8.9 times) higher in the degraded reach than that observed in the engineered reaches. It is suggested that a primary cause of the elevated dilution observed is the series of deep pools (~1m) that are a characterising feature of the degraded reach. The influence of dilution on peak DOC concentration in-stream was evident in the magnitude of expected DOC concentration observed in the contrasting stream reaches, particularly during periods of relatively low flow. The influence of this difference in dilution (reduction in maximum pollutant concentration) is arguably ecologically important, as the rate of many biogeochemical processes such as nutrient uptake are time and concentration dependent (Marti and Sabater, 1996). Perhaps surprisingly, a significant relationship between expected peak DOC concentration and percent uptake was only observed in the underground-engineered reach, and no relationships were observed for expected peak DOC concentration and uptake length. Despite the apparent lack of influence on DOC interception evident in these experiments, the dilution of the point source inputs provided by the degraded reach may provide a level of protection to biotic pathways, particularly if toxic compounds (e.g. heavy metals, pesticides, herbicides, hydrocarbons) are present in point source inputs, as is common in stormwater inputs (Walsh *et al.*, 2004).

8.4.3 Interception of DOC – Uptake Lengths and Percent Uptake

The uptake lengths obtained in the degraded reach (79.91 ±7.41m) were longer than that obtained in a preliminary trial (unpublished results) in a relatively intact stream reach in the 5th Creek catchment (55m), and are longer than those obtained by Munn and Meyer (1990) in another relatively intact stream (Hugh White Creek, North Carolina) with reaches characterised by cobble (47m) and rock outcrops (69 m). The uptake lengths in the degraded reach are however substantially shorter than those obtained in the open-engineered (167 ±25.00m) and the underground-engineered (273.88 ± 43.84m) reach. Recognising the limited data set, and the potential limitations of comparing uptake length between different streams, this comparison indicates that although intact stream reaches are more efficient at retaining DOC than degraded streams, degraded steams are substantially more efficient at retaining DOC than engineered reaches.

Short uptake lengths indicate that stream water DOC is rapidly removed from the water column (Munn and Meyer, 1990). In stream reaches where uptake lengths are short, DOC is intercepted near the input site, and the fate of the majority of the intercepted DOC is likely to be heterotrophic metabolism (Findlay *et al.*, 1993). In reaches exhibiting long uptake lengths, DOC is transported from the reach to be oxidised at some point downstream (Elwood *et al.*, 1983). In effect, resources are lost from the reach, and pollutants have a higher potential to reach the terminal water body. This has major implications with respect to eutrophication and pollution of rivers, lakes and estuaries (Peterson *et al.*, 2001). In catchments where the inflowing DOC is readily bioavailable, downstream transport of un-intercepted labile DOC may result in deoxygenation of the receiving water, a situation that occurs in the Torrens Lake following rain events (Chapter 5).

The mechanisms responsible for retention of DOC in the study reaches were not assessed in this project. However uptake lengths are influenced by contact between the resource and active benthic compartments (Davis and Minshall, 1999), and it is well recognised that sediments, gravels, course particulate material (Baker *et al.*, 1999; Dahm, 1981; Mickleburgh *et al.*, 1984; Mulholland *et al.*, 1985; Munn and Meyer, 1990) and the hyporheic zone are key zones for nutrient uptake in streams

(Baker *et al.*, 1999; Findlay, 1995; Findlay *et al.*, 1993; Vervier *et al.*, 1993). Sediments (Fischer and Pusch, 2001) and biofilms have been identified as major sites for the uptake and storage of dissolved organic carbon (Battin *et al.*, 1999; Kaplan and Bott, 1983), with comparatively little uptake believed to occur in the pelagic zone (McDowell, 1985). The reduction in channel complexity, reduction in surface area available for biofilms, and the elimination of interaction between surface-water and the hyporheic zone in the engineered reaches is therefore a major concern.

Based on the results of these experiments, it is considered likely that a large proportion of the uptake that occurred, particularly in the engineered sections, is abiotic (e.g. adsorption to biofilms on substrates) rather than biotic (e.g. biological uptake via biofilms). The basis for this suggestion is that a number of potentially active benthic compartments (sediments, gravels, course particulate material, hyporheic zone) are not available, and that no relationships were observed between DOC retention (uptake length and percent uptake) and factors generally recognised as influencing biotic uptake processes (e.g. retention time, water temperature). Although a relationship was observed between percent uptake and peak DOC concentrations in the underground-engineered reach, the relationship is dependent on a single observation at a relatively high peak DOC concentration. Furthermore, contact times were substantially shorter in the engineered reaches compared to the degraded reach, and this may have limited the potential for biotic uptake. The suggestion that any substantial uptake that occurs where contact times are short may be primarily through adsorption is supported by Lush and Hynes (1978), Dahm (1981), and McDowell (1985) who propose that chemical or physical uptake is responsible for the initial removal of DOC in streams.

In comparison to the engineered reaches, it is anticipated that a higher proportion of the DOC retention observed in the degraded reach is attributable to biotic uptake. Although no relationships were observed between DOC retention (uptake length and percent uptake) and factors generally recognised as influencing biotic uptake processes (e.g. retention time, water temperature, and peak DOC concentration), more of the potentially active benthic compartments pathways are available. Furthermore, uptake lengths were relatively stable despite variation in key factors such as discharge and retention time, and nutrient uptake lengths are assumed to be stable until biotic uptake pathways approach saturation (Stream Solute Workshop 1990), at which point an increase in uptake length can be expected (Davis and Minshall, 1999). The comparatively stable percent uptake and uptake length in the degraded reach may also be a reflection of the importance of the hyporheic zone. During periods of high discharge, velocity in the hyporheic zone has been shown to remain comparatively low (Vervier *et al.*, 1993), maintaining retention time and potential for interception of resources. Without this "stable" zone, the potential for interception of resources is greatly restricted during periods of high discharge in the engineered reaches.

8.4.4 General Discussion

The results of this project support both the research hypothesis, and the hypothesis presented by Brookes *et al.* (2005), that a primary consequence of simplification of stream geomorphology would be a reduction in the capacity of a stream reach to process nutrients and provide a buffer effect to downstream ecosystems. The underground-engineered reach is characterised by high velocity and long uptake lengths. Key features of the degraded reach are the extended retention time and enhanced dilution of the spike solution that the reach provides. The variability in expected peak DOC concentration, uptake length, and percent uptake observed in the engineered reaches suggests that these reaches are not resilient to a common disturbance such as change in discharge.

In contrast to the engineered reaches, the degraded reach maintains a relative stable expected peak DOC concentration, uptake length and percent uptake despite substantial variation in several key parameters such as discharge, dilution, and retention time. This indicates that despite being in a relatively degraded condition, the reach still provides a substantial ecosystem service to receiving waters by buffering the impact of concentrated inputs. Recognising that stormwater inputs will be comprised of volumes of water several orders of magnitude larger, and will be sustained over a longer time than the inputs studied in this project, the results of this project strongly suggest that restoring stream complexity in urbanised streams such as those in the Torrens Catchment by removal of concrete channels and reconstruction of natural meandering flow paths has a major role for improving the buffering capacity of streams. The observation that the open-engineered reach appears to function at a midway-point between the degraded reach and the underground-engineered reach indicates that even a moderate increase in channel complexity can improve the capacity of a stream reach to buffer downstream ecosystems from DOC inputs.

Increasing dilution, dispersion, retention time, and reducing the uptake length of potential pollutants provides a means to improve downstream water quality (Kronvang *et al.*, 1999). Management of bed and bank erosion in streams that have been restored will however be a major challenge. The increased velocity of surface run-off (Paul and Meyer, 2001) and the direct connection (via constructed stormwater infrastructure) that often occurs between impervious surfaces and receiving waters (Walsh, 2002) not only decreases the potential for a resource to come in contact with pathways (abiotic or biotic) capable of capturing the resource (Triska *et al.*, 1989), but also applies significant hydraulic pressure on receiving water bodies (Hatt *et al.*, 2004). Stormwater generated by frequent small to medium rain events and transported to streams by constructed stormwater infrastructure may be responsible for the majority of channel incision observed in urban streams (MacRae and Rowney, 1992). Although restoration of pools, gravel bars and riffle zones will dissipate energy (Vervier *et al.*, 1993), management of runoff in the terrestrial zone of the catchment (Kronvang *et al.*, 1999) and reducing the connectivity between catchment and stream (Walsh *et al.*, 2004) will also be required to reduce the load of inflowing pollutants and volume of water flowing through streams. In addition to ecological benefits, improving stream complexity can also be expected to deliver important socio-economic benefits to people living within, and visiting those catchments.

Chapter 9. General Discussion.

9.1 Introduction

The six experimental chapters of this thesis have dealt with the impact of urbanisation on the composition, bioavailability and transport of organic carbon in stream water across rural-urban gradients in sub-catchments of the Torrens River. The impact of the change in land use on the relative role of particulate and dissolved organic carbon was assessed in Chapter 3. Change in relative composition of macro-fractions of DOC and the bioavailability of the DOC pool in streams and an urban weir pool was assessed in Chapters 4 and 5 respectively. The influence of vegetation type (native versus exotic) on the composition and bioavailability of DOC entering streams was assessed in Chapter 6. Chapter 7 provided an assessment of the role of internal and external loading of DOC and FRP to the Torrens Lake. The final experimental chapter (Chapter 8) investigated the influence of channel morphology and structure on the buffering capacity of urban streams.

9.2 Synthesis of findings

Substantial shifts in the composition, bioavailability and transport of organic carbon in stream water were observed across the rural-urban gradients in the sub-catchments of the Torrens River. A schematic representation of the shift in organic matter input pathways and bioavailability across the rural-urban gradient in the studied sub-catchments is presented in Figure 9.1. Above the rural-urban gradient in a natural (intact) sub-catchment, a relatively high degree of habitat and biological diversity has been retained. DOC inputs from native leaf litter is comprised of moderately bioavailable DOC characterised by a high proportion of hydrophobic acids (e.g. humic and fulvic acids) with a comparatively low oxygen demand per unit DOC (0.7 ±0.02 mg O_2 mg DOC^{-1}), and a moderate (459:1) DOC:FRP ratio (Chapter 6). DOC inputs are unlikely to be direct to streams but via sub-surface and to a lesser extent overland flow during peak rain events (Walsh *et al.*, 2004). Multiple pathways (Brookes *et al.*, 2005) for the interception and processing of the DOC inputs are likely to be present and functional.

The predominantly intact, meandering channels that have retained extensive pool and riffle sections are likely to provide a buffer to downstream ecosystems by retaining nutrients. In stream reaches where uptake lengths are short, DOC is likely to be intercepted near the input site, and the fate of the majority of the intercepted DOC is anticipated to be heterotrophic metabolism

(Findlay *et al.*, 1993). DOC in stream water samples from the rural catchment is characterised by AHS in summer, and HiN (and to a lesser extent AHS) in winter, and the DOC pool is recalcitrant, delivering a relatively low CBOD:DOC ratio (0.36 ±0.05) in both summer and winter (0.15 ±0.02) storm flows (Chapter 4). It is suggested that this organic material is comprised of material that has been processed by "upstream" pathways during transport into the streams.

Below the rural-urban gradient in the heavily urbanised sub-catchments, there is a loss of habitat and biological diversity. Contrary to expectation, there was not an observable increase in the proportion of oxygen demanding organic material in the particulate phase (Chapter 3). An increased proportion of exotic trees and the introduction of garden waste such as grass cuttings generate inputs of DOC that has a different bioavailability and physicochemical signature than that from native leaf litter. For example, DOC leached from the leaf litter of London Plane tree (a commonly planted street tree in Adelaide) is characterised by a high proportion of HiN with a high oxygen demand per unit DOC (3.1 ±0.25 mg O_2 mg DOC^{-1}), and a low (39.9:1) DOC:FRP ratio.

The proliferation of impervious surfaces in the urban catchment reduces the surface area available for infiltration of rainfall into the soil, and the removal of topsoil during development reduces the infiltration capacity for the remaining surface area (Walsh *et al.*, 2004). The increased velocity of surface run-off (Paul and Meyer, 2001), and the direct connection (via constructed stormwater infrastructure) that often occurs between impervious surfaces and receiving waters (Walsh, 2002) in urbanised catchments shifts the dominant flow path for rain falling in the catchment into streams, from subsurface and groundwater flow to overland flow (Walsh *et al.*, 2004). Consequently a substantial component of DOC inputs to streams are likely to be direct to streams via constructed stormwater infrastructure, and the number, diversity and functionality of pathways (Brookes *et al.*, 2005) available for the interception and processing of the DOC inputs will be reduced.

The streams are likely to have suffered severe bank and channel erosion, with a subsequent simplification of the physical structure of the streambed. Substantial sections of the streams have been engineered to manage flooding, typically via realignment of flow paths, and the conversion of creek beds into concrete channels that in some cases have been diverted underground. Short-term nutrient addition experiments (Chapter 8) demonstrate that those reaches that have retained some complexity of structure (meandering channel with pool and riffle sections) will buffer downstream ecosystems from concentrated inputs of pollutants by maintaining relatively stable peak DOC concentrations, and short uptake lengths (79.9 ±7.4m). The capacity for stream reaches to buffer downstream ecosystems is greatly reduced in engineered reaches; flow velocities are markedly increased, peak DOC concentrations are unstable, and uptake lengths are long (273.9 ±43.8m). In reaches exhibiting long uptake lengths, DOC is transported from the reach to be oxidised at some point downstream (Elwood *et al.*, 1983). In effect, resources are lost from the reach, and pollutants have a higher potential to reach the terminal water body (e.g. Torrens Lake).

Below the rural-urban gradient, DOC in stream water samples was characterised by hydrophobic, pH neutral compounds in summer, and by both hydrophobic neutrals and hydrophilic acids in winter (Chapter 4). The urban DOC pool was more bioavailable than DOC from the rural streams, being depleted in an exponential manner, and delivering a significantly elevated CBOD:DOC ratio during both summer (0.99 ±0.07) and winter (0.42 ±0.07) storm flows. It is proposed that the increase in CBOD:DOC ratios is due to a combination of an increase in synthetic compounds (e.g. synthetic detergents and pesticides) that are not present, or are only present at trace levels (Walsh *et al.*, 2004) in rural catchments, and a higher proportion of unprocessed DOC reaching the creeks.

An assessment of the impact of inflowing stormwater on DOC dynamics and water quality in Torrens Lake (Chapter 5) demonstrated that the load of oxygen demanding organic material contained in inflowing urban stormwater increases the biochemical oxygen demand in the water column of the lake from <2mgL^{-1}, to ~18mgL^{-1}, and induces anoxic conditions throughout the lake. Prior to the rain event inflow, a substantial proportion of the DOC pool in the lake was comprised of AHS and HiN compounds. The rain event inflow induced a significant shift in composition of the DOC pool; during the rain event, DOC at the inlet was characterised by an increased proportion of AHS, HiA and HiN compounds. Assessment of the DOC pool in the lake in the days following the rain event indicated that the DOC fractions most readily depleted and therefore most likely to be the most problematic, oxygen demanding organic compounds were in the AHS (e.g. humic and fulvic acids), and HiN (e.g. fatty acids, sugar acids, hydroxyl acids) macro-fractions.

During periods of base flow (little or no inflow into the lake) oxygen demand from benthic sediments and any resuspended sediment (e.g. sediments disturbed by turbulence generated from boat traffic) potentially contribute to the low dissolved oxygen levels often observed Torrens Lake. However, under conditions of increased external loading due to rain event inflows, oxygen demand in the water column becomes the governing oxygen demanding process that generates an oxygen debt and anoxic conditions in Torrens Lake. Under anoxic conditions a substantial pool of bioavailable phosphorus may be released from the lake sediments (Chapter 6). However, internal loading from FRP remobilisation is not considered to be a primary trigger for the episodic algal blooms observed in Torrens Lake. Pulses of FRP input associated with rain events and ambient water column FRP levels (5-10 μgL^{-1}) in the lake are more than sufficient to support a bloom given the right environmental conditions.

9.3 Implications for catchment management

The finding that the majority (95%) of oxygen demanding organic material was contained in the dissolved phase on both sides of the rural-urban gradient has implications for stormwater management. Models presented for predicting sustainable loads of oxygen demanding material to Australian waterways (Lawrence and Phillips, 2003) are based on only 6% of the total B.O.D.$_5$ being generated by material finer than 0.7μm. Consequently, in the Torrens catchment, calculations of sustainable B.O.D.$_5$ loads based on the default values presented by Lawrence and Phillips (2003) model would be incorrect, with potentially catastrophic results. The particle size of sediments has been shown to be catchment specific (Wong, 2001). In addition, in some catchments, the majority of particulate material measured as suspended solids (TSS) may be comprised of leaf litter, whilst in others, the majority of TSS may be comprised of inorganic particles from eroded road surfaces (Goonetilleke *et al.*, 2005). Consequently, the oxygen demand associated with TSS from different catchments is likely to vary considerably, and therefore management and treatment needs to cater for the catchment in question.

The combination of increased concentration, shift in composition, and increased bioavailability of DOC in stream water samples below the rural-urban gradient and generation of anoxic conditions in receiving waters demonstrates that at-source interception measures in the sub-catchments are required to improve water quality in the Torrens River. The widespread acceptance and application of principles of water sensitive urban design and the installation of appropriate treatment trains (e.g. gross pollutant traps, sedimentation basins, swales and filter strips, wetlands and infiltration systems) (Lawrence and Breen, 1998; Wong, 2000) has potential to improve water quality in the Torrens Catchment.

During development of stormwater management strategies for the Torrens Catchment, it must be kept in mind that generic "solutions" are not likely to be effective at reducing pollutants loads and that structural management approaches need to be tailored to remove specifically targeted pollutants (Goonetilleke *et al.*, 2005). For example, street sweeping, gross pollutant traps, grass swales, and buffer zones will reduce BOD by less than 40%. In comparison, percolation trenches, infiltration basins and detention basins may reduce BOD by 40-60%, and wetlands may reduce BOD by 20-60% (Lawrence *et al.*, 1996). Stormwater treatment systems designed such that the predominant treatment pathway is via interception or sedimentation of particulate material (e.g. detention/sedimentation basins/wetlands) will have little impact on reducing a B.O.D.$_5$ that is predominantly driven by DOC (unless the retention time of water in the system is long enough for the B.O.D.$_5$ to be exhausted via biological degradation of the organic material). At-source measures such as pervious pavements (which can reduce BOD by 60-80% (Lawrence *et al.*, 1996)), and percolation trenches-infiltration basins may be more efficient at reducing B.O.D.$_5$ derived from dissolved material.

Reducing the proportion of the impervious surfaces in the catchments that are connected directly to the receiving water by constructed stormwater infrastructure is likely to produce improvements in water quality, stream condition (Walsh, 2002) and ecosystem function. Even modest improvements in stream channel complexity via rehabilitation projects that maintain flood protection but offer a higher degree of complexity than a flat bottom concrete channel will deliver an improvement in buffering capacity (Chapter 8) and ecosystem functionality of restored reaches. The improvements in aesthetic value can also be expected to deliver multiple socio-economic benefits.

The observed shift in DOC composition, bioavailability and stoichiometry (DOC:FRP ratio) between native and exotic leaf litter should be taken into consideration by council planning authorities when considering the selection of street trees. The composition of macroinvertebrate communities in streams may be affected by the change from native to exotic trees. For example, freshwater shrimps (*Paratya australiensis*) have been shown (Schulze and Walker, 1997) to prefer leaves from the native river red gum (*Eucalyptus camaldulensis*) over leaves from the deciduous exotic willow *Salix babylonica*. Furthermore, inputs from eucalypts typically occurs intermittently throughout the year with a maxima in summer (Barlocher and Graca, 2002; Boulton, 1991; Pozo *et al.*, 1997). In contrast, the peak litter input form deciduous trees is primarily in late autumn (Murphy and Giller, 2000). The shift in quality, quantity and timing can be anticipated to have a series of substantial impacts on biogeochemical cycles.

Initiatives put in place by catchment water management authorities to improve the ecological and social amenity value of urban watercourses by reducing litter and contaminant loads, are compromised by the extensive leaf litter fall from exotic trees within the urban landscape. The scale of the issue of leaf litter is such that the Adelaide City Council allocates approximately $125,000 to clean up the leaf litter annually (Golding, 2002). Although this program goes someway to minimising the amount of leaf material transported via stormwater, the gross pollutant traps installed on major creeks and drains are often overwhelmed during rain events. The efficacy of the gross pollutant traps is also dependent on efficient management. If the traps are not emptied rapidly (e.g. within 48 hours), the majority of the water-soluble compounds will still leach into the water, elevating carbon and nutrient levels in the receiving waters (Chapter 6). Consequently the common practice of wide spread planting of exotic deciduous trees such as London plane tree should be avoided. Management should focus on the use of trees that are indigenous to the region and offer biodiversity conservation values.

Constructed water bodies such as urban lakes often act as stormwater sedimentation basins. If the water body functions as a sink for pollutants, the system provides a buffering effect to downstream ecosystems. However if conditions within the lake remobilise intercepted pollutants (e.g. sediment bound nitrogen, phosphorus, iron and manganese), the system may transform a relatively low impact pollutant into a critical pollutant. An example of this is the transformation of sediment bound TP into readily bioavailable FRP under anoxic conditions. FRP released into the water column is potentially available to support nuisance and or harmful algal blooms. This undermines the role of the sedimentation basin as a buffer to downstream ecosystems (Lawrence and Breen, 1998). The opinion that the Torrens Lake provides a critical ecosystem service by functioning as sedimentation basin for the catchment (TCWMB, 2002) is valid only if the sediments function as a long-term sink for pollutants (Lawrence and Breen, 1998). Considering the FRP release observed in this (Chapter 7) and other studies (Jenkins, 2000), the role of the Torrens Lake as a sedimentation basin is considered questionable.

The impact of increasing urbanisation pressure on catchments utilised for potable supply is also a potential concern. Stormwater flowing into the Torrens Lake was characterised by AHS, HiA and HiN, and generated a substantial increase in the proportion of HiN compounds in the lake (Chapter 5). Although the HiN fraction is readily bioavailable, this fraction represents a major challenge to the treatment of water for potable supply (Chow *et al.*, 2004; Chow *et al.*, 2000) and substantially impacts on the quality of potable water (Prevost *et al.*, 1998; Simpson and Hayes, 1998) that can be delivered to consumers. Urbanisation may not only decrease the quality of water flowing into reservoirs, but also increase the cost and complexity of providing safe drinking water back to the community. This issue will become increasingly important as communities look to stormwater harvesting and reuse to meet their urban water needs.

9.4 Conclusions

Any activity that changes the land use of a given catchment will directly influence the quality, and quantity of the water in that catchment (Goonetilleke *et al.*, 2005). Urbanisation is the most disruptive of all land use changes, altering waterways such as to generate systems that are distinctly different from natural. The objective of this thesis was to investigate the impact of urbanisation on NOM composition, metabolism, and transport within the conceptual framework proposed by Brookes *et al.* (2005) "that degradative processes associated with changes in land use lead to a reduction in resource processing during transport between the terrestrial component of the catchment and the receiving water". It is proposed that the project provides support to the conceptual framework by demonstrating that (a) the capacity of heavily engineered stream reaches to buffer downstream reaches was severely comprised, and (b) that urbanisation induces a substantial shift in the composition and bioavailability of organic material in streams which appears to be due to an introduction of "urban" compounds and a reduction in processing of endemic DOC compounds.

In a recent assessment of sustainability in urban centers (McGranahan and Satterthwaite, 2003), one of the key factors in "meeting the needs of the present without comprising the ability of future generations to meet their own needs" was ensuring that the disposal of biodegradable waste does not exceed the capacity of renewable sinks. The example provided was to ensure that the capacity of a river to assimilate biodegradable material, without degrading the ecological value of the river, was not exceeded. While there remains a distinct lack of understanding of processes that occur in natural systems, this project provides some level of insight into the impact that changes in land use has on those systems, and of how a "restored" stream may function post intervention. The capacity to process resources that the "degraded" stream reach has retained provides a sound basis for stream restoration projects. It is clear that restoring an urban stream to "pristine" condition is not possible, yet reinstatement of substantial ecosystem services can realistically be expected.

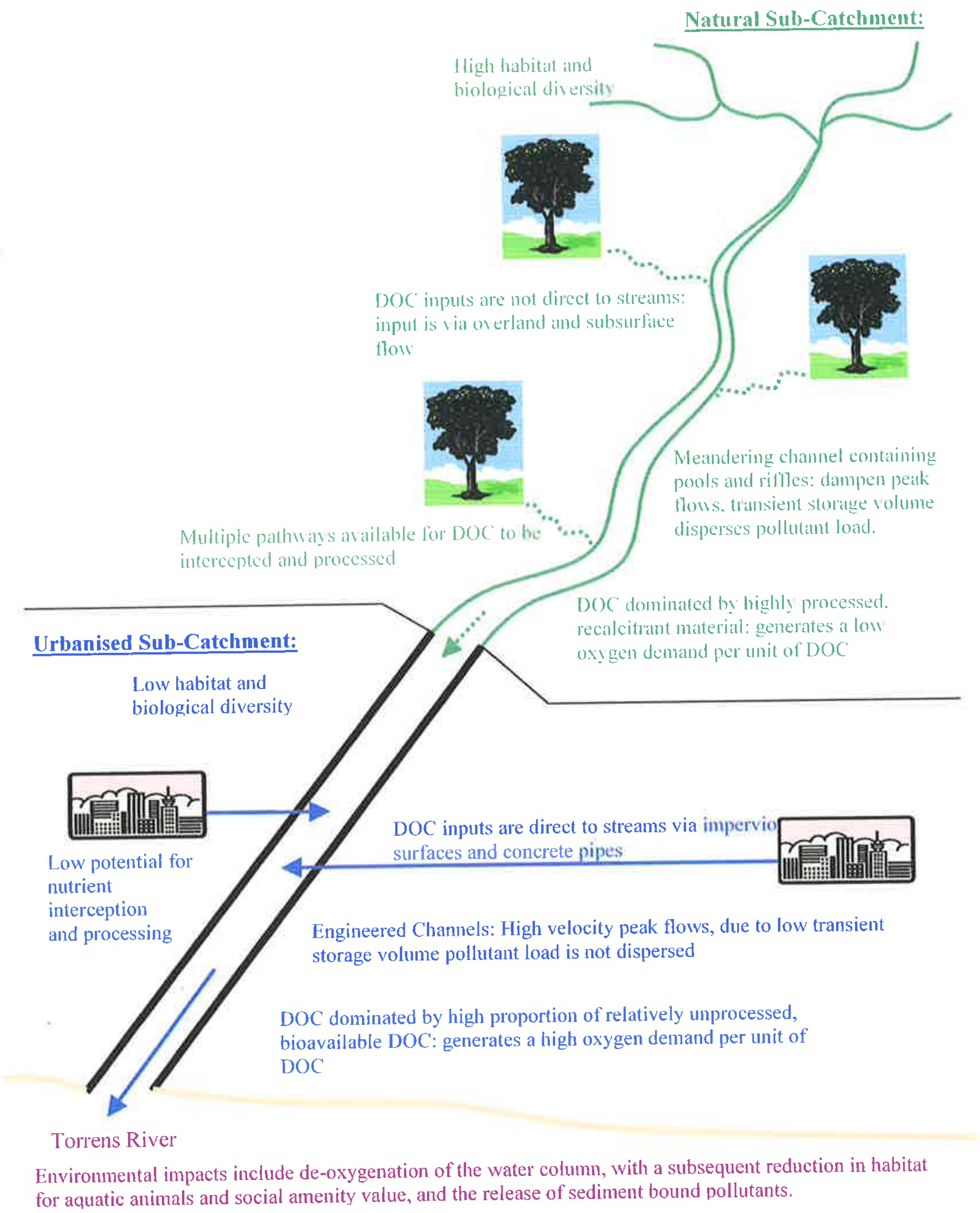

Figure 9.1. Schematic representation of First Creek sub-catchment outlining the shift in organic matter input pathways and bioavailability across the rural-urban gradient.

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