MONASH UNIVERSITY

# NUTRIENT BEHAVIOUR IN URBAN DRAINAGES

***THESIS SUBMITTED TO THE DEPARTMENT OF CIVIL ENGINEERING, FACULTY OF ENGINEERING FOR THE DEGREE OF MASTER OF ENGINEERING SCIENCE (RESEARCH)***

**BY**

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# ABSTRACT

Urbanisation has altered the natural landscape, removing features that previously acted to retain, transform and process nitrogen and phosphorus within catchments. In Melbourne the past legacy of traditional urban design aimed at efficient drainage of stormwater has resulted in higher stormwater volumes with high pollutant concentrations. Excessive concentrations of such nutrients in urban runoff can have an adverse impact on the ecological health of receiving waters.

The aims of this study are to identify the catchment characteristics and mechanisms that influence nitrogen and phosphorus concentrations in dry and wet weather, and to recommend the most appropriate treatment technologies to remediate the situation.

The study used existing data sourced from previous researchers on a number of Melbourne catchments. Standard statistical methods were used to gain insights into concentrations, compositions and relationships between catchment characteristics and nutrient concentrations.

Catchment land use is found to have an impact on dry weather average nitrogen concentrations with residential concentrations (e. g. mean TN=3.2 mg/L, mean $NO_x$=1.868 mg/L) significantly higher than in industrial catchments (mean TN=1.06 mg/L, mean $NO_x$=0.296 mg/L). However, this disparity between land uses could not be evaluated for wet weather due to the lack of data.

In dry weather, the catchment characteristics of catchment (human) population and area both positively influence most nutrients, since they are measures of nutrient loading. Some nitrogen species are affected by the hydraulic conductivity of the catchment's underlying soils, suggesting nitrogen leaching and subsurface flow pathways may be critical in supplying nitrogen oxides and other dissolved nutrient species during dry weather. Older catchments, compared among the urban catchments studied, discharge higher levels of phosphorus and dissolved nitrogen, most likely as a result of degraded and leaking wastewater infrastructure, whereas steeper catchments deliver higher concentrations of ammonia, suggesting retention times may limit the transformation of organic nitrogen and ammonia to nitrate and nitrite. Nitrogen loading is not only generated from current anthropogenic activities but appears to be complicated by past legacies of land use, where

significant long-term leaching of oxidised forms of nitrogen occurred. Unfortunately, inadequate historical land use data were available to test this hypothesis.

In wet weather, catchment population influences nitrogen and phosphorus species, especially the dissolved forms. Curiously, catchment area influences nitrogen oxides and dissolved nitrogen, with higher concentrations observed for larger catchments. The percentage of impervious surfaces influences dissolved nitrogen and total phosphorus. The hydraulic conductivity of soil and bedrock influences dissolved nitrogen, with more permeable soils producing higher concentrations, whereas surprisingly, the catchment slope negatively influences total nitrogen concentrations. A plausible reason is that slope affects water retention time. A steeper slope provides a quicker runoff of rainwater containing less total nitrogen, whereas a flatter slope, with longer retention time, provides more baseflow seepage from soils.

A factor possibly explaining the higher nitrogen oxide concentrations seen in dry weather is that in the process of urbanization, when stormwater drainage networks are built, (especially for buildings and roads), the ground is effectively disturbed and drained. This results in the water table usually being lowered, hence producing a thicker aerobic soil zone that promotes the nitrification process. In wet weather, in contrast, nitrogen oxide concentrations are much lower. In wet weather, particulate nitrogen sourced from soil surface runoff and impervious surfaces is a significant component of stormwater.

The average proportion of nitrogen oxides to total nitrogen found in Melbourne catchments in stormwater (in surface runoff) is similar to the national average for stormwater of urban catchments in the USA, probably due to similarities in urban development.

Based on knowledge of nutrient concentrations and their composition, appropriate treatment technologies can be planned for their removal. The processes targeting removal of particulates and soluble nutrients involve physical and biological processes. It is recommended to apply methods to settle, detain, reduce and assimilate nutrients focussing on particulate removal in stormwater, and dissolved nitrogen, especially nitrogen oxides, in dry weather flows. The main processes for the removal of dissolved nutrients are anaerobic processes and biotic assimilation.

The sources of nitrogen, both natural and anthropogenic, are varied and dispersed throughout the urban catchment. They include both surface sources (e.g. sediment and organic matter) and sub-surface sources (e.g. nitrogen inputs from previous land uses, and leaks from wastewater infrastructure). It is clear that the management of nutrients remains a critical challenge for stormwater managers. In order to address the problem, appropriate treatment technologies should focus particularly on the removal of particulate nitrogen during wet weather flows, given that it comprises 35% of total nitrogen in stormwater under these conditions. During dry weather, the focus should be on the treatment of nitrogen oxides, which make up 64% of total nitrogen in inter-event flows. Ideally, to treat wet weather flows from catchments (where space allows), it is recommended to construct wetlands which are capable of removing sediments, particulate organic matter, and dissolved nutrients. To treat dry weather flows from catchments, it is recommended to build in-line clastic filters or "filter barriers", which are capable of removing dissolved nutrients. These could be built with a range of substrates combined with woodchips, (incorporating reducing cells), and planted with an assortment of sedges and macrophytes. Thus there are methods for treating urban drainages throughout the year.

# TABLE OF CONTENTS

## LIST OF FIGURES

## LIST OF TABLES

# Declaration

This statement is to certify that to the best of the candidate's knowledge the thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other institution and affirms that to the best of the candidate's knowledge the thesis contains no material previously published or written by any other person, except where due reference is made in the text of the thesis. The length of this thesis is less than 50,000 words, exclusive of figures, tables and references.

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David K. W. Choy

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# Chapter 1: Introduction

## 1.1 Background

Urban runoff has been implicated as a major cause of the degradation of the water quality and ecosystems of receiving streams, lakes and near-shore coastal waters (Roesner, 1986; Hunter, 2001). Key pollutants found in urban runoff are nutrients, such as nitrogen and phosphorous, which are in particular harmful to coastal waters and freshwater lakes. This thesis investigates the causes of the variability of nutrient levels in stormwater drains in urban areas. It seeks to identify the important catchment characteristics and mechanisms that influence the concentrations of both nitrogen and phosphorus in dry and wet weather runoff in order to inform the development of the most appropriate management strategies to reduce nutrient levels of urban runoff.

Diffuse pollution is difficult to manage and regulate since its sources and pathways are hard to understand and quantify, and monitoring and treatment programs are usually expensive. An understanding of the causes, in particular the factors that affect the concentrations of particular pollutants, will enable a more targeted approach to the management and treatment of such pollution.

Nutrients are chemical compounds of nitrogen (N) and phosphorus (P) that are essential for plant and animal growth. The supply of N and P influences the rates of growth of algae and vascular plants in freshwater and marine ecosystems (Vollenweider, 1968; Hecky and Kilman, 1988; Howarth, 1988; Smith, 1998). However, high nutrient levels in water lead to over-nourishment, or eutrophication, in freshwater lakes, reservoirs, streams, rivers, estuaries and coastal marine waters (Edmondson, 1995). Eutrophication commonly leads to accelerated growth of microscopic plants and animals, consuming oxygen, in turn producing a condition called hypoxia, a condition when water is depleted of oxygen. Hypoxia causes the death of microorganisms, invertebrates and vertebrates (such as fish), and the breakdown of organic matter produces toxic conditions, including for humans. Eutrophication is the most widespread water quality problem in the USA and many other nations (Carpenter et al., 1998). High nutrient concentrations in receiving waters increase the potential for algal blooms and the loss of biodiversity and habitat (Galloway et al., 2003). Eutrophication has affected approximately half of the impaired area of lakes and 60% of impaired river reaches in the USA (U.S. EPA, 1996). Strong positive relationships between algal biomass and nutrient loading have been observed in lakes and reservoirs (Dillon and Rigler, 1974; Jones and Bachman, 1976; OECD, 1982). The average characteristics of streams in an eutrophic state may be defined as concentrations of total nitrogen (TN) exceeding 1.5mg/L, of total phosphorus (TP) exceeding 0.075 mg/L, of suspended chlorophyll *a* in excess of 30 $mg/m^3$, and of benthic chlorophyll *a* exceeding 70 $mg/m^3$ (Dodds et al., 1998).

The Australia and New Zealand Environment Conservation Council provides guidelines on median and maximum permissible concentrations of nutrients for surface waters (ANZECC, 2000). For example, for TN the threshold concentration for lowland rivers is 0.5 mg/L, and for TP the threshold concentration is 0.05 mg/L. Levels above these are recognised to cause bio-stimulating effects on the aquatic environment (SPCC, 1990). These levels are the default trigger values adopted for south-eastern Australia, above which chemical stress to the ecosystem is likely to occur (ANZECC, 2000). Dissolved forms of nitrogen such as ammonia ($NH_3$) and oxides of nitrogen consisting primarily of nitrates and nitrites, together called nitrogen oxides ($NO_x$), particularly impact on water bodies, since they are readily assimilated by simple organisms (Seitzinger et al., 2002).

Human population growth has placed increasing demands on aquatic and terrestrial ecosystems. Between one third and one half of the land surface has been transformed by land clearing, agriculture, forestry, animal husbandry, urbanization and by changing the hydrological cycles (Vitousek et al., 1997b). When a landscape is cleared of forest, the soil's structure, stability, and filtering capacity are diminished, overland flow of surface water and soil erosion increases, and nutrient cycling, water budgets, and water-release dynamics are altered (Voyer et al., 2011). With increasing human population growth, the impacts on aquatic and terrestrial ecosystems will continue. Human activities have profoundly impacted on the global biogeochemical cycles of carbon (C) (Galloway et al., 1995; Vitousek et al., 1997a; Vitousek et al., 1997b), N and P (Schlesinger, 1991; Vitousek et al., 1997a; Vitousek et al., 1997b). The rate of N input into the terrestrial N cycle has been doubled by humans, and continues to increase (Vitousek et al., 1997a). Human activities **(**primarily by industrial N fixation and the cultivation of N-fixing legumes) produce around 10% more than the total N fixed by all natural terrestrial ecosystems before the advent of agriculture (U.S. EPA, 1994).

In major cities in Australia and in the USA (and in many other places around the world), sewerage and stormwater systems are essentially separate systems. Wastewater from homes and industrial areas is conveyed in pipes (sewers) to centralised wastewater treatment plants to be treated (using typically secondary or tertiary treatment processes to concentrations that are still higher than those of receiving waters) and commonly discharged to receiving waters, either inland or marine. On the other hand, stormwater runs into drains and pipes to discharge directly into streams and rivers, in most cases without treatment. In major urban catchments, stormwater has been identified as the primary source of water quality degradation, though of lower and more variable concentration, but typically of higher volume and therefore providing a greater mass load (Burton and Pitt, 2002). As cities grow, both the concentrations and loads of N and P to small streams increase, with stormwater being the primary driver of such increases (Soranno et al., 1996; Hatt et al., 2004).

The question as to the specific *causes* of urban stormwater-related deterioration in water quality has begun to be addressed in more recent studies. For example, it has been found that concentrations and loads of TP and filterable reactive phosphorus (FRP) increase as more impervious areas are directly connected to receiving waters (Hatt et al., 2004). This has important (and potentially positive) implications for stormwater management; it appears possible that if runoff from impervious surfaces can be intercepted and treated before discharge to receiving waters, a healthy receiving water ecosystem may be able to be sustained. It is, however, worth noting that specific components of nitrogen, such as nitrite and nitrate, may also be influenced by wastewater inputs such as septic tanks, particularly where they are relatively close to streams (ibid).

This study aims to investigate the levels of nutrients in both dry and wet weather emanating from stormwater drains, and to identify the key catchment characteristics that influence the variability of nutrient concentrations. This understanding will ultimately better enable the identification of urban catchments which are prone to generating high nutrient levels in both dry and wet weather, and locations where appropriate remedial actions may be more effectively planned and applied.

## 1.2 Objectives

The main objective of this thesis is to understand the behaviour of nutrients from urban catchments and the catchment characteristics that affect them. This research aims at examining key factors that influence nutrient concentrations and composition from urban catchments during both dry and wet weather. The study is intended to achieve insights into the most appropriate treatment technologies for treat urban runoff in both dry and wet weather.

Specifically, the detailed objectives are to:

1. Quantify dry weather (baseflow) N and P concentrations from urban catchments;
2. Quantify wet weather (storm event) N and P concentrations from urban catchments and their explanatory factors;
3. Understand the composition of N species in both dry weather and wet weather from urban catchments with differing land uses, and explore the mechanisms causing any differences; and
4. On the basis of the results of the above analyses, identify implications for the design of stormwater management strategies aimed at reducing N inputs to receiving waters, including the selection and design of stormwater treatment systems.

## 1.3 Scope of research and Methodology

This thesis focuses on dry and wet weather nutrient concentrations as measured in flows from urban catchment drains, using existing water quality and flow data. Whilst the concentrations of many other pollutants such as sediment, heavy metals and pathogens are also important, this thesis focuses exclusively on N and P and the factors that explain their behaviour.

The important catchment characteristics will be identified, quantified and studied to see what influence they have on nutrient concentrations in different catchments during both dry and wet weather flows. The concentrations and composition of N and P species from particular catchments will be studied and the influence of different land uses and different weather conditions (both dry and wet) will be compared in order to gain insights into the underlying mechanisms that control the differing nutrient concentrations and compositions.

## 1.4 Thesis outline

The structure of the thesis is as follows: Chapter 1 provides the background, objectives, scope of research and the thesis outline. Chapter 2 presents a review of studies which have investigated the concentrations and composition of nutrients in urban stormwater, both in Australia and internationally. In Chapter 3, data sources and study sites are described, and data analysis methods for concentrations, compositions and relationships between nutrient levels and catchment characteristics are presented. Chapter 4 examines nutrient concentrations and composition during dry weather (inter-event) periods, along with the influences of catchment characteristics, while Chapter 5 takes a similar approach, focussing on storm events (wet weather). Chapter 6 gives a comparison of dry and wet nutrient (nitrogen and phosphorus) levels, while Chapter 7 draws together the findings from the previous chapters into a discussion of the implications for receiving waters and for the design of stormwater management strategies aimed at reducing nutrient inputs from stormwater**.** The final chapter (Chapter 8) outlines the conclusions of the work, identifies its contributions to knowledge and discusses the remaining knowledge gaps which need to be addressed.

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# Chapter 2: Literature review

## 2.1 Introduction

Urbanisation is an inevitable consequence of population growth, with the urban population having exceeded the rural population in the world in 2008 (Vairavamoorthy et al., 2009). In developed countries, the urban population is expected to increase from 0.9 billion to 1 billion by 2030, at an overall growth rate of 1% (Brockerhoff, 2000). With increased urbanisation, the natural landscape and drainage patterns are replaced by more uniform gradients and greatly reduced vegetation cover, along with a much more efficient drainage network (Walsh et al., 2004a; Walsh et al., 2004b). Urban catchments generally deliver higher concentrations and loads of pollutants to their receiving waters (Chocat et al., 2001; Hatt et al., 2004). Urbanisation is the most likely primary determinant of stream water quality degradation, with drainage connection and imperviousness and sub-basin indicators of urban density explaining much of the observed variation in pollutant concentrations (Hatt et al., 2004). In urban areas, stream and lake impairment also occur due to habitat destruction (e.g. channelization, removal of stream canopy and riparian zone loss, turbidity, siltation, etc), physical and chemical contaminant loadings from impervious areas (e. g. parking lots, streets) and construction sites within industrial, commercial, and residential areas (Burton and Pitt, 2002).

Adverse impacts to waterways from urbanisation are many and varied and include sedimentation which smothers aquatic ecosystems along with scouring of aquatic habitats by the increased volume and velocity of flows (Rohrer and Roesner, 2005). Elevated levels of nitrogen (N) and phosphorus (P) contribute to the eutrophication of receiving waters (Carpenter et al., 1998; Kendall and Aravena, 2000; Fenn et al., 2003). Examples of such eutrophication include Chesapeake Bay in the USA (Novotny and Olem, 1994; Galloway et al., 2003) and Port Philip Bay (Harris et al., 1996) and Moreton Bay in Australia (Abal et al., 2001). All such examples have environmental, social and economic impacts.

## 2.2 Impacts of stormwater

### 2.2.1 Changes to hydrology

Urbanisation dramatically changes a catchment’s hydrology. The increasing imperviousness results in reduced infiltration, and loss of vegetation decreases evapotranspiration; these in turn increase the frequency and magnitude of stormwater flow events, as well as reducing both groundwater levels and baseflow (Roesner et al., 2001; Fletcher et al., 2010). The effects exacerbate flooding downstream. More impervious surfaces such as roofs, tarmac roads and paved surfaces will contribute to increased runoff. It has been identified that elevated runoff occurs due to two primary mechanisms; (i) an increased imperviousness and (ii) an increase in the hydraulic efficiency of the drainage network (Leopold, 1968; Codner et al., 1988; Schueler, 1992; Wong et al., 2000). The increased quantity and rate of stormwater runoff generated also results in bank erosion.

As a consequence of these hydrological disturbances brought about by urbanisation, stormwater management has traditionally focussed on flow control (Schueler and Helfrich, 1988), with the primary objective of safely and economically conveying stormwater runoff from urbanised areas to receiving waterways (Wong et al., 2000). However such rapid stormwater conveyance approaches have compounded hydrologic impacts and disturbance to receiving waters (Fletcher et al., 2001; Urbonas, 2001; Walsh et al., 2004a; Wong, 2006).

The impacts of urbanisation on hydrology have been documented for several decades, with benchmark studies in the USA identifying the extent of changes brought about by impervious areas (Leopold, 1968). A case study of the hydrologic effects of urbanisation in an Australian context identified hydrologic changes from a rural catchment to a low density urban catchment (Codner et al., 1988). Even early studies such as that of Leopold (1968) identified that the nature of the drainage connection was important for determining the eventual consequence of impervious areas on stream hydrology. More recently, an Australian study showed that the hydraulic efficiency of the drainage network may account for up to 95% of the increase in observed peak discharge where all channels are lined (Wong et al., 2000). The relative contribution of imperviousness and hydraulic efficiency of drainage works have been examined to provide guidelines for future stormwater management (Wong and Somes, 1997; Wong et al., 2000) and recent studies have shown that the decline in receiving aquatic ecosystem health is directly linked to the proportion of impervious surfaces in a catchment that is connected to the stream by drainage pipes (Hatt et al., 2004; Walsh et al., 2004a). This suggests that the extent of degradation of receiving water hydrology by urbanisation may be reduced through the use of careful design processes which minimise the connection between impervious areas and receiving waters by the use of appropriately designed stormwater retention and treatment systems, such that most ‘everyday’ rainfall events are retained within the catchment for treatment and potentially for infiltration or use.

### 2.2.2 Changes to water quality

Not surprisingly, urbanisation also results in substantial degradation of receiving water quality, as a result of increased generation and mobilisation of pollutants in the catchment. With a change in hydrology, the quality is also affected - urban stormwater runoff is generally of poorer overall quality than runoff from both rural (Fletcher et al., 2010) and forested catchments (Duncan, 1999; Fletcher et al., 2010). The result is a progressive deterioration of the environmental values of the aquatic ecosystems in urban environments. The hydraulically efficient nature of urban drainage systems means that the transport of pollutants is more efficient than in forested or agricultural catchments where natural filtering removes a substantial proportion of pollutants (Fletcher et al., 2010). Pollutant types include sediments, nutrients, heavy metals, organic matter, hydrocarbons, pathogens (bacteria, viruses, protozoa) and micro-pollutants (including hormones and other chemical products). A summary of each pollutant type, including their sources, impacts and typical levels in stormwater, is given in the following sections.

#### *2.2.2.1 Sediments*

Suspended solids (SS) has frequently been used as a generic or indicator measure of urban runoff pollution (Duncan, 2006), in part because it is a carrier of other pollutants (such as adsorbed metals, pathogens, etc). Suspended solids comprise inorganic and organic components.

Sources of inorganic sediments in drainage waters include: soils, exposed bedrock of the catchment, erosion of drains, stream banks and stream beds during stormwater erosion, products of wear of vehicles and roads, and erosion from construction and demolition sites (Burton and Pitt, 2002). Sources of organic sediments are primarily human or animal wastes (human wastes may occur as a result of leaking or cross-connected wastewater systems), plants and parts of plants such as decaying vegetation: leaves, twigs and branches entrapped in the stormwater drainage.

Suspended solids may cause pipe blockages, and changes in flow conditions in channels, and aquatic habitats (Duncan, 2006). Excessive sediments carried in stormwater have a number of physical impacts. Coarse sediments settle quite rapidly and can bury or smother benthic flora and fauna on the beds of receiving waters such as small streams and lakes. Fine sediments such as silts and clays can remain suspended in water for an extended period of time and have the potential to choke the respiratory organs (gills) of fish and filter feeders such as molluscs. Combined, these ecological effects result in the death of vulnerable species and reduced biodiversity. Contaminants such as hydrocarbons, heavy metals and phosphorus are linked to suspended solids, being readily adsorbed to sediments (Walesh, 1986; Preul and Ruszkowski, 1987; Urbonas, 1991). In some circumstances, adsorbed or attached pollutants may later desorb, rendering them bioavailable. The effective treatment of suspended solids is thus a fundamental requirement of stormwater quality management (Lawrence and Breen, 2006).

#### *2.2.2.2 Nutrients*

Nutrients are natural compounds of nitrogen and phosphorus, which are essential for the growth of algae and aquatic plants. However, urban areas generate nutrients and deliver them to receiving waters at a greater rate than their rural or forested counterparts (Fletcher et al., 2010). When the concentrations and loads of nutrients are high, they become pollutants. For example, industrial or vehicle emissions in urban areas result in substantially higher atmospheric deposition of nitrogen (Taylor et al., 2005). Other sources of N are from washoff of impervious and pervious surfaces, and washout of pervious areas. Nutrients in excessive concentrations and loads are of concern; the relative importance of nitrogen or phosphorus will depend on which is limiting in a particular ecosystem. Eutrophication is the most widespread water quality problem in the USA and many other nations (Carpenter et al., 1998). High nutrient concentrations in receiving waters increase the potential for the proliferation of algal blooms and the loss of biodiversity and habitat (Galloway et al., 2003). Eutrophication has affected approximately half of the impaired area of lakes and 60% of impaired river reaches in the USA (U.S. EPA, 1996). Strong positive relationships between algal biomass and nutrient loading have been observed in lakes and reservoirs (Dillon and Rigler, 1974; Jones and Bachman, 1976; OECD, 1982). The average characteristics of streams in an eutrophic state may be defined as concentrations of total nitrogen (TN) exceeding 1.5mg/L, of total phosphorus (TP) exceeding 0.075 mg/L, of suspended chlorophyll *a* in excess of 30 mg/m$^3$, and of benthic chlorophyll *a* exceeding 70 mg/m$^3$ (Dodds et al., 1998).

Nitrogen (N) compounds play an important role in eutrophication, impact on the oxygen content of receiving waters, and their high concentrations cause toxicity to aquatic invertebrates and vertebrates (Kadlec and Wallace, 2009). High N levels (over-enrichment) support the rapid growth of microscopic plants and animals in aquatic environments leading to eutrophication and toxicity which may be further compounded by the proliferation of cyanobacteria which produce toxins, resulting in a health risk to aquatic and human life. Humans drinking water with very high levels of nitrates in excess of about 50 mg/L nitrate may suffer a serious illness, methaemoglobinemia, due to the oxidation of haemoglobin, resulting in the reduced capacity of the blood to transport oxygen (WHO, 2012).

Phosphorus (P) is a key nutrient required for plant growth and is a limiting factor for vegetative productivity (Kadlec and Wallace, 2009). With many waters often being P limited, the introduction of trace amounts of P into receiving waters can have profound effects on the structure and functioning of the aquatic ecosystem (Kadlec and Wallace, 2009). Sources of P include decaying vegetative and animal matter, garden fertilisers, household detergents, and the droppings of animals and pets. Phosphorus exists in the organic and inorganic forms. Both exchangeable and colloidally bound phosphorus have been found in eutrophic wetlands (Baldwin, 1988; Hens and Merckx, 2002). Phosphorus readily combines with dissolved organic compounds to form dissolved organic phosphorus (DOP), which has been found to consist of several kinds of organics (Turner and Newman, 2005). Some are readily hydrolysed by enzymes of soil microbes, and together with $PO_4$-P are called soluble reactive phosphorus (SRP) (Kadlec and Wallace, 2009). The organic components of SRP can move readily in solution, through soils and sediments (Anderson and Magdoff, 2005). Phosphorus may also be associated (be bound to) with suspended particles, when it is called particulate phosphorus (PP) (Kadlec and Wallace, 2009). Under certain conditions, phosphate may be precipitated by certain cations, e.g. as apatite ($Ca_5(Cl,F)(PO_4)_3$), and hydroxyl-apatite ($Ca_5(OH)(PO_4)_3$) (Reddy and D'Angelo, 1994). In addition to direct chemical reaction, P can co-precipitate with other minerals, such as ferric oxyhydroxide and carbonate minerals such as calcite (calcium carbonate, $CaCO_3$) (Reddy and D'Angelo, 1994). In acid soils, P may be fixed by Al and Fe, if available; in alkaline soils, P may be fixed by Ca, and Mg, if available; whereas reducing conditions lead to the solubilisation of Fe minerals and the release of P co-precipitates (DOP and SRP) (Reddy and D'Angelo, 1994).

Nutrients tend to have a long duration of impact on receiving waters, in particular because N can be cycled between soil and water, in complex routes with the biota and vice versa. Similarly, P trapped in sediments in a treatment system or aquatic environment, may, under low oxygen conditions, be released back into the water column, causing subsequent problems. Nutrient accumulation and eutrophication thus tend to be problems that persist for years, with long-term ecological impacts.

#### *2.2.2.3 Heavy metals*

Heavy metals in urban runoff may be derived from metal roofs, vehicle wear, and the corrosion of urban infrastructure, and these lead to the high concentrations of heavy metals such as Zn, Cu and Pb found in receiving waters (Fletcher et al., 2010). Stormwater runoff thus commonly contains elevated levels of heavy metals and metalloids, particularly in urban areas (USEPA, 1983; Pitt et al., 1995). Some are toxic at low concentrations (Kadlec and Wallace, 1996). The main metals of concern in urban runoff, which can impair the health of humans or aquatic animals are Pb, Zn, Cd, Cr, Hg, Cu and As. Pb is harmful to both humans and aquatic life, Zn is deadly to aquatic life, Cd and Hg can bioaccumulate, and Hg is considered a neurotoxin (Oregon_Environmental_Council, 2012). Cu has been found to impair the olfactory organs of salmonid fish (Sandahl et al., 2004). Metal bioavailability is reduced by higher hardness, by sorption to solids, and by dilution (Kadlec and Wallace, 1996). Most metals are bound to particulates and are thus subsequently deposited in stream and lake sediments (Pitt et al., 1995). However, heavy metals such as Zn and Cu are often present in runoff in soluble forms (Schueler, 1987). Episodic exposure of organisms to stormwaters laden with metals can produce stress and lethality (Kadlec and Wallace, 1996). . Amphipods bio-accumulate Zn from episodic *in situ* exposures, with repeated exposures increasing their sensitivity (Ellis et al., 1992).

#### *2.2.2.4 Organic matter*

Organic matter includes both plant and animal material. The organic load in stormwater originates mainly from leaves and garden litter, and contributes significantly to biological oxygen demand (BOD) in receiving waters (Lawrence and Breen, 2006). The cycle of plant growth, death and partial decomposition produces gases, dissolved organics and solids. Decomposition by microbes is the respiration of sugars, starches, and low molecular weight celluloses in the dead plant material (Kadlec and Wallace, 1996) which result in methane and carbon dioxide gases being produced with a spectrum of soluble, large organic molecules (humic substances) being released into soils (and possibly transported in water), and the solid residues of plant decomposition (which originate as celluloses and lignins in plants) becomes peat or organic sediment. The organics are classed as fulvic (acid soluble), humic (base soluble) and humin (insoluble) (Peat Testing Manual, 1979). While the primary result of decomposition is a range of carbon-bearing compounds, organic N is formed as a result of biomass decomposition, and proteins degrade to organic species such as amines, which in turn degrade to ammonium N (Kadlec and Wallace, 1996). Impervious surfaces are good collectors and accumulators of organic matter, which provide a long-term supply of N in the form of ammonium N. While urban catchments may have lower overall vegetation density than the pre-developed state, the nature of impervious areas and the drainage system means that material deposited far away from the receiving water is transported directly to it, rather than being retained, biodegraded and integrated into the catchment landscape.

#### *2.2.2.5 Pathogens*

Pathogens cause illness in humans and are present in untreated domestic wastewaters as well as in runoff which contains animal sources (Kadlec and Wallace, 2009). These organisms range from sub-microscopic viruses to parasitic worms (Kadlec and Wallace, 2009), divided into five groups: viruses, bacteria, fungi, protozoa and helminths. Principal pathogen sources in stormwater include leaks from sewer pipes or cross-connections with sanitary sewers. Since the measurement of human pathogens in natural and wastewaters is expensive, contamination is often detected with the use of a number of indicator organisms which are easy to monitor and correlate with other pathogenic organisms. From the higher than usual specific pathogen counts, management will be able to focus on repairing certain pipes or eliminating particular sources. However, this can be complicated if there are large populations of animals in the catchment, as animals are also a source of pathogenic organisms (Kadlec and Wallace, 2009), or where the sources are highly dispersed.

#### *2.2.2.6 Organic compounds and hydrocarbons*

Organic compounds, including hydrocarbons, are major constituents of biochemical oxygen demand (BOD), or chemical oxygen demand (COD) (Kadlec and Wallace, 2009). The major routes for hydrocarbon removal includes volatilization, photochemical oxidation, sedimentation, sorption, biological (microbial) degradation, and plant uptake, where microbial processes contribute to fermentation, aerobic and anaerobic respiration (Kadlec and Wallace, 2009). However, specific organic chemicals pose a difficult set of problems due to their toxicity to plants and the limitations of aerobic and anaerobic degradation (Kadlec and Wallace, 2009). Aliphatic compounds, of straight chained and branched structure (natural waxes) degrade more slowly with increasing molecular weight, and aromatic compounds (with ring molecular structures) also degrade much more slowly than polyaromatic hydrocarbons (PAHs). Those with more than three rings cannot support microbial growth (Zander, 1980) and therefore are more resistant to degradation. Some PAHs are considered to be toxic and mutagenic and have carcinogenic properties, posing a risk to the environment and human health (Kadlec and Wallace, 2009). Due to their resistance to degradation, PAHs may be transferred into living organisms with the potential to affect their physiology.

Oils and grease are common substances in runoff from roads and car parks. Oils and grease tend to float on water, posing a barrier to the water surface, reducing oxygen solubility and a threat to gill respiration of fish and molluscs, and the larvae of certain insects that use their proboscis for aerial breathing (e. g. mosquito larvae may be controlled by oil on water). Both invertebrate and vertebrate populations will be reduced.

Persistent chemicals such as pesticides and herbicides are numerous. Many pre - 1950 pesticides such as DDT are very persistent in the environment. They cause death to insects, and may be harmful to humans. Their affinity to certain particulates could be used in a mechanism for their removal. Although data on pesticide removal are sparse, some success has been reported in treating polychlorinated biphenyls (PCBs) and Lindane in sub-surface flow (SSF) systems which essentially treat water by allowing water to permeate deep in the media so that by interaction with the media, and the activity of anoxic bacteria the pollutants in question can be denatured. (Winter, 1991). Pesticides: DDT, DDE and dieldrin; and herbicides such as Atrazine, a triazine herbicide are commonly observed in stormwater and receiving streams, while phenol is a frequent pollutant of industrial effluents (Kadlec and Wallace, 1996). Many of these chemicals have received increasing recent attention, as they now fall under the European Union's Water Framework Directive, which identifies 'priority pollutants' (Vogt and Petersen, 2003; Becouze et al., 2011).

#### *2.2.2.7 Summary*

Whilst the range of pollutants in stormwater is broad, this thesis focuses on nutrients – N and P. The rationale is to explain the mechanisms that drive the transport of nutrients in urban catchments, which are as yet unclear. Subsequent sections will discuss in more detail the sources, transformations and impacts of these nutrients in urban stormwater.

## 2.3 Pollutant sources in urban stormwater

Pollutants found in urban runoff have many sources, including anthropogenic and infrastructure (from the weathering of buildings and roads) sources. Both atmospheric deposition and surface erosion of land are major pollutant sources. Anthropogenic sources can be from industrial and commercial activities, runoff from roads, vehicle emissions, spills of chemicals and fuel, along with surface runoff from household gardens that can carry fertilizers. The combination of land-use activities in conjunction with a hydraulically efficient drainage system results in increased contaminants being delivered to receiving waters (Prowse, 1987; Soranno et al., 1996; Carpenter et al., 1998; Chiew and McMahon, 1999; Brezonik and Stadelmann, 2002).

Physical and chemical contaminant loadings come from runoff from impervious areas (e.g. parking lots, streets), construction sites, and industrial, commercial and residential areas (Burton and Pitt, 2002). The extent of urbanisation and the state of receiving waters have been examined by bodies such as by the US EPA documenting nonpoint source pollution under the categories: General urban, Storm sewers, Sanitary sewers, Construction sites, and Surface runoff (USEPA, 1983). Other contaminant sources are even more difficult to assess. They include accidental spills, unintended discharges and atmospheric pollution (Burton and Pitt, 2002).

It has been recognized that pollutants in stormwater runoff vary with watershed characteristics and land uses. Certain pollutants are associated with specific activities (e.g. automobile service areas), and with uses (e.g. parking lots, construction) (Burton and Pitt, 2002).

## 2.4 Key sources of nutrients in urban runoff

In general terms, the main sources of nutrients are: soil erosion, cleared land, fertilisers, human waste, animal waste, fuel combustion, industrial and household chemicals, industrial processes and stormwater facilities (Schueler, 1987; Lawrence and Breen, 2006). In catchments with combined sewers, wastewater constitutes the main source of organic and nitrogenous pollution (Gasperi et al., 2010). In catchments where sewage is piped to a centralised sewerage treatment plants, there is still the risk of leakages, and accidental connections to the stormwater drains, but in these catchments, it is stormwater that is the primary driver of nutrient concentrations and loads (Hatt et al., 2004).

The type of land use may be an important driver of nutrients and land-use zoning has thus been used as a predictor of nutrient loads (Soranno et al., 1996; Carpenter et al., 1998). However, the US EPA reported that land use has little power in explaining site-to-site differences in nutrient loads (Novotny and Olem, 1994); Duncan (2006) made a similar observation.

In a recent study in Perth (an area with very sandy soils and rapid infiltration to groundwater), nutrient inputs to residential land were measured in a survey (Kelsey et al., 2010). It was found that the highest input came from fertilisation of gardens, followed by lawns, and pets, with most of the fertilisers being organic manures, mulches and composts. Where there is a variation of these elements (particularly the permeability and hydraulic conductivity of catchment soils), the magnitude of nutrient input will change. For example, a reduction of household garden spaces may drastically reduce fertilizer application, and in commercial or industrial areas the mix of nutrient sources and transport pathways will be different.

Catchments with heavy traffic may have more atmospheric nitrogen oxides as a result of automobile combustions of fuel. Likewise stationary power generating plants may provide atmospheric pollutions, and a fraction is nitrogen oxides. In storms, the atmospheric nitrogen oxides dissolve readily in rainwater falling onto land or impervious areas, to supply the stormwater network. Atmospheric deposition as a result of lightning producing nitrogen oxides is recognised as a source (Ophardt, 2003), although this may form a minor (< 1%) part of the overall $NO_x$ budget (DOE, 2014).

## 2.5 Nutrient species

### 2.5.1 Nitrogen

Nitrogen compounds occur in a number of forms, including inorganic and organic along with constituents in both the dissolved and particulate phase. Total N is thus broken up into total dissolved nitrogen (TDN) and particulate organic nitrogen (PON). Each of these are further broken down, with the dissolved forms including nitrate and nitrite, ammonia/ammonium (collectively forming dissolved inorganic nitrogen (DIN)) and dissolved organic nitrogen (DON) (Figure 2.1). Transformation between forms can happen through microbially mediated processes such as mineralisation, nitrification and denitrification, as part of the nitrogen cycle (Figure 2.3).

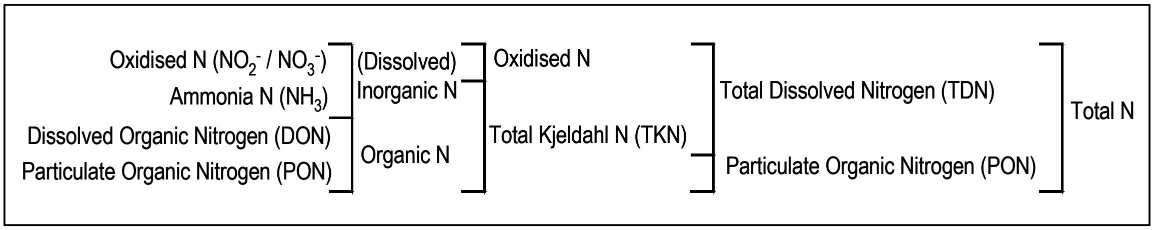



**Figure 2.1** Composition of nitrogen (source: Taylor et al., 2005).

#### *2.5.1.1 Typical concentrations of total nitrogen (TN)*

The literature shows that there is a wide variation in total nitrogen (TN) levels in stormwater from various sources. For example, Duncan (1999) examined 212 separate studies, including 139 from high urban areas, finding an observed range from 0.194 mg/L for the largely forested Tieton River in Washington State to 56.6 mg/L for an urban road in Washington State affected by the eruption of Mt. St. Helens, and agricultural land use provided a median TN concentration of 4.4 mg/L. Despite this, Duncan did not find a significant difference in TN concentrations between urban land-uses, the results range from 2.0 mg/L to 2.7 mg/L (Table 2.1).

**Table 2.1** Typical average total nitrogen (TN) concentrations from different urban land-uses and other sources (Duncan, 1995, 1999).

| **Source** | **No. of samples** | **Median TN (mg/L)** | **Mean TN (mg/L)** |
|---|---|---|---|
| ***Urban sources*** | | | |
| All high urban | 139 | 2.5 | 2.6 |
| Residential | 58 | | 2.7 |
| Industrial | 6 | | 2.4 |
| Commercial | 13 | | 2.15 |
| Other high urban | 62 | | 2.6 |
| All medium urban | 4 | | 2.5 |
| All low urban | 52 | | 2.0 |
| Other low urban | 25 | | 2.2 |
| ***Other sources*** | | | |
| Roads | 12 | 2.2 | |

| | | | |
|---|---|---|---|
| Agricultural | 14 | 4.4 | |
| Forest | 12 | 0.95 | |
| Urban rainfall | | 1 to 2 | |

#### *2.5.1.2 Nitrates and nitrites (NOx)*

Nitrogen oxides ($NO_x$), made up of nitrate ($NO_3^-$) and nitrite ($NO_2^-$), are the most abundant nitrogen forms in water systems (Oms et al., 2000). They are colourless, odourless, and highly soluble in water, are retained weakly in soils, and are easily transported through the soil profile to reach the groundwater (Oms et al., 2000). Nitrate in water is persistent, does not volatilize, and remains in water until consumed by plants or other organisms, or is denitrified (which occurs under low oxygen conditions, Taylor et al, 2005).

A high concentration of $NO_3^-$ in drinking water leads to methemoglobeinemia ("blue baby syndrome" in infants) and possibly other pathological conditions such as cancer (Frewtrell, 2004). Many freshwater lakes undergo eutrophication with the increasing input of nitrates and nitrites (Zhang et al., 2008). Groundwater N pollution was investigated in 14 cities and counties in northern China, where more than half of the 69 locations investigated, over an area of 140,000 $km^2$, reported $NO_3^-$ content in ground and drinking water exceeded 50 mg/L, the allowable limit for drinking water (Zhang et al., 1996) (Chen et al., 2008).

Natural sources of $NO_3^-$ and $NO_2^-$ include gaseous nitrogen fixation due to the activity of microorganisms such as bacteria and blue-green algae, soil degradation, geological deposits, and decomposition of plant and animal residues in which organic N and ammonia are converted to nitrate and nitrite ions (Oms et al., 2000).

Anthropogenic sources of $NO_3^-$ and $NO_2^-$ include the intensive use of nitrogenous fertilizers, improper disposal of plant and animal wastes, municipal and industrial wastewater discharge, sewage disposal systems, landfills, aerial emissions from industrial processes and vehicular emissions (Puckett, 1995). Elevated $NO_3^-$ and $NO_2^-$ levels in water systems thus usually result from human activities (Puckett, 1995). High concentrations of $NO_2^-$ may also be due to very high levels of microbial activity, typically caused by polluted water (Grasshoff, 1983). In urban areas, non-point sources include lawn fertilizer, sanitary landfill leachate, atmospheric fallout, nitric oxide and $NO_2^-$ discharges from automobile exhausts and other combustion processes, and losses from natural sources such as mineralization of soil organic matter (Burton and Pitt, 2002). Atmospheric deposition of $NO_3^-$ and other nitrogen-bearing compounds may be a significant source, particularly near industrial areas, where atmospheric concentrations tend to be elevated (Brimblecombe, 1982; Paerl et al., 1990; Owens et al., 1992; Paerl et al., 1993; Cornell et al., 1995a).

Due to its stability and solubility, $NO_3^-$ has been used by many studies as an indicator for potential water pollution (Oms et al., 2000), such as for estuaries or point-source outfalls (Grasshoff, 1983; Puckett, 1995). Elevated levels may also indicate the presence of other contaminants, microbial pathogens or pesticides (Oms et al., 2000). Nitrate concentrations in oceans are usually below 0.05 mg/L $NO_3^-$-N (Kamykowski and Zentara, 1985). Nitrate levels in ambient groundwater are generally less than 1 mg/L, e. g., (British_Columbia_Canada, 2007). In shallow groundwater and surface streams concentrations range from <0.1 mg/L $NO_3^-$N to 20 mg/L $NO_3^-$N (Oms et al., 2000), depending on soil type, land use practices and well depth, whereas in wastewater discharges and wastewater effluent plants, $NO_3^-$ concentrations can be as high as 30 mg/L $NO_3^-$N (Oms et al., 2000). Table 2.2 gives typical stormwater $NO_2^-$ and $NO_3^-$ Event Mean Concentrations (EMCs) from the USA. The median $NO_3^-$ concentration for separate stormwater systems around the world is 0.8 mg/L (Brombach et al., 2005).

**Table 2.2** Typical stormwater Event Mean Concentrations (EMCs) of nitrite and nitrate from the USA (Smullen et al., 1999).

| **N species** | **Source** | **Mean EMC (mg/L)** | **Median EMC (mg/L)** | **No. of events** |
|---|---|---|---|---|
| Nitrite & Nitrate | Pooled | 0.658 | 0.533 | 2016 |
| Nitrite & Nitrate | NURP | 0.837 | 0.666 | 1234 |

The Nationwide Runoff Program (NURP) was the first comprehensive study of urban stormwater pollution in the USA (USEPA, 1983). Since 1983, further USA urban stormwater pollution data collected have been reported as “pooled data” by Smullen et. al. (1999). Nitrates impact both groundwater and surface waters and $NO_3^-$ is the most common contaminant in groundwater (Oms et al., 2000). Nitrite concentrations in water systems are generally below 0.5

mg/L $NO_2$-N because it oxidises readily to $NO_3^-$ (Oms et al., 2000). The presence of high $NO_3^-$ levels causes aquatic plants and algae to become over-productive (eutrophic), eventually leading to negative impacts on the environment including the death of fish and other aquatic species, sunlight blocking resulting in the elimination or reduction of photosynthesis by submerged aquatic vegetation, and the settling of dead algae and macrophytes to the bottom of the water body, stimulating bacteria proliferation, changes in colour and odours (Allaby, 1989).

#### *2.5.1.3 Dissolved organic nitrogen (DON)*

Organic N is found in all locations, including urban, rural, and remote sites, and also in all types of substrates, including snow and rainwater, lakes and estuaries, seawater and rivers (Cerda et al., 2000). Several studies have shown that dissolved organic nitrogen (DON) may represent more than half the TN loading (Knap et al., 1986; Mopper and Zika, 1987; Cornell et al., 1995b; Bronk et al., 1999). Taylor et al. (2005) found that organic N made up around 50% of the N concentration in both dry weather and wet weather flows in urban catchments of Melbourne. Organic N is defined as organically bound N in the tri-negative oxidation state (Cerda et al., 2000). It includes a wide variety of organic molecules containing N, such as urea and other amines, amino acids, proteins, and other nitrogen containing macromolecules (Mopper and Zika, 1987). In analytical terms, the term organic N is generally applied to the N fraction remaining after nitrate, nitrite, and ammonium have been subtracted (Cerda et al., 2000) (see Figure 2.2).

Typical organic N concentrations vary from < 1mg/L in lakes and marine environments to 20 mg/L in raw waste water (Cerda et al., 2000). Several studies have demonstrated the impact of organic N on estuarine and lake eutrophication, with massive algal blooms, extended bacterial production and poor water quality (Hammer, 1993; Bronk et al., 1994; Cornell et al., 1998). Potential sources of DON are point sources such as wastewater effluents, and non-point sources such as atmospheric deposition, agriculture, combustion, and runoff from forest and urban areas (Knap et al., 1986; Cornell et al., 1995b; Puckett, 1995; Cornell et al., 1998). Dissolved organic nitrogen may also be produced by phytoplankton and bacteria (Pavlou et al., 1974; Hammer, 1993; Bronk et al., 1994; Cornell et al., 1995b). In oceanic, coastal and estuarine environments, an average of 25-41% of DIN (dissolved inorganic nitrogen, made up of ammonia and nitrate) taken up by phytoplankton is estimated to be released as DON (Bronk et al., 1994).

#### *2.5.1.4 Ammonia ($NH_3$)*

Ammonia exists as un-ionized ammonia ($NH_3$), or ionized ammonia ($NH_4^+$, ammonium ion) depending on water temperature and pH, as shown in equation 2.1 (Kadlec and Wallace, 2009):

$NH_3 + H_2O \leftrightarrow NH_4 + OH^-$ Eqn 2.1

$NH_3$ is the toxic form and predominates in high pH and warm water. $NH_4^+$ is relatively less toxic and is predominant in moderate pH and temperature. The sum of $NH_3$ and $NH_4^+$ may be referred to as $NH_x$. Great changes in the supply of ammonia have occurred over the last 100 years as a result of fertiliser use, urbanisation and industrial processes (Gibb, 2000).

In the natural world, animals contribute $NH_3$ through excretion (Gibb, 2000). Natural sources of ammonia also include those of biogenic origin where bacteria produce $NH_x$ via the decomposition of proteins, amino acids, and other nitrogenous compounds (Gibb, 2000). Bacteria are capable of fixing atmospheric N and of reducing $NO_2^-$ and $NO_3^-$ to $NH_x$ (Gibb, 2000). Approximately 83% (as of 2004) of ammonia is used as fertilizers either as salts or as solutions(Appl, 2011). Waste from livestock, feedlots and grazing land also make a significant contribution to $NH_x$ (Gibb, 2000).

Industrial sources of $NH_4^+$ are common because $NH_x$ is used in many industrial processes (Gibb, 2000). Residential and urban sources contribute $NH_4^+$ since $NH_x$ is introduced into the air and wastewaters from the usage and disposal of $NH_x$-containing cleaning and domestic products (Gibb, 2000). Atmospheric deposition of $NH_4^+$ occurs from volatilization and combustion processes including waste disposal, internal combustion, and fuel combustion (Gibb, 2000). Atmospheric deposition of $NH_x$ from rain, particulates, aerosols, and gas exchange contributes a significant proportion of TN inputs to natural water systems (Gibb, 2000). The significance of these inputs increases with the remoteness of the receiving water from anthropogenic influence (Gibb, 2000). Deposition of organic matter such as leaf material, transported from impervious areas into the receiving waters, will also contribute $NH_3$, through bacterially-mediated mineralisation.

Although the aquatic N cycle and the turnover and concentrations of $NH_x$ may once have been in steady state, anthropogenic activities are likely to have caused a significant perturbation of any natural balance (Libes, 1992). Ammonia typically comprises more than half of TN in a variety of municipal and domestic effluents, where the range is between 20-60 mg/L (Kadlec and

Wallace, 2009). Ammonia concentrations from food processing wastewaters can exceed 100 mg/L (Van Oostrom and Cooper, 1990; Kadlec et al., 1997). Landfill leachates especially from recently closed and capped landfills can show concentrations of $NH_3$ in hundreds of mg/L (Bulc et al., 1997; McBean and Rovers, 1999; Kadlec, 2003).

However, the typical median $NH_4$-N concentrations from world data for separate stormwater systems is much lower, being 0.80 mg/L (ATV-DVWK, 2003; Brombach et al., 2005). In Melbourne, for separate stormwater systems, the typical median $NH_3$ (un-ionized) concentration ranges from 0.05 mg/L during baseflow to 0.17 mg/L in stormflow (Taylor et al., 2005). Taylor et al.'s study found that $NH_3$ made up only around 10% of TN in stormwater.

Plants assimilate $NH_x$ to construct cellular amino acids and proteins, and the role of $NH_x$ as a preferred micro-nutrient makes it a key water-quality parameter in studies of eutrophication (Gibb, 2000). Due to its basic character, $NH_x$ may be highly influential in the regulation of the acid-base chemistry of the atmosphere (Gibb, 2000). Experiments have shown that the lethal concentration of $NH_x$ for a variety of fish species ranges from 0.2 mg/L (trout) to 2 mg/L (carp) (Zlotorzynski, 1995). Un-ionized $NH_3$ is toxic to fish and other forms of aquatic life at low concentrations, typically >0.2 mg/L (Kadlec and Wallace, 2009).

#### *2.5.1.5 Total dissolved nitrogen (TDN)*

The proportion of nitrogen in dissolved form within receiving waters depends on the sources and transport pathways of the nitrogen. In urban stormwater, total dissolved nitrogen (TDN) is typically around 75% of the TN concentration (Taylor et al., 2005), while in agricultural catchments, the form of N load varies with land use and intensity (Heathwaite and Johnes, 1996). Analytically, TDN is measured through the filtering of a sample through a filter of known mesh size (typically 0.45 um membrane filter) (Eaton et al., 2005). Therefore: TDN = $NO_x$ + DON + $NH_3$ (Figure 2.2).

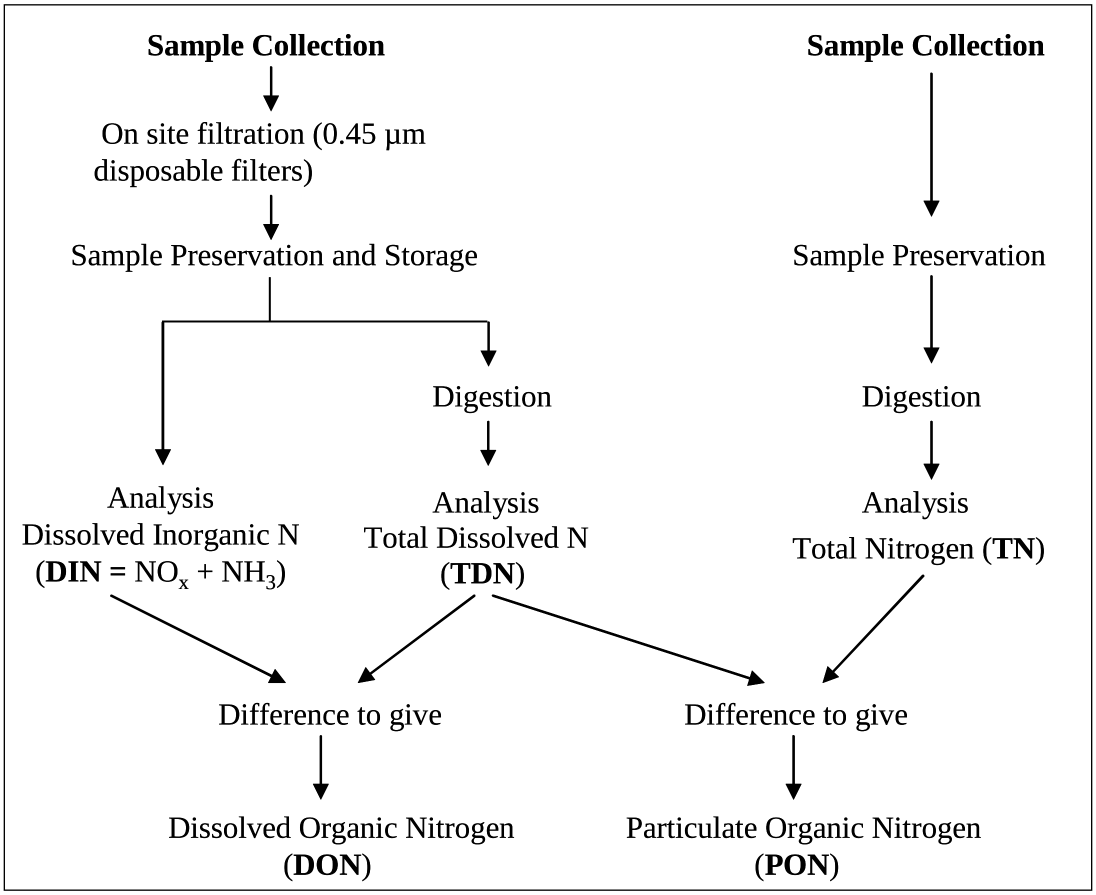



**Figure 2.2** Laboratory analysis of nitrogen (Source: Taylor et al., 2005).

The components of TDN – $NO_x$, DON and $NH_3$ have been described above. These N compounds all augment plant growth, and in turn stimulate the biogeochemical cycles of the wetland (Kadlec and Wallace, 2009), or receiving waters. Since TDN compounds are the most readily available plant nutrients, their high concentrations can stimulate algal growth, leading to eutrophication.

#### *2.5.1.6 Total particulate nitrogen (TPN)*

In laboratory analysis, total particulate nitrogen (TPN) is derived by subtracting TDN from TN (eqn 2.2).

$$TPN = TN - TDN \qquad \text{Eqn 2.2}$$

Being attached to organic or mineral particles, particulate N tends to be less biologically available. However, particulate N can later be released into the water column, for example through the mineralisation of organic N into $NH_3$. In a study of intensive agricultural watersheds, the proportion of particulate N was found to account for between ~5% to ~9% of the total N flux

(Vanni et al., 2001), whereas from urban catchments, particulate N may be approximately 25% of TN (Taylor et al., 2005). In the urban context, particulate N may result from erosion and sediments, leaf litter and other vegetative matter, along with faecal inputs (either from animals or from wastewater inputs).

### 2.5.2 Phosphorus (P)

Phosphorus is classed as a trace element (McKelvey, 1973). In the lithosphere it occurs usually as phosphates, and may be leached into the hydrosphere by weathering (McKelvie, 2000). In aquatic systems, both freshwater and marine, P occurs in a wide variety of inorganic and organic forms, and the dissolved component is operationally defined by filtration before chemical analysis. The term filterable is thus preferable to either dissolved or soluble, although both of these latter terms are used extensively (McKelvie, 2000). In urban stormwater, P is typically found mainly (around 60-70%) in particulate form (Taylor et al, 2005), which is not surprising, given its affinity to sediments. Phosphorus in aquatic systems may originate from natural sources such as mineralization of algae to dissolution of phosphate minerals, and from anthropogenic point sources such as discharge of sewage and industrial effluents to diffuse inputs from grazing and agricultural land (McKelvie, 2000). Erosion of soils is another primary source of P.

Environmental interest in P stems from its critical role in the process of euthrophication. In many aquatic systems, P may be a limiting nutrient for the growth of algae. The analysis of P in waters has historically been based on the photometric measurement of 12-phosphomolybdate or the phosphomolybdenum blue species produced when phosphmolybdate is reduced, and P species that are determined in this manner are referred to as reactive.

TP therefore includes the insoluble portion attached to fine particles (the particulate form) and the soluble portion (FRP). Total phosphorus (TP), and filterable reactive phosphorus (FRP) are perhaps the most commonly measured (McKelvie, 2000). TP is frequently used to measure discharge compliance for wastewaters, and it represents the maximum potentially bioavailable phosphorus discharged. As FRP comprises mostly orthophosphates, it provides an indication of the amount of most readily bioavailable P.

Periphyton and phytoplankton contribute to water column P dynamics since they can assimilate both organic and inorganic P fractions, especially in shallow streams (Bentzen et al., 1992; Whitton et al., 1998; Dodds, 2003). Soluble forms of P are readily assimilated by aquatic organisms. For example, one study of the Frome River (England) reported that 50% of the soluble reactive phosphate (SRP) was removed by biological uptake in spring (House and Casey, 1989).

Given the largely particulate nature of P in stormwater, removal processes generally focus on the sedimentation, filtration or removal of sediments, particularly fine mineral materials such as clay particles (David et al., 2011).

## 2.6 Typical nutrient concentrations in urban wet and dry weather flows

### 2.6.1 Nutrient concentrations in urban wet weather flows

Concentrations of nutrients in urban stormwater tend to be highly variable as a result of variations in land-use, catchment activities and in flow. In one of the most extensive metastudies to date, Duncan reviewed TN concentrations for various land use categories described as: All Urban, Residential, Industrial, Commercial and Other Urban. Across each of these land uses, the mean TN concentration ranged from 2.0 – 2.7 mg/L, with no statistically significant differences between urban land-uses. However, significant variations were found when the urban catchments were compared with agricultural and forest land-uses, with agricultural catchments producing the highest median TN concentration (4.4 mg/L) and forested catchments the lowest (0.95 mg/L) (Duncan, 2006). Duncan also found a similar pattern for TP concentrations. For the urban catchments (All Urban, Residential, Industrial, Commercial and Other Urban), the mean TP concentrations varied from 0.3 mg/L to 0.35 mg/L, again with no significant differences between the urban land-uses (Duncan, 2006). However, he identified agricultural catchments as having the highest mean TP concentration (5.25 mg/L) and the forested catchments as having the lowest mean TP concentration (0.75 mg/L).

In addition to Duncan (2006), other studies have shown that concentrations of nutrients are highly variable. For example, Fletcher et al. reviewed a large number of studies and found that storm event concentrations for TN varied between 0.6 to 8.6 mg/L, and for TP between 0.12 and 1.6 mg/L (Fletcher et al., 2005). A summary of typical nutrient concentrations compiled by Lawrence and Breen (2006) in urban runoff and urban streams are shown in Table 2.3.

**Table 2.3** Typical nutrient concentrations for urban runoff and urban streams (Lawrence and Breen, 2006).

| **Variable** | **Urban runoff: Typical concentration (range) (mg/L)** | **Urban stream water quality: Typical range (mg/L)** |
|---|---|---|
| Total Phosphorus (TP) | 0.6 (0.1-3) | 0.02-1.2 |
| Ammonium ($NH_4^+$) | 0.7 (0.1-2.5) | 0.002-0.16 |
| Oxidised nitrogen ($NO_x$) | 1.5 (0.4-5) | 0.34-3.2 |
| Total nitrogen (TN) | 3.5 (0.5-13) | 0.39-4.9 |

Typical nitrate and ammonia concentrations are shown in Table 2.4. These world data compiled by Brombach et al. (2005) show that concentrations from storm sewers in separate systems are, not surprisingly, lower than in overflows from combined systems.

**Table 2.4** Median pollutant concentrations for selected nutrients (Brombach et al., 2005)

| **Source** | **$NH_3$-N (mg/L)** | **$NO_3$-N (mg/L)** |
|---|---|---|
| Storm sewer (separate system), world | 0.80 | 0.80 |
| Overflows (combined sewage, combined system), world | 1.94 | 1.13 |

References: $NH_4$-N concentrations (ATV-DVWK, 2003), $NO_3$-N concentrations (NRW, 2000)

### 2.6.2 Nutrient concentrations in urban dry weather flows

The large-scale reviews by Duncan (1999 & 2006) and by Fletcher et al. (2005) all reveal that dry weather flows tend to have lower TP concentrations, whilst having similar concentrations of TN during dry and wet weather. Whilst TP concentrations tend to be around 0.3-0.35 mg/L during wet weather, dry weather flows were found to have typical concentrations of around 0.15 mg/L. More recently, Taylor et al. (2006) went further in attempting to explain such observations. They identified a secondary pollutograph for TN and TP (consisting predominantly of dissolved N and P constituents), suggesting that inter-event concentrations do not exhibit steady concentrations (but varied) even when flow remains relatively constant (Taylor et al., 2006). The effect was more pronounced for N, which is not surprising, given that a greater proportion of N tends to be dissolved than is the case for P. An investigation of the chemical composition of N species in urban runoff by Taylor (2006) identified that dissolved nitrogen (DN) dominates during both dry-weather ($\mu$=84%) (baseflow) and wet-weather ($\mu$=76%) (storm event) conditions, and that $NO_x$ and DON account for the majority of this dissolved N. He found that although TN species and TN concentrations were highly stochastic, little difference existed between dry-weather and wet-weather flows in terms of concentrations. Importantly, Taylor et al. (2006) observed that fluctuations in baseflow concentrations were comparable to (and in some cases higher than) peak pollutographs observed during stormflows, particularly for dissolved N species. It thus appears that in the urban context, dry weather flows cannot necessarily be assumed to have constant nor low concentrations of nutrients.

## 2.7 Processes, mechanisms and transformations of nutrients

Pollutant sources, pathways and concentrations associated with urban storm runoff have been studied extensively (Duncan, 1999; Victorian Stormwater Committee, 1999; Wong and Breen, 2006). The processes that affect nutrients include the physical *translocation* of N and P compounds from point to point. N and P are both transported in urban runoff.

### 2.7.1 Translocation of nutrients, and nutrient transport pathways

As discussed above, urbanisation has increased the rate of translocation of nutrients. The loss of native vegetation, as a result of urbanisation, typically results in major increases of nitrate leaching from soils (Edwards et al., 1985; Edwards et al., 1990). When a landscape is cleared of forest, the soil's structure, stability, and filtering capacity are diminished, overland flow of surface water increases, as does erosion, and nutrient cycling, water budgets, and water-release schedules are altered (Voyer et al., 2011). This has particular implication for P transport, with erosion and sediment transport being a principal source of P. In urban environments, the replacement of naturally ‘inefficient’ flow paths with a network of hydraulically efficient channels and pipes minimises the possibility of the retention, transformation and processing of nutrients. Catchment imperviousness and hydraulically efficient drainage infrastructure are major contributors to increased delivery efficiency of nutrients to receiving waters.

Whilst wet weather translocation pathways have been generally well studied (Novotny and Olem, 1994), dry weather nutrient levels are also of critical importance, since many pollutants stored in flow pathways during low flow periods can be transferred to the downstream environments (river reaches, reservoirs, coastal zones) during subsequent flow events (Obermann et al., 2009). For example, Taylor et al. (2006) suggest that a secondary pollutograph (in the inter-event period) may originate from delayed stormflows conveyed through pervious soils, as part of interflow and throughflow processes. In the urban context, interactions with infrastructure such as wastewater and drinking water systems may further impact these subsurface processes.

The land surface can have a major impact on nutrient transport pathways, as summarised by the three pathway typologies proposed by Lawrence and Breen (2006): Deep porous soils, Duplex shallow soils, and impervious areas (roofs and pavements). Particulate nutrients, attached to fine sediments are mobilised in surface flows (Muthukumaran et al., 2002), whereas dissolved nutrients: $NO_x$, phosphate ($PO_4^{3-}$), and $NH_4^+$ are conveyed by both surface and sub-surface flows.

#### *2.7.1.1 Deep porous soil pathways*

In these pathways, rapid infiltration of rainfall occurs at source, filtering out particulates. Throughflow of fine colloidal organic material and dissolved forms of nutrients to groundwater or perched groundwater systems may be possible. Discharges are mainly by soil throughflow and groundwater aquifers, altering the quality of storm event discharges which are low in total suspended solids (TSS), but potentially high in colloidal and dissolved nutrients. In these pathways, biofilms may play a major role in N retention and transformation, particularly by denitrification, resulting in the release of $N_2$ gas to the atmosphere. Phosphorus will generally be retained by filtering of sediments and by adsorption of dissolved P to soil particles.

In urban catchments with deep porous soils, discharges may be partly routed through the soil as through-flow (Lawrence and Breen, 2006). Contaminants entering deep soil may leach into groundwater reserves, escalating contamination to groundwater, particularly for $NO_3^-$. On the other hand, subsurface flow through deep porous soils may result in denitrification, facilitated by soil-based biofilms, resulting in the net loss of N gas (Bourgues and Hart, 2007), but there may also be a delayed leaching of soluble N from the soil media (Dolezal and Kvitek, 2004).

Particulate organic N deposited on pervious surfaces eventually breaks down in aerated conditions through mineralisation, nitrification and subsequent denitrification in the low-oxygen components of the soil matrix (Meyer et al., 2000), reducing N in washoff.

#### *2.7.1.2 Duplex shallow soils*

Duplex soils are sand overlying impermeable clay where infiltration rates are lower due to rapid filling of soil moisture storages, leading to more frequent surface overflow. Such shallow, compacted soils will have reduced infiltration capacity and thus increased transport of particulate nutrients through overland flows. Modifications to soil properties as a result of urbanisation (compaction, removal of organic topsoils, etc.) can also affect nutrient pathways.

Rapid runoff mobilises soil particles, increasing the washoff of sediments and its attached nutrients. This is particularly the case for P and will thus result in the transport of high loads of sediment-attached nutrients, into received waters. The ‘tail’ of the storm pollutograph typically reflects interflow (flow through the soil B Horizon) and where present, sewer exfiltration/stormwater infiltration-related discharges, with elevated levels of leached cations, anions, and faecal bacteria (ex-sewer). For these surfaces, the primary contaminant interception mechanism is sedimentation of TSS, followed by bacterial breakdown, oxidation of organic material and associated nutrients in the sediments with release of $N_2$ gas (denitrification), and burial of ferric phosphate in sediments.

#### *2.7.1.3 Impervious areas (roofs and pavements)*

Most rainfall intercepted by impervious areas becomes surface runoff. The wetting and drying of such areas and the depth of surface runoff promotes:

- Leaching and abrasion of surfaces (bitumen, concrete, metal roofing)
- Washoff of particulate materials accumulated on the surface
- Flushing of litter, organic matter and debris accumulated on impervious surfaces
- Washoff of soil, fertilisers and pesticides (spillages from adjacent pervious surfaces) accumulated on impervious areas

Impervious surfaces contribute to increased peak discharge rates and rapid rates of supply of contaminants to receiving waters. Typical flows from impervious surfaces are high in sediments and nutrients, along with other pollutants. Runoff from small rainfall events is predominantly generated by impervious areas, but with increased rainfall depth, pervious surfaces will also contribute. Impervious areas, without the natural features of interception such as vegetation with high filtration rates, respond rapidly to rainfall and generate higher peak discharges during storm events (Roesner et al., 2001; Rohrer and Roesner, 2005). Consequently, there is little opportunity for nutrient transformation and retention, meaning that both particulate and dissolved nutrient species are readily transported to receiving waters. Nutrients are efficiently conveyed in drains and pipes, transporting dissolved nutrients, as well as fine and coarse particulates.

The primary focus of research in urban catchments of contaminant pathways has been associated with storm events (Wong, 2006), with very much less for baseflow pathways. The reasons may be that in urbanised catchments with high levels of imperviousness, surface flow is more important as it is dominant in terms of volume. However, from a temporal perspective, receiving waters in urban environments experience low-flows for the majority of the time and recent studies (e.g. Taylor et al 2006) suggest that dry weather flows may still have elevated levels of nutrients, particularly in the dissolved form. Such behaviour may suggest that water infiltrated into soils during storms results in a subsequent flushing out (leaching) of nutrients (Taylor et al., 2006). Regardless of the exact cause, it appears important to consider the behaviour and mechanisms of nutrient transport in both wet weather and dry weather flows.

#### *2.7.1.4 Emerging new approaches to addressing the nutrient problem*

New approaches are being taken to mitigate the nutrient problem from urban areas. These methods alter the flow path of runoff to devices that can take up nutrients or denitrify nitrites and nitrates. One way is to incorporate green roofs for buildings (Green roofs, 2014). These roofs, intercept roof runoff so that nutrients are removed by growing plants. Another approach is to use biofilters to remove nutrients from drainages. The biofilters operate by the use of appropriate plants to take up nutrients and utilise anoxic zones to denitrify nitrites and nitrates through bacterial activity (Zinger et al., 2013). Other approaches include the use of rain gardens and the use of porous pavements where possible.

### 2.7.2 Nitrogen transformations

In nature, nitrogen occurs in different forms, as depicted in the nitrogen cycle in Figure 2.3, For N, there are recognised five principal processes which *transform* N from one form to another (Kadlec and Wallace, 1996):

1. Ammonification (mineralisation)
2. Nitrification

3. Denitrification
4. Nitrogen fixation
5. Nitrogen assimilation

These processes are considered in the following sections.

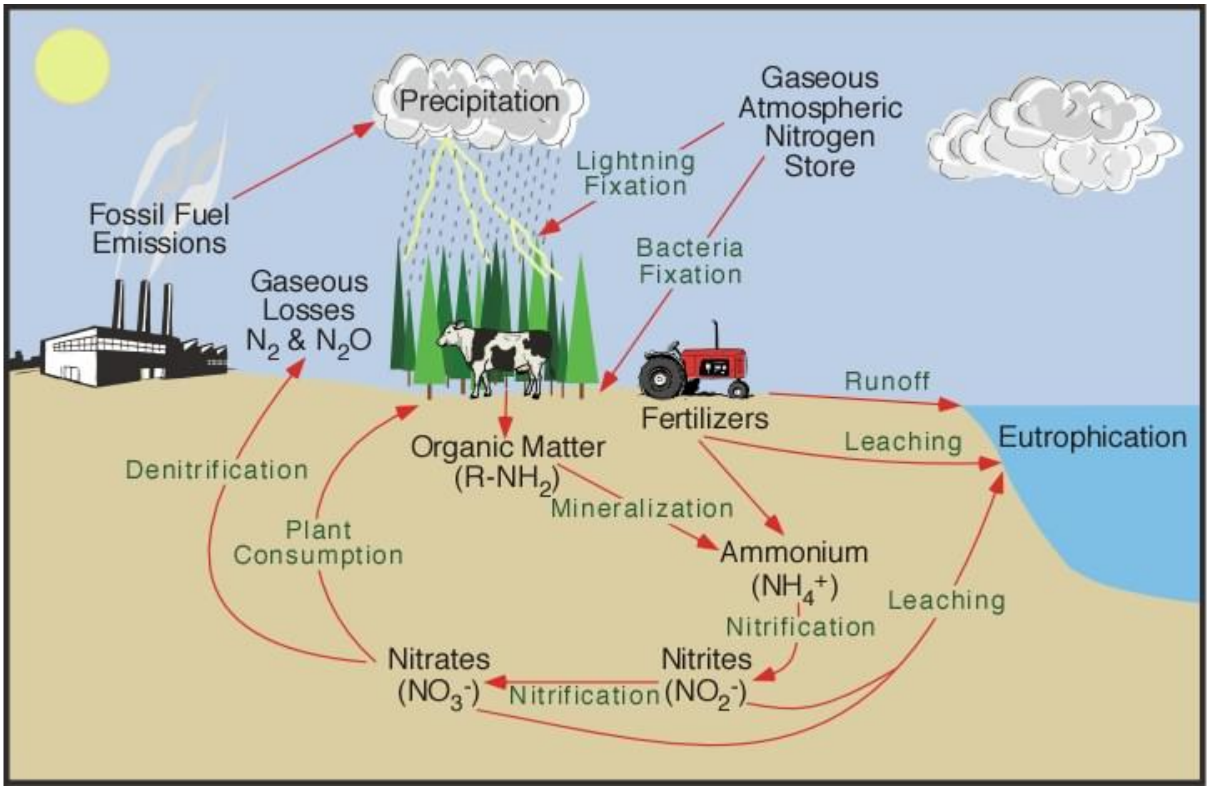



**Figure 2.3** The nitrogen cycle (PhysicalGeography.net, 2014)

### *2.7.2.1 Ammonification (mineralisation)*

Ammonification of organic N to $NH_3$ is the first step in the mineralization of organic N (Reddy and Patrick, 1984). This process occurs aerobically and anaerobically, releasing $NH_3$ from dead and decaying cells and tissues (Kadlec and Wallace, 2009), with heterotrophic microorganisms being involved (U. S. EPA, 1993). Enzymes act upon proteins, nucleic acids and urea, both intra- and extra-cellularly (Maier et al., 2000). The typical ammonification reactions are given in Equations 2.3 and 2.4 (Kadlec and Wallace, 2009):

Urea breakdown: $NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$ Eqn 2.3.

Amino acid breakdown: $R\mathrm{CH(NH_2)COOH} + H_2O \rightarrow NH_3 + CO_2$ Eqn 2.4.

The process of ammonification is not instantaneous, and kinetically ammonification proceeds more rapidly than nitrification (Kadlec and Wallace, 2009). Ammonification proceeds twice as fast as nitrification, since ammonification is a single-step bacterial process, nitrification is a two-step bacterial process (Section *2.7.2.2*).

#### *2.7.2.2 Nitrification and denitrification*

Nitrification is the principal transformation mechanism by which $NH_3$ is converted to $NO_x$ (Kadlec and Wallace, 2009). Nitrification is defined as the biological formation of $NO_3^-$ or $NO_2^-$ from compounds containing reduced N with oxygen as the terminal electron acceptor (van der Graaf et al., 1996). Nitrification is a two-step, microbially mediated process, involving two species of bacteria: *Nitrosomonas* and *Nitrobacter*. Both steps require the presence of oxygen (Reddy and Patrick, 1984).

The two-step microbially mediated processes are given in Equations 2.5 and 2.6 (U. S. EPA, 1993):

Nitritation: $2NH_4^+ + 3O_2$ ----*(Nitrosomonas)*→ $2NO_2^- + 2H_2O + 4H^+$ Eqn 2.5.

Nitrification: $2NO_2^- + O_2$ ----*(Nitrobacter)*--→ $2NO_3^-$ Eqn 2.6.

Denitrification is defined as the process in which $NO_3^-$ is converted to $N_2$ via the intermediates: nitrite, nitric oxide (NO) and nitrous oxide ($N_2O$) (Hauck, 1984; Jetten et al., 1997). In denitrification, nitrates are microbially transformed to nitrogen gas which is transferred to the atmosphere, a process which occurs in low-oxygen conditions. The de-nitrifiers require reduced organic carbon for heterophic growth (Kadlec and Wallace, 1996). Denitrification ($NO_3^-$ dissimilation) is carried out by facultative heterotrophs; organisms that use either oxygen or $NO_3^-$ as terminal electron acceptors (Kadlec and Wallace, 2009). There is a sequential process by which $NO_3^-$ is converted to $NO_2^-$, then to NO, then $N_2O$ and finally nitrogen gas which escapes from water back to the atmosphere, as depicted in Equation 2.7 (Cox and Payne, 1973; Koike and Hattori, 1978; Kadlec and Wallace, 2009):

$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2$ Eqn 2.7.

Nitrification and subsequent denitrification in combination is the primary mechanism for permanent N removal from water. The paired processes can act on pools of N stored in the soil or water column, allowing later removal, particularly during low-flow periods (David et al., 2011). **Nitrification** is an aerobic process (Kadlec and Wallace, 1996), occurring in the oxidized (unsaturated) zone where nitrification by bacterial activity tends to produce $NO_x$ from precursors such as $NH_3$ (Reddy and Patrick, 1984). Conversely, **denitrification** is an anaerobic process occurring in the reducing (saturated) zone of the soil profile, where denitrifying bacteria convert $NO_x$ to produce nitrogen gas, which escapes back to the atmosphere. The presence of dissolved organic carbon (DOC) functions as a reducing agent to reduce various oxidized species (Champ and Gullens, 1979), one of the species being $NO_3^-$. In the soil profile, the degree of thickness of the oxidizing zone is an important factor in providing a medium for nitrification and denitrification.

#### *2.7.2.3 Nitrogen fixation*

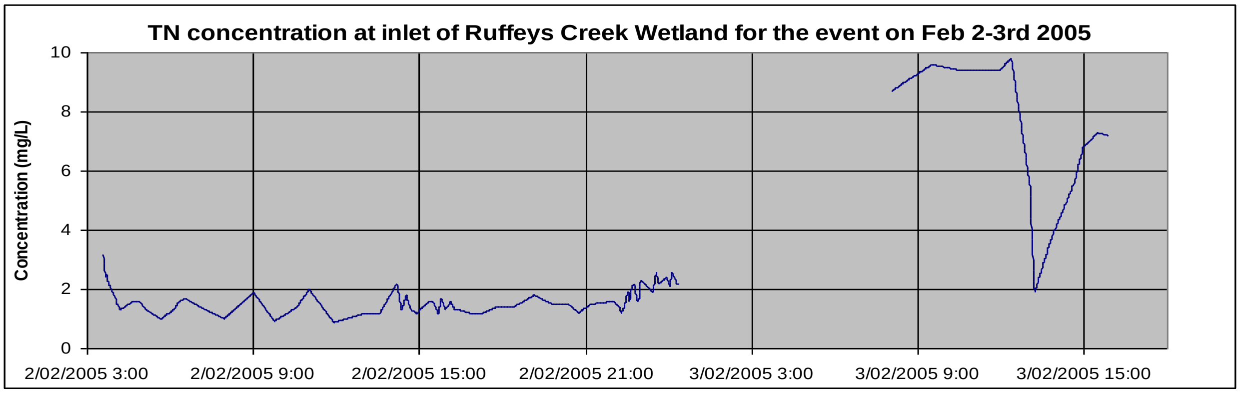
Nitrogen fixation is a biological process in which nitrogen gas in the atmosphere diffuses into solution and is reduced to ammonia by autrophic and heterophic bacteria, blue-green algae and higher plants (Kadlec and Wallace, 1996). Autotrophic bacteria can produce their own food, eg. cyanobacteria, green sulphur bacteria, purple bacteria, methogens and halophiles). Photosynthetic bacteria (which obtain energy through photosynthesis, eg. dinoflagellates, cyanobacteria, purple and green bacteria) are capable of N fixation as are some aerobic heterothrophs (bacteria which can feed on a variety of organic substances such as carbohydrates and proteins), e. g. *Azotobacter*; anaerobic bacteria such as *Clostridium*, and many facultative bacteria under anoxic conditions. The filamentous algae that are N fixers include the blue-green *Anabaena*, *Gloeotrichia*, and *Nostoc* (Kadlec and Wallace, 1996). The aquatic fern, *Azolla*, and other transitional wetland vascular plants such as *Alnus*, and *Myrica* have been observed to fix atmospheric N (Waughman and Bellamy, 1980). Some wetland plants are thus able to fix N, and one of the factors of variation in N mass balances for $NH_4^+$-poor treatment wetlands may be the fixation of atmospheric N (Kadlec and Wallace, 1996). Nitrogen can also be fixed from the atmosphere during lightning strikes (Ophardt, c. 2003).

#### *2.7.2.4 Nitrogen assimilation*

Nitrogen assimilation is the biological process whereby nitrogen compounds are taken up into cells of organisms and converted from inorganic nitrogen into organic compounds such as amino acids, carbohydrates and fats, the building blocks for cells and tissues (Kadlec and Wallace, 1996). The assimilation can be by riparian vegetation and biological consumption by heterotrophic organisms, such as biological assimilation by autotrophic organisms followed by consumption by heterotrophic organisms such as zooplankton and fish. Ammonium is more reduced energetically and is the preferable source of N for assimilation. Aquatic macrophytes produce enzymes such as nitrate reductase and nitrite reductase to convert $NO_x$ to useable forms, and the production of these enzymes decreases when $NH_3$ is present (Melzer and Exler, 1982). In a study of sub-surface flow (SSF) gravel wetland mesocosms, it was shown that 70-85 % of $NO_3^-$ loss was due to plant uptake (Zhu and Sikora, 1994). Nitrogen assimilation supports the growth of macrophytes, microorganisms and algae. N assimilation by plants is a primary mechanism for the storage of N in vegetation, microorganisms and algae. Subsequent to vegetation storage of N, the decay of vegetation releases $NH_3$ from organic N breakdown, the first step in the mineralization of organic N (Reddy and Patrick, 1984) and the N cycle continues (Figure 2.3). N assimilation by plants such as sedges and macrophytes is an important mechanism used for water purification.

## 2.8 Summary of previous studies

Nutrient concentrations in stormwater have been studied in detail and considerable worldwide data exist for urban runoff (Duncan, 1999; Smullen et al., 1999; Fuchs et al., 2004) In Australia, further wet weather data are found (Taylor et al., 2005; Wong et al., 2006; Francey et al., 2010). Most data compilations, however focus on wet weather concentrations while few dry weather studies have been conducted. The water quality of discharges from stormwater drains during dry weather in five coastal catchments in the Sydney region by O'Brien et al. (1992), who observed that TN concentrations in at least 96% of samples exceeded 0.5 mg/L, and in three of the five catchments, TP concentrations exceeded 0.05 mg/L, the limits considered to cause bio stimulating effects in receiving waters (SPCC, 1990; O'Brien et al., 1992). They emphasised the poor quality of dry weather flows, but there were no wet weather data for comparison. A study of nutrient behaviour from some Melbourne (Australia) catchments, conducted by sampling both wet and dry weather discharges from stormwater pipes, identified a secondary (ie. Immediately post event) pollutograph for TN and TP, showing their concentrations increased during the storm recession as shown in Figure 2.4 (Taylor, 2006). Nutrient levels were elevated during the storm event, and during the storm recession when flow was constant, the concentrations of TN, and dissolved species: $NO_x$, DON and $NH_3$ showed distinct increments, as given in Figure 2.5 (Taylor, 2006). Elevated levels of P were found during a storm event and there were distinct increases for dissolved species (TDP and FDP) during baseflow, as shown in Figure 2.6 (Taylor et al., 2006).



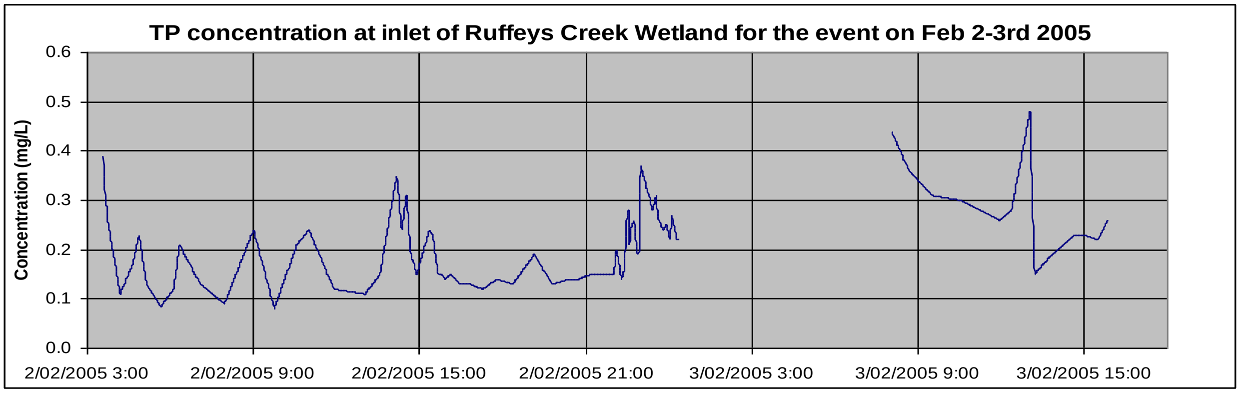




**Figure 2.4** Typical TN and TP concentrations during the storm recession on 3/02/2005 (Taylor, 2006). Stormwater flow had receded to baseflow at 21.00 hrs, 2/2/2005.

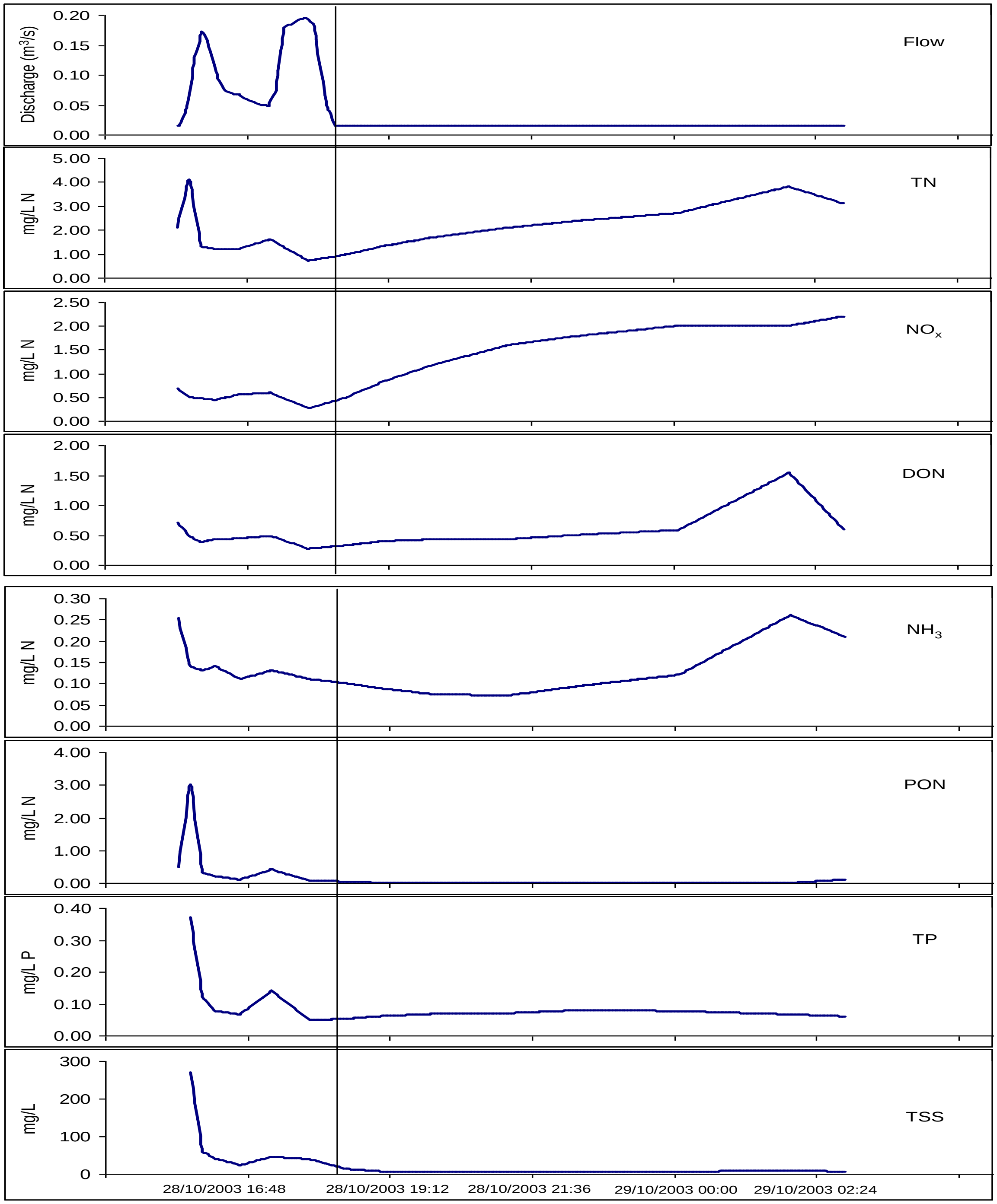



**Figure 2.5** Comparison of inlet hydrograph with pollutographs of TN, $NO_x$, DON, $NH_3$, PON, TP and TSS during and following a storm from 28/10/2003-29/10/2003. TN concentrations demonstrate a distinct increase after the storm. The vertical line represents the time at which flow had receded to baseflow conditions (Taylor, 2006).

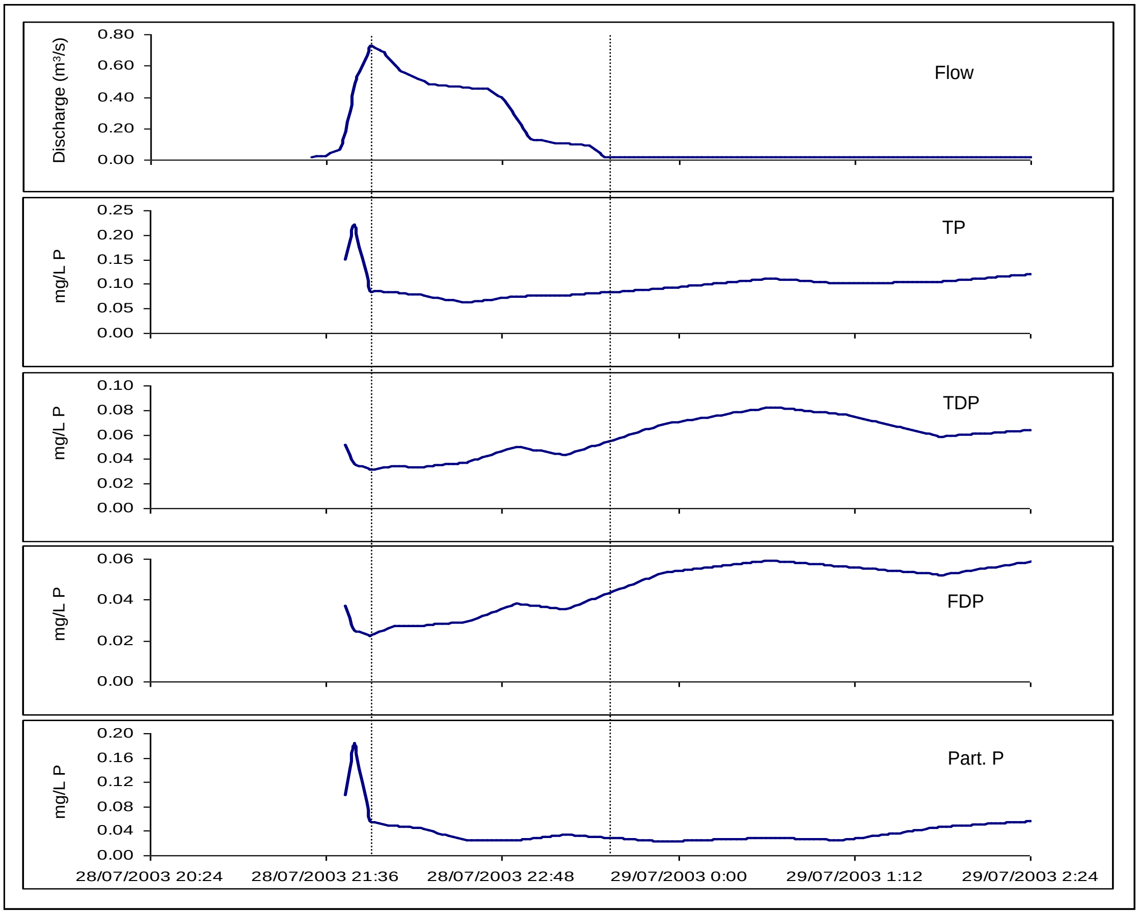



**Figure 2.6** Dissolved and particulate phosphorus constituents showing dissolved P increasing during baseflow from 28/7/2002-29/7/2003 (Taylor et al., 2006).

Taylor et al. (2006) showed that whilst particulate pollutants followed a typical storm hydrograph response in receding with the hydrograph, dissolved N and P constituents began to increase after the storm, and it was suggested that this was due to delayed stormflows through pervious media; critically they found that dry weather flows often contained higher N concentrations than wet weather flows. Recently, stormwater monitoring in Melbourne catchments has revealed that concentrations of total suspended solids (TSS) were higher in wet weather than in dry, whereas TN and TP concentrations were lower in wet weather than in dry (Francey et al., 2010).

## 2.9 The relative importance of wet and dry weather flows

The work of Taylor et al. (2006) described above highlights that wet weather flows cannot be assumed to be the only source of impacts to receiving waters. In Melbourne, it is estimated that the greater proportion of TN and TP loads (around 70%) is transported in wet weather flows (Poullain, 2012). This dominance is not surprising given that, in contrast to the situation in rural environments, urban catchments are dominated by surface runoff (Walsh et al. 2012). Pollutant loads are important to large (ie. Lentic) receiving waters which have high buffering capacities but are sensitive to the long-term accumulation of pollutants (e.g. Taylor et al. 2006). However, for flowing receiving waters, pollutant concentrations are likely to be more important (since in these systems their accumulation in the water column is less important), with variations in concentration likely to result in direct ecological consequences such as algal biomass (Hart et al. 1999, Sonneman et al. 2001, Taylor et al. 2004). Given that in terms of time of exposure, streams are subject to dry weather flows the majority of the time (for example in Melbourne rainfall events sufficient to cause impervious runoff occur on average around 70-90 days a year (Walsh et al. 2005)), elevated nutrient concentrations during dry weather are an important stressor to urban streams.

## 2.10 Key Knowledge Gaps

The review of literature has identified a number of important knowledge gaps. They are summarised as follows:

(1) The reasons for variations in nutrient concentrations between urban catchments in both dry and wet weather remain poorly understood. It is clear that both low flow and wet weather flow can contain high nutrient concentrations, but the mechanisms driving these concentrations and their variability are not well understood. Previous work has highlighted that one or more important explanatory variables are yet to be quantified (Duncan, 1999). Studies that explore these potential explanatory factors are thus required.

(2) The relationship between land use in a catchment and nutrient concentrations in the outlet stormwater drain is also not well understood; for example Duncan (1999) showed that variations in concentrations within a particular land-use were such that variations

between land-uses were essentially ‘masked’. No significant differences were detected between urban land-use zonings for N or P concentrations, despite the very large sample size of their study (Duncan, 1999). However, differences in both (i) infrastructure and (ii) activities between land uses suggest that differences in the concentration and form of nutrients are likely.

(3) Other catchment characteristics that influence nutrient concentrations in urban stormwater are as yet not well defined. For example, in a study (Duncan, 1999) of urban stormwater quality where data from many sources were analysed, it was concluded that some other catchment characteristic, factor or process might be able to explain more of the observed variability of nutrient concentrations between catchments (Duncan, 1999). As a result of his study, Duncan suggested that more specific investigations into the influence of catchment characteristics on pollutant concentrations were required.

(4) Variations in the concentrations and composition of nutrients between dry weather and wet weather need to be better understood and explained, along with their implications for stormwater treatment. Taylor et al (2006) showed that concentrations during dry weather can, perhaps surprisingly, often exceed those during stormflows, suggesting either external (non stormwater-related) inputs or pervious area inputs, perhaps as a result of throughflow processes.

Diffuse pollution such as posed by nutrients is difficult to manage and regulate since its sources and pathways are hard to understand and quantify, and monitoring and treatment programs are usually expensive. A better understanding of nutrient dynamics and behaviour in urban catchments is a prerequisite to improving the efficiency and effectiveness of stormwater treatment for the protection of receiving waters. By addressing the above knowledge gaps, in understanding the factors, the mechanisms and causes that affect the concentrations of particular pollutants, will enable a more targeted approach to the management and treatment of such pollution.

## 2.11 Conclusions

Urbanisation significantly impacts on the hydrology and water quality of receiving waterways. Catchment imperviousness appears to be one of the important drivers of variations in water quality, including for nutrients, which are pollutants with important consequences, since they result in eutrophication. Nutrients occur in a number of species, with the capability of being transformed from one species to another depending on the physical, biological and chemical conditions of the water. The biologically available forms are those found in solution, such as $NH_4^+$, $NO_x$, DON, and FRP. While particulate forms like TPN may be removed by physical filtration methods, the soluble forms are much more difficult to treat, generally requiring biological uptake or other microbial-mediated removal processes. The full range of possible factors controlling dry weather nutrient and wet weather nutrient concentrations has not been explored to-date. Thus far, although variations in N concentrations between wet and dry weather, and distinct increases soon after storm events have been reported, the mechanisms driving the concentrations and variability of nutrients both in dry and wet weather are as yet largely unknown. Since high nutrient concentrations discharged from stormwater drains in urban areas are detrimental to the aquatic environment, it is important to study the factors that drive their variability. By understanding the controls on nutrient concentrations and their composition, and identifying the problematic nutrient species and the underlying mechanisms driving nutrient concentrations and composition, the appropriate treatment technology can be applied.

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# Chapter 3: Methods

## 3.1. Introduction

This chapter describes the data sources for both dry and wet weather, the catchments studied and their characteristics, along with the sampling and laboratory analyses for the water quality data, and finally the analyses applied to derive the relationships between the catchment characteristics and the nutrient levels and composition.

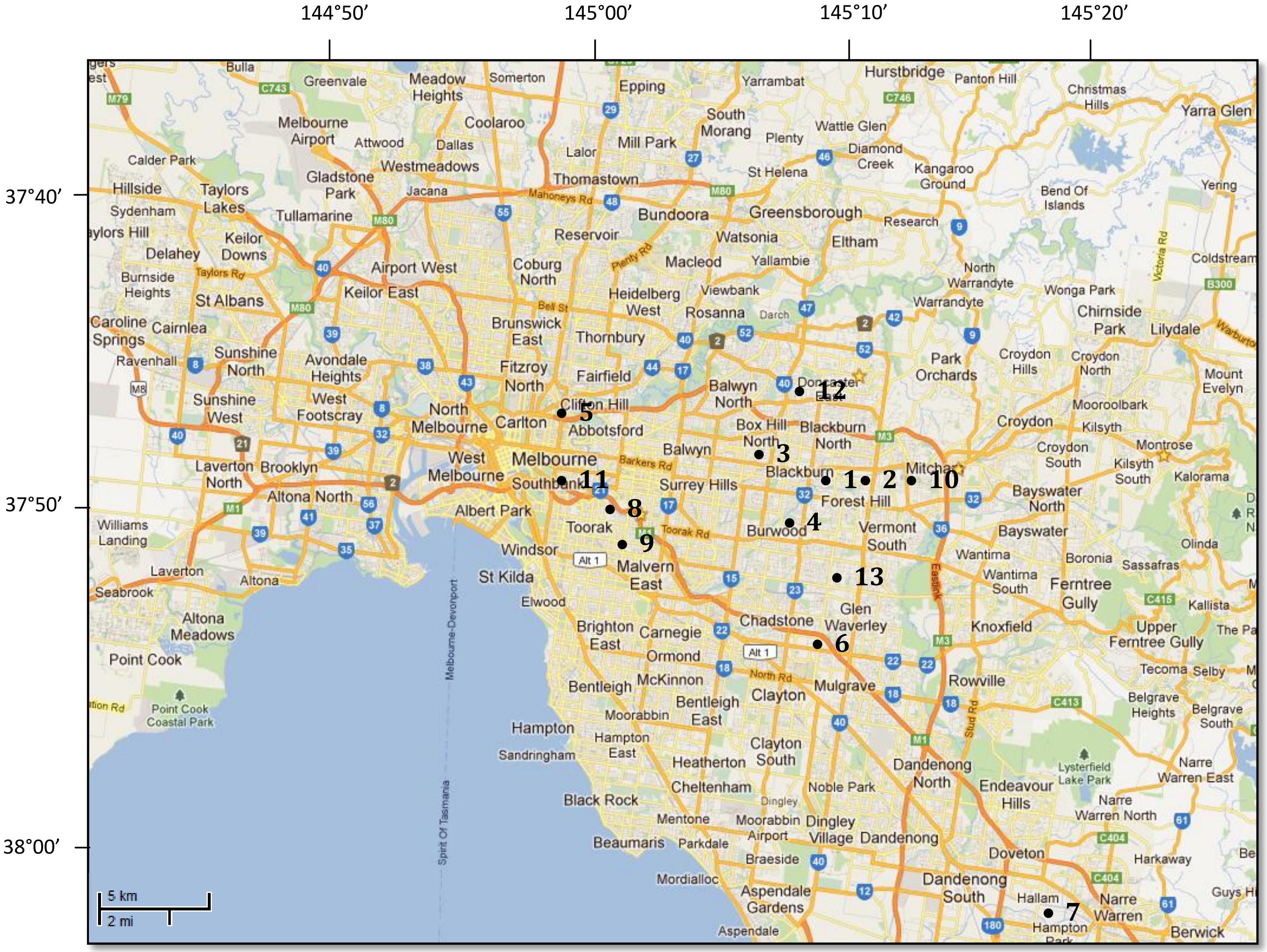
## 3.2. Data sources & study sites

The data used for this study were obtained from a number of large stormwater quality sampling programs conducted in Melbourne, Australia (Fletcher and Poelsma, 2004; Taylor et al., 2005; McCarthy et al., 2009a; Francey et al., 2010). Melbourne’s climate is of the Mediterranean type, with cool winters and warm to hot, dry summers. Rainfall predominantly occurs in winter and spring with mean annual rainfall ranging from 600 to 800 mm/year (BOM, 2010).

### 3.2.1 Dry weather

The dry weather water quality data were from water samples collected from stormwater drains in 11 catchments in the south-eastern suburbs of Melbourne. (Stormwater drains in Melbourne are separate from the sewer drains.) The sampling locations are shown in Figure 3.1. Sampling was undertaken from February 2003 to May 2009.

Dry weather samples were taken manually in all the studies using a consistent method: a clean 1L polyethylene bottle was held in the flow 20-50 mm above the invert of the stormwater pipe at a suitable point upstream of the flow-monitoring and auto-sampling equipment. This sampling method has been used for other studies (e.g. Eleira and Vogel, 2005; Fletcher and Deletic, 2007; Soonthornnonda and Christensen, 2008). Dry weather samples were usually collected between storm events on a monthly basis (e.g., Ruffeys Creek (Taylor, 2006)). In the case of the Hampton Park site, samples were collected on a weekly basis for the first two months and fortnightly thereafter, provided that there was no rainfall in the previous 48 hours (Fletcher et al., 2004) A detailed dry-weather sampling campaign was also conducted at Hampton Park in 2009, where three samples per day were collected (Fletcher and Poelsma, 2004). Similarly, three samples per day were collected at some other sites (e. g. Blackburn), except for occasions when it was not possible to collect all three samples per day due to insufficient flow (McCarthy et al., 2009a). A summary of the sources of dry weather water quality data is presented in Table 3.1.




Sampling points

1 Blackburn

2 Blackburn Lake

3 Box Hill

4 Eley Rd

5 Fairfield

6 Gilby Rd

7 Hampton Park

8 Hedgeley Dene

9 Lara St

10 Nunawading

11 Richmond

12 Ruffeys Ck

13 Glen Waverley

**Figure 3.1** Location of sampling points of Melbourne catchments studied (source: Google map, 2012)

**Table 3.1** Dry weather summary of water quality data: TN, total nitrogen; TDN, total dissolved nitrogen; $NH_3$, ammonia; $NO_x$, nitrate/nitrite; TPN, total particulate nitrogen; DON, dissolved organic nitrogen; TP, total phosphorus.

| Catchment name | No. samples | | | | | | | Sampling period | Source of data |
|---|---|---|---|---|---|---|---|---|---|
| | TN | TDN | $NH_3$ | $NO_x$ | TPN | DON | TP | | |
| Blackburn | 21 | 21 | 21 | 21 | 21 | 21 | 0 | 12/05/09 – 19/05/09 | (McCarthy et al., 2009a) |
| Box Hill | 21 | 21 | 21 | 21 | 21 | 21 | 0 | 12/05/09 – 19/5/09 | (McCarthy et al., 2009a) |
| Eley Rd | 16 | 0 | 0 | 0 | 0 | 0 | 16 | 13/11/03 – 30/3/05 | (Francey et al., 2010) |
| Fairfield | 9 | 9 | 9 | 9 | 9 | 9 | 0 | 10/2/09 – 16/2/09 | (McCarthy et al., 2009a) |
| Gilby Rd | 14 | 0 | 0 | 0 | 0 | 0 | 14 | 13/11/03 – 22/2/05 | (Francey et al., 2010) |
| Hampton Park | 167 | 0 | 62 | 62 | 0 | 0 | 136 | 5/2/03 – 7/12/04 | Melbourne Water & CRC (Fletcher and Poelsma, 2004) |
| Hedgeley Dene | 9 | 9 | 9 | 9 | 9 | 9 | 0 | 13/2/09 – 16/2/09 | (McCarthy et al., 2009a) |
| Lara St | 9 | 9 | 9 | 9 | 9 | 9 | 0 | 13/2/09 – 16/2/09 | (McCarthy et al., 2009a) |
| Nunawading | 21 | 21 | 21 | 21 | 21 | 21 | 0 | 12/5/09 – 19/5/09 | (McCarthy et al., 2009a) |
| Ruffeys Creek | 10 | 0 | 0 | 0 | 0 | 0 | 10 | 12/5/04 – 30/3/05 | (Francey et al., 2010) (Taylor et al., 2005) |
| Shepherds Bush | 16 | 0 | 0 | 0 | 0 | 0 | 16 | 13/11/03 – 22/2/05 | (Francey et al., 2010) |

### 3.2.2 Wet weather

The wet weather data sources and catchments studied derive from the same stormwater quality sampling programs conducted in south-east Melbourne as for the dry weather data. The wet weather sites are listed in Table 3.2 (with the nutrient species analysed described in Table 3.3), and their locations are shown in Figure 3.1. The stormwater quality data were collected from stormwater drains in seven catchments with varying land uses and catchment sizes. Sampling was undertaken from January 1996 to June 2009.

**Table 3.2** Wet weather summary of sources of water quality data and catchments studied.

| Catchment Name | Number of Events | Sampling period | Sources of data |
|---|---|---|---|
| Blackburn Lake | 48 | 20/1/96-14/11/97 | (RossRakesh et al., 1999) |
| Eley Rd, Burwood East | 15 | 17/4/04-24/9/04 | (Francey et al., 2010) |
| Gilby Rd, Mt Waverley | 42 | 12/12/03-31/8/05 | (Francey et al., 2010) |
| Hampton Park | 8 | Dec 02-Apr 03 | (Fletcher and Poelsma, 2004) (Fletcher et al., 2004) |
| Richmond | 35 | 9/3/04-30/8/05 | (Francey et al., 2010) |
| Ruffeys Creek | 9 | Jul 03-Oct 03 | (Taylor et al., 2005)(Taylor, 2006) |
| Shepherds Bush | 15 | 30/11/03-7/7/04 | (Francey et al., 2010) |

**Table 3.3** List of wet weather nutrient species analysed. TN, total nitrogen; TDN, total dissolved nitrogen; $NH_3$, ammonia; $NO_x$, nitrate/nitrite; TPN, total particulate nitrogen; DON, dissolved organic nitrogen; TP, total phosphorus; FRP, filterable refractory phosphorus.

| Catchment | Number of samples | Nutrient species analysed |
|---|---|---|
| Blackburn Lake[1] | 917 | TN, TP |
| Eley Rd, Burwood East[2] | 120 | TN, TP, $NH_3$, FRP, $NO_x$, TDN, TPN, DON |
| Gilby Rd, Mt. Waverley[2] | 461 | TN, TP |
| | 133 | TN, TP, $NH_3$, FRP, $NO_x$, TDN, TPN, DON |
| Hampton Park[1] | 370 | TN, TP |
| | 72 | $NH_3$, $NO_x$, FRP |
| Richmond[1] | 574 | TN, TP |
| Ruffeys Ck, Doncaster [1] | 216 | TN, $NH_3$, $NO_x$, TDN, TPN, DON |
| Shepherds Bush, Glen Waverley[2] | 311 | TN, TP, $NH_3$, FRP, $NO_x$, TDN, TPN, DON |

Catchments denoted by [1] were sampled by automatic samplers, and those denoted by [2] were sampled by a combination of event automatic samplers and composite (grab samples).

For all wet weather sampling, Doppler-based flow meters (Sigma 950) located in pipes close to the catchment outlets were used for measuring stormwater flow. Either automatic samplers (Sigma 900) or manual grab samples were used to collect samples for water quality analysis. Where automatic samplers were used, flow-weighted samples were collected (detailed descriptions are given in each of the studies used). The methods used in sampling each catchment are detailed in Table 3.3. For a storm event, up 24 one litre samples were collected in polyethylene bottles to derive the Event Mean Concentration (EMC).

## 3.3 Laboratory analysis

All water quality samples for both dry weather and wet weather were analysed by an Australian National Association of Testing Authorities (NATA) accredited laboratory for TN, total dissolved nitrogen (TDN), $NH_3$, $NO_x$ and TP using standard methods and quality control procedures (Hosomi and Sudo, 1986; APHA/AWWA/WEF, 2005). Total particulate nitrogen (TPN) and dissolved organic nitrogen (DON) were derived by calculation. Concentrations of DON were calculated by subtracting the sum of $NH_3$ and $NO_x$ from TDN, while TPN was calculated by subtracting TDN from TN. The instrument detection limits were 0.02 mg/L for TN, TDN and TP, and 0.001 mg/L for $NH_3$ and $NO_x$ (Hines T. (pers. com.), 2011).

## 3.4 Catchment characteristics

It was hypothesised that catchment characteristics could explain the variations in nutrient concentrations between the different catchments, under both dry and wet weather. The selection of pertinent catchment characteristics was based on the review of literature in Chapter 2, but was constrained by the ability to obtain data to quantify the chosen characteristic.

Eight catchment characteristics were considered as potential correlates with nutrient concentrations. Five are indicators of potential impacts of urbanisation; *land use, total imperviousness* (the proportion of sum of the areas covered by roofs, pavements, sealed roads and other impervious surfaces, measured as a percentage of total catchment area), *population* (i.e. total number of inhabitants in the catchment), *population density* (number of inhabitants/km$^2$), and the *average year of infrastructure construction* (the average year of the initial development phase, reflecting the age of stormwater infrastructure within the catchment). The other three catchment characteristics – *area, slope,* and *hydraulic conductivity of catchment soils* – are factors which could influence the behaviour of nutrients through transport and retention pathways within the catchment. As previously mentioned, other catchment characteristics were identified as potentially also being important, but unfortunately no reliable data were available to quantify them. For example, past farming intensity could not be adequately quantified and was therefore excluded from the data analysis, despite hypothesising that it may impact on nutrient levels within catchment soils and groundwater. The potential influence of septic tank density was another potential characteristic that may have an impact for some nutrient species (Hatt et al., 2004) but was not included since the monitored catchments had few if any septic tanks present, being mainly in well established urban areas. The characteristic of ground water depth, and the thickness of saturated and unsaturated soil were not covered in this study, through lack of data.

The population of each catchment was determined using the Australian national census data (BOS, 2006). Catchment population density was calculated simply by dividing the population by the catchment area. It is to be noted that population density is more often used for measuring population pressure on a physical resource (Drechsel et al., 2001; Stoner et al., 2011) rather than the raw populations of catchments. However, in this study, both population density and raw population data were considered, to take into account potential threshold effects in terms of total population size within a catchment. The average year of infrastructure was derived from the age of drainage works using drainage maps provided by Melbourne Water Corporation (Francey et al., 2010) and the use of local historical records (e. g. for Ruffeys Creek; Pertzel and Williams, 2001).

Catchment areas were calculated with the use of the GIS software package, MapInfo (MapInfo Corporation, 2002), in conjunction with underground drainage plans and 1 m contour maps to calculate drainage sub-areas (Francey et al., 2010). Not surprisingly, catchment area and catchment population were highly correlated ($R^2 = 0.85$, $p<0.05$) due to the population densities being similar. Land use was defined using local planning schemes (e.g. DSE, 2005) and by visual examination of aerial photographs of the catchments.

Indicative total impervious fractions were determined for each land use within a catchment based on aerial orthophotos and site inspections conducted by Francey (2010), for the catchments of Gilby Rd, Shepherds Bush, Eley Rd and Ruffeys Creek. For the other catchments, published figures were used (Fletcher and Poelsma, 2004; McCarthy et al., 2009b). The weighted average of area of land uses was used for calculating the total impervious fraction for the catchment (Francey et al., 2010). Imperviousness data for the catchments of Lara St, Hedgeley Dene, Fairfield and Nunawading were as estimated by McCarthy (2009a). Unfortunately, the data necessary to calculate effective imperviousness (Walsh and Kunapo, 2009) were not available for these catchments.

The soil hydraulic conductivity of each catchment was assessed by identifying the bedrock type from geological maps (Thomas, 1959; Douglas and Spencer-Jones, 1977) and topographical maps (Royal Australian Survey Corps, 1982). The mean hydraulic conductivities were then calculated using the hydraulic conductivity ranges as given for the relevant bedrock types (Quaternary basalts and Silurian sandstones and mudstones (Leonard, 1992), Tertiary gravels and sands (DEWHA, 2009)). For catchments with a mixture of rock types, the spatially-averaged catchment hydraulic conductivity was determined by calculating the weighted average of the percentage of each bedrock type found in the catchment.

Finally, the average slope of each catchment was calculated by dividing the average change in elevation by the change in horizontal distance as determined from 1:25,000 topographical maps and other maps (Thomas, 1959; Douglas and Spencer-Jones, 1977; Royal

Australian Survey Corps, 1982). A summary of the catchment characteristics is shown in Table 3.4.

**Table 3.4** Summary of catchment characteristics used in dry and wet weather analyses: land use, catchment area (Area), total imperviousness (Imp), catchment population (Pop), catchment population density (Pop Density), the year of catchment infrastructure installation (Infrastructure), catchment hydraulic conductivity ($K_s$), and mean catchment slope (Slope).

| Catchment name | Land use | Area (ha) | Imp (%) | Pop. (no.) | Pop. Density (no./km$^2$) | Infra-structure (Year) | $K_s$ (m/day) | Slope (%) |
|---|---|---|---|---|---|---|---|---|
| Blackburn[1] | Industrial | 44 | 65 | 907 | 2061 | 1946 | 0.51 | 2.5 |
| Blackburn Lake[2] | Industrial | 221 | 56.1 | 3391 | 1534 | 1946 | 0.51 | 2.5 |
| Box Hill[1] | Industrial | 16 | 80 | 394 | 2463 | 1945 | 0.51 | 0.6 |
| Eley Rd[3] | Residential | 186 | 24 | 4330 | 2328 | 1968 | 0.51 | 1.5 |
| Fairfield[1] | Residential | 337 | 68 | 4876 | 1447 | 1906 | 3.5 | 1.1 |
| Gilby Rd[3] | Industrial | 28 | 45 | 539 | 1925 | 1970 | 4.33 | 3.8 |
| Hampton Park[3] | Residential | 118 | 40 | 1868 | 1583 | 1987 | 4.75 | 0.4 |
| Hedgeley Dene[1] | Residential | 160 | 45 | 4125 | 2578 | 1905 | 4.20 | 0.7 |
| Lara St[1] | Residential | 110 | 55 | 2836 | 2578 | 1905 | 2.21 | 3.0 |
| Nunawading[1] | Industrial | 11 | 85 | 217 | 1973 | 1946 | 0.51 | 1.1 |
| Richmond[2] | Residential | 89 | 74 | 5263 | 5914 | 1922 | 3.5 | 0.95 |
| Ruffeys Creek[3] | Residential | 106 | 25 | 2877 | 2714 | 1969 | 1.92 | 3.2 |
| Shepherds Bush[3] | Residential | 38 | 21 | 865 | 2276 | 1970 | 0.51 | 1.2 |

Catchments denoted by [1] and [3] provided data for dry weather analysis, and those denoted by [2] and [3] were used for wet weather analysis.

## 3.5 Data analysis

### 3.5.1 Concentrations of nutrients

All data of the concentrations of nutrients were first checked for errors. Outliers were not excluded unless the original authors had identified a reason for doing so (for example, a known laboratory error or suspected sample contamination) or where an *a priori* rationale for removal was apparent.

#### *3.5.1.1 Dry weather*

The dry weather concentrations of the nutrient species were tabulated and the mean, as well as the 2.5$^{th}$ and the 97.5$^{th}$ percentiles were calculated for each pollutant, in order to derive the 95% confidence interval of nutrient species concentrations for each catchment. The overall means of concentrations, 2.5$^{th}$ and 97.5$^{th}$ percentiles were derived by calculation of the arithmetic means.

#### *3.5.1.2 Wet weather*

The data sets that were accepted for inclusion in the data analysis were from catchments where five or more storm events were sampled (catchments with less than five samples were considered not to provide a representative sample).

For wet weather data, the basic statistics were computed as follows:

*Event Mean Concentration*

An EMC is defined as the total mass load of a chemical parameter yielded from a site during a storm divided by the total runoff water volume discharged during the storm. For sampling programs based on flow-weighted techniques, the EMC is taken as simply the flow-weighted mean concentration (Smullen et al., 1999). The flow-weighted mean concentration of each storm event was calculated as the integral of the product of concentrations and flow volumes divided by the sum of flow volumes for the event (Eqn 3.1). Grab samples for storm events with no accompanying flow volume data were excluded.

$$EMC = \frac{\Sigma(C_i \text{ x } Q_i)}{\Sigma Q_i} \qquad \text{Eqn 3.1}$$

where EMC is the event mean concentration, $C_i$ is the concentration of the sample, and $Q_i$ is the volume of sample i.

*Site Mean Concentration*

The site mean concentration (SMC) for the catchment was the sum of the product of EMCs and sum of flow volumes divided by the total volume all samples taken for all events (Eqn 3.2).

$$SMC = \frac{\Sigma\ (EMC_n \times Q_n)}{\Sigma Q_n} \qquad \text{Eqn 3.2}$$

where SMC is the site mean concentration, $EMC_n$ is the event mean concentration of event n, and $Q_n$ is the sum of the volume of all samples taken for all events over the entire period of record.

*Statistics*

The arithmetic mean of the EMCs was calculated for each catchment, along with the 95% confidence interval, derived from the difference between the $2.5^{th}$ percentile and the $97.5^{th}$ percentile. The median of all EMC values was also calculated.

### 3.5.2 Composition

The composition of TN was calculated, based on the concentrations of the individual species. Concentrations of each of the species, $NO_x$, $NH_3$, DON, TDN and TPN, were calculated as well as their contribution to TN (in terms of percentage of TN). The contribution of each of these species to TN gives further insight into the forms and transformations of N within the catchment, which may help explain processes governing N behaviour.

### 3.5.3 Relationships between nutrient levels and catchment characteristics

#### *3.5.3.1 Dry weather*

Dry weather sample data were from water samples after stormwater had receded to baseflow. Box-plots were prepared using SPSS v18 to compare dry weather nutrient concentrations between each of the land uses. Comparisons were undertaken for concentrations of TN, TDN, $NO_x$, TPN, $NH_3$, DON and TP in catchments where a full complement of data was available. It should be noted that only two land-use types, residential and industrial, were represented due to the availability of dry weather data, and commercial land use was not evaluated through lack of data. Whilst this limits the analysis, it does allow these two important land uses to be compared. Paired t-tests were used to test for significant differences in nutrient concentrations between the land uses (significant at $p<0.05$), after first checking that the data sets complied with the assumption of normality.

The other catchment characteristics – area, total imperviousness, population, population density, average year of infrastructure, bedrock hydraulic conductivity and the mean catchment slope – were compared to the mean nutrient concentrations by scatterplots and subsequent regression analysis. The relationships were assessed using both linear and non-linear regression analysis; in each case the regression with the highest $R^2$ value and lowest p-value was chosen.

#### *3.5.3.2 Wet weather*

The impact of land use was not analysed for the wet weather data, since there were insufficient industrial catchments for comparison with residential catchments. However, the relationships between the SMCs of each catchment and the catchment characteristics were analysed by regression analysis, using the same methods as for dry weather. As with the dry weather analysis, linear and non-linear regressions were undertaken, with the regression with the highest $R^2$ value and the lowest p-value being presented.

## 3.6 Conclusion

Data from several existing studies in Melbourne, Australia provided information on nutrient concentrations and composition from 13 catchments. Of these, 11 catchments were analysed for their dry weather nutrient behaviour, whereas seven catchments were analysed for their wet weather nutrient behaviour. Characteristics of each of the study catchments were defined using eight defined parameters which describe the land use and physiography of the catchments. The data were analysed using standard statistical methods, box plots and regression analysis, in order to derive relationships between the catchment characteristics and the nutrient concentrations and composition. In the next two chapters, the results of these analyses are presented for dry weather (Chapter 4) and wet weather (Chapter 5).

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# CHAPTER 4: Impact of catchment characteristics on nutrient concentrations in dry weather

## 4.1 Introduction

In this chapter, the concentrations of nutrients in dry weather flows (baseflows) from eleven Melbourne catchments, where stormwater drains are separate from the sewer pipes and drains, (Blackburn; Box Hill; Eley Rd, Burwood East; Fairfield; Gilby Rd, Mt Waverley; Hampton Park; Hedgeley Dene, Malvern East; Lara St, Malvern East; Nunawading; Ruffeys Ck, Doncaster, and Shepherds Bush, Glen Waverley) are investigated. The relationships between nutrient concentrations and catchment characteristics are analysed using the methods described in Chapter 3. This chapter thus presents and discusses the results; the manner by which catchment factors impact on nutrient levels in dry weather flows is detailed and their implications are discussed.

## 4.2 Nitrogen and phosphorus concentrations

The basic descriptive statistics for TN, N species and TP measured across the 11 catchments studied are presented in Table 4.1. The dry weather mean TN concentration for all sites is 2.2 mg/L, which is, interestingly, higher than Duncan's (2003) mean wet weather TN concentration of 2.0 mg/L. The range of means is from 0.3 mg/L (Nunawading) to 3.7 mg/L (Lara St), while the 95% confidence interval (CI) varies from 1.0 to 6.5 mg/L, indicating considerable variability in TN concentrations between the catchments. These persistently high concentrations during dry weather at all sites, except for Nunawading, have negative implications for receiving waters, particularly if they are small streams with little buffering capacity (Hatt et al., 2004). As a guideline to the ecological health of receiving waters in New South Wales, TN concentrations in excess of 0.5 mg/L and TP concentrations in excess of 0.05 mg/L are considered to have bio-stimulating effects (SPCC, 1990). These levels equate to default trigger values for south-eastern Australian lowland rivers above which chemical stress to the ecosystem is likely to occur (ANZECC, 2000). This is not only the case for freshwater systems in Australia but applies worldwide. For example, the influx of high levels of nutrients of 3-9 mg/L TN and 0.08-0.38 mg/L TP has been identified to have caused hypereutrophic conditions in Lake Apopka, Florida, USA (Coveney et al., 2002).

The mean for all sites for TDN is 1.9 mg/L (CI=1.0-4.1). This concentration is of concern as it is a component of TN which is readily bio-available for micro-organism uptake. This dissolved nitrogen component alone also exceeds the trigger level for TN (0.5 mg/L) for lowland rivers in south-eastern Australia (ANZECC, 2000).

The mean $NH_3$ concentration for all sites is 0.15 mg/L (CI=0.010.93 mg/L) which is high compared to the trigger value of $NH_4^+$ of 0.02 mg/L (ANZECC, 2000), while the upper range (0.93 mg/L) is of particular concern due to its ready bio-availability with the potential to cause eutrophication. Ammonia is readily assimilated by microorganisms, and since it is un-ionized, less energy is expended in its assimilation and converted to organic matter. Many plants, especially phytoplankton, have evolved transport mechanisms that favour the uptake of ammonia, and the role of $NH_3$ as a preferred micronutrient makes it a key parameter in studies of eutrophication potential (Gibb, 2000).

The mean for all sites for $NO_x$ is 1.31 mg/L (CI = 0.53-4.49 mg/L), as a fraction of TN itself exceeds the trigger value for TN, which is 0.50 mg/L (ANZECC, 2000), and has the potential to cause eutrophication. The ANZECC trigger value for $NO_x$ is 0.04 mg/L.

**Table 4.1** Summary of dry weather nutrient concentrations, under baseflow conditions, (mean (95% confidence interval)) from the 11 Melbourne catchments: TN, total nitrogen; TDN, total dissolved nitrogen; $NH_3$, ammonia; $NO_x$, nitrate/nitrite; TPN, total particulate nitrogen; DON, dissolved organic nitrogen; TP, total phosphorus. Blank space denotes that no data were available. The overall means (bottom row) are calculated as the arithmetic mean of all catchments with available data.

| **Catchment** | **TN (mg/L)** | **TDN (mg/L)** | **$NH_3$ (mg/L)** | **$NO_x$ (mg/L)** | **TPN (mg/L)** | **DON (mg/L)** | **TP (mg/L)** |
|---|---|---|---|---|---|---|---|
| Blackburn | 1.9 (0.3-8.5) | 1.6 (0.26-7.0) | 0.42 (0-3.2) | 0.56 (0.075-1.6) | 0.28 (0.01-2.0) | 0.62 (0.13-3.0) | |
| Box Hill | 0.9 (0.4-2.1) | 0.76 (0.32-1.8) | 0.035 (0.005-0.12) | 0.18 (0.010-0.90) | 0.18 (0.05-0.42) | 0.54 (0.20-1.7) | |
| Eley Rd, Burwood East | 3.4 (0.6-12.1) | | | | | | 0.63 (0.15-2.8) |
| Fairfield | 3.2 (2.6-4.4) | 3.0 (2.08-4.2) | 0.14 (0.014-0.35) | 2.1 (1.6-2.8) | 0.26 (0-0.82) | 0.69 (0.17-1.2) | |
| Gilby Rd, Mt. Waverley | 1.1 (0.4-2.3) | | | | | | 0.22 (0.03-0.61) |
| Hampton Park | 2.5 (0.5-20.0) | | 0.05 (0-0.60) | 2.7 (0-20.38) | | | 0.07 (0.01-0.30) |
| Hedgeley Dene, Malvern East | 2.7 (1.5-5.3) | 2.2 (1.5-3.0) | 0.018 (0.010-0.03) | 1.4 (0.91-2.0) | 0.48 (0-2.4) | 0.75 (0.40-1.0) | |
| Lara St, Malvern East | 3.7 (2.0-8.1) | 3.5 (2.0-8.2) | 0.35 (0.012-2.27) | 2.0 (1.0-3.6) | 0.20 (0-0.64) | 1.1 (0.40-2.5) | |
| Nunawading | 0.3 (0.2-0.4) | 0.24 (0.17-0.31) | 0.012 (0.010-0.20) | 0.14 (0.10-0.18) | 0.02 (0-0.06) | 0.08 (0.05-0.12) | |
| Ruffeys Creek, Doncaster | 2.4 (1.2-4.4) | | | | | | 0.24 (0.11-0.50) |
| Shepherds Bush, Glen Waverley | 2.3 (0.8-4.3) | | | | | | 0.23 (0.09-0.46) |
| **Overall mean** | 2.2 (1.0-6.5) | 1.9 (1.0-4.1) | 0.15 (0.01-0.93) | 1.31 (0.53-4.49) | 0.24(0.01-1.05) | 0.63 (0.23-1.59) | 0.27 (0.08-0.92) |
| **ANZECC trigger values** | 0.50 | | | 0.04 | | | 0.05 |

The mean TPN concentration for all sites is 0.24 mg/L (CI=0.01-1.05 mg/L). Not surprisingly, the concentrations of particulate nitrogen are low relative to typical wet weather concentrations (see for example Duncan 2003 or Chapter 5), because in low flow conditions there is not enough energy to transport large amounts of particulate matter. While particulate nitrogen may not have major direct consequences, there is the possibility that, under the right conditions, TPN could be later transformed into other species of N (e.g. by bacterial oxidation to $NO_x$) which may then be more readily assimilated by aquatic microorganisms.

The mean concentration of DON for all sites is 0.63 mg/L (CI=0.23-1.59 mg/L). Typical organic N concentrations vary from <1 mg/L in lakes and marine environments to 20 mg/L in raw waste water (Cerda et al., 2000). Although the mean DON level detected is not of concern in most catchments, the level from Lara Street (DON=1.1 mg/L) was elevated. Several studies have demonstrated the impact of organic nitrogen on estuarine and lake eutrophication, with massive algal blooms, extended bacterial production, and poor water quality (Hammer, 1993; Bronk et al., 1994; Cornell et al., 1998)

The mean dry weather TP concentration for all sites is 0.27 mg/L (CI=0.08-0.92 mg/L). Again, this concentration, not surprisingly, exceeds the default trigger level (TP=0.05 mg/L) above which impacts on ecological health in south-eastern Australian lowland rivers, as defined by ANZECC, including the rivers and streams that flow through Melbourne, are likely (ANZECC, 2000). The catchment with the lowest mean (0.07 mg/L) was Hampton Park (a residential catchment) whereas Eley Rd, Burwood East (an industrial catchment) had the highest mean concentration at 0.63 mg/L. The mean TP concentrations from all catchments exceeded 0.05 mg/L and thus have the potential to accelerate microscopic plant growth in aquatic environments.

The variability of concentrations of nutrient species are consistent with the observations of several other studies (e. g. Terstriep et al., 1986; Duncan, 2003; Taylor et al., 2005). Most importantly, most of the concentrations were elevated beyond important ecological thresholds (SPCC, 1990; ANZECC, 2000), meaning that discharge of these dry weather flows risks having impacts on receiving waters. Of the 11 Melbourne catchments studied, all except for Nunawading exceeded the TN threshold *during dry weather* (Table 4.1). The mean dry weather TP concentration was 0.27 g/L for the Melbourne catchments studied, which also exceeded the bio-stimulating threshold for lowland streams (ANZECC, 2000). Further, in some catchments, the 97.5 percentile concentrations for TN, TDN and $NO_x$ were particularly high and likely to cause acute effects in receiving waters such as streams and shallow lakes.

That most of the dry weather concentrations exceed the recognized biochemical thresholds in dry weather is significant because dry weather flows occur for the majority of the time of the year (even if they do not carry the majority of the load, which will be more important to the larger, buffered downstream ecosystems such as estuaries and bays). Therefore, they have the potential to cause eutrophication in small streams and lakes in dry weather.

## 4.3 Composition of total nitrogen

Within the eleven monitored catchments, the dominant nitrogen species was $NO_x$ (Figure 4.1). On average (across all sites), $NO_x$ comprised around 64% of TN. This was followed, in descending order of importance, by DON (22%), TPN (9%) and $NH_3$ (5%). Total dissolved nitrogen therefore made up around 91% of TN in dry weather. This dominance of dissolved (and thus readily bioavailable) forms of nitrogen can allow rapid assimilation by microscopic aquatic plants in receiving waters. Conversely, as previously noted, the proportion of TN made up of particulate forms during dry weather was quite low, at around 9%.

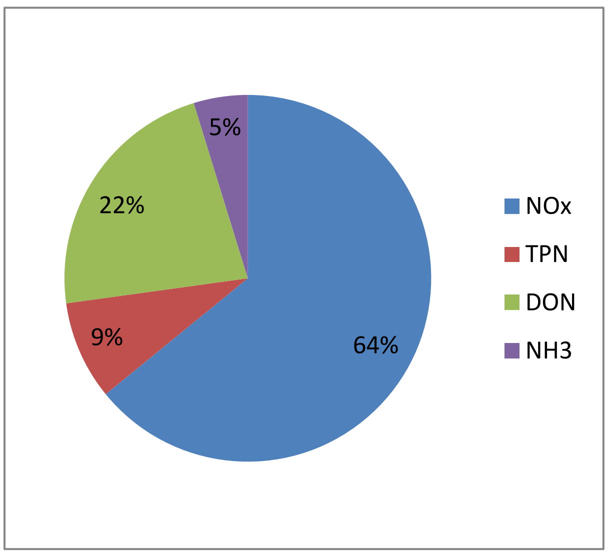


**Figure 4.1** Dry weather overall average percentages of nitrogen composition.

### 4.3.1 Comparison of nitrogen concentrations and composition from residential and industrial land-uses

The impacts of land use (comparison between residential and industrial land-use) on nitrogen were investigated by comparing N concentrations and their composition from catchments of the two different land-use types (Table 4.2); it should be noted that a subset of the eleven catchments had adequate data to be included in this analysis. The N compositions of the catchments are illustrated in Figures 4.2-4.4.

**Table 4.2** Mean dry weather nitrogen concentrations and compositions.

| Catchment | Variable | Concentration (mg/L) | % of TN |
|---|---|---|---|
| Fairfield (residential) | $NO_x$ | 2.1 | 66 |
| | TPN | 0.26 | 8 |
| | DON | 0.69 | 21 |
| | $NH_3$ | 0.14 | 4 |
| | TN | 3.2 | |
| Box Hill (industrial) | $NO_x$ | 0.18 | 19 |
| | TPN | 0.18 | 19 |
| | DON | 0.54 | 58 |
| | $NH_3$ | 0.035 | 4 |
| | TN | 0.94 | |
| Hedgeley Dene (residential) | $NO_x$ | 1.4 | 54 |
| | TPN | 0.48 | 18 |
| | DON | 0.75 | 28 |
| | $NH_3$ | 0.018 | 1 |
| | TN | 2.7 | |
| Blackburn (industrial) | $NO_x$ | 0.56 | 30 |
| | TPN | 0.28 | 15 |
| | DON | 0.62 | 33 |
| | $NH_3$ | 0.42 | 23 |
| | TN | 1.9 | |
| Lara St. (residential) | $NO_x$ | 2.0 | 54 |
| | TPN | 0.20 | 5 |
| | DON | 1.1 | 29 |
| | $NH_3$ | 0.46 | 12 |
| | TN | 3.8 | |
| Nunawading (industrial) | $NO_x$ | 0.14 | 40 |
| | TPN | 0.02 | 6 |
| | DON | 0.08 | 22 |
| | $NH_3$ | 0.20 | 33 |
| | TN | 0.36 | |
| **Residential averages** | $NO_x$ | 1.9 | 58 |
| | TPN | 0.31 | 10 |
| | DON | 0.84 | 26 |
| | $NH_3$ | 0.17 | 5 |
| | TN | 3.2 | |
| **Industrial averages** | $NO_x$ | 0.3 | 28 |
| | TPN | 0.16 | 15 |
| | DON | 0.41 | 39 |
| | $NH_3$ | 0.19 | 18 |
| | TN | 1.1 | |

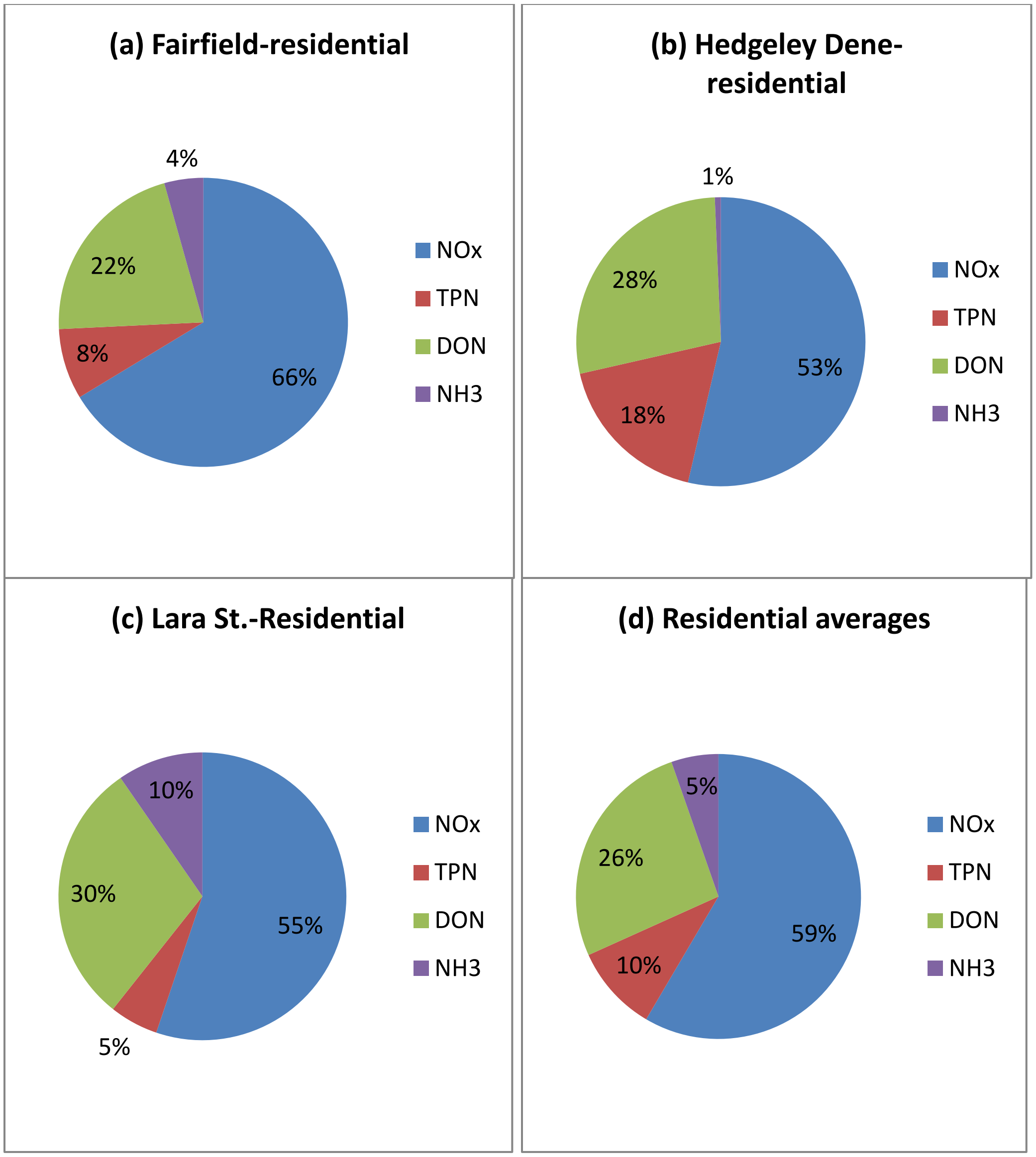


**Figure 4.2** Typical dry weather N compositions from residential catchments. Charts (a)-(c) are of individual catchments. Chart (d) shows the average N compositions.

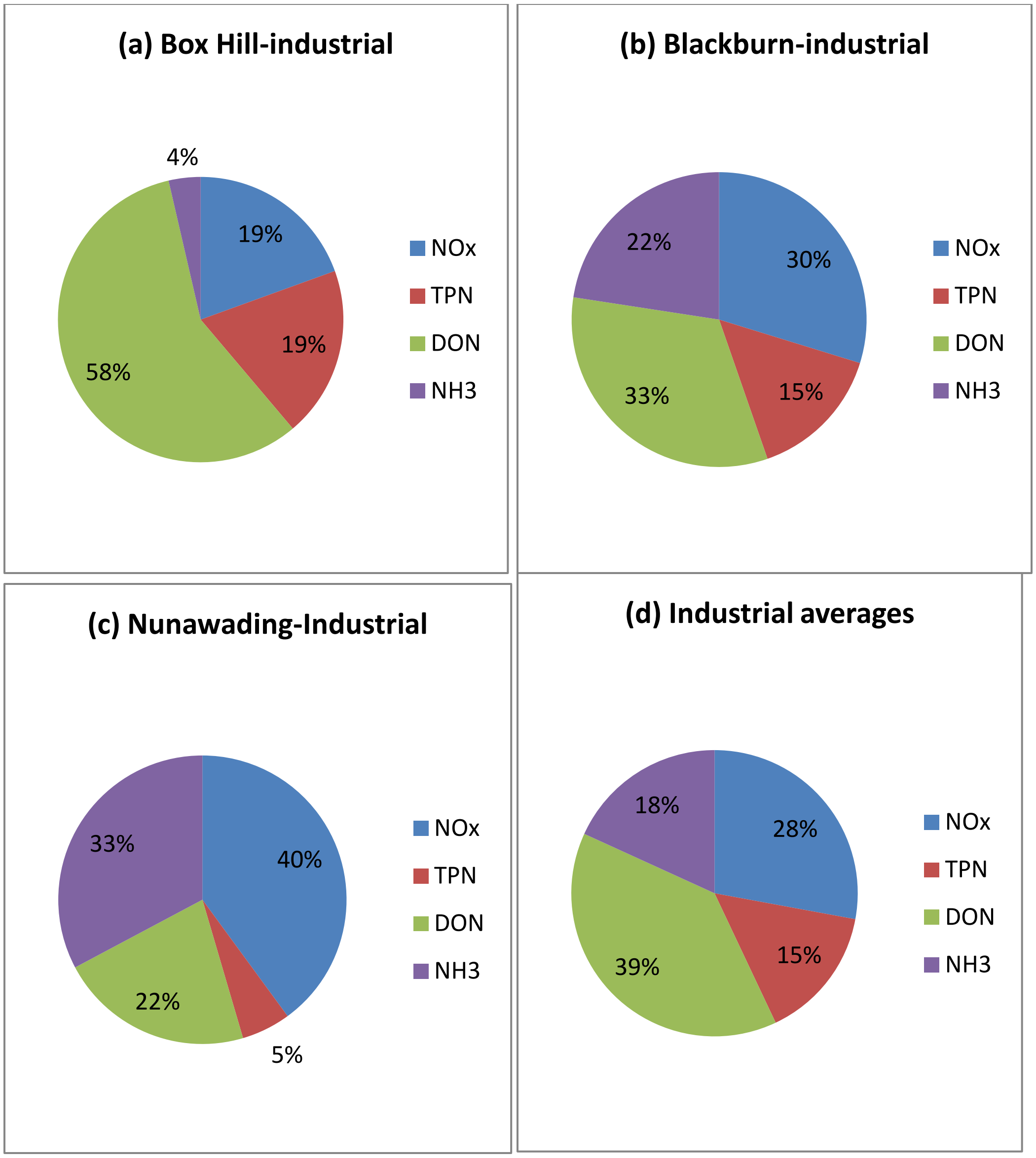


**Figure 4.3** Typical dry weather N compositions from industrial catchments. Charts (a)-(c) are of individual catchments. Chart (d) shows the average N compositions.

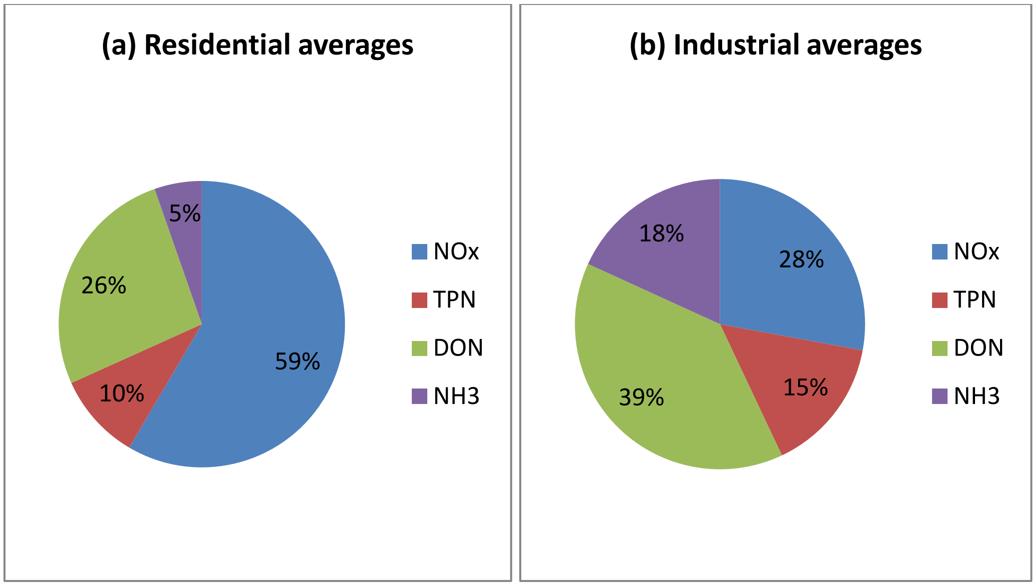


**Figure 4.4** Comparison of (a) residential and (b) industrial nitrogen compositions

In residential catchments there is thus a clear dominance of $NO_x$, followed by DON, with TPN and $NH_3$ making up significantly smaller contributions (Table 4.2). In industrial catchments, the composition is much more variable and although DON on average is higher (followed by $NO_x$), there are distinct differences between each of the industrial catchments (Figure 4.2). In the industrial catchments catchments, $NO_x$ makes up on average around 28% of TN and around half of that in residential catchments. This is possibly due to a difference in anthropogenic sources of $NO_x$ (Grasshoff, 1983; Puckett, 1995) between industrial and residential catchments. DON comprises 39% of TN in industrial catchments, and 26% in residential catchments. DON is primarily sourced from decaying organic matter, and possibly from industrial sources like organic chemicals; given the relatively higher DON concentrations within industrial areas, it would appear that industrial sources of organic nitrogen may be present.

These quite distinct differences in N composition between industrial land-uses would suggest that treatment methods may need to be tailored to the given land-use. **A very important, significant conclusion:** In residential areas, systems that promote denitrification only will be required, whilst in industrial areas, mineralisation and ammonification will be necessary to deal with the relatively large proportion of organic nitrogen.

## 4.4 Effect of catchment characteristics on nutrient concentrations

### 4.4.1 Influence of land use

As shown in Table 4.2, residential catchments generally produce higher N concentrations than industrial catchments. The average TN concentration from residential catchments is some three times that of industrial catchments. Concentrations of $NO_x$ in residential catchments are approximately six times that in industrial catchments, and DON concentrations in residential catchments are about twice that from industrial catchments. Residential catchments produce about twice the TPN concentration of industrial catchments. Hence, despite the differences in composition between the two land-use types investigated in this study, it appears that concentrations of N are consistently higher from residential catchments (Figure 4.5). Indeed, most concentrations of N species were found to be significantly different between the two land-uses (t-tests, $p<0.05$), with the exception of $NH_3$. Conversely, the concentrations of TP did not vary significantly between the two land-uses.

Previous studies have not found definitive differences between land-use and nutrient levels in urban settings e. g. (Duncan, 1999, 2003) where no significant differences were detected between urban land use zonings. Although land-use zoning has been used as a predictor of water quality (Soranno et al., 1996; Carpenter et al., 1998), the relationship between landscape attributes and water quality has not been resolved (Soranno et al., 1996). One possible explanation for the differences observed in this study is that residential catchments have more N input than industrial catchments since residential catchments have more gardens, lawns, household pets, sewer and water supply infrastructure, when compared with industrial catchments. In a recent survey, nutrient inputs to residential land were measured, and the highest input came from fertilisation of gardens, followed by lawns and pets, and most of the fertilisers are organic manures, mulches and composts (Kelsey et al., 2010). Similarly, it was found that N inputs from a subcatchment in Estonia were due to intensive use of mineral fertilizers and manure application (Mander et al., 1998). These inputs may contribute to groundwater N concentrations, which then find their way back into stormwater pipes in addition to overland wash-off (Young et al., 1976; Shepherd et al., 2006).

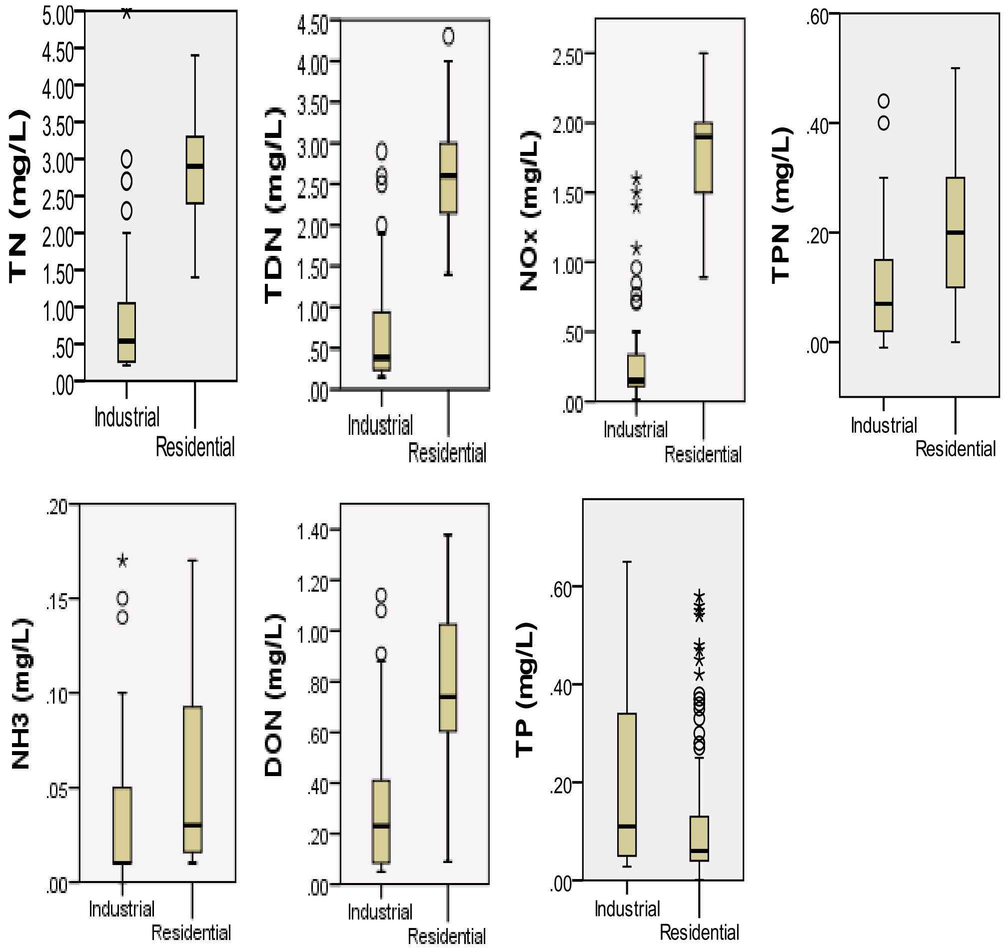


**Figure 4.5** Range of dry weather nutrient concentrations for industrial and residential land uses across the study urban catchments.

### 4.4.2 Influence of population and population density

The relationships between the catchment population and nutrient concentrations are shown in Figure 4.6. Whilst population density has no influence on concentrations, interestingly, raw catchment population was found to significantly influence all nutrient species, except for $NH_3$. The $R^2$ values for the regressions between catchment population and TN, TDN, $NO_x$, TPN, DON and TP are: 0.86, 0.84, 0.67, 0.54, 0.62, and 0.54 respectively, all with $p < 0.05$.

One possible explanation of catchment population influencing nutrient levels is that a higher population is likely to provide a *higher loading (input)* of nutrients to the catchment. It is also possible that the relationship between population and concentration is a co-correlation with land-use type. Populations were, not surprisingly, significantly higher ($p<0.01$) in residential catchments than in industrial catchments. Given that residential catchments have been shown (section 4.4.1) to have greater concentrations for most N species than do industrial catchments, the observed population influence is at least partly an artifact of land-use. As shown in Figure 4.7, the catchment population has a general influence on TN concentrations, whereas the landuse has a dominant influence. TP concentrations are moderately influenced by the residential catchment population as shown in Figure 4.8. There are insufficient data to correlate TP concentrations with residential populations.

One would of course expect that *population density* would be in itself a useful indicator, given that this could result in higher loads per unit catchment area. It is thus surprising that no significant relationships between population density and nutrient levels have been found in this study. This is likely to be (a) because the range of population densities of the catchments studied was quite small (ranging from 1447 to 2714 inhabitants/$km^2$), a bigger range may provide a more rigorous test; and (b) because there is no significant difference ($p=0.54$) in *population density* between industrial and residential land use in this study. These suggest that the influence of land-use on nutrient concentrations is stronger than is the influence of population density.

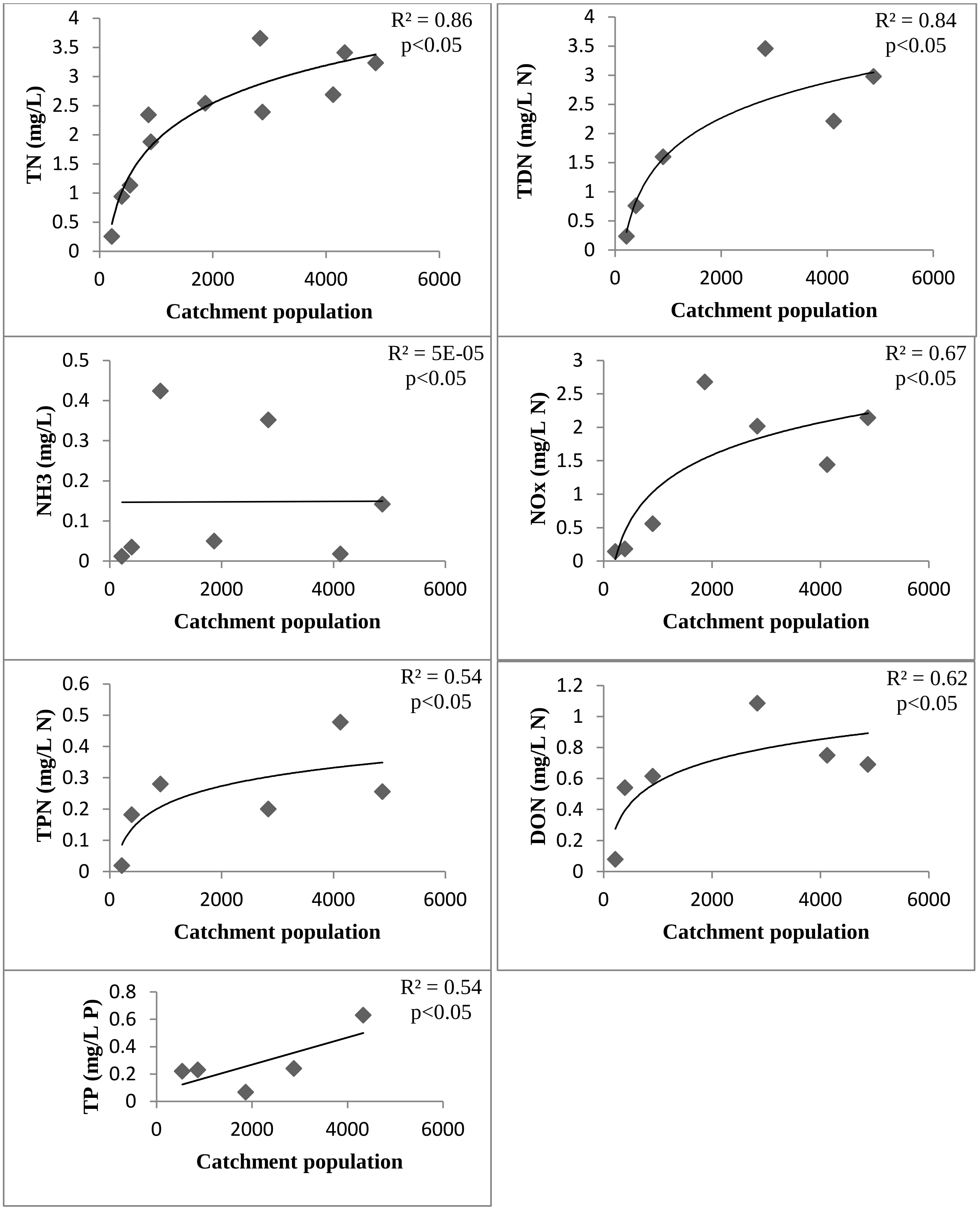


**Figure 4.6** Regression relationships between catchment population and mean nutrient concentrations. TN, total nitrogen; TDN, total dissolved nitrogen; $NH_3$, ammonia; $NO_x$, nitrate/nitrite; TPN, total particulate nitrogen; DON, dissolved organic nitrogen; TP, total phosphorus.

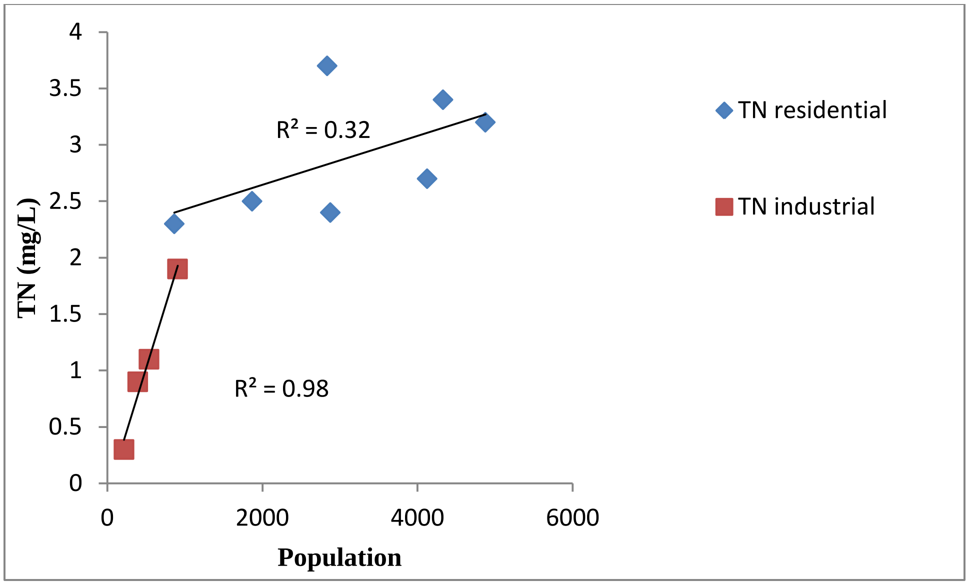


**Figure 4.7** Regression relationship between catchment population and mean TN (total nitrogen) concentrations with residential and industrial data differentiated

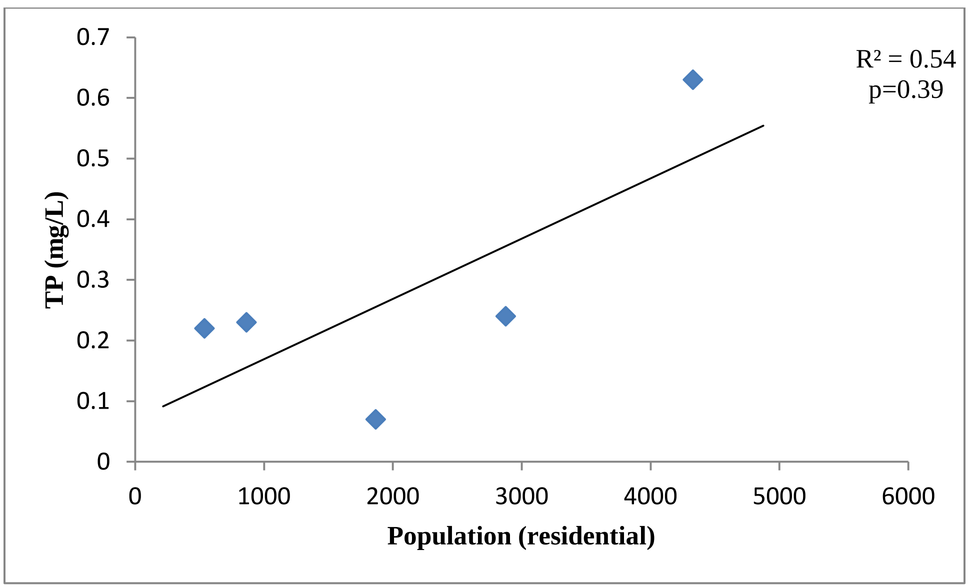


**Figure 4.8** Regression relationship between residential populations and TP (total phosphorus) concentrations.

The populations of catchments influence nutrient levels in general; and as shown in Figures 4.7 and 4.8, residential catchment populations strongly influence TN and TP concentrations. In Figure 4.7, the regressions of residential and industrial TN concentrations follow different trends.

### 4.4.3 Influence of catchment area

Catchment area was a strong positive predictor of TN concentrations ($R^2 = 0.82$, p=0.01) and TDN ($R^2 = 0.80$, p = 0.08), and a moderate predictor of $NO_x$ ($R^2 = 0.47$, p = 0.04). However, there was only a weak relationship between catchment area and DON ($R^2 = 0.50$, p = 0.08) and TP ($R^2$=0.39), while catchment area did not correlate with $NH_3$ ($R^2$=0.00, p=0.04) and TPN ($R^2$=0.20, p=0.08) (Figure 4.9).

Again, a possible explanation for the relationship between catchment area and concentration is a co-correlation with land-use type. While the catchment area did not vary significantly between the two land uses (t-test p = 0.12), the average catchment area for residential land use (150 ha) was more than twice that of industrial catchments (64 ha). Given that residential catchments have been shown (section 4.4.1) to have greater concentrations for most N species than do industrial catchments, the observed catchment area influence may be at least partly an artifact of land-use. It is also possible that the size of the catchment area plays some role in terms of the length of the pathway that baseflow takes, (by increasing residence time), increasing the chance for baseflow to intercept N sources (e.g. Taylor et al., 2005). Previous studies reported that the loss of vegetation from a catchment would result in major increases in nitrate leaching (Edwards et al., 1985; Edwards et al., 1990), in some cases by up to six to ten times (Stevens and Hornung, 1988). It is therefore possible that, in response to an increase in urbanisation and the clearing of native vegetation, nitrate leaching of the soil will substantially increase. Coupled with the longer distances travelled by groundwater and longer drainage pipe and drain networks in the larger catchments, N is postulated to be accumulated along the way in groundwater as it makes its way through the soil to the drainage outlet. Therefore, with the removal of native vegetation, and taking into account the nutrient-rich condition of the soil and sub-soil (from N input, leaching and bacterial N fixation), the size of the catchment (which determines the distance and time of groundwater travel) may play some role in influencing nutrient levels, through the accumulation of dissolved nutrient forms from the soil media.

Dry weather N pollution is hypothesized to be sourced not only from the ground surface, but more importantly from sub-surface groundwater flows, from the contaminated soil media itself which can possess current sources of pollution, plus past legacies of N pollution. In dry weather, the quality of the soils, sub-soils and ground water become important considerations.

Furthermore, during the dry season, it is postulated that a lower water table creates a thicker vadoze zone, producing oxidizing conditions ideally suited for bacterial nitrification of any N-bearing precursors sourced from the soil surface or the sub-surface of the ground. Therefore, N sources will be from the leaching of surface N sources (atmospheric, fertilizers, and the leaching of N-bearing accumulated organic plant debris deposited on surfaces of the extensive impervious drainage network itself), and sub-surface N sources such as leaky water and sewer infrastructure, and N species generated from bacterial nitrification. Therefore, the catchment area, the sub-surface strongly oxidising media, and extensive drainage network operate to contribute, transform (nitrify) and convey most N species.

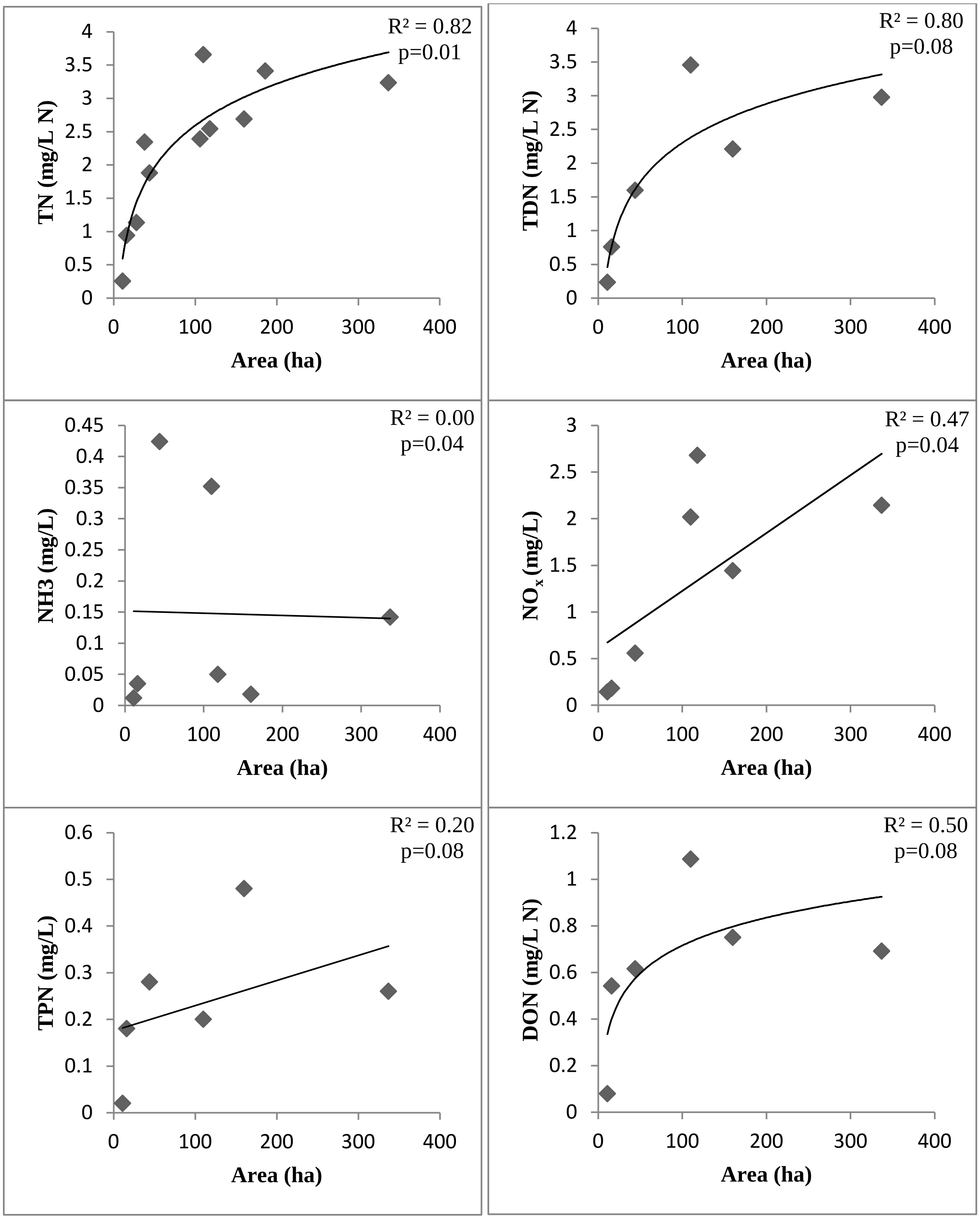


**Figure 4.9** Regression relationships between catchment area and mean dry weather nutrient concentrations. TN, total nitrogen; TDN, total dissolved nitrogen; $NH_3$, ammonia $NO_x$, nitrate/nitrite; TPN, total particulate nitrogen; DON, dissolved organic nitrogen.

It is also important to note that catchment area and population are, logically, highly co-correlated (Figure 4.10), meaning that their relationships with nutrient concentrations are somewhat confounded, given that both vary between industrial and residential land uses.

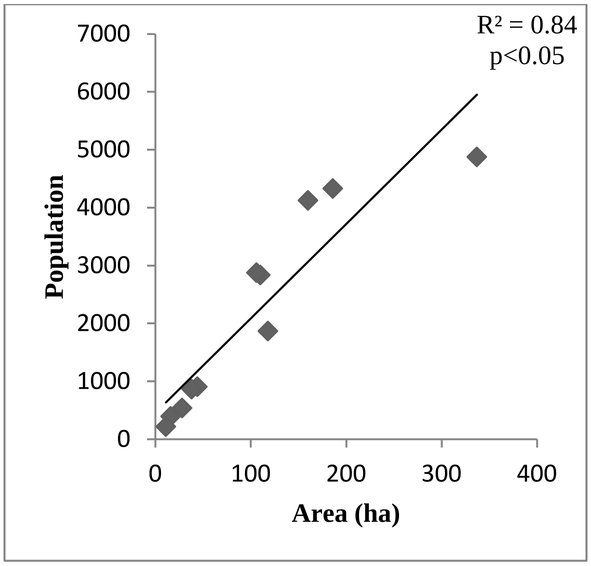


**Figure 4.10** Relationship between catchment population and catchment area.

### 4.4.4 Influence of surface imperviousness

Catchment imperviousness exerted only a weak influence on TN ($R^2$=0.26, p=0.01) and TP ($R^2$=0.24, p=0.00), but had a strongly significant negative influence on TPN ($R^2$ = 0.73, p=0.01, $NO_x$ ($R^2$ = 0.62, p=0.00), TDN ($R^2$ = 0.54, p=0.01) and DON ($R^2$ = 0.60, p=0.01) (Figure 4.11).

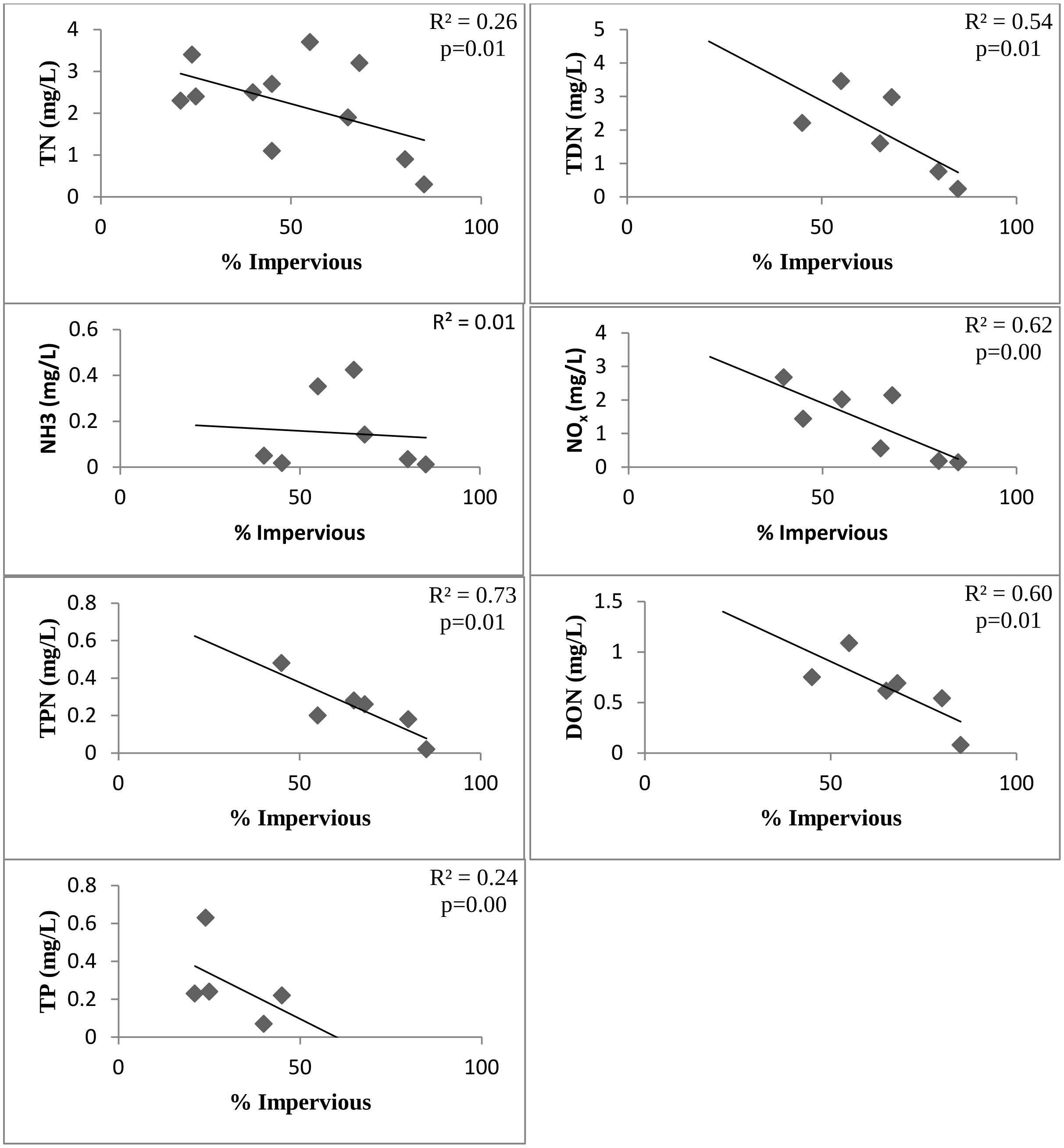


**Figure 4.11** Regression relationships between catchment imperviousness and mean dry weather nutrient concentrations. TN, total nitrogen; TDN, total dissolved nitrogen; $NO_x$, nitrate/nitrite; TPN, total particulate nitrogen; DON, dissolved organic nitrogen; TP, total phosphorus.

A higher surface imperviousness reduces infiltration into sub-soils, thus reducing the potential leaching of soil-resident N through interflow, through-flow and groundwater flows (Linderfelt and Turner, 2001). Reduced infiltration will also limit the ongoing supply of nutrients to the soil, resulting in higher concentrations of N during stormflows (i.e. from impervious area runoff), but potentially reducing dry weather concentrations (Arnold and Gibbons, 1996). Nitrogen can also be accumulated on catchment surfaces from atmospheric deposition which can be a significant component (Stevens et al., 1990), along with gardens, lawns, and pets (Kelsey et al., 2010) and possibly leaking water infrastructure. One recent study showed that smaller residential blocks in Perth, with higher imperviousness, tended to have lower N input rates of surface runoff (Kelsey et al., 2010). The hypothesis of these researchers was that increasing the impervious fraction operates *(during dry weather)* by reducing the surface area for N input to the sub-surface, leaching, production, and mobilisation of nutrients, and reducing infiltration of delayed stormwater through urban soils, implying the significance of sub-surface pathways in urban soils in dry weather. Again, however, it is hard to tease out the exact mechanisms occurring, as industrial catchments (which exhibit low dry weather N concentrations) have significantly higher imperviousness (t-test $p=0.02$) than do residential catchments. It thus may be the difference in imperviousness that explains the lower dry weather N concentrations in industrial catchments, rather than, or as well as, differences in nutrient-generating activities within the catchment (Kelsey et al., 2010).

### 4.4.5 Influence of average age of stormwater infrastructure

The average year of infrastructure had a significant influence on the concentrations of some forms of N, as well as on P: TDN ($R^2 = 0.78$, $p=0.02$), TP ($R^2 = 0.80$, $p=0.04$). Its influence on DON was ($R^2 = 0.53$, $p = 0.01$) (Figure 4.12). There was, however, no influence of infrastructure age on the overall concentration of nitrogen (TN).

It is suggested that older catchments are more likely to produce elevated concentrations of dissolved nutrient species than recently developed catchments because older infrastructure is more likely to leak, particularly old wastewater infrastructure. For example, it is recognised that the problem of leaky infrastructure is most acute in historic cities with old and failing infrastructure (Shepherd et al., 2006).

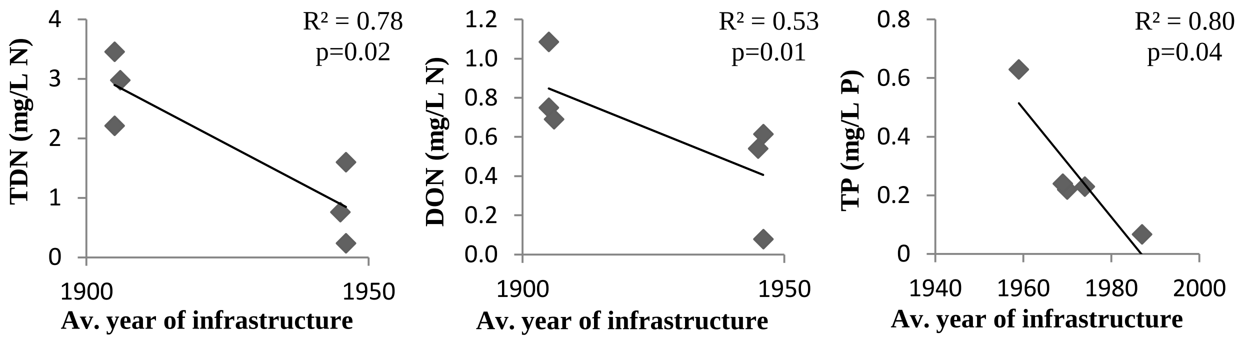


**Figure 4.12** Regression relationship between the average year of infrastructure with mean dry weather nutrient concentrations. TDN, total dissolved nitrogen; DON, dissolved organic nitrogen; TP, total phosphorus.

### 4.4.6 Influence of catchment hydraulic conductivity and slope

Both slope and hydraulic conductivity of the underlying soils could potentially play a role in dry weather nutrient concentrations, given their role in influencing subsurface flow pathways and residence time. Indeed, in this study, the hydraulic conductivity of the underlying soils significantly and positively influenced $NO_x$ ($R^2$ = 0.84, p=0.00), TDN ($R^2$ = 0.65, p=0.02) and TPN ($R^2$ = 0.53, p=0.01), while the average catchment slope significantly influenced only the concentrations of $NH_3$ ($R^2$ = 0.85, p=0.00) (Figure 4.13), and there was no correlation of catchment slope with TN ($R^2$=0.05, p=0.01).

A previous study of the delayed conveyance of TN and dissolved N species following storm events suggested throughflow and interflow as possible mechanisms (Taylor et al., 2006). It was hypothesized that catchment hydraulic conductivity may play an important role, with levels of $NO_x$ being particularly influenced by this variable. It is likely that catchments with high underlying soil permeability have more efficient conveyance pathways of dissolved nitrogen, particularly oxidised N during dry weather, the higher hydraulic conductivity providing a thicker oxidising pervious media. Conversely, a lower hydraulic conductivity implies that $NO_x$ is detained for long periods in very slow moving pore water (e. g. (Scholefield and Stone, 1995) providing greater opportunity for de-nitrification to take place. In agriculture, a result of ploughing is to increase nitrate concentrations (Neill, 1989; Thornton and Dise, 1998; Stoate et al., 2001). The inference is that ploughing effectively aerates the soil, allowing for more oxidation and nitrification to occur. Therefore catchments with higher hydraulic conductivities can potentially provide a larger and thicker oxidising volume of soil and bedrock for water infiltration, thus generating higher concentrations of N species from microbial activity, especially $NO_x$.

However, TP levels were inversely related to catchment hydraulic conductivity, implying that lower hydraulic conductivities facilitate TP removal by contact with more clay mineral adsorption, or fine particles are screened by the soil. This is not surprising, given the high fraction of TP in the particulate state (Taylor et al., 2006).

Slope plays a significant role only in the dry weather concentrations of $NH_3$ (Figure 4.13). Ammonia is produced by ammonification of organic N (Canter, 1997). It is likely that a steep slope provides a fast transport mechanism to deliver $NH_3$ in the stormwater drains before there is sufficient time for complete oxidation to form nitrite and nitrate. To remove $NH_3$, catchments with steep slopes will benefit from devices that will increase retention time, for example wetlands (Wong and Geiger, 1997; Bavor et al., 2001; Bourgues and Hart, 2007), and biofiltration systems, particularly those incorporating design modifications such as saturated zones and incorporation of zeolite (known for its ability to remove $NH_3$ and $NH_4^+$ (Lenntech, 2014)), aimed at maximizing nitrogen removal, (by plant uptake and denitrification) (Hunho et al., 2003; Henderson et al., 2007; Zinger et al., 2007; Bratieres et al., 2008; Hatt et al., 2009; Li et al., 2009). It is noted that as $NH_3$ comprises a small percentage of dry weather runoff, the focus should be on other constituents.

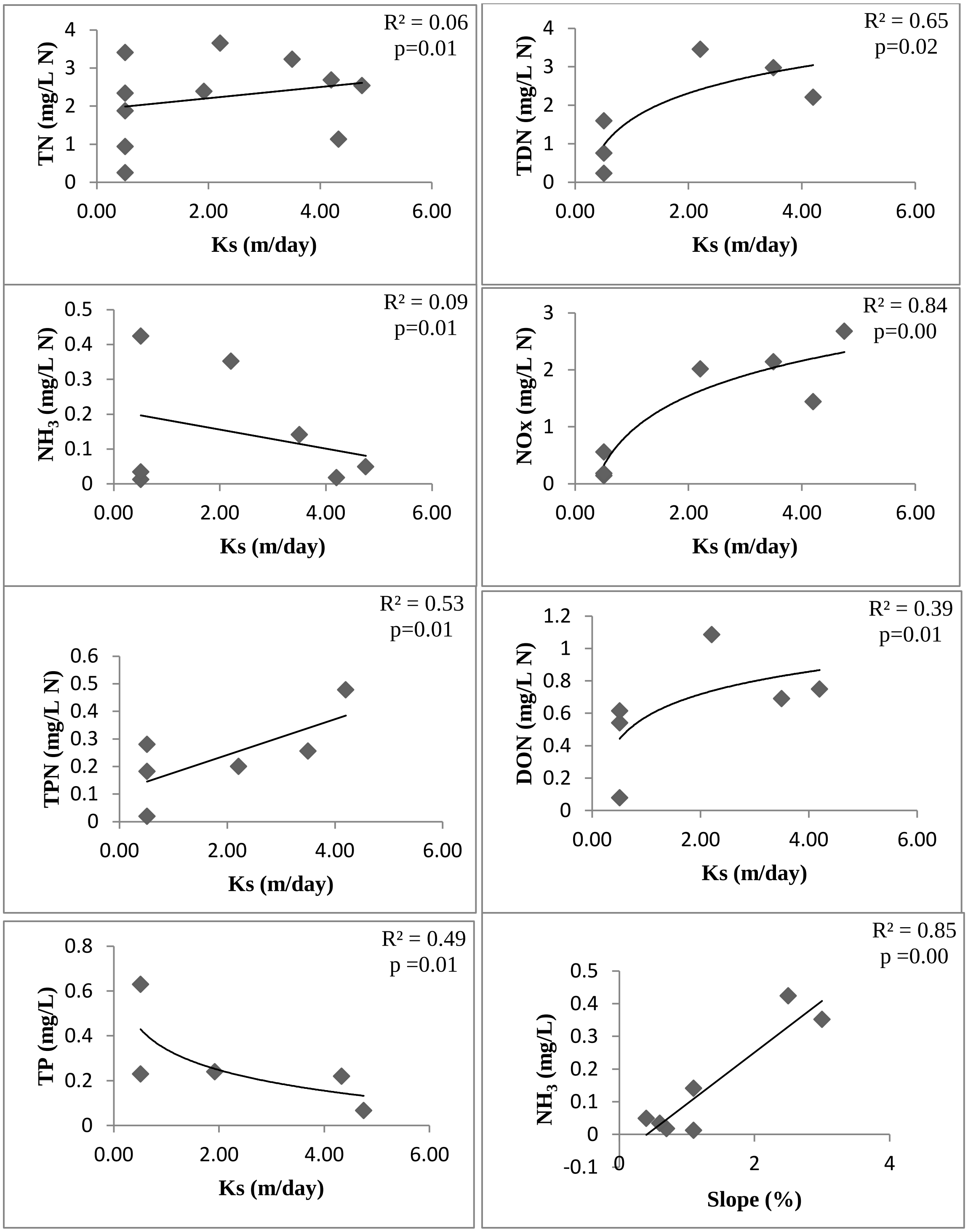


**Figure 4.13** Regression relationships between hydraulic conductivity and slope with mean dry weather nutrient concentrations. TN, total nitrogen; TDN, total dissolved nitrogen; $NH_3$, ammonia; $NO_x$, nitrate/nitrite; TPN, total particulate nitrogen; DON, dissolved organic nitrogen; TP, total phosphorus.

## 4.5 Conclusions

In dry weather, mean nutrient concentrations in drains from 11 Melbourne catchments studied mostly exceeded bio-stimulating thresholds, and are therefore of concern with respect to the ecological health of receiving waters. Due to a potential combination of sub-surface sources (e.g. leaking wastewater infrastructure) and flows through nutrient-rich soil media, dry weather flows may often contain very high concentrations of nutrients, dispelling the common observation (Duncan, 1999) that urban storm runoff is always more polluted than urban dry weather flows.

Nitrogen concentrations in dry weather flows from residential catchments were significantly higher than from industrial catchments, whereas concentrations of phosphorus appeared to be similar across the two land uses. The residential and industrial N compositions also showed characteristic differences, and dry weather N composition in residential areas was dominated by nitrites and nitrates which form two thirds of TN.

The land use differences appear to explain in part the positive correlations observed between nutrient concentrations and two explanatory factors; catchment area and population. The other characteristics tested: imperviousness, hydraulic conductivity, average age of infrastructure and the mean catchment slope had mixed effects, with imperviousness generally resulting in lower concentrations, suggesting a reduced opportunity for subsurface N sources to be mobilized. Steeper slope catchments had higher $NH_3$ concentrations, suggesting that increased flow velocities reduced the time available for nitrification and then subsequent denitrification of organic and ammonia forms of N.

Concentrations of some N species were also found to be apparently positively influenced by catchment hydraulic conductivity, again suggesting that subsurface flow pathways and leaching of soil N may play a critical role. To a lesser extent, catchment age may influence dry weather concentrations, with older catchments apparently discharging higher levels of P and dissolved N, demonstrating the potential for leaking wastewater infrastructure and potentially even water infrastructure (through its increase on groundwater flows) to contribute to dry weather N concentrations. The influence of land-use was, however, found to be of particular importance, with residential catchments tending to be larger, have greater populations, yet have lower impervious coefficients.

It is likely that N loading to receiving waters increases as a function of urbanisation, but that this is not simply a product of current loading rates (for example due to the current anthropogenic activities), but rather a combination of past 'legacy' contributions and current activities. For example, through a loss of forest cover, there is a significant long-term leaching of soil N, particularly in oxidised forms. These may be further worsened in catchments with old, leaking infrastructure.

To address the problem of elevated nutrient levels in dry weather flow, catchment management should focus attenuation measures by prioritising attention to residential catchments ahead of industrial catchments. It is likely that catchments with old infrastructure and soils with high hydraulic conductivity are more likely to be problematic, but this requires further research. A combination of source control through structural and non-structural means, retention and planting of nutrient assimilating and retaining vegetation, and upgrading of leaking drainage, water and wastewater infrastructure are all required. Finally, the design of stormwater treatment measures such as wetlands and biofiltration systems to reduce nutrient loads, which to date has focused on treatment of stormflows, needs to also consider the treatment of baseflows, which often have very high nutrient concentrations. In the next chapter, the behavior of nutrients in wet weather flows will be examined.

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# Chapter 5: Impact of catchment characteristics on nutrient concentrations in wet weather

## 5.1 Introduction

In this chapter, the concentrations of nutrients in stormwater in wet weather from seven Melbourne catchments (Blackburn Lake; Eley Rd, Burwood East; Gilby Rd, Mt Waverley; Hampton Park; Richmond; Ruffeys Ck, Doncaster and Shepherds Bush, Glen Waverley) are the focus of investigation. Details of the sampling locations and methods, along with analysis methods, have been presented in Chapter 3. The manner by which catchment factors impact on nutrient levels during storms is thus explored and the implications of these relationships are discussed.

## 5.2 Wet weather nitrogen species and total phosphorus concentrations

The catchments studied, the number of storm events sampled, the sampling periods and the sources of data were all presented in Table 3.3, with the number of samples taken and the nutrient species analysed shown in Table 3.4. The data are used to calculate event mean concentrations (EMCs) and site mean concentrations (SMCs). The composition of nitrogen and phosphorus during wet weather is presented below, prior to an examination of the relationship between catchment and pollutant characteristics.

### 5.2.1 Event Mean Concentrations (EMCs)

The ranges of EMCs of nutrients vary substantially between the catchments, as shown in Table 5.1 and Figure 5.1. For TN, the average EMC varies between 0.65 and 2.1 mg/L, while for TP, it ranges between, 0.13 and 0.43 mg/L. In general, there is also a substantial degree of variability in EMCs, as exemplified by the range in TN EMCs at Richmond (refer to Figure 5.1).

**Table 5.1** Wet weather nutrient Event Mean Concentrations (EMCs) for the seven Melbourne catchments. EMCs were calculated from flow volumes and nutrient concentrations as detailed in Section 3.2.2, Chapter 3.

| Catchment | Blackburn Lake | Eley Rd | Gilby Rd | Hampton Park | Richmond | Ruffeys Creek | Shepherds Bush |
|---|---|---|---|---|---|---|---|
| Mean TN (95%CI) (mg/L) | 1.77 (0.99-3.19) | 1.59 (0.98-2.74) | 1.19 (0.43-4.34) | 1.66 (0.98-3.68) | 2.34 (0.99-5.34) | 1.58 (0.85-2.90) | 1.82 (0.65-4.48) |
| Median TN (mg/L) | 1.58 | 1.35 | 0.99 | 1.53 | 1.94 | 1.28 | 1.46 |
| Mean $NH_3$(95%CI) (mg/L) | | 0.07 (0.01-0.13) | 0.08 | 0.67 (0.006-0.52) | 0.16 (0.07-0.27) | 0.14 (0.07-0.27) | 0.12 (0.1-0.14) |
| Median $NH_3$ (mg/L) | | 0.08 | 0.06 | 0.03 | 0.14 | 0.12 | 0.12 |
| Mean $NO_x$ (95%CI) (mg/L) | | 0.74 (0.53-1.27) | 0.46 | 0.70 (0.02-1.64) | 0.52 (0.40-0.83) | 0.50 (0.25-0.79) | 0.39 (0.20-0.62) |
| Median $NO_x$ (mg/L) | | 0.65 | 0.38 | 0.64 | 0.48 | 0.43 | 0.36 |
| Mean TDN (95%CI) (mg/L) | | 1.14 (0.79-1.77) | 0.66 (0.25-1.45) | | 1.08 (0.72-1.75) | 0.96 (0.58-1.40) | 0.76 (0.51-1.08) |
| Median TDN (mg/L) | | 0.99 | 0.58 | | 0.98 | 0.89 | 0.71 |
| Mean TPN (mg/L) | | 0.45 (0.19-0.97) | 0.53 (0.18-2.89) | | 1.52 (0.27-3.59) | 0.62 (0.09-1.5) | 1.06 (0.14-3.40) |
| Median TPN (mg/L) | | 0.36 | 0.41 | | 1.12 | 0.35 | 0.75 |
| Mean DON (mg/L) | | 0.33 (0.28-0.49) | 0.28 (0.11-0.79) | | 0.39 (0.20-0.78) | 0.32 (0.21-0.42) | 0.29 (0.10-0.50) |
| Median DON (mg/L) | | 0.28 | 0.20 | | 0.33 | 0.35 | 0.28 |
| Mean TP (mg/L) | 0.24 (0.09-0.61) | 0.16 (0.09-0.27) | 0.18 (0.06-0.63) | 0.15 (0.02-0.67) | 0.42 (0.13-1.04) | | 0.25 (0.10-0.66) |
| Median TP (mg/L) | 0.20 | 0.16 | 0.14 | 0.07 | 0.30 | | 0.22 |
| Mean FRP (95%CI) (mg/L) | | 0.05 (0.03-0.09) | 0.01 | 0.04 (0.001-0.32) | 0.06 (0.03-0.11) | | 0.03 (0.02-0.04) |
| Median FRP (mg/L) | | 0.05 | 0.01 | 0.16 | 0.06 | | 0.03 |

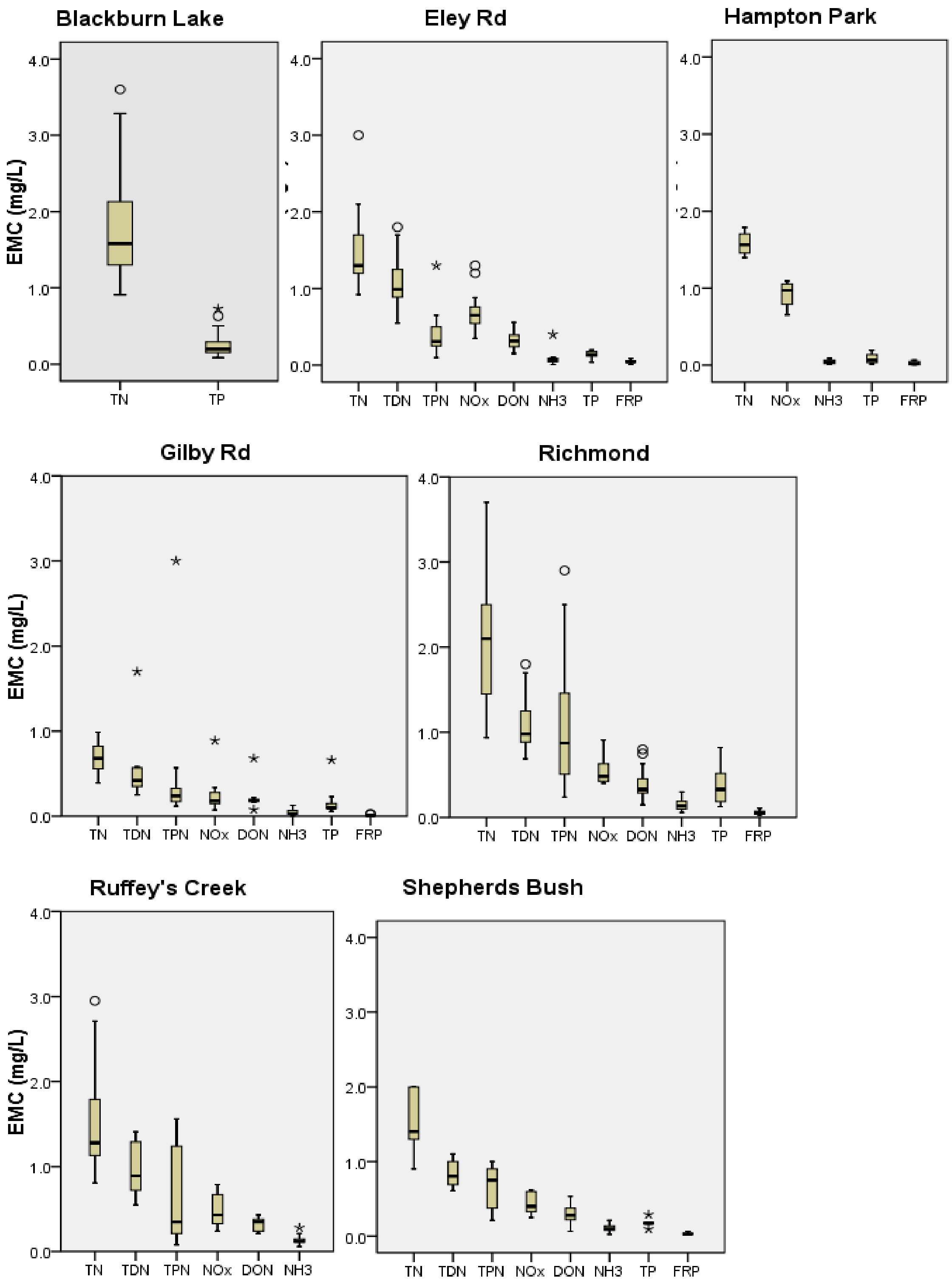


**Figure 5.1** Ranges of nutrient concentrations from the seven Melbourne catchments studied. EMC (Event Mean Concentrations).

### 5.2.2 Site Mean Concentrations (SMCs)

Given the variation in concentrations between events (as shown in Figure 5.1), the Site Mean Concentrations, which account for the weighting between individual events (using the method detailed in Section 3.3 ) provides the most useful overall estimate of wet weather nutrient concentrations (Table 5.2).

**Table 5.2** Summary of wet weather nutrient SMCs (mg/L) (data for individual nutrient species were not available at all sites).

| Site | TN | TP | $NH_3$ | FRP | $NO_x$ | TDN | TPN | DON |
|---|---|---|---|---|---|---|---|---|
| Blackburn Lake | 1.6 | 0.21 | | | | | | |
| Eley Road | 1.6 | 0.11 | 0.07 | 0.06 | 0.87 | 1.3 | 0.37 | 0.32 |
| Gilby Road | 0.99 | 0.16 | 0.04 | 0.013 | 0.23 | 0.67 | 0.32 | 0.40 |
| Hampton Park | 1.7 | 0.16 | 0.05 | 0.005 | 0.82 | | | |
| Richmond | 1.9 | 0.35 | 0.12 | 0.060 | 0.54 | 1.1 | 0.82 | 0.42 |
| Ruffey's Creek | 1.5 | | 0.13 | | 0.53 | 0.96 | 0.53 | 0.30 |
| Shepherd's Bush | 1.4 | 0.20 | 0.079 | 0.036 | 0.39 | 0.76 | 0.64 | 0.29 |
| Median | 1.5 | 0.18 | 0.090 | 0.040 | 0.49 | 0.90 | 0.58 | 0.32 |
| Mean | 1.7 | 0.23 | 0.10 | 0.043 | 0.54 | 0.94 | 0.81 | 0.33 |

### 5.2.3 General statistics

Table 5.2 indicates that the SMCs of TN are variable, ranging from Richmond with the highest SMC at 1.9 mg/L, to Gilby Rd which has the lowest of 0.99 mg/L. Richmond also has the highest TP SMC at 0.35 mg/L, whereas Eley Rd shows the lowest TP SMC of 0.11 mg/L.

The concentrations of nutrient species shown in Table 5.1 and Figure 5.1 are also variable between the catchments. This nutrient concentration variability is consistent with previous studies (Terstriep et al., 1986; Duncan, 2003; Taylor et al., 2005).

The median and the arithmetic mean of the EMCs of each catchment are given in Table 5.1. The median SMCs for the nutrient species studied are shown in Figure 5.2, and the range of wet weather nutrient concentrations from the seven Melbourne catchments are given in Figure 5.3.

The median values for TN and TP concentrations exceed the default trigger values of south-eastern Australian lowland rivers (TN=0.5 mg/L, TP=0.05 mg/L), which indicate that chemical stresses to the ecosystem of lowland rivers are likely to occur (ANZECC, 2000), and are therefore of concern.

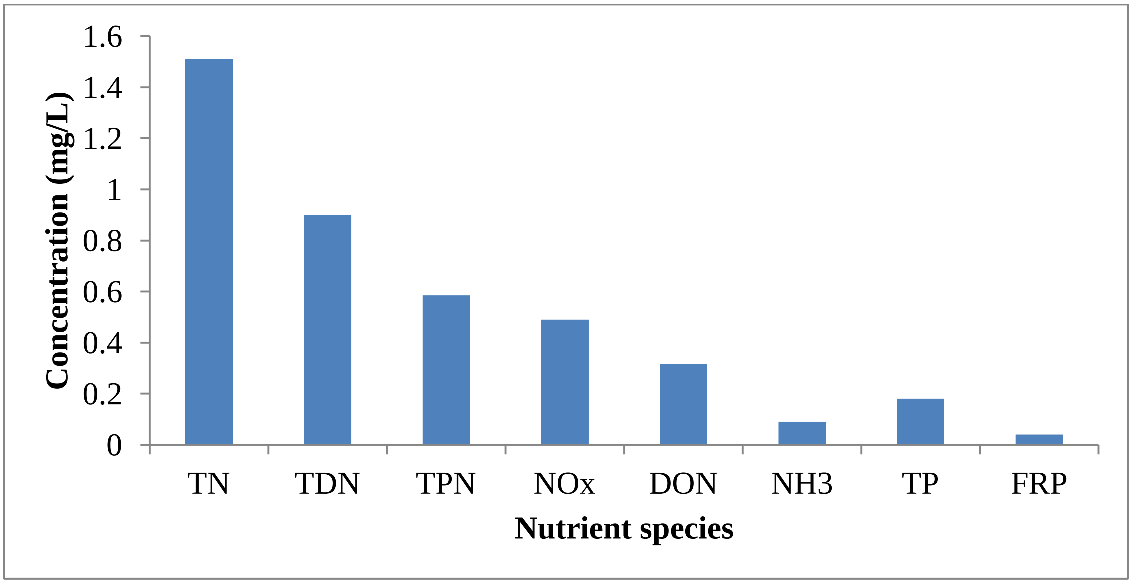


**Figure 5.2** Median SMCs of nutrient species across the seven Melbourne catchments.

## 5.3 Wet weather total nitrogen composition

Data from which to assess the composition of nitrogen were available for five of the seven catchments (Table 5.3 and Figure 5.4). This list does not include the catchments of Blackburn Lake and Hampton Park as some N species were not measured at these sites. As shown in Table 5.2 and Figure 5.4, the total nitrogen composition is unique for each catchment. This is perhaps not entirely surprising, given the variation in catchment characteristics.

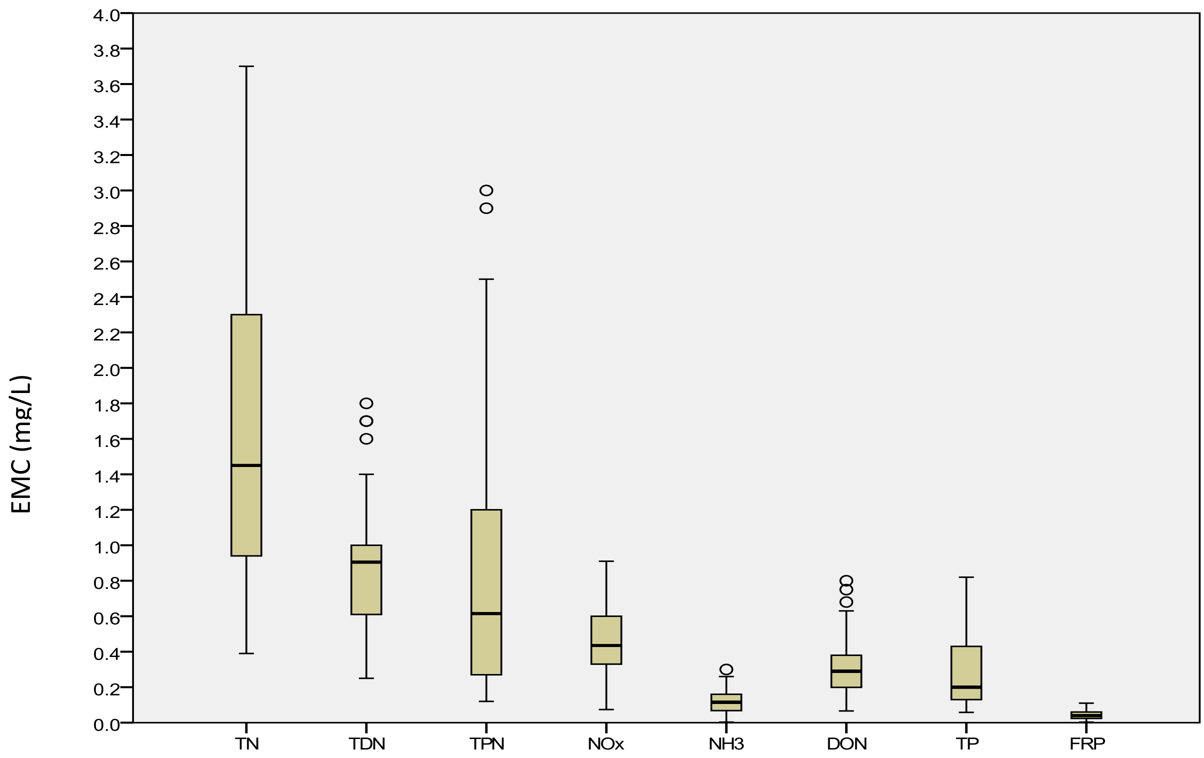


**Figure 5.3** Ranges of wet weather nutrient concentrations across the seven Melbourne catchments studied. EMC (Event Mean Concentrations).

**Table 5.3** The wet weather composition of total nitrogen from five Melbourne catchments

| Catchment | $NO_x$ (%) | TPN (%) | DON (%) | $NH_3$ (%) | TDN (%) |
|---|---|---|---|---|---|
| Eley Rd | 53 | 23 | 20 | 4 | 77 |
| Gilby Rd | 23 | 33 | 40 | 4 | 67 |
| Richmond | 29 | 43 | 22 | 6 | 57 |
| Ruffeys Ck | 35 | 36 | 20 | 9 | 54 |
| Shepherds Bush | 28 | 46 | 21 | 6 | 54 |
| Mean | 37 | 35 | 23 | 5 | 65 |

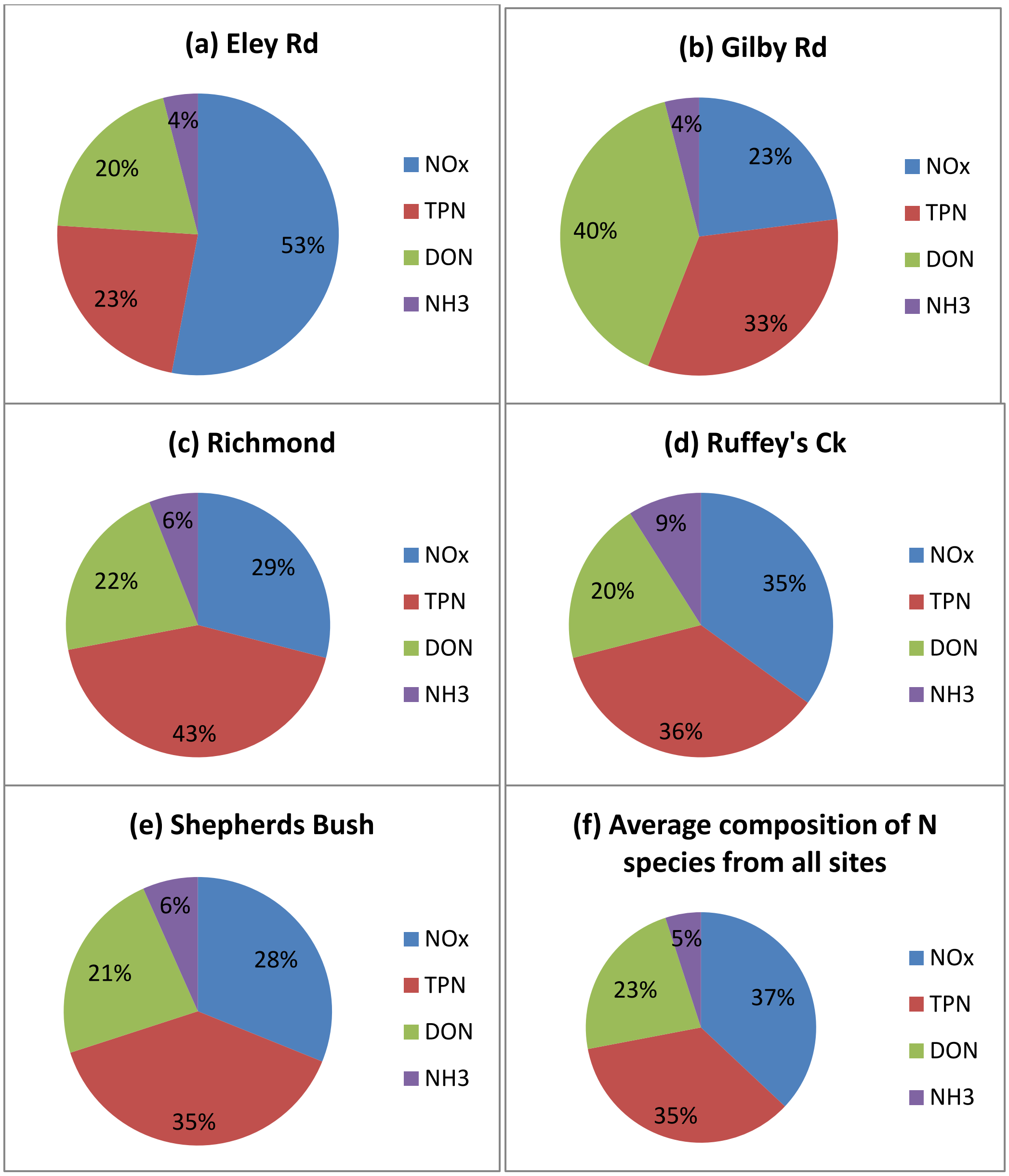


**Figure 5.4** Pie charts showing the relative proportions (expressed in percentage) of nitrogen species from the catchments in wet weather. Charts (a)-(e) are of individual catchments whereas chart (f) shows the average composition from all sites.

### 5.3.1 Observations on the composition of total nitrogen

With reference to Table 5.3 and Figure 5.4, the wet weather composition of total nitrogen is typically made up of one third total particulate nitrogen (TPN), one third nitrogen oxides ($NO_x$), 23% of dissolved organic nitrogen (DON) and 5% of ammonia ($NH_3$). On average, two thirds of TN is composed of total dissolved nitrogen (TDN), meaning that treatment processes for nitrogen cannot rely primarily on particulate removal mechanisms.

### 5.3.2 Wet weather N composition in Melbourne compared with USA data.

The Melbourne N data are compared with data from the USA to explore if there any similarities or differences. The Melbourne data are compared with N data compiled from the USA by Smullen et al. (1999) in which total Kjeldhal nitrogen (TKN), nitrite and nitrate ($NO_x$) concentrations were measured. The comparison of TN, $NO_x$ and TKN (TN-$NO_x$) concentrations from the USA are made with those in Melbourne are given in Table 5.4.

**Table 5.4** Comparison of USA and Melbourne nitrogen concentrations in storm events.

| | USA pooled (Smullen et al., 1999) (mg/L) | No. events | Melbourne (this study) (mg/L) | No. events |
|---|---|---|---|---|
| | Mean | | Mean | |
| TN | 2.39 | 2016 | 1.72 | 138 |
| $NO_x$ | 0.66 | 2016 | 0.54 | 67 |
| TKN | 1.73 | 2693 | 1.18 | 67 |
| | Median | | Median | |
| TN | 2.00 | 2016 | 1.51 | 138 |
| $NO_x$ | 0.53 | 2016 | 0.49 | 67 |
| TKN | 1.47 | 2693 | 1.02 | 67 |

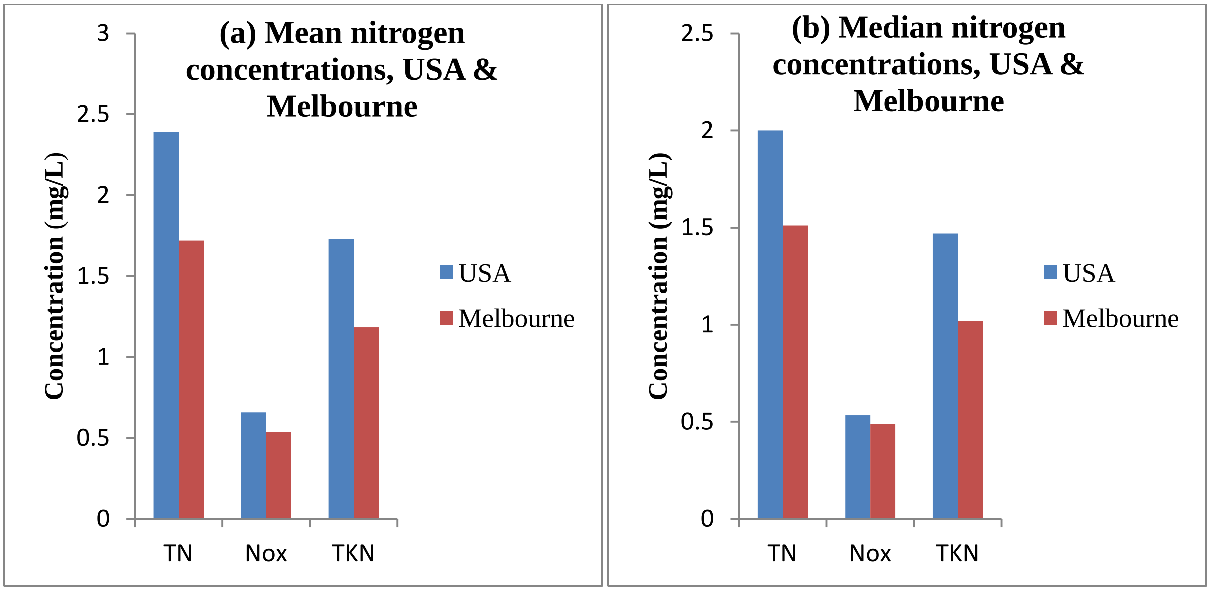


**Figure 5.5** Comparison of (a) mean and (b) median nitrogen concentrations from the USA and Melbourne**.** The USA values are from Smullen et al., 1999.

As shown in Table 5.4 and Figure 5.5, the mean and median wet weather TN, $NO_x$ and TKN, concentrations in the USA as given by Smullen et al. (1999) are higher than those in Melbourne. The higher values in the USA data set may be due to older urban catchments and values which also include stormwater and combined sewer overflow discharges. However, interestingly, the proportion of $NO_x$ in TN in the USA is similar to that in Melbourne (Figure 5.6), possibly suggesting that their origins are similar, since modern urban drainage systems in the USA came into being soon after World War II (Openbook, 2013), similar to that in Melbourne.

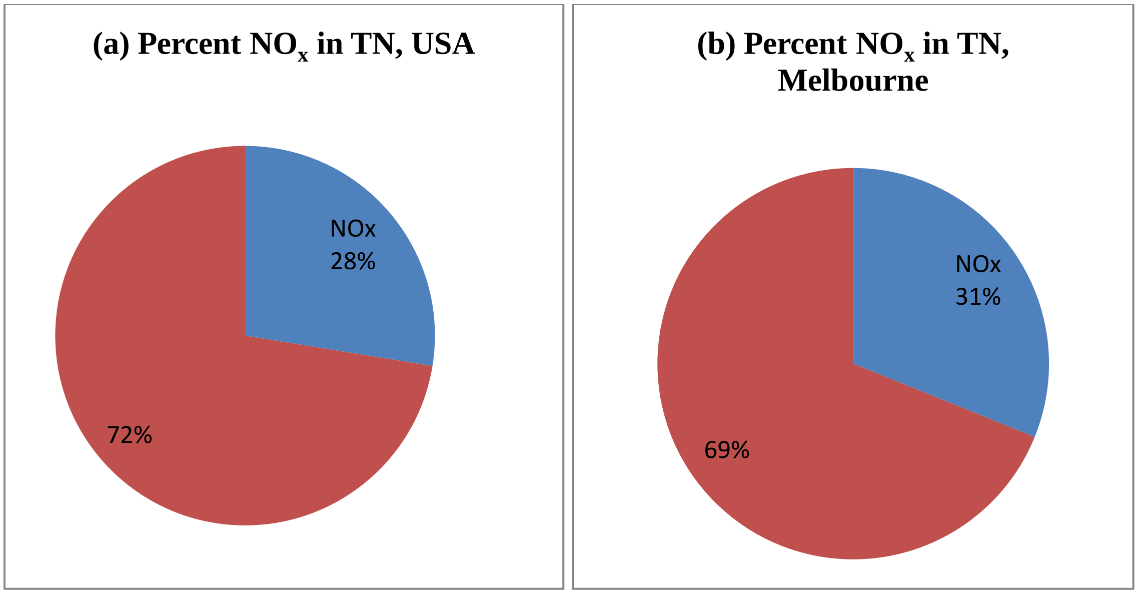


**Figure 5.6** Wet weather percent of $NO_x$ in TN. Charts (a) and (b) show the percent of $NO_x$ in TN in USA catchments and in Melbourne catchments respectively.

### 5.3.3 Implications of nutrient compositions

As Figure 5.4 indicates, for the catchments of Richmond, Ruffeys Creek and Shepherds Bush, the relative N species percentages are remarkably similar. In the residential catchment of Shepherds Bush, TPN predominates whereas in Ruffeys Ck, there is an equal proportion of $NO_x$ and TPN. In an industrial catchment such as Gilby Rd, DON predominates, while Ruffeys Ck shows a high $NH_3$ concentration.

The average TN composition in Melbourne catchments is dominated by dissolved N, with approximately two thirds comprising TDN and one third TPN (Figure 5.4). The TDN comprises in order of importance $NO_x$, DON and $NH_3$. The average TPN component for wet weather (35% of TN) is much higher than the dry weather fraction of TPN (9% of TN) reported in Melbourne catchments (see Chapter 4) reflecting the higher energy environment of stormwater flow as compared to dry weather flow. During storm events, due to substantially increased flows, there is increased mobilization of sediments and particulate organic matter in the drainage networks, leading to increased concentrations of TPN.

Knowledge of the nutrient composition from a particular catchment would enable the planning and use of the appropriate treatment technology to focus on the removal of particular nutrients and the main components such as $NO_x$ and TPN. TPN can be removed using a combination of detention ponds and wetlands (Wong and Geiger, 1997; Bavor et al., 2001; Bourgues and Hart, 2007) to remove the particulates, and $NO_x$ could be removed by incorporating treatment systems that facilitate denitrification or biological uptake. Biofiltration processes are particularly effective at this, (Hunho et al., 2003; Henderson et al., 2007; Zinger et al., 2007; Bratieres et al., 2008; Hatt et al., 2009; Li et al., 2009), although carefully designed wetlands may also be effective (e.g. Wong and Geiger, 1997). One way to avoid the implementation of extensive treatment works at stormwater drain outlets is to use diversion (where possible) of catchment drainage at upstream tributary points for stormwater harvesting such as turf and garden irrigation. Such techniques would substantially reduce the large hydrological loads to be dealt with in any downstream treatment measures.

## 5.4 Effect of catchment characteristics on nutrient concentrations

The aim of this analysis is to understand how catchment characteristics influence nutrient concentrations. The relationships between the catchment characteristics (originally quantified in Table 3.5) and the nutrient SMC values (Table 5.1) are shown as regression plots in Figures 5.7 to 5.13. (note that only relationships with ($R^2 > 0.5$, and $p<0.05$) are presented).

### 5.4.1 Influence of land use

Insufficient data were available to analyse the effect of land use on stormwater nutrient concentrations, since all the catchments except Gilby Road are residential.

### 5.4.2 Influence of catchment population and population density

As shown in Figures 5.7 and 5.8, population significantly influences concentrations of TN, TDN and FRP, and moderately influences $NO_x$. In this dataset, differences in land use (ie. between residential and industrial) do not explain the difference, although there is a strong negative correlation between the catchment age (in terms of drainage infrastructure) and catchment population (Figure 5.13), meaning that there may be a degree of spurious correlation present. Population and population density may, however, operate by increasing the nutrient load to the catchments, with dissolved species such as TDN, $NO_x$ and FRP being especially noteworthy. The sources are mixed, inclusive of products of nitrification processes from nature, such as atmospheric and biological fixation (USEPA, 1994) with additions from human sources, possibly from septic sources (leaks in the sewer system), fertilizers and detergents. Biological fixation could be enhanced by a change in land use, with the drains and pipes often laid well below ground surface, increasing the thickness of the oxidising (vadose) soil zone and allowing for the occurrence of transformation processes (Canter, 1997) which could increase the process of nitrification. A piped drainage system is a drastic change from the previous stream environment, and a concrete and piped system would efficiently convey the N and P species rather than allow their removal in normal stream beds by coupled in-stream processes of retention and denitrification (David et al., 2011). Since the main length of stormwater transport will be in pipes, there will be a lack of light, and the N and P normally removed through assimilation by periphyton and phytoplankton (Bentzen et al., 1992; Dodds, 2003) will persist unabated.

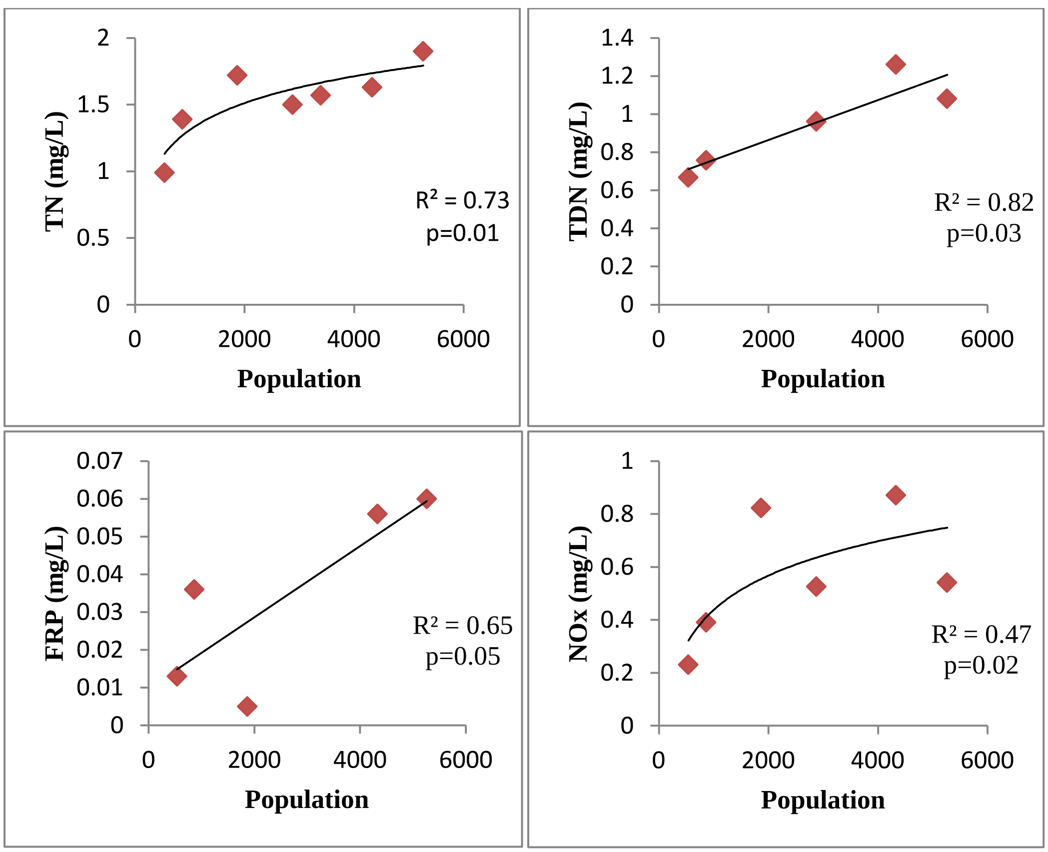


**Figure 5.7** Regression relationships between site mean concentrations (SMCs) of nutrient species and catchment population. TN, total nitrogen; TDN, total dissolved nitrogen; FRP, filterable reactive phosphorus; $NO_x$, nitrogen oxides.

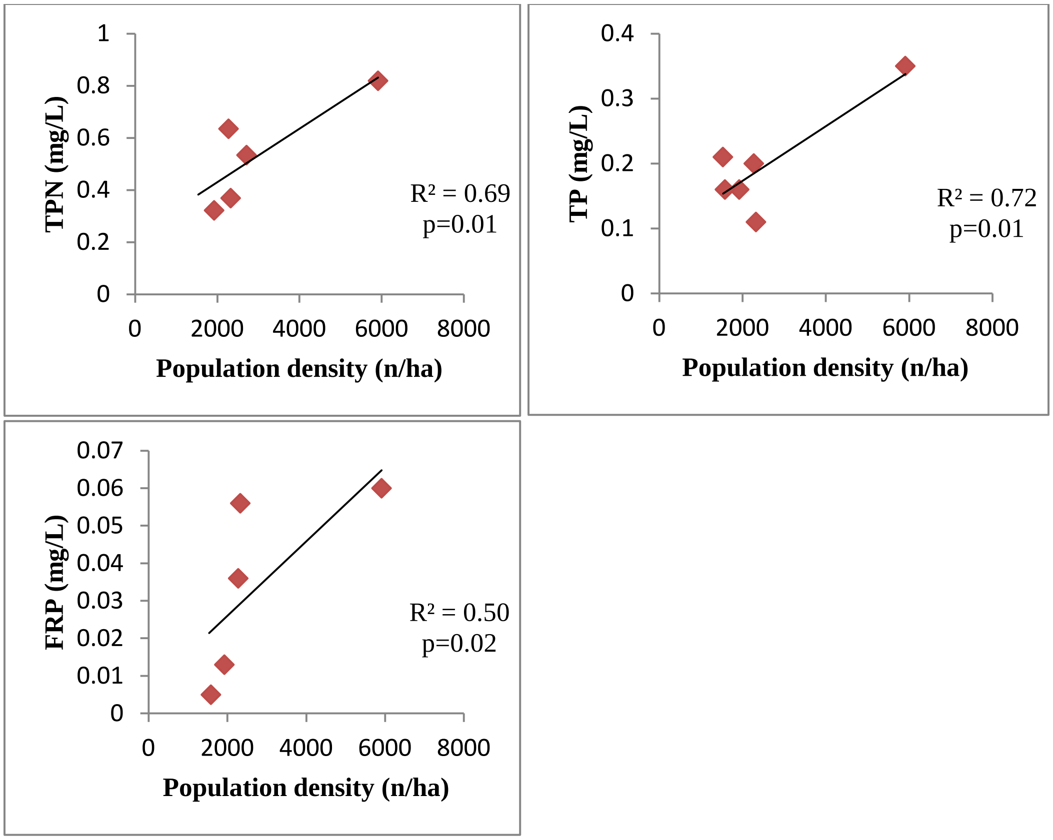


**Figure 5.8** Regression relationships between nutrient species and population density. TPN, total particulate nitrogen; TP, total phosphorus; FRP, filterable reactive phosphorus.

### 5.4.3 Influence of catchment area

Figure 5.9 shows that the catchment area significantly influences the concentrations of $NO_x$ and TDN. A strong regression relationship exists between catchment area and $NO_x$ as a fraction of TN, whereas there is a moderate regression relationship between area and TDN as a fraction of TN. It is difficult to find an explanation for such a relationship, although it is possible that this is due to processes occurring within the drainage network itself, or from leaching of nitrate from soils after the removal of vegetation (Edwards et al., 1985; Stevens and Hornung, 1988; Edwards et al., 1990). Soil N can also be accumulated from atmospheric deposition (Stevens et al., 1990), with larger catchments accumulating more N. Urbanisation, accompanied by deforestation and change of land use has a significant influence on N levels. This fosters the ability to accumulate soil N by atmospheric deposition and nitrification with the propensity to leach nitrates, supporting the relationship with $NO_x$. Larger catchments require water in the drainage system to travel longer distances, thus potentially increasing travel time and accumulating more nitrates in the process. However, it must be noted that these relationships, despite their strength, still rely on relatively small numbers of data points, and would require further confirmation before recommending changes to stormwater management policy.

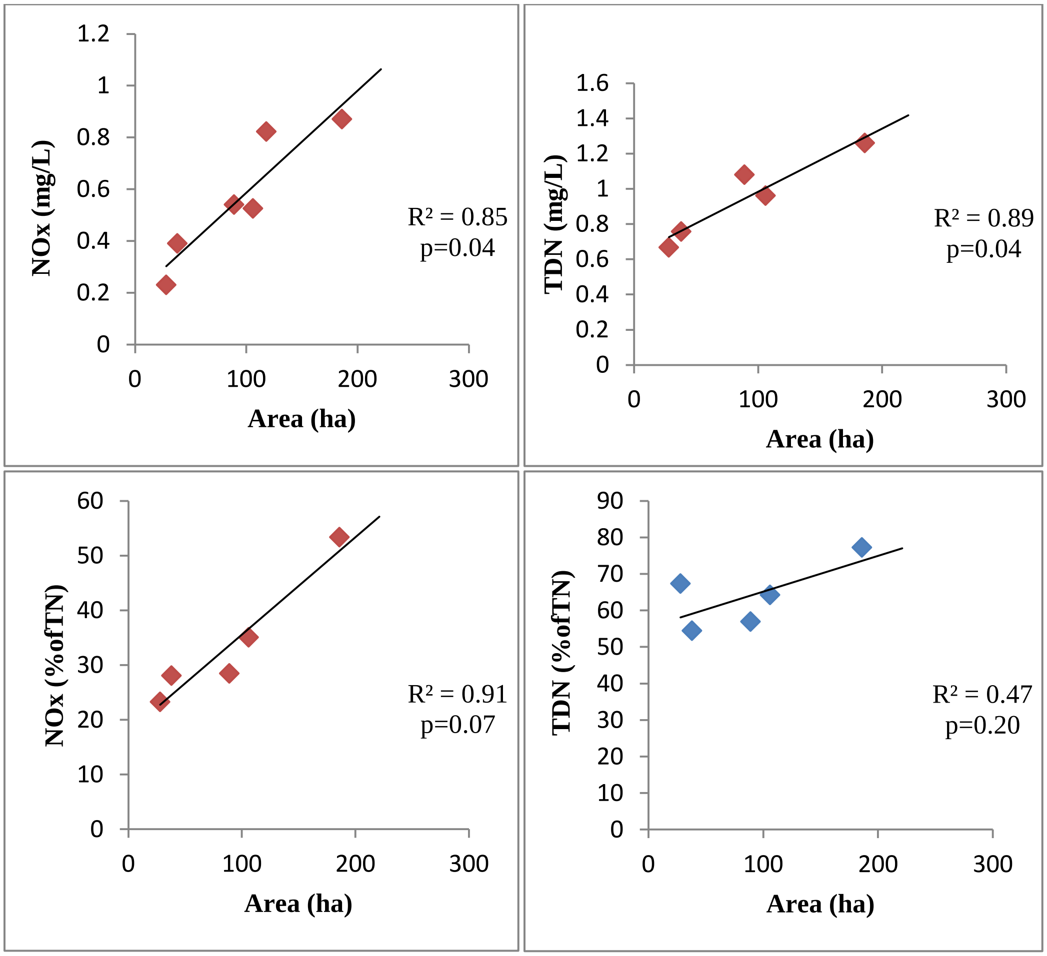


**Figure 5.9** Regression relationships between catchment area (ha) and nutrient concentrations of $NO_x$ and TDN, and regressions between area and the percentage of $NO_x$, TDN and TPN in TN.

### 5.4.4 Influence of surface imperviousness

It can be seen that the impervious percentage significantly influences DON and TP concentrations, as shown in Figure 5.10. The source of DON is most likely the leaching of decomposing vegetation that has accumulated on impervious surfaces. The vegetation includes debris such as leaves, woody twigs, branches and other garden waste. One of the methods of DON production is most likely from the breakdown of accumulated *in-situ* organic matter (Taylor, 2006). The role of impervious surfaces in affecting N concentrations is supported by the work of (Arnold_Jr and Gibbons, 1996). When DON is produced from decaying vegetative debris, it does not infiltrate the soil if it is on impervious surfaces, and is instead conveyed in stormwater. TP in stormwater is most likely derived from excess fertilizers sourced from gardens and lawns, and also from pets and detergents (Kelsey et al., 2010), as well as the transport of sediments from impervious surfaces. Therefore, impervious surfaces operate by accumulating organic and surface pollutants and, while not allowing losses through seepages into soils, act as efficient transporters serving to convey surface pollutants such as DON and TP through the system.

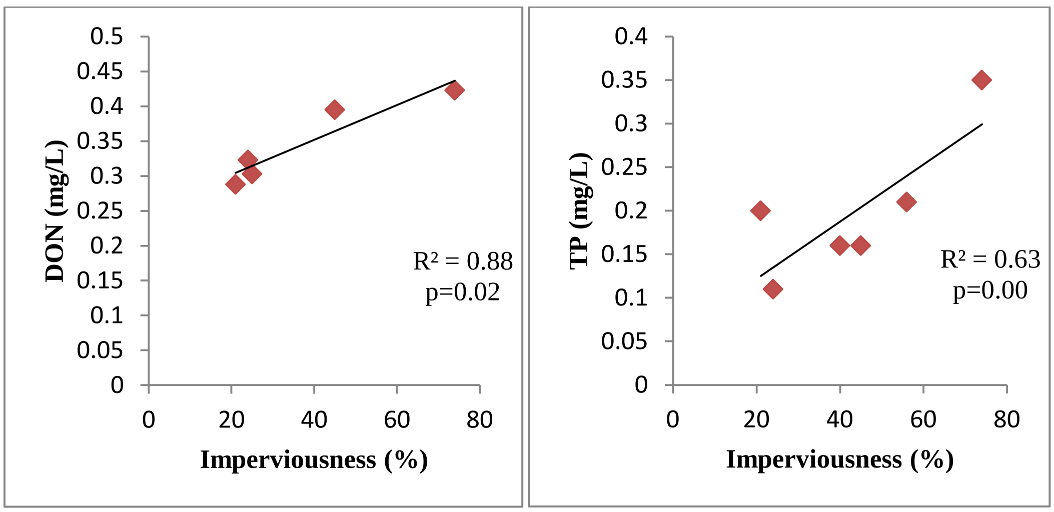


**Figure 5.10** Regression relationships between nutrient species and percent imperviousness. DON, dissolved organic nitrogen; TP, total phosphorus.

### 5.4.5 Influence of bedrock hydraulic conductivity

Figure 5.11 shows that the sub-surface hydraulic conductivity ($K_s$) within a catchment significantly influences both DON concentrations and DON as a fraction of TN. A higher $K_s$ favours the transport of DON, but it is noteworthy that $K_s$ does not influence other nutrient species. Given that stormwater derives primarily from impervious surfaces, it is perhaps not surprising that underlying soil permeability is less important. DON is a surface-sourced pollutant, sourced most likely from decomposing vegetation such as leaf litter and debris produced from the decomposition of accumulated vegetation. Although it tends to be retained in clayey soils through ionic attraction, in media with higher $K_s$ which contains less clay and more quartz, there is less DON retention. It may therefore be the case that leaching of water from soils of high $K_s$ into the stormwater system during storms brings with it elevated concentrations of DON.

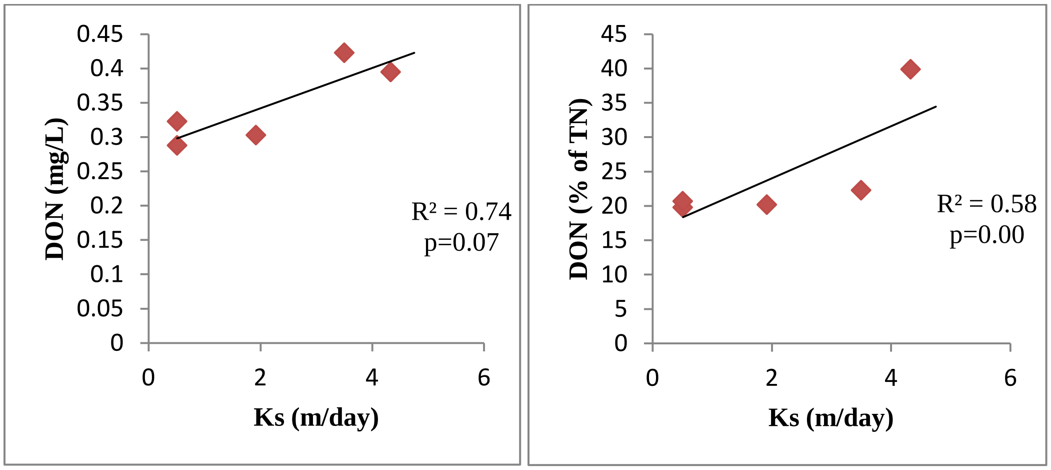


**Figure 5.11** Regression relationships between dissolved organic nitrogen (DON) with soil and bedrock hydraulic conductivity ($K_s$).

### 5.4.6 Influence of average catchment slope

It is surprising to find that average slope has a significant inverse influence on TN concentrations, and moderately influences TPN and $NO_x$ concentrations (Figure 5.12). This finding suggests that urban stormwater may have contributions from shallow groundwater (other sources) or throughflow processes (some stormwater taking alternate pathways, like through porous soils and fractured bedrock), which are likely to have high levels of $NO_x$, as discussed in Chapter 4. Stormwater from steeper slopes comprises relatively more impervious runoff and less subsurface contributions. Flatter slopes tend to have more rainwater infiltrating the soil and generating more groundwater flows, since flat land produce less runoff than rolling and steep sloping land (Poullain, 2012). Gentler slopes also require longer travel times for stormwater, allowing more ingress of groundwater which carries higher TN concentrations to the drainage system, since groundwater contributions of nutrients can be significant – particularly for nitrate (Dubrovsky and Hamilton, 2010) A likely explanation is that a less steep slope contributes to a higher water residence time in the catchment when the effects of bacterial activity (the oxidizing type) may be seen.

In Figure 5.12, it can be seen that the fraction of TN that is DON is moderately influenced by the average slope, although this relationship is highly skewed by a single point.

The observed relationship also differs to that of TPN, which appears to have a slight negative relationship with slope (albeit non-significant). It is thus unclear from these data what the influences on the mobilisation and transport of organic nitrogen are.

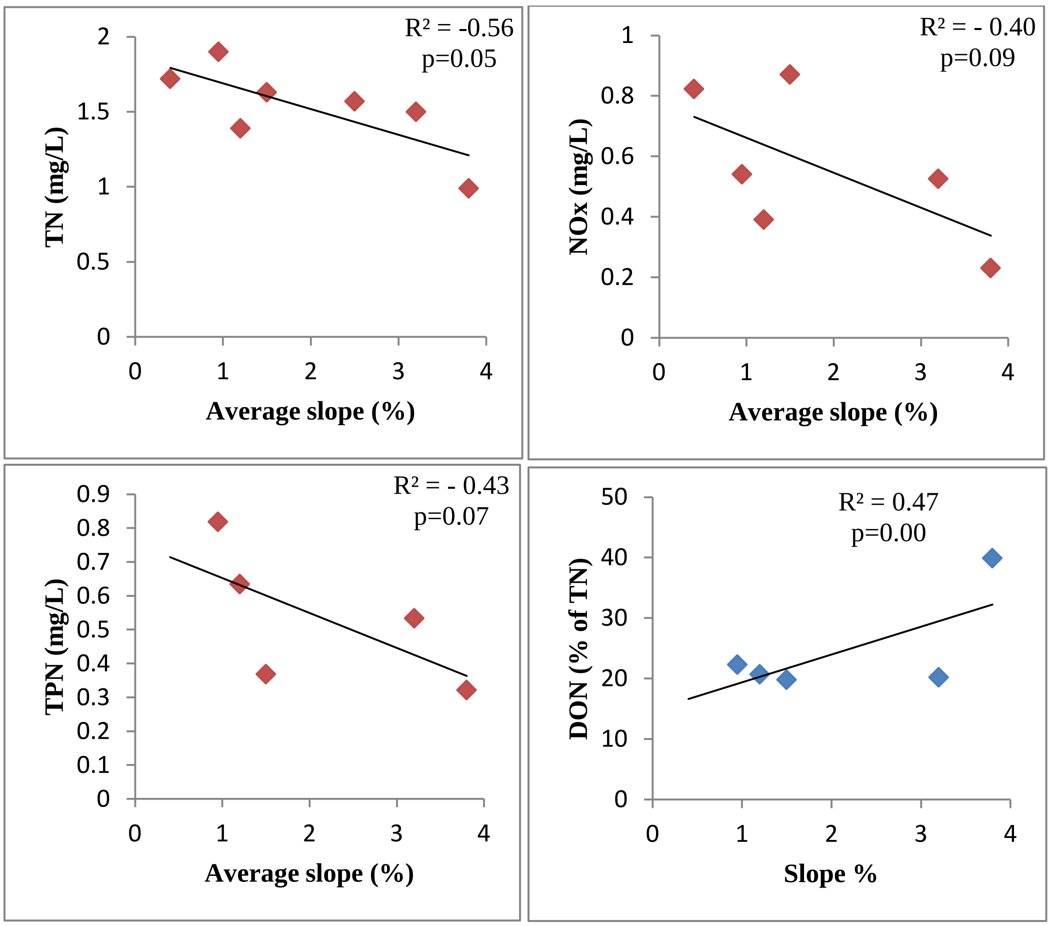


**Figure 5.12** Regression relationships between nutrient species and Average slope %. TN, total nitrogen; $NO_x$, nitrogen oxides; TPN, total particulate nitrogen; DON, dissolved organic nitrogen.

### 5.4.7 Influence of average year of stormwater infrastructure construction

Figure 5.13 shows that the year of stormwater infrastructure construction has significant inverse influences on TPN, DON, TP and FRP concentrations during wet weather. It has been recognised that nutrients in runoff are more problematical in historic cities that have old and failing infrastructure (Shepherd et al., 2006). Therefore, older catchments with a longer legacy of urbanisation where nutrients have accumulated and ageing wastewater infrastructure, tend to produce more nitrogen and phosphorus concentrations, possibly from sewer leaks or other cross connection. Similarly, if there is a contribution from leaking sewers, it has been found that the pollutant loads of stormwater are significant but the hydrocarbons and heavy metal concentrations associated with settled solids from a separate stormwater network are lower than the concentrations measured in solids sampled in detention tanks situated on a combined sewer system (Jacopin et al., 1999). At an experimental catchment in Paris it was found that the organic layer at the water-sediment interface in the (combined) sewer is the main source of wet weather flow pollution for suspended solids, volatile solids, particle-bound COD and BOD, and copper (Chebbo and Gromaire, 2004). Recent studies in Paris have found that entry-exit mass totals at the scale of all catchments and for a large number of rain events indicate that wastewater constitutes the primary source of organic and nitrogenous pollution (Gasperi et al., 2010). While these studies are of combined sewers, the higher N and P concentrations associated with older infrastructure and catchments appear to implicate wastewater sources from failing sewer infrastructure. However, it must be noted that the observed relationships in this study are fairly limited, because most of the catchments are of a generally similar period, with one catchment being much older (dating back to the 1920s).

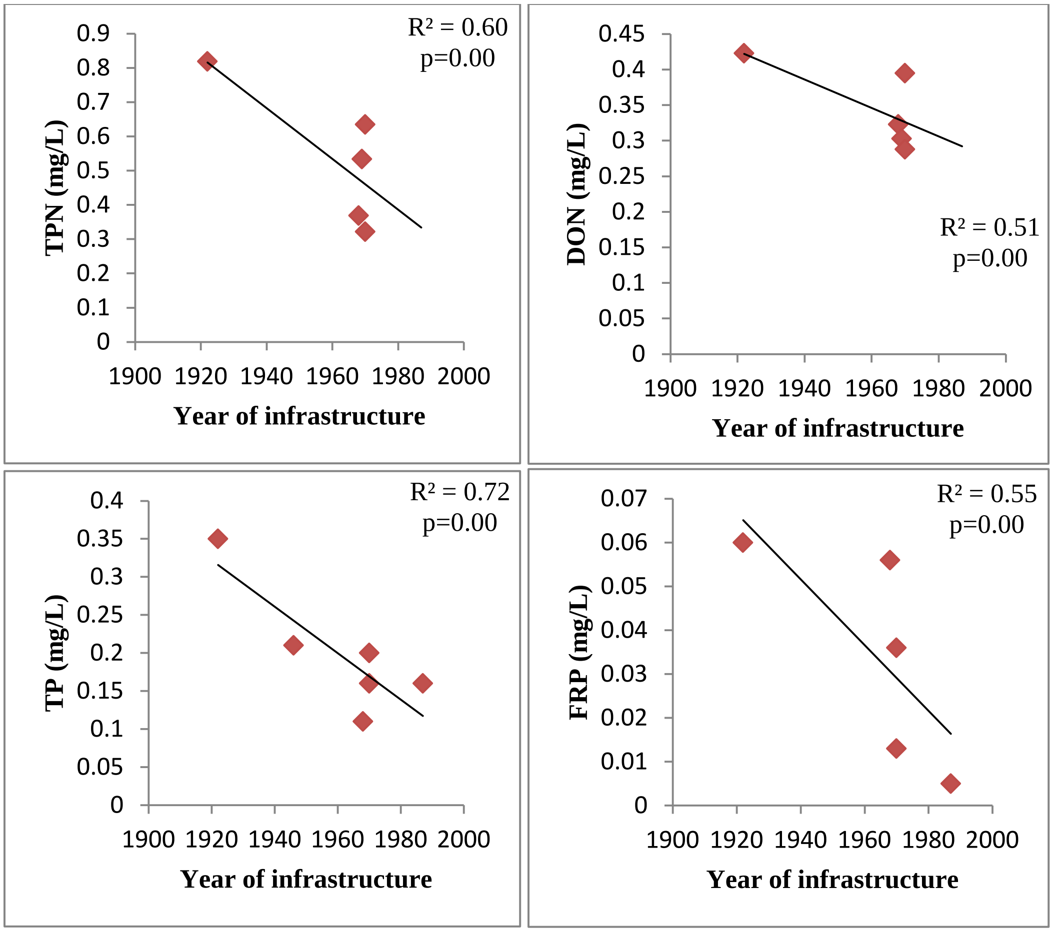


**Figure 5.13** Regression relationships between nutrient species and year of infrastructure. TPN, total particulate nitrogen; DON, dissolved organic nitrogen; TP, total phosphorus; FRP, filterable reactive phosphorus.

### 5.4.8 Correlation between catchment characteristics

Graphs of correlation between some catchment characteristics are shown in Figure 5.14, where the year of infrastructure correlates strongly with the impervious percentage, while population correlates moderately with the year of infrastructure. These correlations provide some explanation for the nutrient relationships observed. For example, imperviousness was found to influence wet weather concentrations of DON and TP, while infrastructure age also influenced TP and DON concentrations (along with TPN and FRP). Perhaps unsurprisingly, older catchments tend to be those that are (now) more densely populated (being the inner suburban catchments). It is thus difficult to tease out the relative contribution of each of these measures, given the relatively small number of data points and their relatively discontinuous distribution (at least for infrastructure age). Similarly, the relationship between infrastructure age and catchment population suggests that the observed influence of population on nutrient concentrations may be affected to some extent by the co-correlation with infrastructure age. Unfortunately, the relatively small number of data points (seven) means that trying to tease these out with techniques such as multiple regression or hierarchical partitioning (Chevan and Sutherland, 1991) is not possible.

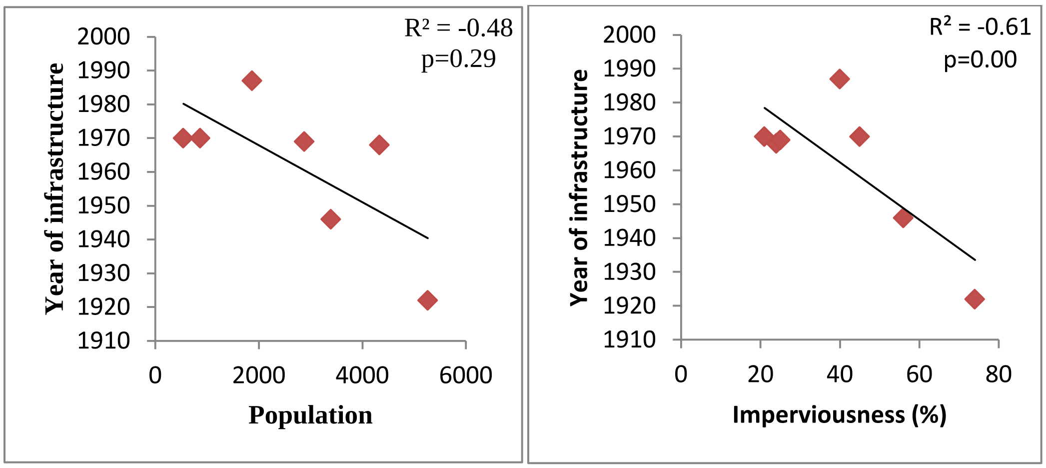


**Figure 5.14** Correlations between year of infrastructure installation and population, and imperviousness.

## 5.5 Conclusions

A compilation of wet weather nutrient data indicates that the average TN and TP concentrations exceed the ANZECC (2000) default trigger values and, together with high TDN, TPN and $NO_x$ concentrations, are a concern for the environment.

An analysis of the composition of nitrogen species in TN reveals that on average, one third is $NO_x$, one third is TPN and the other one third comprises DON and $NH_3$. As a comparison, TN levels in Melbourne are lower than those in the USA, however the proportion of $NO_x$ in TN in both Melbourne and the USA are similar, possibly implying similarities in origin.

The analysis of catchment characteristics that influence the concentrations of different nutrient species are summarised in Table 5.5.

**Table 5.5** Summary of significant regression relationships between nutrient species and catchment characteristics. +, nutrient concentration increases with the catchment characteristic; -, nutrient concentration decreases as the catchment characteristic increases.

| **Catchment characteristic** | **Significant regressions ($R^2$>0.5)** | **Possible causes** |
|---|---|---|
| Population | TN (+), TDN (+), FRP (+) | Nutrient loading |
| Population density | TPN (+), TP (+), FRP (+) | Nutrient loading |
| Year of Infrastructure | TPN (-), DON (-), TP (-), FRP (-) | Nutrient loading, possibly from leakages |
| Area | TDN (+), $NO_x$ (+), $NO_x$ % (+) | Nutrient loading: Area increases $NO_x$ supply |
| Impervious % | DON (+), TP (+) | DON, TP sourced from impervious surfaces. DON sourced from decomposing vegetation |
| $K_s$ | DON (+), DON% (+) | DON is transported in high $K_s$ media |
| Slope | TN (-) | Steeper slope results in reduced subsurface processes and leakage input |

The following conclusions can be drawn:

**TN** is significantly influenced by population, and inversely by slope. Population affects nutrient loading, while the steep slope may reduce inputs from infrastructure leakage and subsurface leaching.

**TDN** is significantly influenced by population and catchment area, factors that affect nutrient loading and supply.

**$NO_x$** is primarily controlled by the size of catchment area, a factor that affects *nutrient loading* through modifying transport distances and thus opportunities for nitrification of organic nitrogen. Urbanisation represents a departure from previous forest cover, with lower nutrient loading, to the current higher nutrient loading and soils with oxidising conditions. The larger catchment areas tend to leach more $NO_x$, most likely as a result of conversion of organic nitrogen to $NO_x$ along the drainage pathways to the receiving waters.

**TPN** is strongly controlled by population density and year of infrastructure, factors which contribute to the input of TPN, with older infrastructure being more problematic, possibly because of sewer leaks, other cross connections (a potential source of particulates) and the likely permeable nature of the stormwater infrastructure (allowing input from other water sources).

**DON** is significantly related to year of infrastructure, imperviousness, and hydraulic conductivity since DON concentrations are affected by leaky infrastructure, efficient delivery system, and the rate of transport, respectively.

**FRP** is strongly associated with population, population density, and year of infrastructure, characteristics which contribute to nutrient loading, as previously discussed.

**TP** is strongly affected by population density, year of infrastructure, and imperviousness, factors which affect nutrient loading.

The factors that control urban wet weather nutrient concentrations are complex and, of course, inter-related. Catchment characteristics of population, population density, age of infrastructure, and area influence concentrations of particular nutrient species by influencing nutrient loading. Other factors such as hydraulic conductivity affect only DON and surprisingly, slope inversely controls TN concentrations. A possible explanation is that slope affects the detention time of stormwater and thus influences the opportunity for leaching of resident sources. The age of infrastructure strongly correlates with both population and imperviousness, meaning that the influences of these factors on nutrient concentrations in wet weather are to some extent co-correlated. Unfortunately, a larger dataset would be needed to tease out these individual relationships.

In this study, the larger, older catchments (which have older infrastructure and relatively high population density) tend to be problematic. Higher DON concentrations are likely sourced from decomposing vegetation decaying on impervious surfaces, as well as from wastewater inputs, and high $K_s$ facilitates DON transport through soils. Steeper slopes tend to produce lower TN concentrations by potentially reducing the relative impact of leaching of in-situ sources within the catchment. However, this observation remains surprising and is an important area for future research.

Nutrient concentrations for all nutrient species are variable between catchments. The SMCs for N and P, although generally low, still exceed the recognised chemical concentrations that can cause ecological stress for receiving waters. The average composition of nutrient species from all sites shows that dissolved nitrogen forms two thirds of the total, meaning that treatment systems targeting wet weather flows must be designed to promote the processes and detention time necessary for treatment of dissolved nitrogen. Half of TDN comprises the $NO_x$ fraction, while the other half of TDN comprises DON and $NH_3$. Three residential catchments show remarkable similarity in the proportions of N species composition, although the actual N species concentrations are different. A possible explanation is that the relative proportion of the sources and transformation processes in these three catchments are similar. The importance of year of infrastructure shows significant inverse relationships with TPN, DON, TP and FRP, suggesting that leaking stormwater and wastewater infrastructure may combine to result in elevated wet weather nutrient concentrations. The size of the catchment area strongly influences $NO_x$, $NO_x$ as a fraction of TN, and TDN. The inference is that larger catchments tend to produce more nitrites and nitrates, possibly by allowing sufficient retention space and time for oxidation and nitrification processes. Impervious surfaces significantly influence DON and TP concentrations, both of which are surface-sourced pollutants. DON is likely sourced from the leaching of decaying vegetation trapped on impervious surfaces, whereas TP is likely sourced from garden fertilizers and washing detergents. Not surprisingly, hydraulic conductivity of catchment soils is less important, given the dominant role of impervious surfaces during weather. However, the surprising negative influence of slope remains an important knowledge gap.

Wet weather nutrient concentrations in stormwater are therefore controlled by some catchment characteristics which particularly affect nutrient loading, whereas other characteristics influence retention times and rates of transport, thus influencing the measured concentrations within the waterway.

Wet weather pollution abatement should firstly aim at the reduction of nutrients at source, such as renovation of old infrastructure, and the application of treatment technologies designed for the removal of dissolved nutrient forms, in particular. Even during wet weather, these dissolved forms dominate, meaning that treatment technologies relying on particulate removal alone will not be adequate.

Despite the extensive datasets compiled for this analysis, it is apparent that the relationships between catchment characteristics and nutrient concentrations and composition are multi-factorial and interactive. Very large datasets or targeted research are thus required to enable the individual and joint contributions of each factor to be quantitatively assessed.

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# Chapter 6: Comparison between dry and wet weather

## 6.1 Introduction

In Chapters 4 and 5, the behaviour and influences on nutrient concentrations in dry weather and wet weather were presented and discussed. In this chapter, comparisons are made between the dry weather and wet weather concentrations and their composition (in terms of the nutrient species). The factors influencing these comparisons are also discussed.

## 6.2 Comparison of dry and wet weather concentrations

**Question: What are the differences/similarities in nutrient concentrations in wet weather and dry weather (and why do such similarities and differences occur)?**

The aim of this section is to compare nutrient concentrations between dry weather and wet weather and to briefly discuss differences and similarities. A comparison of the dry and wet weather average nutrient concentrations from the Melbourne catchments studied is given in Figure 6.1.

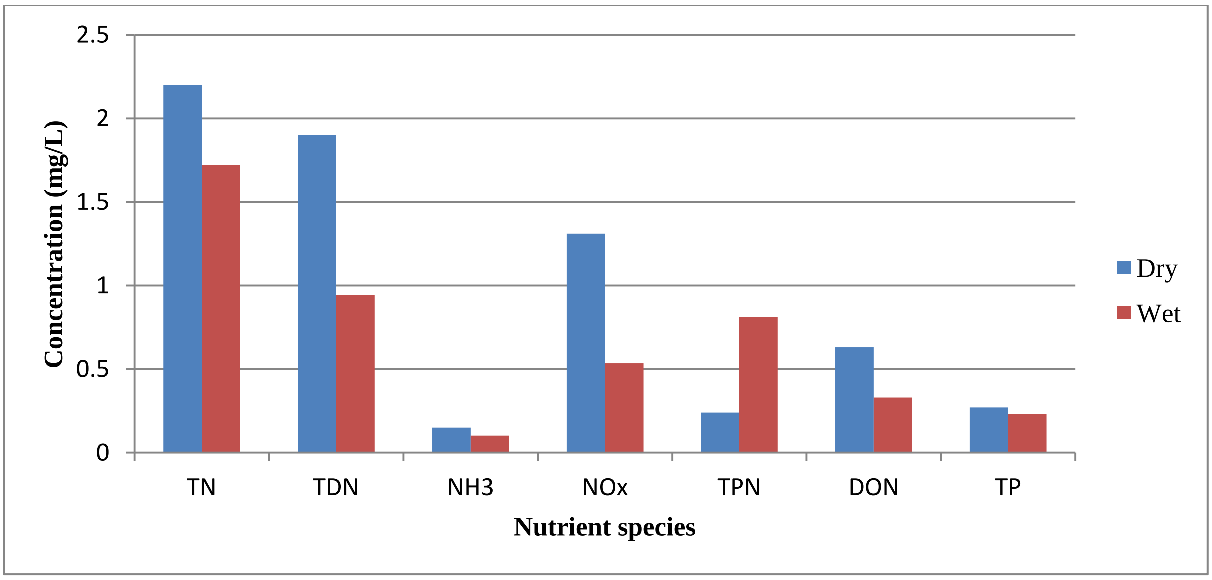


**Figure 6.1** Comparison of dry and wet weather mean nutrient concentrations for Melbourne catchments studied. FRP (TDP) data are insufficient to present a comparison.

In dry weather and in wet weather, the concentrations of $NH_3$ and TP are similar, whereas the dry weather concentrations of TN, TDN, $NO_x$ and DON are significantly higher than those seen in wet weather. The FRP (TDP) data are insufficient to provide a comparison. The dry weather TPN concentration is significantly lower than in wet weather.

These observed differences are attributed to the very different pathways that the bulk of water flows in dry and in wet weather. In wet weather, there is a high proportion of contribution from impervious (and less frequently, pervious) runoff, whereas in dry weather, the primary contribution is from sub-surface flow processes, or by external sources, such as leaking wastewater. In dry weather, there are likely proportionally higher impacts of interactions with infrastructure, such as wastewater and water supply pipes. Dry weather flows are thus filtered through soils except where wastewater pipes connect into the stormwater network, while surface runoff is conveyed through channels, pipes and other drainage systems (or as direct overland flows). These differences in pathways account for, in dry weather, the much lower concentration of particulates (e.g. TPN), as flow through soil and bedrock filters out particulates, while potentially allowing or even augmenting the passage of higher concentrations of dissolved nutrient species such as TDN, $NO_x$ and DON. Indeed, the flow through subsurface pathways may also mobilise and transport soluble forms of nitrogen, such as $NO_x$ produced from bacterial nitrification in oxidising conditions (Meyer et al., 2000; Oms et al., 2000), or residual nitrogen from past land uses.

## 6.3 Comparison of dry and wet weather compositions

**Question: What are the differences/similarities in nitrogen compositions in wet weather and dry weather (and why do such similarities and differences occur)?**

The composition of nutrient species is compared between wet weather and dry weather flow conditions in Figure 6.2.

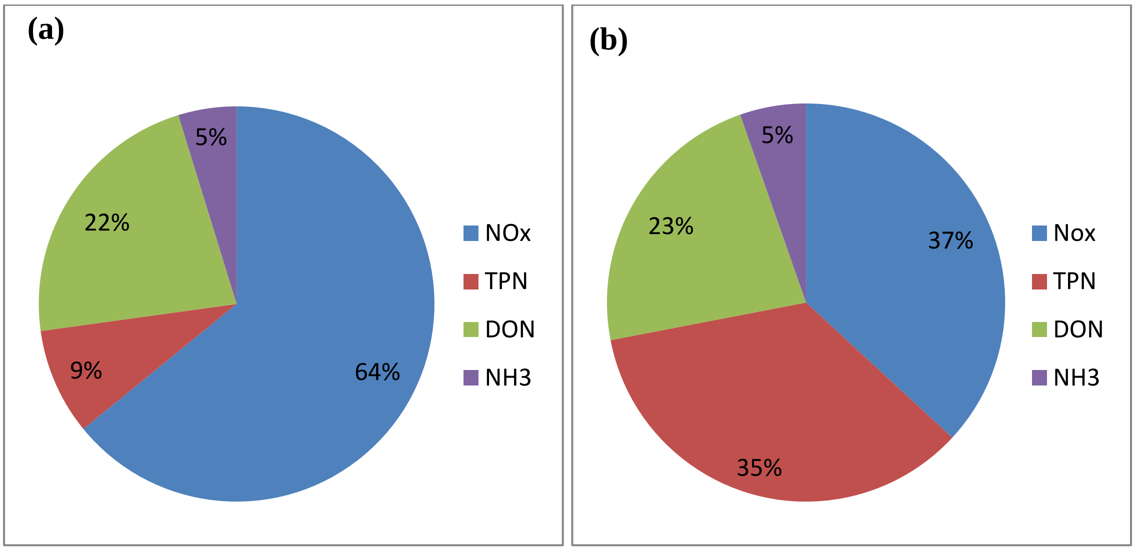


**Figure 6.2** Comparison of (a) dry and (b) wet weather N compositions.

The contribution of DON and $NH_3$ proportions to TN remains relatively constant between dry and wet weather. However, the contributions of $NO_x$ and TPN vary quite substantially. In dry weather, the percentage of $NO_x$ of TN is much higher than in wet weather; whereas the percentage of TPN of TN is much lower than in wet weather. These results differ from those of Taylor et al. (2005), who observed larger variations in DON between baseflow ($\mu$=36%) and stormflow ($\mu$=28%) (Taylor et al., 2005). Taylor et al. (2005) observed that the proportion of $NO_x$ was similar during dry weather (39%) and wet weather (36%). The higher DON % of TN in Taylor et al., 2005 compared to this study for dry and wet weather could possibly be due to more industrial catchments, higher surface imperviousness and higher bedrock hydraulic conductivity. The higher $NO_x$ of TN found in this study compared to that in Taylor et al., 2005 for dry weather is likely due to the catchments having deeper soil and subsurface pervious media.

The difference in the proportion of TPN during wet and dry weather is likely due to the difference in flow energy, with the faster, turbulent flow seen in wet weather transporting a higher proportion of TPN (35% of TN) as compared to that in dry weather (9% of TN) when flow is much more subdued, and when mobilisation of surface material is unlikely. Particulate forms of nutrients are more significant as a function of the strength of stormwater flow which has the power to erode and suspend sediments in its turbulent path, as has been shown by many studies (Sartor et al., 1974; Chiew and McMahon, 1997; Kanso et al., 2003). The decreased *proportion* of dissolved pollutants is therefore primarily a mathematical result of the increased particulate contribution during wet weather. It is also possible that during dry weather, $NO_x$ results from the nitrification of organic matter, as a result of biodegradation of particulate nitrogen deposited during storm events.

## 6.4 Comparison of the influence of catchment characteristics during dry and wet weather

**Question: What are the differences/similarities in the factors influencing concentrations and composition, in wet weather and dry weather? Why do these occur?**

As described in Chapter 3, the catchment characteristics studied were: land-use, catchment population, catchment population density, catchment area, imperviousness, the age of infrastructure, hydraulic conductivity of catchment bedrock, and catchment slope. Tables

6.1 to 6.8 summarise the observed relationships between these parameters and nitrogen concentrations and composition during dry weather (from Chapter 4) and wet weather (Chapter 5).

### 6.4.1 Influence of land-use

The influence of two types of land-uses on nutrient concentrations was studied and the results are given in Table 6.1.

**Table 6.1** Influence of land-use on nutrient concentrations in dry and wet weather, their similarities, differences, and likely reasons for their behaviour.

| Influence during dry weather | Influence during wet weather | Similarities/Differences & reasons for nutrient behaviour |
|---|---|---|
| Concentrations of TN, TDN, $NO_x$, TPN & DON from residential catchments are significantly higher than those from industrial catchments. No significant differences are seen for $NH_3$ & TP. | Concentrations of TN are significantly higher from residential catchments as compared to industrial catchments. TP concentrations from residential catchments are similarly higher than from industrial catchments. | TN concentrations are influenced in a similar way for both residential and industrial catchments. TP concentrations are similarly influenced as TN concentrations in wet weather, but differently in dry weather. The type of land-use thus affects nutrient concentrations both in dry and wet weather. Residential landuse is likely to contribute greater sources of nutrients due to factors such as use of fertilisers (Water_Encyclopedia, 2013), potential for wastewater leaks or cross-connections (eHow, 2013), and potentially greater pervious area contributions. In contrast, the industrial catchments tend to be highly impervious, with less potential for subsurface contributions. |

### 6.4.2 Influence of catchment population

The influence of catchment population on nutrient concentrations is summarised in Table 6.2.

**Table 6.2** Influence of catchment population on nutrient concentrations in dry and wet weather, their similarities, differences, and the reasons for their behaviour.

| **Influence during dry weather** | **Influence during wet weather** | **Similarities/Differences & reasons for nutrient behaviour** |
|---|---|---|
| Catchment population has positive influences on the concentrations of most nutrient species, specifically: TN, TDN, $NO_x$, TPN, DON and TP. However, the catchment population density is the more important variable and these results have to be read with caution. | Catchment population significantly influences concentrations of TN, TDN and FRP. However, the population density is the more acceptable variable, and these results are to be taken with caution. | There is no obvious mechanistic link between catchment population and nutrient concentrations. It is possible that the apparent relationship between catchment population and nutrient concentrations is confounded by land-use, in that the higher catchment populations are residential catchments and the lower catchment populations are industrial catchments, as noted above. |

### 6.4.3 Influence of catchment population density

The influence of catchment population density on nutrient concentrations is summarised in Table 6.3.

**Table 6.3** Influence of catchment population density on nutrient concentrations in dry and wet weather, their similarities, differences, and the reasons for their behaviour.

| Influence during dry weather | Influence during wet weather | Similarities/Differences & reasons for nutrient behaviour |
|---|---|---|
| No significant correlations. | | The range of population densities in the study catchments is relatively small, reducing the potential to observe a relationship. |
| | Catchment population density significantly positively influences concentrations of TPN, TP and FRP. | It is possible that the lower population densities in industrial catchments contribute to the lower concentrations of dissolved nitrogen. Residential catchments are more likely to have sources of particulate pollutants, including vegetative material and soils (Wetern_Australian_Government, 2000; USEPA, 2003). |

### 6.4.4 Influence of catchment area

The influence of catchment area on nutrient concentrations is given in Table 6.4.

**Table 6.4** Influence of catchment area on nutrient concentrations in dry and wet weather, their similarities, differences, and the reasons for their behaviour.

| Influence during dry weather | Influence during wet weather | Similarities/Differences & reasons for nutrient behaviour |
|---|---|---|
| Catchment area significantly positively influences TN, TDN, and DON concentrations. | Catchment area significantly positively influences concentrations of $NO_x$, $NO_x$ (as a % of TN) and TDN. | This observation is most likely an artefact of the fact that the small catchments generally have industrial land use, while the larger catchments contain residential land use. Dissolved nitrogen was found to be higher in residential catchments. |

### 6.4.5 Influence of surface imperviousness

**Table 6.5** Influence of imperviousness in dry weather and wet weather, their similarities, differences, and the reasons for their behaviour.

| Influence during dry weather | Influence during wet weather | Similarities/Differences & reasons for nutrient behaviour |
|---|---|---|
| Catchment imperviousness significantly negatively influences TPN, $NO_x$, TDN and DON. There is no influence on TN. | Catchment imperviousness is found to have no influence on TN. | Several factors may explain this observation. Firstly, the most impervious catchments are those with an industrial land use. It is these catchments which exhibit the lowest dissolved nutrient concentrations. Imperviousness most likely limits supply of water and nutrients to groundwater, hence producing lower dry weather concentrations of some nitrogen species. Despite the obvious negative influence of impervious areas to hydrology and water quality, the mechanisms that cause water quality degradation in dry weather by urbanisation are poorly understood. |
| | Imperviousness significantly positively influences DON and TP concentrations. | The contrasting behaviour between dry and wet weather is somewhat confounding. It is likely that increased impervious area contributes to the hydraulic efficiency of drainage pathways, thus increasing the transport of particulate pollutants. The reason why DON would be increased in these catchments is less clear, given that other dissolved forms of N do not show this relationship. It is hypothesised that the increase in DON could be a result of contaminants resulting from varying activities in residential and/or industrial areas. |

### 6.4.6 Influence of the age of stormwater infrastructure

The influence of the age of stormwater infrastructure on nutrient concentrations is given in Table 6.6.

**Table 6.6** Influence of the age of infrastructure on nutrient concentrations in dry and wet weather, their similarities, differences, and the reasons for their behaviour.

| **Influence during dry weather** | **Influence during wet weather** | **Similarities/Differences & reasons for nutrient behaviour** |
|---|---|---|
| The average age of infrastructure significantly negatively influences TDN, TP, and DON. | The average age of infrastructure has significant inverse influences on TPN, DON, TP and FRP. | The dry weather data shows that older infrastructure provides a higher input of nutrients, particularly phosphorus and dissolved nitrogen, most likely from leaky sewers. The wet weather result implies that there are possible leakages from older infrastructure (primarily from wastewater) to the drainage system, the same for wet and dry. |

### 6.4.7 Influence of bedrock hydraulic conductivity

The influence of bedrock hydraulic conductivity on nutrient concentrations is summarised in Table 6.7.

**Table 6.7** Influence of hydraulic conductivity of soils on nutrient concentrations in dry and wet weather, their similarities, differences, and the reasons for their behaviour.

| **Influence during dry weather** | **Influence during wet weather** | **Similarities/Differences & reasons for nutrient behaviour** |
|---|---|---|
| Hydraulic conductivity of the catchment soils significantly influences nutrient species: $NO_x$, TDN, and TPN | | In dry weather, it is most likely that soils with higher hydraulic conductivities (such as Tertiary gravel and fractured basalt) provide more efficient and faster groundwater pathways for $NO_x$ and other forms of dissolved nitrogen. It is less clear why particulate N would be higher in such catchments. |
| | Hydraulic conductivity significantly positively influences DON and DON (as a % of TN), and no other nutrient species. | In wet weather, a surface-sourced nutrient such as DON is strongly influenced by hydraulic conductivity. This could suggest a flushing of DON from soils during wet weather periods. |

### 6.4.8 Influence of catchment slope

The influence of catchment slope on nutrient concentrations is summarised in Table 6.8.

**Table 6.8** Influence of catchment slope on nutrient concentrations in dry and wet weather, their similarities, differences, and the reasons for their behaviour.

| Influence during dry weather | Influence during wet weather | Similarities/Differences & reasons for nutrient behaviour |
|---|---|---|
| Catchment slope strongly influences $NH_3$ concentrations. | Catchment slope has a significant inverse influence on TN. | The fact that only $NH_3$ was found to have a significant relationship with slope during dry weather is curious; it would be expected that other dissolved forms of nitrogen would behave similarly.<br>The wet weather correlation with TN is explained by steeper slopes providing a more efficient transport pathway. Again, however, the results are not consistent. |

## 6.5 Conclusions

There is a distinct contrast in the behaviour of dissolved and particulate nutrients during both dry and wet weather. This difference is attributed to the differing pathways that water takes in dry and wet weather, and to the respective effects of these pathways on particulate and dissolved forms of nitrogen. In dry weather, nutrients are mainly composed of dissolved species (91%) and less of particulate species (9%), whereas in wet weather dissolved N reduces to 65% whereas nutrients associated with particulates increase to 37%. The difference in composition is due to the different pathways that water takes in dry and wet weather. In wet weather, surface runoff occurs with higher energy, capable of transporting more particulates, whereas in dry weather, flow is through the sub-surface pathways, thus interacting with soils and underground infrastructure.

Residential land-use contributes higher nutrient concentrations than industrial landuse, both in dry and wet weather. In dry weather, the nutrient species influenced are more varied, implying that the sources are more varied, from the land surfaces as well as the sub-surface media. A higher population density in wet weather contributes to a higher loading of TPN, TP and FRP, whereas no correlations are found for dry weather since there is insufficient variation in the population densities to reveal a finding.

In wet weather, it is inferred that DON is contributed by a range of surface-related sources, including from the flushing of decomposing vegetation trapped on impervious surfaces, whereas TP is most likely generated by the transport of sediments in the catchment. Imperviousness influences the wet weather concentration of surface-derived nutrients such as DON and TP, implying that surface loading in wet weather is important. However, imperviousness has an inverse influence on dry weather nutrient concentrations. With increasing imperviousness, dry weather dissolved concentrations are decreased, suggesting that the decreased infiltration may result in reduced release of dissolved nutrients from subsurface pathways. Despite the obvious negative influence of impervious areas to hydrology and water quality, the mechanisms that cause water quality degradation in dry weather by urbanisation are poorly understood.

In dry weather, it is most likely that soils with higher hydraulic conductivities (such as Tertiary gravel and fractured basalt), being more porous than soils with lower hydraulic conductivities (e.g., the Silurian Mudstone), provide more efficient and faster groundwater pathways for dissolved nutrient forms such as $NO_x$. In wet weather, a surface-sourced nutrient such as DON is strongly influenced by hydraulic conductivity.

In dry weather, slope significantly affects $NH_3$ concentrations, implying a steeper slope provides a faster transport mechanism for $NH_3$ (before its eventual conversion to nitrate), whereas no correlations for the other nutrient species were found for catchment slope.

In summary, the relationship between catchment characteristics and the concentration and composition of nutrients is complex, varying with flow conditions (dry weather vs wet weather), as well as with land use, catchment geology and other catchment characteristics. The complexity makes prediction of nutrient concentrations difficult, but importantly demonstrates that simplistic approaches to inferring likely concentrations based on flow or catchment characteristics are unlikely to be very accurate.

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# Chapter 7: Implications for urban runoff management

## 7.1 Introduction

This chapter summarises the factors affecting nutrient concentrations in urban runoff, and discusses the implications of these findings to runoff management practices with recommendations for remedial action to arrest nutrient problems.

## 7.2 Impacts of catchment characteristics on nutrient behaviour

**Land use** is found to have an impact on dry weather nutrient behaviour. Nitrogen concentrations from residential catchments are significantly higher than from industrial catchments, whereas phosphorus concentrations are similar between the two land uses. This finding differs from results found for wet weather flow which do not identify land use as a significant driver of nitrogen concentrations, although in part this observation results from high levels of variation in concentrations within each land use (Duncan, 1999). In this study, it was found that residential land use tends to produce more nutrients than industrial land use.

In dry weather, **catchment population and area** have significant positive influences on most nutrient concentrations, whereas increasing **imperviousness** decreases nutrient levels. These factors are likely to interact with land use, although the size of the dataset precludes statistical separation of these interactions. Despite the obvious negative influence of impervious areas on hydrology and water quality, the mechanisms that cause water quality degradation by urbanisation are complex.

The concentrations of some nitrogen species are positively influenced by **catchment hydraulic conductivity**, suggesting that subsurface flow pathways and leaching of soil nitrogen may play an important role. The **catchment age and slope** influence dry weather concentrations to a lesser extent. **Older catchments** discharge higher levels of phosphorus and dissolved nitrogen, and **steeper catchments** deliver higher ammonia concentrations.

Clearly, **nitrogen loading** is determined by catchment characteristics such as population and area and increases with the intensity of urbanisation. This is not only a product of current anthropogenic loading rates, but past land use legacies can be a significant contributor to the current nutrient concentrations. For example, the loss of forest cover contributes to significant long-term leaching of soil nitrogen, particularly nitrogen oxides. This situation is made more acute with old, leaky infrastructure, leading potentially to contributions from wastewater, or mobilisation of in-situ sources by subsurface contributions of potable water. Indeed, the **year of infrastructure** is significantly inversely related to TPN, DON, TP and FRP, implying that older infrastructure is more problematical due to failures such as leaks or accidental cross-connections between sewer and stormwater drains.

**In wet weather**, the **catchment population** significantly influences TN, TDN and FRP, especially soluble nutrients, and the population density strongly influences TPN, TP and FRP.

**Impervious areas** significantly influence DON and TP. It is hypothesised that DON is sourced from decaying organic matter, whereas TP is from a number of sources such as garden fertilizers and detergents. Impervious areas and the piped network serve as efficient transport mechanisms.

**Catchment hydraulic conductivity** influences DON and DON% of TN, implying a faster rate of subsurface flow, facilitates DON transport. Hydraulic conductivity in wet weather plays a minor role for other nutrient species studied since a high proportion of stormwater flow is surficial.

A surprising finding is that the **average catchment slope** significantly inversely influences total nitrogen. Steeper slopes reduce TN levels in stormwater runoff. The explanation is possibly because steeper slopes results in less water infiltrating soil and bedrock, generating less groundwater, which is implicated as the main source of TN contamination. However, the mechanisms explaining this observation remain unclear and require further research.

**Catchment characteristics** influence particular suites of nutrients. There are two categories of characteristics. The first category of factors defines **nutrient loading** (population density, year of infrastructure and percentage of imperviousness). The second category of factors includes catchment area, hydraulic conductivity and slope that influence the mechanisms of **retention, transformation and transport.**

## 7.3 Impacts of the weather on water and nutrient pathways

Melbourne has a moderate climate with mild springs (Sep-Nov, average range: 20-10$^{o}$C), warm to hot summers (Dec-Feb, average range : 25-14$^{o}$C), mild autumns (Mar-May, average range: 20-11$^{o}$C) and cool winters (Jun-Aug, average range: 14-7$^{o}$C) (BOM, 2013). Rain usually falls in winter and spring, and summers are usually relatively dry. In dry weather, the water table will be low and in wet weather it will be high. The depth of unsaturated soil contributes to the degree of soil oxidation. Unsaturated oxidised soils facilitate bacterial oxidation of any introduced organic matter, which is **transformed** to nitrogen oxides. Saturated soils in wet weather will slow down the nitrifying bacterial activity. Therefore, the pathway that water takes through soil will determine whether the water is loaded with nitrogen oxides. Dry weather flow is basically flow from groundwater (and potentially from leaking infrastructure), whereas stormwater runoff is made up of a greater proportion of surface flow than groundwater flow. In wet weather, the high water table produces less nitrogen oxides, whereas in dry weather, the lower water table tends to produce more nitrogen oxides.

In Melbourne, in dry weather, the water table is low, meaning that baseflow is primarily sourced mainly from groundwater flow. Groundwater flow is composed of delayed stormwater flow which has infiltrated the soil and bedrock. Water from leaky sewer pipes and water supply pipes can also be included in groundwater. Groundwater flow through oxidising media will typically be loaded with nitrogen oxides, nitrites and nitrates (Egboka, 1984) since nitrification involves *Nitrosomanas and Nitrobacter* species of bacteria and requires the presence of oxygen (Reddy and Patrick, 1984).

In a prolonged drought, much of the groundwater table will eventually drop below the drainage network, in which case there will be no flow. However, if leaky infrastructure continues to supply nutrients to the depressed groundwater, where oxidation converts organic matter to nitrogen oxides, its effect will find expression in the next storm event, when infiltrating rainwater will once again raise the groundwater table to supply water with nitrogen oxides to the drainage network. This may be the mechanism that occurs at Richmond where the underlying basaltic bedrock, with its cracks, fractures and high porosity, has the ability to store nutrients in its groundwater, supported by a high population density and old infrastructure. The rise and fall of the water table affects the water pathways, and the nutrient levels seen in drainages. Unfortunately, inadequate data exist to test this hypothesis for the sites examined in this thesis.

With the flow of water, nutrients in subsurface pathways are conveyed. The nutrients are predominantly in dissolved form, with the particulate forms being more significant as a function of the strength of stormwater flow, which has the power to erode and suspend sediments in its turbulent path, as has been shown by many studies (Sartor et al., 1974; Chiew and McMahon, 1997; Kanso et al., 2003).

## 7.4 Implications for dry and wet weather treatment

### 7.4.1 Current urban runoff management practices

Over time, stormwater management has evolved based on new studies. In a study of Port Philip Bay, Melbourne, it was recommended to reduce the annual TN load by 1000 tonnes to reduce the risk of eutrophication (Harris et al., 1996). Subsequently, reductions in mean annual loads of total suspended solids (TSS), TP and TN were specified for new urban developments (Victorian Stormwater Committee, 1999).

Urban stormwater management has evolved from flood control arising from rainfall for the protection of urban areas (Roesner et al., 2001). Low-level urbanisation has been shown to have major degrading impacts on aquatic ecosystems (Walsh et al., 2004). Stormwater impacts on stream health through three primary mechanisms (1) changes to catchment hydrology, (2) changes to hydraulics and (3) changes to the water quality (Wong et al., 2000). Recent Australian guidelines (Wong, 2006) have attempted to provide a more detailed framework linking load reduction targets to trigger concentrations according to ANZECC water quality guidelines (ANZECC, 2000) that aim to protect the environment of receiving waters (Lawrence and Phillips, 2006). The following table gives the objectives for the post-construction phase of stormwater management in regard to nutrients.

**Table 7.1** Objectives for post-construction phase of stormwater management of nutrients

| **Pollutant** | **Receiving water objective** | **Current best practice performance objective** |
|---|---|---|
| Total Phosphorus (TP) | Comply with SEPP (baseflow concentration not to exceed 0.08 mg/L) | 45% retention of the typical urban annual load |
| Total nitrogen (TN) | Comply with SEPP (baseflow not to exceed 0.9 mg/L | 45% retention of the typical urban annual load |

Source: SEPP: State Environment Protection Policy: Waters of Victoria, 1988

TN and TP concentration values indicate potentially bioavailable N and P, and since TN and TP include a variety of N and P species respectively, some of which are readily absorbed and assimilated by biota, whereas the particulate species may not be immediately available to the biota but are more persistent, there may be a requirement for more nutrient-specific targets.

Urban stormwater management has now evolved to new, multiple objective approaches such as "Low Impact Design" (LID) (Holman-Dodds et al., 2003), "Sustainable Urban Drainage Systems" (SUDS) (Marsalek and Chocat, 2002), and " Water-Sensitive Urban Design" (WSUD) (Lloyd et al., 2001; Lloyd, 2004; Wong and Breen, 2006).

The primary objectives of WSUD are described as:

1. The reduction of potable water demand through water efficient appliances, rainwater and grey water reuse.
2. The minimisation of wastewater generation and the treatment of wastewater to a standard suitable for effluent reuse opportunities and/or release to receiving waters.
3. The treatment of urban stormwater to meet water quality objectives for reuse and/or discharge to surface waters.
4. The preservation of the natural hydrological regime of catchments.

The treatment processes can be placed in series, commonly called a "treatment train" where coarse pollutants are removed first, and particles of finer grain sizes are gradually removed, until nutrients are taken up through biological assimilation (Wong, 2006). Nutrient removal is through the processes of sedimentation, enhanced sedimentation, adhesion and filtration, and finally biological uptake (Wong, 2006). To support the latest stormwater management practices, there is a requirement to understand nutrient concentrations during both dry weather and storm events.

### 7.4.2 Recommendations for urban runoff management

Prior to urbanisation, small streams and creeks existed together with natural vegetation, but as they have been replaced by concrete drains and pipes, the natural sinks for nutrients have been drastically reduced (Groffman et al., 2002; Walsh et al., 2005; Klocker et al., 2009). Where the former streams with their established vegetation would have trapped and retained the particulates, the particulate nutrients of N and P, and dissolved nutrients (which were readily absorbed and assimilated by plants), are conveyed in the impervious drainage network and present in urban runoff.

#### *7.4.2.1 Prioritise catchment treatment*

The results of this study indicate that urban stormwater management – *purely from a nutrient reduction point of view* - should prioritise treatment for catchments that tend to be more problematic in terms of nutrient concentrations in runoff. They are likely to be residential rather than industrial catchments, catchments with high population densities, old infrastructure, high impervious percentages and bedrock of high hydraulic conductivity. Of course, pollutants other than nutrients may often be important, and so the overall approach to stormwater management will need to be multi-dimensional.

#### *7.4.2.2 Treatment technology*

The treatment technology applied should aim for the removal of all pollutant species in both dry and wet weather. The ideal treatment system should aim for the removal of both particulate and dissolved nutrient species. Since particulate nitrogen and phosphorus in stormwater is the main form to be removed, an allowance for particulate removal is a priority. Ways of providing space for runoff treatment need to be incorporated to allow for the retention of particulates. Wetlands, dams and ponds provide means of water retention to allow time, and still water, for particulates to be removed by settlement. In dry weather, long-term phosphorus uptake (for example by plants and sediments) and complete nitrogen removal (primarily by promoting a full sequence of transformations through to de-nitrification) should be facilitated.

#### *7.4.2.3 Create denitrification (reducing) cells*

In traditional urbanisation, a draw-back of the efficient drainage network and impervious surfaces is the production of conditions of increased oxidation. The potential for oxidation of nutrients, especially bacterial nitrification to produce nitrogen oxides, is enhanced. To counter-act this feature of urbanisation, the treatment system should incorporate, in the drainage pathway, a reducing process in which de-nitrification to remove dissolved N species takes place (Groffman and Crawford, 2003; McClain et al., 2003; Klocker et al., 2009). Previously, along stream and creek beds, in the gravel and sediment media, nitrification and de-nitrification processes could occur with the presence of oxic and anoxic subsurface media. Therefore, the provision of reducing conditions provided by carbon in the form of wood and wetlands is one way of providing the environment for nitrification and de-nitrification to take place to remove $NO_x$, since the primary dissolved N species that is problematic is $NO_x$. The technology could also use aquatic plants for N assimilation and anaerobic zones for treatment to denitrify $NO_x$ for example, employing biofiltration systems which use both oxic and anoxic zones (Hunho et al., 2003; Zinger et al., 2007).

### *7.4.2.4 Treatment for wet weather flows*

For wet weather, the technology applied should target the removal of the main N species of TPN and $NO_x$. In wet weather treatment, a combination of detention ponds with attached wetlands designed to remove N by trapping particulates and thereby TPN, the removal of nutrients by their uptake by aquatic plants, and the provision of anoxic cells to denitrify $NO_x$ are recommended, using systems (Hunho et al., 2003; Zinger et al., 2007; Bratieres et al., 2008) which are ideally designed for high volume flows. The lower volume dry weather flows also need to be addressed.

The removal of TP and FRP can be accomplished by the use of media such as gravel, sand and soil with a clay fraction and suitable macrophytes to remove them by assimilation. Where TPN and particulate P are removable by physical methods, the soluble fractions such as TDN can be removed by a combination of the use of rooted vegetation that provides N and P sinks, and the appropriate media and chemical conditions to enable nitrification and de-nitrification processes to occur, with the emphasis on providing retention and filtration, and assimilation and de-nitrification conditions along the treatment train (Reddy and D'Angelo, 1994; Verhoeven et al., 1994; Boudraa et al., 1999; Hoagland et al., 2001).

### *7.4.2.5 Treatment for dry weather flows*

Priority should be given to the removal of the main polluting nutrient species. The priority nutrient species to be removed are $NO_x$ in dry weather flow, and primarily TPN and $NO_x$ in stormwater. The removal of these specific target species using physical, chemical and biological processes will lead to significantly reduced levels of TN and TP in urban runoff.

Dry weather flow will be substantially lower in volume than stormwater flow. The dry weather treatment cells (discussed further below) should be ideally located downstream of wetlands, where they can treat any dissolved nutrients, especially nitrogen oxides derived from the breakdown of organic matter from the wetland.  Such systems will need high levels of flow control to protect them from damage during storms.

It has been the practice to provide for the treatment of stormwater, with a lower priority for dry weather flows. In dry weather, the main problematic nutrient species are soluble forms NOx, DON and NH3 which are readily assimilated by microscopic aquatic plants and algae.In dry weather, dissolved, oxidised species of N form the major proportion of totalnitrogen. High nutrient levels are problematic, causing eutrophication leading to hypoxia, which may cause receiving waters to become toxic as a result of the accelerated growth of microscopic aquatic plants, particularly by high $NO_x$ levels (as discussed in Chapter 2). This problem is particularly acute in small streams which have little buffering ability. The nutrient species which are mainly the oxidised forms are most appropriately treated by the use of anaerobic treatment cells which are recommended to be placed in the dry weather flow path. The treatment will have to include a sequence, which firstly promotes the conversion of any ammonia to nitrate, before the anaerobic (or at least low oxygen) phase (Zinger et al., 2013). Facilities to raise the water table in the treatment media would be the ideal remediation process to treat dry weather flows.

#### *7.4.2.6 Clastic filters for treating dry weather flows*

To treat dry weather flows, it is preferable to locate the interception devices such as biofilters, or low cost clastic filters are proposed with anaerobic treatment cells at the drain outlets before and after water retention structures such as constructed wetland systems. These will provide for the removal of dissolved nutrients, especially nitrogen oxides, prior to their discharge into small dams, other wetlands and streams. Instead of currently having long, straight concrete drains that discharge urban flows to creeks and rivers, every opportunity should be taken to build low cost clastic "filter barriers", which are made of boulders of rock, gravel, wood and sand and planted with an assortment of sedges and macrophytes. These clastic "filter barriers" located in drains will provide deep subsurface flow to de-nitrify the nutrients, and in addition to these clastic barriers, the plants will take up the surplus nutrients from water seeping through the clastic filters. Species planted could be sedges such as *Phragmites australis*, *Carex appressa* (the roots of which provide a carbon source for denitrification), and *Lomandra sp.*; and tea trees such as *Melaleuca ericifolia* thrive in such environments. Such filter barriers will also remove nutrients held in particulate form. Hence, the full spectrum of nutrient species can be eliminated from the dry weather flows. Such structures will obviously be swamped during flood conditions. Therefore, the use of large clastics such as boulders, cobbles, gravel and logs will ensure that they will be still working after storm events. A basic clastic filter has been designed and presented in Figure 7.1. The residence time for dry flow in the clastic filter is estimated to be 20 days, allowing nutrient uptake by plants and denitrification to take place. The residence time can be adjusted by varying the depth of the reducing cell, the grain-size of clastics used, and the length of the filter. Optimisation of the filter will be the subject of further research.

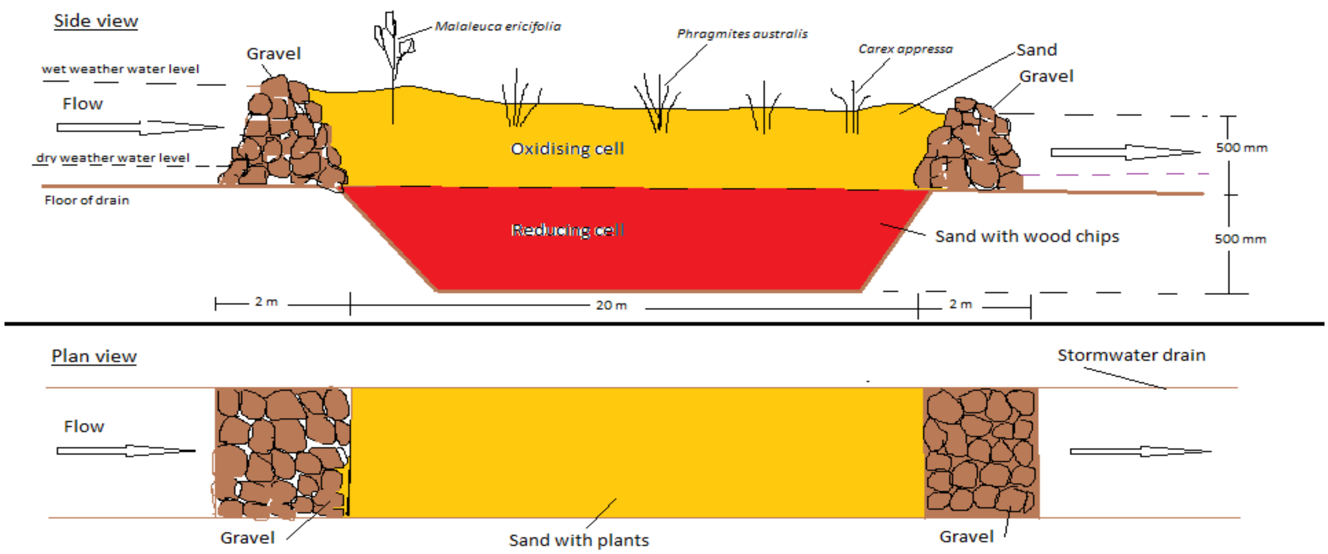


**Figure 7.1** Clastic filter barrier for treatment of dry weather flow

## 7.5 Conclusion

Increased concentrations and fluxes of nutrients are an inevitable consequence of urbanisation under 'traditional' drainage management. Previous approaches to urban drainage have aimed to remove stormwater efficiently, with more recent attempts focussing on improving stormwater quality and reducing hydrological disturbance. It is clear from this study that the approach to stormwater treatment needs to take into account the composition of nutrients and its likely variability with climate and relationship with catchment characteristics.

The species that are most problematic in dry weather are dissolved nitrogen and oxidised nutrients. A combination of filtration barriers with anaerobic cells and plants that will assimilate nutrients will be necessary to ensure their removal. The filtration barriers will remove both dissolved and particulate nutrients during dry weather flow.

For wet weather, the aim is to remove the most problematic TPN and particulate phosphorus species by removing the particulates from stormwater. Detention ponds and wetlands will accomplish this aim.

The present study indicates that residential catchments require more attention than industrial catchments. Ideally, wetlands are preferable where flood prone areas are large and offer opportunities. In practice it is usually easier to find several smaller areas where smaller wetlands, scaled to catchment size (a distributed approach to treatment) allows relatively smaller hydraulic loadings to be treated at each wetland. In addition, old infrastructure should be examined and leakages remedied. In catchments with high bedrock hydraulic conductivity, since sub-surface flows may be a significant source of highly oxidised nitrogen species, more filtration barriers with anaerobic cells will often be required, for example using the riparian approaches explored by Groffman and others (Groffman and Crawford, 2003). Their approach involves the recognition that pristine riparian zones function as “sinks” for nitrate ($NO_3^-$) and should be preserved where possible. The denitrification potential of urban riparian zones can be raised or lowered (affected) by certain urban hydrologic factors, eg, water pooling, and the raising or lowering of the water table.

Nutrient reduction from urbanised and urbanising catchments will thus require a combination of approaches, focussed on both wet weather and dry weather. Such approaches will need to be integrated within the broader context of stormwater management, where management of other water quality problems, as well as hydrologic disturbance, must also be taken into account.

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# Chapter 8: Conclusions and Future Research

## 8.1 Variation of nutrient concentrations and composition in dry and wet weather

**Nutrient concentrations** in runoff from most of the 13 Melbourne catchments studied **exceed the chemical thresholds for lowland rivers** and are of concern with respect to the ecological health of receiving waters. **Dry weather flows may often contain even higher concentrations of nutrients than wet weather flows**, due to a likely combination of subsurface sources such as leaking wastewater infrastructure and flow through nutrient-rich soil media.

Nitrogen concentrations in dry weather runoff were affected by land use, such that residential catchments show significantly higher nitrogen concentrations than do industrial catchments. Such differences, however, do not exist for phosphorus. Concentrations of $NO_2^-$ and $NO_3^-$ were the highest of the nitrogen species found in dry weather from residential catchments, whereas the concentration of DON was the highest of nitrogen compounds from industrial catchments, reflecting the difference in sources and the degree of loading. A negative relationship between imperviousness and nutrient concentrations suggests that despite the obvious negative influence of impervious areas on hydrology and water quality, the mechanisms causing water quality degradation by urbanisation are more complex and likely to be affected by a more important co-factor such as land use.

The **dry weather concentrations** of some nitrogen species are positively influenced by catchment hydraulic conductivity, suggesting that subsurface flow pathways and the leaching of nitrogen may be critical. Catchment age and slope play a lesser role in influencing dry weather concentrations. Older catchments discharge higher concentrations of phosphorus and dissolved nitrogen, and steeper catchments deliver higher concentrations of ammonia. Nitrogen loading increases as a function of urbanisation, including not only from the present anthropogenic activities but also contributions from a past legacy such as significant long-term leaching of soil nitrogen especially in oxidised forms, which are aggravated by old, leaking infrastructure.

During wet weather, nutrient concentrations for all nutrient species were variable both within and between catchments. The TN and TP concentrations were generally low but still exceed the recognized chemical concentrations that can cause ecological stress to lowland rivers

(ANZECC, 2000). Population density strongly influences dissolved forms of N and P. The age of infrastructure strongly influenced TPN, DON, TP and FRP. Larger catchments were strongly related to the concentrations and proportion of $NO_x$ in stormwater. This may be related to flow paths and therefore travel times, or may be influenced by co-correlates such as land use. Imperviousness significantly influenced DON and TP concentrations. The observation of higher TN concentrations with flatter slopes was surprising, while the influence of infrastructure age and imperviousness were more predictable.

**The compositional patterns of nutrients from dry and wet weather are significantly different.** The proportions of $NH_3$ and DON with respects to TN are similar in both dry and wet weather. In dry weather, $NO_x$ comprises about two thirds of TN whereas in wet weather, it comprises approximately only one third of TN. In dry weather, TPN forms 9% of TN whereas in wet weather it forms a third of TN. In dry weather, industrial catchments are characterised by higher proportions of $NH_3$ and DON than do residential catchments. Residential catchments produce higher proportions of $NO_x$ and TPN than industrial catchments. Different land uses discharge differing total nitrogen compositions.

## 8.2 Nutrient pathways and nutrient transformation mechanisms

The results of this thesis add weight to the observation that urbanisation changes not only surface flow paths (through creation of impervious areas and constructed drainage networks), but also changes subsurface processes, through the contributions of drainage, water and wastewater infrastructure, and the creation of 'legacy effects' in soils, which results in in-situ contributions of nutrients.

Additionally, seasonal changes in soil moisture and oxygen availability likely influence the degree of bacterial nitrification and de-nitrification. A lower water table in dry weather produces a thicker soil-oxidising zone, resulting in a higher amount of bacterial nitrification taking place. Conversely, in wet weather, a much higher water table will probably result in a lower rate of bacterial nitrification, producing less nitrogen oxides. The water table falls even faster in dry weather where urbanisation has increased impervious cover, effectively reducing the soil surface area and the underlying soils receiving rainfall. In dry weather, coupled with a much more rapidly falling water table, the thicker, very well-drained oxidising soil layer provides an aerobic environment that is conducive to bacterial nitrification to generate more nitrites and nitrates.

## 8.3 Management implications

Treatment technologies aimed at reducing nutrient concentrations are aimed broadly at replacing the losses of retention, filtration, transformation and assimilation processes inherent in natural catchments (Vitousek et al., 1997; Voyer et al., 2011). A combination of source control through structural and non-structural means, retention and planting of nutrient retaining vegetation are required, with catchment prioritisation based on factors shown to influence nutrient concentrations (in particular old infrastructure, high population densities and highly porous soils). The design of stormwater treatment measures such as wetlands and biofiltration systems to reduce nutrient loads, to-date focussed largely on treatment of stormflows, needs to better consider treatment of baseflows, which often have very high nutrient concentrations. In understanding the processes and mechanisms contributed by the catchment characteristics, nutrient pollution abatement should aim at nutrient reduction at source, targeting specific suites of nutrient species, particularly the dissolved and the oxidised forms such as nitrites and nitrates during the dry weather and particulate nitrogen in wet weather. A focus on source remediation programs to ensure the integrity of water infrastructure is required, to restore old, leaky infrastructures, along with techniques (such as harvesting) to reduce overall pollutant loads.

## 8.4 Recommendations for future research

A number of knowledge gaps have been identified by this research and insights gained in this thesis. Addressing these will further increase our understanding of nutrient behaviour, to help design the appropriate technology to remove nutrients from urban runoff.

Further research into specific treatment trains to effectively remove nutrients in dry and wet weather is required. Currently treatment trains are usually designed in series, with relatively little attention paid to the relative importance or variation of dry weather and wet weather concentrations. Research needs to consider systems (either integrated or separate) which target both wet weather and dry weather flows, specifically to remove particulates in storms, and dissolved forms of nitrogen (primarily nitrates and nitrites) and phosphorus (primarily orthophosphate) in dry weather, while providing and maintaining the important downstream baseflow.

Specifically, dry-weather filtration systems use a relatively small treatment footprint to confer a benefit to the stream/environment for a large proportion of time. Therefore they are efficient in space and capital costs. It is recommended that research be focussed into potential designs, treatment efficiencies and modelling.

To address the differing nutrient concentrations and compositions, an option of designs for parallel treatment streams (one drainage pathway designed for wet weather flows and a parallel drainage pathway designed for dry weather flows) may need to be researched in order to be more effective. The explanation is as follows: In such a design, one stream may be designed for dry weather to remove soluble nutrients, particularly for nitrogen, using anoxic cells and biotic assimilation (followed by re-aeration to ensure phosphorus is not released), and contributing to downstream flow to the river, and the other parallel stream designed specifically for the removal of particulates in stormwater - with large water storage capacities, long detention times, and biological assimilation with macrophytes.

As the drainage outlets of catchments are often space-constrained, conventional treatment facilities will have to be efficient. Research into space-saving but effective treatment devices that remove nutrients with the use of suitable aquatic plants is required. Further research is required into the behaviour and performance of dry weather flow clastic filters.

Catchments with commercial land use were not studied in this research because of the lack of available data. Such catchments form an important sector contributing to urban drainage, where spaces for locating treatment devices are at a premium. Smaller, space-saving, low energy treatment systems become critical in this context. Design of stormwater treatment systems should take into account subsurface flow pathways and therefore the influence of catchment geology and potential legacy impacts. Further work is needed in this area, for specific catchments that produce exceptionally high nutrient concentrations, in dry and wet weather flows.

Research into the occurrence of dry weather flows in urban catchments, its sources, causes and its contribution to annual pollutant loads would also help to provide a much greater ability to target and prioritise catchments for treatment.

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