Chapter 3 Nutrient origins and pathways in the Manning Valley

3.1 Introduction

Stream ecosystems are predominantly influenced by catchment geology, climate and land use (Hynes 1975, Johnes et al. 1996, Moss 1998, McKee et al. 2001). The strong influence of geomorphic and hydrological processes on the physical characteristics of streams is supplemented by biotic components such as land use. Stoate et al. (2009) found that land use change is a major contributor to habitat loss and degradation, particularly when riparian vegetation is absent, through the modification of biogeochemical cycling and water availability (Naiman et al. 2000).

Changes in catchment land use and riparian degradation since European settlement in Australia have led to the emergence of both point and non-point sources of pollution to streams, with the control of these pollution sources as a major issue facing rural communities in Australia (McKergow et al. 1999). The removal of riparian vegetation has resulted in the loss of filtration capacity, reduction in allochthonous organic inputs, and increased sediment and nutrients into waterways (Campbell et al. 1992, Naiman and Décamps 1997, McKergow et al. 1999, McKee et al. 2000, Reid et al. 2008a). Riparian loss may also result in decreased terrestrial detritus inputs and increased macrophytes and algae, altering stoichiometric interactions within stream networks (Giling et al. 2012). Along with its influence on stream interactions such as energy transfer, riparian vegetation affects stream temperatures through shading and by modifying air temperature and humidity (Brosofske et al. 1997, Naiman et al. 2000), with stream water temperatures highly correlated to riparian soil temperatures (Brosofske et al. 1997).

The rehabilitation of streams to address impacts resulting from land use changes through riparian revegetation is found to be more effective when managed systems imitate natural ones by introducing a multispecies riparian buffer strip suited to the stream type and location within the catchment (Naiman and Décamps 1997). Giling et al. (2013) found that revegetation in an Australian lowland river, even at a small scale, resulted in a shift in stream ecosystem processes. However the extent of this shift depended on stream size and age of replantings (Giling et al. 2013).

Stream size also influences how catchments may be compartmentalised. Upland ecosystems are generally where materials are transformed and transported, while lowland aquatic ecosystems act as depositional zones for water and materials from upland ecosystems and may be further transformed (Fisher et al. 1998). Mulholland and Rosemond (1992) demonstrated that nutrient uptake within streams reduces nutrient availability, influencing the structure and functioning of downstream periphyton communities. The influence of upland ecosystems on lowland reaches can be substantial, regulating the form and concentration of nutrients and organic matter during downstream transport (Mulholland et al. 1995, Fisher et al. 1998, Dodds and Oakes 2008). In turn, these transformational processes also influence the response of aquatic biota, particularly through algal community structure and biomass (Pringle 1990, Valett et al. 1994, Mulholland et al. 1995, Suren et al. 2003).

When looking at longitudinal trends, one study on three Australian rivers, two located in the Murray-Darling Basin and one in south-east Queensland, found that heterotrophic microbial respiration was limited by dissolved organic carbon, with higher nutrients having a limited impact on respiration, with only minor increases recorded (Hadwen et al. 2010a). Hadwen et al. (2010a) suggested that drought, the loss of floodplain connection and transport of allochthonous carbon sources into river channels could further increase the relative importance of instream algal carbon sources within Australian rivers. Cortez et al. (2012) found that disrupted longitudinal processes as a result of regulation within the Hunter River, NSW, increased nitrogen concentrations and created significant changes in benthic algal assemblages with increases in diatom abundance.

While the relative abundance of species within benthic algal communities are affected by N:P ratios and total nutrient concentrations (Stelzer and Lamberti 2001), the degree to which nutrients influence aquatic community structure is determined by interactions with other factors such as temperature, flow, shading and disturbance (Pickett et al. 1987, Dodds and Welch 2000, Newall and Walsh 2005, Finlay et al. 2010). Local climate conditions also regulate the magnitude, temporal patterns and variability relating to nutrient retention by influencing disturbance and resource availability in streams (von Schiller et al. 2008). The consistencies of threshold values found across habitats have been found to be ecologically relevant and useful in providing nutrient criteria for anticipating likely algal responses (Black et al. 2011).

Understanding the source of nutrients and the transport mechanisms of upland ecosystems will determine likely impacts on lowland rivers, which may be exacerbated under low flow conditions (Suren et al. 2003). Evaluating the form (organic or inorganic) and magnitude of nutrient inputs from the upper catchments can also guide land use management decisions by allowing a focus on sub-catchments or point sources with disproportionately high nutrient inputs. As establishing or protecting riparian zones or large watershed areas to mitigate impacts of land use on water quality can be costly or politically difficult, it is essential that these areas are identified to guide rehabilitation to produce substantial water quality benefits (Dodds and Oakes 2008).

3.1.1 Catchment-relevant nutrient threshold values

The determination of catchment-relevant water quality threshold values and possible thresholds that indicate impacts on algal communities within subcatchments helps identify possible sources and nutrient impacts to aquatic system. A threshold or breakpoint occurs when a system responds to a driver by rapidly changing to an alternate steady state (Groffman et al. 2006, Dodds et al. 2010). Predicting thresholds that can cause potential instability and ecosystem change is an important aspect of managing systems (Dodds et al. 2010). The thresholds are useful as they may influence the ecosystem service values people place on processes and functions (Martin et al. 2009, Dodds et al. 2010) but can be difficult to infer due to lack of ecological information to make predictions of where thresholds will occur (Dodds et al. 2010). Analysis of these thresholds is further complicated by the nonlinear behaviour and multiple factors that operate at a variety of spatial and temporal scales (Groffman et al. 2006).

In 2000, water quality threshold values were developed for use in Australia and New Zealand for the purpose of protecting the 'environmental values' for public benefit, welfare, safety or health (DEC 2006). These values include the protection of aquatic ecosystems, drinking water, primary and secondary recreation and agricultural water. The Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand guidelines (ANZECC/ARMCANZ 2000) provide a framework for assessing water quality, based on whether the physical, chemical and biological characteristics of a waterway support environmental values by defining the type of water quality needed to protect these values (DEC 2006).

While the default threshold values provided in the ANZECC/ARMCANZ (2000) may be an adequate guide to water quality for specific purposes such as recreation or drinking, for other environmental values the default guidelines may not be suitable in setting thresholds for ecological change. The development of catchment-derived thresholds, based on the type of water resource and inherent differences in water quality across a region, may provide more suitable values. As catchments plays an important role in regulating stream water chemistry (Chuman et al. 2012), assessing water quality thresholds at a smaller scale and moving away from the use of conventional standards, human-caused imbalances are better identified and addressed (Poole et al. 2004). This occurs through the creation of more applicable water quality standards which describe the desirable distribution of conditions over space and time within a catchment (Black et al. 2011, Poole et al. 2004).

For a water resource manager with an environmental goal of aquatic ecosystem protection or restoration, guidelines need to be adapted to suit the local area or region (ANZECC/ARMCANZ 2000). These catchment-derived water quality threshold values enable the effectiveness and relevance of water quality monitoring and prioritisation of on-ground actions to be improved. By using catchment-derived water quality standards, more effective strategies for management options to protect aquatic ecosystems and support beneficial uses in streams could be facilitated (Poole et al. 2004). These types of standards would also help managers to identify the most cost-effective and efficient path toward creating the desired distribution of conditions across a catchment rather than management plans for individual water-bodies (Bohn and Kershner 2002). Water quality reference values on which to compare overall catchment water quality performance and appropriate threshold values for ecological responses can further inform catchment and water management.

3.1.2 Response of periphyton to nutrients

Understanding what controls periphyton biomass is important for understanding food webs in aquatic ecosystems. Benthic periphyton can be a crucial component within streams, providing the main form of energy and driving production (Bunn et al. 2003, Hadwen et al. 2010). While upland stream production has thought to be dominated by allochthonous input, studies looking at range of lowland and tropical Australian rivers found that, particularly under low flow conditions, in-stream producers not only support consumers in mid to lower river reaches but headwater streams as well (Douglas et al. 2005, Hadwen et al. 2010).

Several studies have shown that a strong relationship exists between algal biomass and the spatial distribution of nutrient inputs in streams (Pringle 1990, Valett et al. 1994, Black et al. 2011). Substantial increases in algal biomass can alter habitats through smothering substrates or trapping fine-grained particles that can lead to a decrease in species composition (Carpenter et al. 1998, Sand-Jensen 1998). Biggs and Smith (2002), when investigating the impacts of flood and nutrients on benthic algae in New Zealand gravel streams, found taxa richness was highest under low to moderate flood disturbance, but negatively related to soluble nutrients. However, establishing a relationship between nutrients and benthic periphyton biomass can be difficult, as periphyton growth rates may be more limited by light, grazers or flow than by nutrients and the relationship varies seasonally (Mosisch et al. 2001a, Munn et al. 2010, Black et al. 2011).

Ecological stoichiometry investigates the balance of carbon (C) in relation to nutrients (nitrogen-N and phosphorus-P). The use of stoichiometry allows the examination of trophic interactions as autotrophs typically exhibit high and variable C:N and C:P ratios, whereas heterotrophs typically have constrained and low C to nutrient ratios (Cross et al. 2003, Giling 2012). Ecological stoichiometry also includes the principle that the N:P ratio of primary producers should closely match that from environmental nutrient supplies (Sterner and Elser 2002). It is thought that mismatches in elemental composition between consumers and their resources may regulate food web structure by constraining species interactions (Sterner and Elser 2002, Hall et al. 2005). Shifts in the relative abundance of primary producers are likely to occur along a N:P ratio gradient without exploitative use of nutrients (Stelzer and Lamberti 2001). An example of this is when supply N:P ratios are high, a greater maximum growth rate may allow a species with a high affinity for phosphorus to grow much faster than a species with a low affinity (Stelzer and Lamberti 2001). Therefore, environmental N:P supply gradients, which drive elemental flexibility, should be examined to increase understanding of possible effects on food webs (Hall et al. 2005).

As N and P are often seen as the key limiting nutrients for primary producers (Winterbourn 1990, Valett et al. 1994, Stevenson et al. 2008), it is important to focus on concentrations of these nutrients and their ratios to each other, as primary producers, such as benthic algae, are thought to respond to the variation in N:P ratios (Tilman 1985, Stelzer and Lamberti 2001). In general terms, a N:P ratio >16:1 is thought to indicate phosphorus limitation, but nutrient concentrations must also be considered to determine actual thresholds of nutrient limitation (Bothwell 1985).

Studies have examined dissolved forms of N and P to determine how stream particulate and solute concentrations relate to catchment differences (Holmes et al. 1996, Neill et al. 2001). Dissolved nutrients are known to have a major influence on the types, abundance and activity of organisms within streams, with inorganic nutrients providing an indication of the underlying geology and organic materials indicative of vegetation, soil and microbial processes (Welch et al. 1998). Stelzer and Lamberti (2001) found that, under experimental conditions, periphyton biomass was limited by dissolved inorganic N and soluble reactive P, despite high N:P ratios, indicating that predicting nutrient limitation by ratios alone has limitations. Instream retention of inorganic N and P has also been found to be strongly seasonal with high retention rates in winter and lower rates in summer (Mulholland 1992).

Differences in abiotic factors such as velocity, discharge, water temperature, electrical conductivity and turbidity have been correlated to variations in nutrient limitation and periphyton biomass (Meyer 1979, Mosisch et al. 2001ab, Irvine and Jackson 2006). These variations can be the result of riparian removal, deforestation and seasonal changes (Francour et al. 1999, Mosisch et al. 2001b, Neill et al. 2001). Examples of how abiotic variables may influence periphyton biomass include physiological responses to temperature, decreases in dissolved oxygen increasing denitrification processes and the over-riding influence of shade (Holmes et al. 1996, Francour et al. 1999, Mosisch et al. 2001b, Neill et al. 2001).

To overcome the complexities of the relationship among nutrients, other chemical and physical factors and algal communities, nutrient-diffusing substrates (NDS) have been frequently employed as they promote the growth of colonizing autotrophs without substantially changing other physico-chemical or biological conditions (Winfield Fairchild and Everett 1988, Bernhardt and Likens 2004, Marcarelli et al. 2009). Previous research has shown that the use of artificial substrates allows observations of algal responses to demonstrate autotrophic nutrient limitation (Chessman et al. 1992, Francour et al. 1999, Neill et al. 2001). Studies found that nutrient limitation may vary at small temporal and spatial scales, and is driven by local processes (Wold and Hershey 1999, Irvine and Jackson 2006).

3.1.3 Aims and hypotheses

The aim of this chapter is to determine baseline condition from reference sites and develop threshold values to assess non-reference sites. These catchment-scale reference water quality thresholds will assist in the protection and restoration of natural flow regimes in the Manning River system. Further to this aim, an assessment of overall catchment water quality and its influence on aquatic ecosystems was undertaken.

I hypothesise that identification of the origin and pathways of nutrients in the Manning system under various flows and seasonal conditions will better inform catchment and water management within the Manning system. I predict that nutrient concentrations in surface water are dependent on flow. The strength of interactions with flow and land use are evaluated using water quality data collected across the catchment at various temporal scales.

I predict that, within upland reference sites, stoichiometric ratios may be limiting autotrophic production. Nutrient enrichment experiments were used to determine if C, N and P ratios are indicative of autotrophic limitation in the upland reference sites.

3.2 Study sites

The Manning catchment has a total catchment area of approximately 8,190 km^2 with rainfall falling in the upland ranges of around 1,200 mm $year^{-1}$. The Manning is unregulated by large structures but small weirs may influence discharge patterns and water quality. Water is extracted for a range of uses that include irrigation and stock water, rural and domestic use and urban reticulated supply. The lower Manning floodplain is extensively modified with almost 40 per cent cleared for grazing and cropping, with 1.5 per cent cleared for urban areas (see Chapter 2 for details). The extent of modification in the lower Manning River landscape made appropriate reference sites for the lowland difficult to locate.

Various water quality datasets have been used to compare historical information to more recently collected data. Figure 3.1 indicates the location of these sites within the Manning catchment. Water quality variables and the source of data for these sites are in Table 3.1.

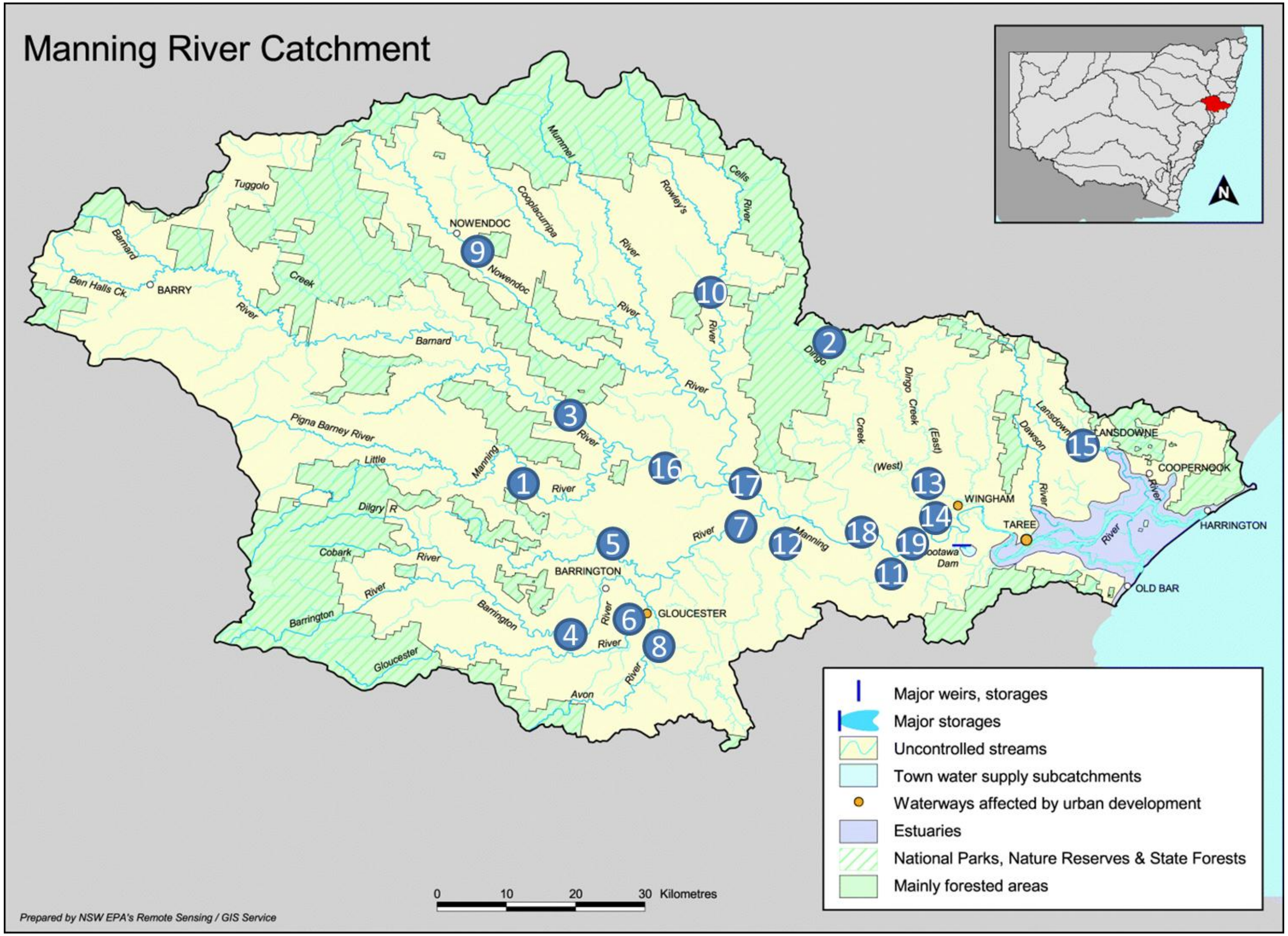


Figure 3.1 Locations of Manning catchment long-term water quality sites (Refer to Table 3.1 for site names)

Table 3.1 Water quality variables and source of data collected at long-term Manning catchment sites

Site No. and Name	Water quality variables	Monitoring program	Years and Source
1. Little Manning River at Curricabark Road	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study; Manning Community water quality monitoring program	1994-97 and 2006-07; MCW[1]
2. Caparra Creek at Wheerol Flat	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study; Manning Community water quality monitoring program	1994-97 and 2006-07; MCW
3. Barnard River at Thunderbolt Highway	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2006-07; MCW
4. Barrington River at Rocky Crossing	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study; Manning Community water quality monitoring program	1994-97 and 2006-07; MCW
5. Bowman River at Bowman Farm Road	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2006-07; MCW
6. Gloucester River at Gloucester	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2006-07; MCW
7. Gloucester River at Bundook	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2006-07; MCW
8. Avon River at Bucketts Way	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study; Manning Community water quality monitoring program	1994-97 and 2006-07; MCW
9. Nowendoc River at Nowendoc	Turbidity, EC, NO_x, TP	Manning Community water quality monitoring program	1994-97; MCW
10. Rowleys River at Bullocks Bow	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study; Manning Community water quality monitoring program	1994-97 and 2006-07; MCW
11. Burrell Creek at Kimbriki Road	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2006-07; MCW
12. Bakers Creek at Bakers Creek Road	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2006-07; MCW
13. Dingo Creek at Belbourie	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study; Manning Community water quality	1994-97 and 2002-07; MCW

Site No. and Name	Water quality variables	Monitoring program	Years and Source
		monitoring program	
14. Dingo Creek at Clarkes	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2006-07; MCW
15. Lansdowne River	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study; Manning Community water quality monitoring program	1994-97 and 2006-07; MCW
16. Manning River at Gloryvale	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2006-07; MCW
17. Manning River at Tiri	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2006-07; MCW
18. Manning River at Charity Creek Bridge	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study; Manning Community water quality monitoring program	1994-97 and 2002-07; MCW
19. Manning River at Killawarra	Temperature, EC, TP, SRP, TN, NOx, NH_4^+	Catchment water quality study	2002-07; MCW

[1]Midcoast Water – Water quality results analysed using same protocols as used in this thesis
EC=Electrical Conductivity; TP=Total Phosphorus; SRP=Soluble Reactive Phosphorus; TN=Total Nitrogen; NOx=Nitrate/Nitrite; NH_4^+ =Ammonium.

3.2.1 Water quality threshold values - reference sites

In terms of water quality, the Manning is a moderately disturbed east flowing freshwater coastal waterway within south-eastern Australia. The catchment supports upland (>150m above sea level) and lowland streams (<150m above sea level). Three reference sites were selected from an upland catchment (>150m above sea level), a midland catchment (<150m, >30m) and a lowland catchment (<30m). Resulting in a total of nine reference sites.

When selecting water quality reference sites condition must be consistent with the level of protection proposed for the ecosystem in question, in this case moderately disturbed. Sites were located in the same biogeographic and climatic region and had pre-existing water quality information available. Reference site catchments had similar geology, soil types and topography and contained a range of habitats similar to those at the treatment sites.

Three reference sites within each of the three catchment area types were selected to allow adequate comparisons of water quality variables. These sites were chosen due to their position in minimally modified sub-catchments, mostly containing a high percentage of intact native riparian vegetation. Locations of each of these sites are in Figure 3.2. Site selection took into account pre-existing water quality assessments, as this allowed historical data to be incorporated at some sites when calculating threshold values. These selected sites were also evaluated based on representativeness, surrounding land use, riparian condition and upstream influences.

Three sites were selected in the upland catchment. The Little Manning River at Curricabark Road (Site 1 in Fig. 3.2) is a community water quality monitoring site at an altitude of approximately

210m ASL (Fig. 3.3). Upper Craven Creek at Craven Creek Road (Site 2 in Fig. 3.2), at an altitude of approximately 250m above sea level (ASL) (Fig. 3.4). Caparra Creek at Jack Fahey Bridge (Site 3 in Fig. 3.2), is near another community water quality monitoring site, at an altitude of approximately 160m ASL (Fig. 3.5). These sites are in forested areas but have some minor grazing and weed impacts. Riparian cover for these sites provided over 70% cover dominated by natives (Table 3.2).

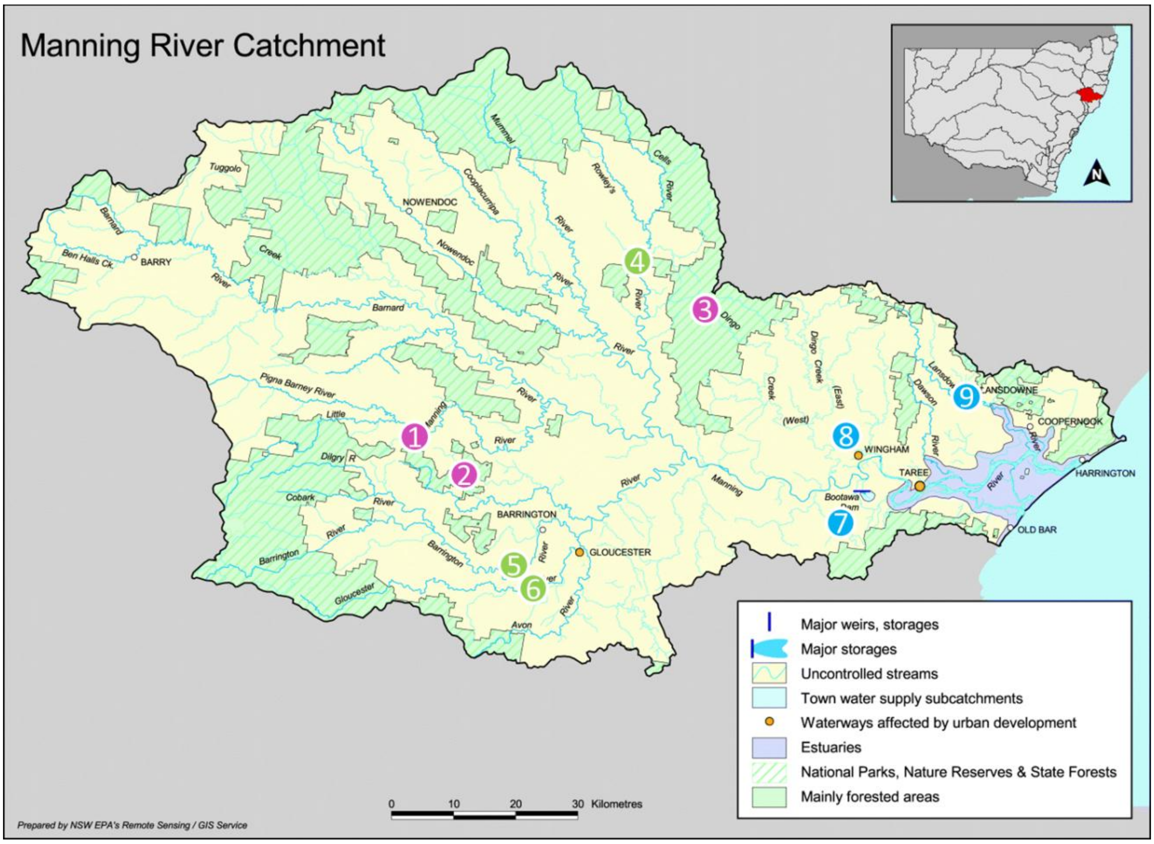


Figure 3.2 Locations of catchment reference sites.

Legend

Pink=Upland sites: site 1 – Little Manning River; site 2 - Craven Creek; site 3 – Caparra Creek

Green=Midland sites: site 4 – Rowleys River; site 5 – Barrington River; site 6 – Gloucester River

Blue=Lowland sites: site 7 – Bobo Creek; site 8 – Dingo Creek; Site 9 – Lansdowne River

Figure 3.3 Little Manning River at Curricabark Road (Looking downstream)

Figure 3.4 Upper Craven Creek at Craven Creek Rd (Looking upstream)

Figure 3.5 Caparra Creek at Jack Fahey Bridge (Looking downstream)

Table 3.2 Physical characteristics of Manning catchment reference sampling sites

Site	Subcatchment Area (km^2)	Riparian Cover and Taxa	Shading	Geology	Land use
Caparra Creek	108	100% riparian cover – Weeping Myrtle (*Waterhousea floribunda*); Water Gum (*Tristaniopsis laurina*); River Oak (*Casuarina cunninghamiana*); Creek Sandpaper Fig (*Ficus coronata*); Brush Box (*Lophostemon confertus*), Lilly Pilly (*Acmena smithii*); Lomandra (*Lomandra longifolia*) Exotics: Privet (*Ligustrum lucidum*)	30%	Metasediment and metamorphosed sediment (sandstone, schist and basalt)	Site located downstream of Tapin Tops National Park; some grazing impacts
Upper Craven Creek	49	70% riparian cover - River Oak (C. *cunninghamiana*); Lilly Pilly (*A. smithii*); Lomandra (*L. longifolia*) Exotics: Privet (*L. lucidum*); Willow (*Salix sp.*)	45%	Metasediment and metamorphosed sediment (sandstone, schist and basalt)	Low impact stock grazing
Little Manning River	720	100% riparian cover - River Oak (*C. cunninghamiana*); Weeping Bottlebrush (*Callistemon viminalis*); Water Gum (*T. laurina*); Creek Sandpaper Fig (*F. coronata*); Lomandra (*L. longifolia*)	30%	Basalt dominated	Site located downstream of Woko National Park
Gloucester River	207	70% riparian cover – River Oak (*C. cunninghamiana*); Weeping Bottlebrush (*C. viminalis*); Water Gum (*T. laurina*), Lomandra (*L. longifolia*) Exotics: Willow (*Salix sp.*); Privet (*L. lucidum*)	5%	Metasediment and metamorphosed sediment (sandstone, schist and basalt)	Moderate grazing impacts
Barrington River	630	90% riparian cover – River Oak (*C. cunninghamiana*); Weeping Bottlebrush (*C. viminalis*); Water Gum (*T. laurina*); Creek Sandpaper Fig (*F. coronata*);Lomandra (*L. longifolia*) Exotics: Willow (*Salix sp.*)	10%	Metasediment and metamorphosed sediment (sandstone, schist and basalt)	Located downstream of Barrington Tops National Park
Rowleys River	730	95% riparian cover: River Oak (*C. cunninghamiana*); Weeping Bottlebrush (C. *viminalis*); Lilly Pilly (*A. smithii*); River Grass (*Potamophila parviflora*); Lomandra (*L. longifolia)*	20%	Metamorphic and sedimentary derivatives	Minor grazing impacts

Site	Subcatchment Area (km^2)	Riparian Cover and Taxa	Shading	Geology	Land use
Lansdowne River	96	80% riparian cover – Weeping Myrtle (*W. floribunda*); Water Gum (*T. laurina*); River Oak (*C. cunninghamiana*); Weeping Bottlebrush (*C. viminalis*);Lomandra (*L. longifolia*) Exotics: Willow (*Salix sp*.); Lantana (*Lantana camara)*	50%	Sedimentary (conglomerate, mudstone and sandstone)	Moderate grazing impacts
Dingo Creek	492	95% riparian cover - Weeping Myrtle (*W. floribunda*); River Oak (*C. cunninghamiana*); Water Gum (*T. laurina*); Weeping Bottlebrush (*C. viminalis*); Creek Sandpaper Fig (*F. coronata*); River Grass (*P. parviflora*); Lomandra (*L. longifolia*) Exotics: Lantana (*L. camara)*	35%	Sedimentary (conglomerate and sandstone); Intermediate volcanics	Small-scale cattle-grazing; site located upstream of dairy and abattoir impacts.
Bobo Creek	80	90% riparian cover - Weeping Myrtle (*W. floribunda*); River Oak (*C. cunninghamiana*); Water Gum (*T. laurina*); weeping bottlebrush (*C. viminalis*); Lomandra (*L. longifolia*.	70%	Sedimentary (conglomerate, sandstone, mudstone)	Site fenced. Some grazing impacts upstream of site.

Three reference sites were chosen in the mid-catchment. Rowleys River at Nowendoc Road (Site 4 in Fig. 3.2), is a community water quality site with some grazing impacts, at an approximate altitude of 140m (Fig. 3.6). Barrington River at Rock Crossing (Site 5 in Fig. 3.2), downstream of the Barrington Tops National Park, is a well-forested site at an altitude of approximately 130m (Fig. 3.7). Gloucester River at Faulklands Road (Site 6 in Fig. 3.2), has some grazing and weed impacts and is at an altitude of approximately 130m (Fig. 3.8).

Figure 3.6 Rowleys River at Nowendoc Road (Looking downstream)

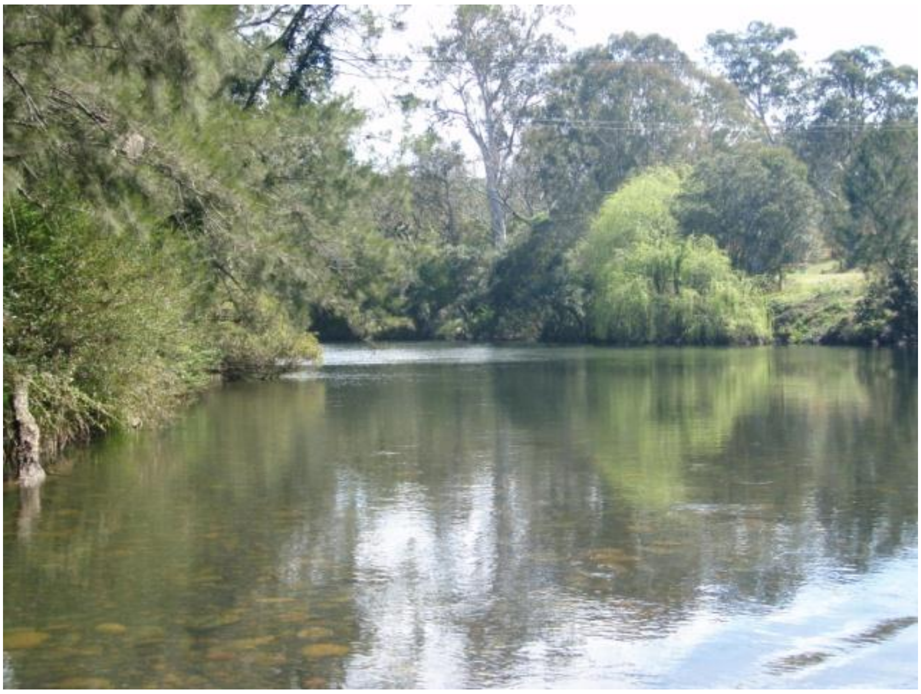


Figure 3.7 Barrington River at Rocky Crossing (Looking downstream)

Figure 3.8 Gloucester River at Faulklands Road (Looking upstream)

Lower Catchment sites selected were Bobo Creek at Gloucester Road (Site 7 in Fig. 3.2), at approximately 20m above sea level (Fig. 3.9). Dingo Creek at Belbourie Bridge (Site 8 in Fig. 3.2), at an approximate altitude of 20m (Fig. 3.10) and the Lansdowne River at Upper Lansdowne Road (Site 9 in Fig. 3.2), at an approximate altitude of 20m (Fig. 3.11). Each of these sites have greater grazing pressure and weed impacts than the upland or mid-catchment sites but the associated riparian vegetation is in good condition compared to many other areas in the lower catchment (Table 3.2).

Figure 3.9 Bobo Creek at Gloucester Road (Looking upstream)

Figure 3.10 Dingo Creek at Belbourie Bridge (Looking downstream)

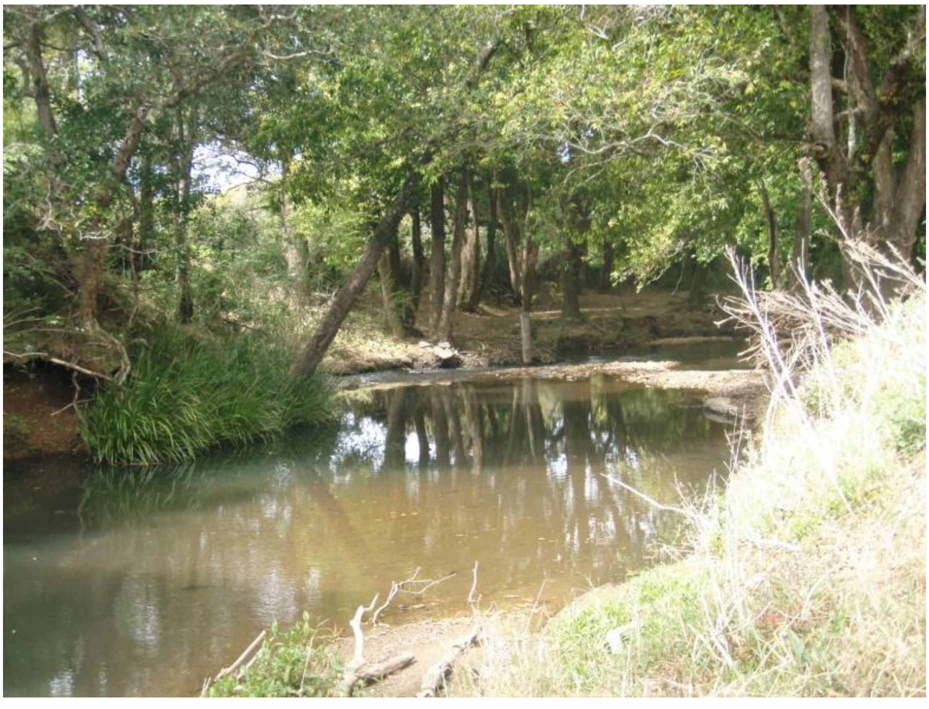


Figure 3.11 Lansdowne River at Upper Lansdowne Rd (Looking downstream)

3.2.2 Experimental nutrient enrichment sites

The Little Manning River at Woko National Park (Figs. 3.12 to 3.14) and Caparra Creek (Figs. 3.15 to 3.17) were selected for deployment of the artificial substrates. Both are in the upper Manning catchment and have mostly undisturbed catchments.

Figure 3.12 Site 1 Little Manning River (Looking upstream)

Figure 3.13 Site 2 Little Manning River (Looking downstream)

Figure 3.14 Site 3 Little Manning River (Looking upstream)

Figure 3.15 Site 1 Caparra Creek (Looking upstream)

Figure 3.16 Site 2 Caparra Creek (Looking downstream)

Figure 3.17 Site 3 Caparra Creek (Looking downstream)

3.3 Methods

3.3.1 Field sampling

The reference condition approach is one of the most common methods for deriving site-specific water quality objectives (de Rosemond et al. 2009). This approach involves the selection of relatively unmodified sites to estimate baseline condition and determine reference water quality thresholds (Warry and Hanau 1993). Water quality measured at reference sites provides a benchmark against other streams or sites which have greater human disturbance. To determine overall catchment conditions, water quality information collected from non-reference sites were compared to threshold values derived from reference sites.

Catchment-scale water quality threshold values for the Manning River were determined through sample collection at 9 reference sites. Water samples were collected monthly, dependent on discharge, from September 2008 to September 2009. The objectives of this study mean the pattern of sampling is important, as a range of hydrologic conditions needs to be captured to best reflect water quality. The sample regime shows a range of hydrologic conditions that have been captured over a 12-month period (Fig. 3.18).

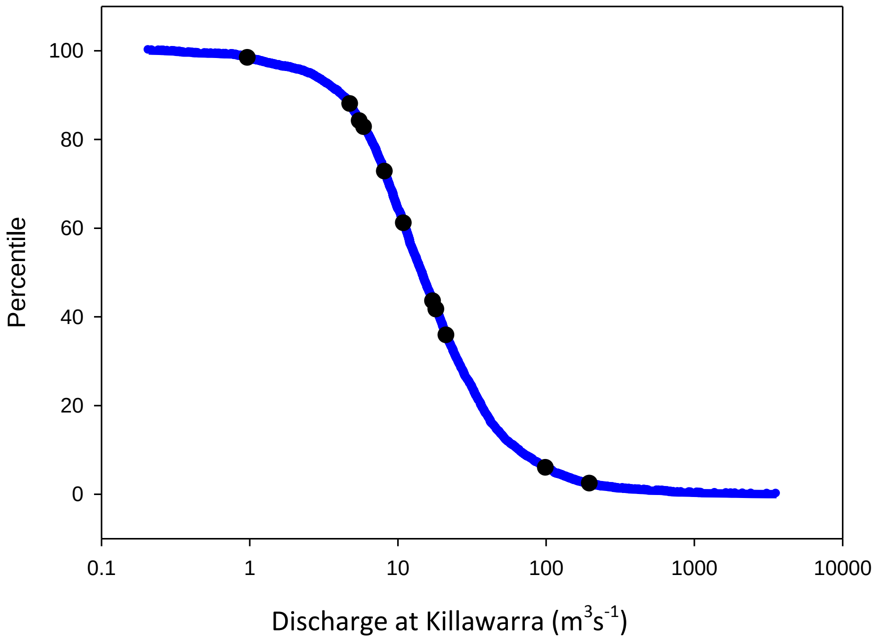


Figure 3.18 Sampling occasions (indicated by black dots) and percentile flows

Where possible, data collected during 2008-09 were added to long-term water quality information collected from several sources from 1994 to 1998 and 2002 to 2007 (Table 3.1). Turbidity, EC, NO_3-N and TP were collected as part of the long-term water quality data set. The inclusion of the long-term data allowed for an assessment of temporal variation of these water quality factors under varying flow conditions. Details of the data sources and analyses undertaken using this combined data and 2008-09 water quality data only can be found in Section 3.3.3.1.

Water column samples were collected from fixed locations at each reference site. Samples were collected for analysis of TN (mgL^{-1}), TP (mgL^{-1}), nitrite/nitrate (NO_3-N mgL^{-1}), ammonia ($NH_{3/4}$-N

mgL^{-1}), soluble reactive phosphorus (SRP mgL^{-1}) and turbidity (NTU). All nutrient analyses were undertaken by the Midcoast Water (MCW) laboratory and the methods described below are taken from MCW laboratory protocols (MCW 2010).

All water column nutrient samples were frozen in PET bottles at -20°C as soon as possible after collection. Prior to analysis samples were thawed by immersion in warm water, with occasional mixing to ensure uniform sample temperature. All methods were calibrated using standards prepared in ultra-pure water.

The TP analysis involved the oxidation of the phosphorus compounds to orthophosphate (PO_4^{3-}) by digesting with potassium persulphate. The determination of SRP (PO_4^{3-}) was based on the method of Murphy and Riley (1962) adapted for Flow Injection Analysis in which the two reagents are added separately for greater reagent stability.

Ammonia-nitrogen, nitrite-nitrogen and organic nitrogen were converted to nitrate by alkaline persulphate digestion. TN was then determined by measuring nitrate-nitrogen contributed by the above nitrogen species plus any nitrate nitrogen originally in the sample, at 520nm.

The determination of ammonia was based on the Berthelot reaction based on an alkaline solution of phenol and hypochlorite (Rhine et al. 1998). Total oxidised nitrogen was determined through nitrate being reduced to nitrite by passage of the sample through a copperized cadmium column.

The QuikChem 8500 Flow Injection Analysis System was used to perform colorimetric and ion specific electrode analysis. The samples and standards were drawn into the main chemistry unit by means of a peristaltic pump. The main chemistry unit consists of three manifolds which include a low-pressure sample injection valve, reaction module and a detector/electrode.

Turbidity was determined in situ using a Hach field meter and a sample was taken for verification in the laboratory. All laboratory samples were cooled to 4 °C, to minimise microbiological decomposition of solids and analysed as soon as possible after collection. Before analysis the samples were gently agitated to ensure representative measurement. A Hach 2100N laboratory turbidimeter was used for the analysis was designed to DIN 3804, NFEN 27027, and ISO 7027 criteria. The turbidimeter measures turbidity from 0 to 10,000 NTU (Nephelometric Turbidity Units) with automatic range selection and decimal point placement (MCW 2010)

On each sampling occasion, pH, temperature, conductivity (µS cm^{-1}), and dissolved oxygen (mg L^{-1} and % saturation) were measured using a Hydrolab DS 5X multiprobe which supported a Hach luminescent dissolved oxygen (LDO) sensor (Table 3.3).

Table 3.3 Details of Hydrolab multiprobe and field turbidity meter

Sensor	Range	Accuracy	Resolution
Hach LDO	0-60 mg L^{-1}	± 0.1 mg L^{-1} at <8 mg L^{-1} ± 0.2 mg L^{-1} at >8 mg L^{-1}	0.01 mg L^{-1}
Temperature (30k ohm thermistor)	-5 to 50 °C	± 0.10°C	0.01°C
Conductivity (graphite electrodes)	0-100 mS cm^{-1}	± 0.5% reading + 0.001 mS cm^{-1}	0.001 mS cm^{-1}
pH (reference electrode)	0 to 14 pH units	± 0.2 units	0.01 units
Turbidity (Hach portable turbidity meter)	0 to 1000 NTU	≤ 0.02 NTU	0.01 NTU

3.3.2 Nutrient enrichment design

To determine if autotrophic production within each treatment was limited by C, N, and/or P, nutrient enrichment experiments were conducted at 3 sites located within the Little Manning River and 3 sites within Caparra Creek, over 21 days during summer in two cobble bed streams. Changes in algal biomass (measured as chlorophyll-a) were measured in response to different nutrient treatments, diffusing from amended agar in small plastic pots (80 mL volume, 4.2 cm diameter). Eight treatments were tested: (1) N-supplemented; (2) P-supplemented; (3) C supplemented; (4) N+P supplemented; (5) N+C supplemented; (6) P+C supplemented; (7) N+P+C supplemented, and (8) agar only (control) (Table 3.4).

Agar pot preparation

The different nutrient enrichment treatments were prepared by amending 1% agar solution with different combinations of salts (Table 3.4). The N substrate was enriched added using $NaNO_3$ at 21.25 gL^{-1}, the P substrate used KH_2PO_4 at 34 gL^{-1} and C using $C_6H_{12}O_6$ at 45 gL^{-1}.The agar and agar plus nutrient solutions were heated to boiling point using a microwave and poured into the 80 mL plastic containers. The level of the set agar was above the lip of the pot, to ensure maximum diffusion from the agar upon deployment. Each pot was covered with a damp glass fibre filter (0.7 µm pore size Whatman GF/F), and a 5 cm^2 piece of material (650 mm poresize, red waterproof polyester, Broadway Textiles, Sydney), and was secured using the rims cut out from each container lid. All pots were stored between 24 and 48 hours, at 4°C, before being deployed at the sites.

Table 3.4 Nutrient treatments and the salts used to amend the 1% agar.

Treatment	0.25 M $C_6H_{12}O_6$	0.25 M $NaNO_3$	0.25M KH_2PO^{4-}
C	×		
N		×	
P			×
C + N	×	×	
C + P	×		×
N + P		×	×
C + N + P	×	×	×

Note: No nutrients were added to the control substrate.

A total of 24 agar pots (8 x treatments, 3 x replicates) were deployed at each site for 21 days in January/February 2012. At each site the pots were randomly arranged into six lengths of rigid, plastic mesh (5 mm mesh size). Each length of mesh had pre-cut holes. The mesh and pots were placed in a random section of each channel, perpendicular to the direction of flow (Fig. 3.19). Eight tent pegs were used to secure the mesh and pots to the stream bed.

Water column samples were collected from each site at each deployment and collection time. The concentration of TN, TP, NO_3-N and SRP were determined using the methods outlined above.

Measurements of pH, temperature units, turbidity units, conductivity (µS cm^{-1}), and dissolved oxygen (mg L^{-1}) were also made at these times.

The mesh and pots were removed from the stream bed after 21 days. The material was lifted from the pots and cut into 4 cm diameter disks. All samples were kept dark and cool while being transported back to the laboratory.

As a measure of autotrophic growth, chlorophyll-a was extracted from each colonised polyester material using 90% acetone and the concentration determined spectrophotometrically, following the method of Parsons et al. (1984).

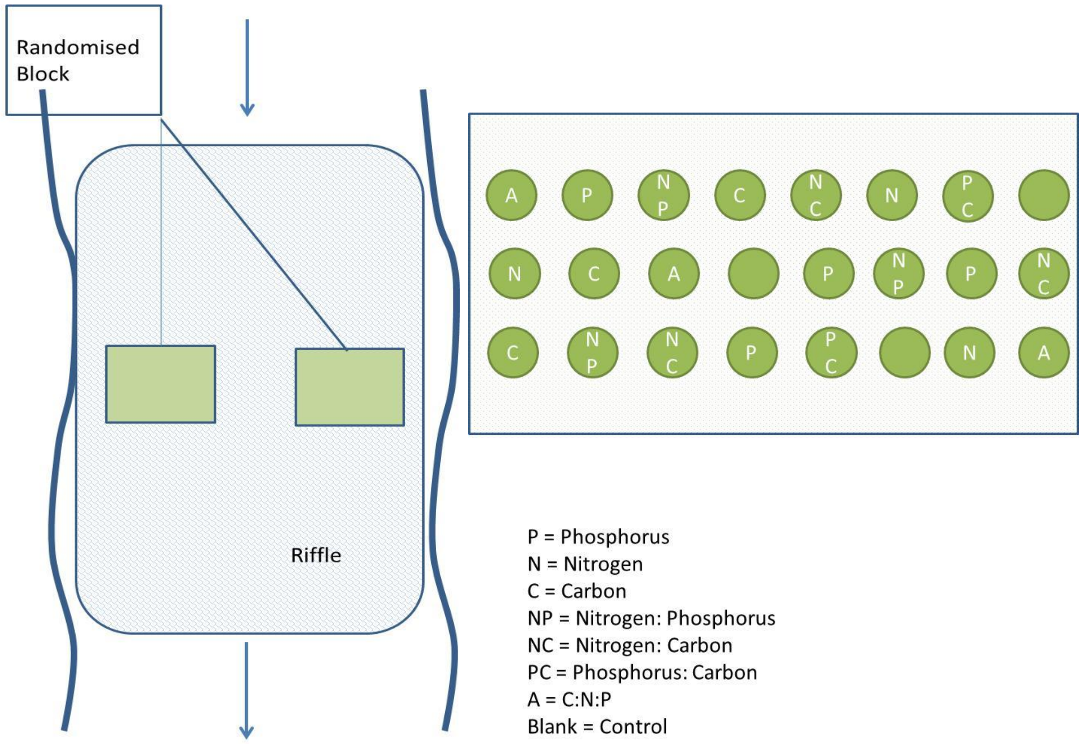


Figure 3.19 Position of trays in riffle and randomised block arrangement

3.3.3 Data analysis

3.3.3.1 Catchment–derived water quality thresholds

To ascertain temporal changes in water quality and to better inform catchment water quality thresholds for the protection of aquatic ecosystems in a moderately disturbed catchment, comparisons were made between historical datasets and more recently collected water quality data by looking for differences over time.

Sites with available historical water quality information were assessed for long-term changes and trends by comparing with data collected for this study in 2008/09, with further comparisons to ANZECC and ARMCANZ (2000) water quality threshold values. Historical water quality data was collected under a number of programs including monthly data sampled from November 1994 to

November 1997, as part of the Manning Community Water Quality Monitoring Program. Variables collected included turbidity, EC, NO_3-N and TP. Data from Rowleys River, Little Manning River, Caparra Creek, Dingo Creek at Belbourie Bridge, lower Dingo Creek, Lansdowne River and Manning River at Charity Creek Bridge were included in this investigation (see Table 3.1 and Fig. 3.1):

Other historical water quality data was collected on a monthly basis as part of MCW Manning River Water Quality Monitoring Program between 2002 and 2007. Water quality variables used for this study were TN and TP collected at Dingo Creek, the Manning River at Charity Creek Bridge and the Manning River at Killawarra Bridge.

Changes over time, differences among sites and whether reference site water quality met ANZECC/ARMCANZ (2000) guidelines were assessed. Long-term data, including data collected by the community, and samples collected over 2008/09 were used to determine representative water quality reference profiles for the Manning catchment. Graphical comparisons using the means and standard errors of EC, TP and NO_3-N, collected as part of the historical and reference sampling, were created using SIGMAPLOT® 10.

All ANOVAs were done using SYSTAT for Windows, Version 13.0 (SYSTAT, Evanston, Illinois, USA). One-way ANOVAs were performed using historical and 2008/09 data to test for differences in water quality variables (EC, NO_3-N and TP) among sites over time. The ANOVA included the term 'stream' which was classed as a random factor as the streams were chosen as representatives of reference condition, and was used to discriminated between sub-catchment effects. The term 'time' was classed as a fixed factor.

Data for ANOVAs were checked for normality and homogeneity of variance using residuals and the relationship between the mean and variance (Quinn and Keough 2002) and were log (x+1) transformed when required. The transformation improved normality and normalised to a common measurement scale to facilitate comparison using Euclidean distance (Clarke and Warwick 2001). Tukey's mean separation technique was used to determine where significant differences existed among treatments.

MCW data taken from a catchment-wide pilot-study was used to assess possible nutrient impacts from tributaries on the Manning River. As there were limited samples available for comparison, only means and standard errors were used to compare differences between sites to identify areas of potential interest or impacts within the Manning catchment.

Relationships between nutrients and discharge were investigated using linear regressions. Nutrient results from long-term, recent datasets and discharge data, taken from the nearest river gauging station (sourced from the NSW Water Information website - www.waterinfo.nsw.gov.au; accessed 14 July 2012) were used in the analyses which were undertaken to determine links between catchment runoff and nutrients. As the risk of making Type I errors increase with single linear regressions, the regressions were only accepted if $p \leq 0.025$ (Quinn and Keogh 2002). Only results of interest are presented in this thesis.

Principal components analysis (PCA) was used to investigate the resemblance in suites of environmental conditions between sites. Values for water temperature, discharge, DO% saturation, EC, pH and nutrients were averaged for each site. All values except for average temperature and pH were log-transformed to improve normality and normalised to a common measurement scale for comparison using Eucildean distance (Clarke and Warwick 2001). Multivariate statistical analyses were performed using PRIMER version 6 (PRIMER-E Ltd, Plymouth).

Exceedance curves are based on cumulative frequency distributions and indicate the percentage of samples which were above or below a certain threshold. Cumulative exceedance curves were used to indicate the percentage of time water quality at sites was higher than recommended levels (ANZECC and ARMCANZ 2000). These recommended levels, based on threshold values for coastal rivers in south-east Australia, were obtained from the Australian and New Zealand Guidelines for Fresh and Marine Waters (ANZECC and ARMCANZ 2000) uses default threshold values calculated using the statistical distribution of reference data collected from appropriate Australian studies (Table 3.5). Reference data was derived from data collected from ecosystems considered unmodified or slightly-modified, however, the choice of reference systems was not based on any objective biological criteria (ANZECC and ARMCANZ 2000). Threshold values for slightly to moderately disturbed ecosystems have been defined using the 80th and/or 20th percentile of reference data (ANZECC and ARMCANZ 2000).

Catchment-derived threshold values were formulated using the results from the reference site water quality data and comparing to the 80th percentile values given by ANZECC and ARMCANZ (2000). Threshold values were changed to reflect those found at reference sites. The derived catchment-relevant threshold values were then validated using exceedance curves populated by data collected at non-reference sites. Water quality data used for the validation was sourced from MCW.

Table 3.5 ANZECC and ARMCANZ (2000) default water quality threshold values for NSW coastal rivers

Ecosystem type	**TP** (mg L^{-1})	**SRP** (mg L^{-1})	**TN** (mg L^{-1})	**NO_x** (mg L^{-1})	**NH_4^+** (mg L^{-1})	**DO%**	**pH**	**EC** (µS cm^{-1})	**Turbidity** (NTU)
NSW Upland River	0.020	0.015	0.20	0.015	0.013	60-120	6.5-9.0	200	2
NSW Coastal Lowland River	0.025	0.008	0.35	0.04	0.020	60-120	6.5-9.0	200	6

3.3.3.2 Nutrient enrichment experiment

The nutrient enrichment experiment was conducted to test whether nutrient stoichiometric ratios were indicative of nutrient limitation of autotrophic production by benthic algae. The experiment was also undertaken to determine whether autotrophic production was limited by the same nutrients or a combination of nutrients within reference sites. Autotrophic nutrient limitation was determined by assuming that the highest concentration of chlorophyll-a had accumulated on the most limiting nutrient or combination of nutrients. The increased concentration of chlorophyll-a on a particular treatment indicates that the added nutrient, or combination of nutrients, is facilitating growth and is likely to be lacking under normal conditions.

A mixed-model ANOVA was used to compare chlorophyll-a concentrations among treatments. The data matrix consisted of chlorophyll-a concentrations (g m^{-2}) from the eight treatments. The chlorophyll-a data were transformed (log x+1) prior to analysis to reduce the effects of heterogeneous dispersions, which can increase type 1 error rates and violates an assumption of the ANOVA test.

Significant differences were assessed using Tukeys mean separation technique. Variance components for ANOVAs were calculated using the estimated mean square of each term and its associated error term (Quinn and Keogh 2002).

Principal components analysis (PCA) was used to investigate the resemblance of algal biomass among sites. Values for each treatment were averaged for each site and log-transformed to improve normality and normalised to a common measurement scale for comparison using Eucildean distance (Clarke and Warwick 2001). Multivariate statistical analyses were performed using PRIMER version 6 (PRIMER-E Ltd, Plymouth).

3.4 Results

3.4.1 Temporal trends

Discharge in the Manning River varied considerably over sampling years (Figs. 3.20 and 3.21). Flooding during 1995 is followed by comparatively low discharge volumes during 1996 and 1997 indicating drought (Figs. 3.20 and 3.21). Discharge during 2008/09 indicates three periods of high flows which is reflected in the high total discharge volume recorded in 2008 (Figs. 3.20 and 3.21). These differences between years may mask long-term temporal changes in water quality.

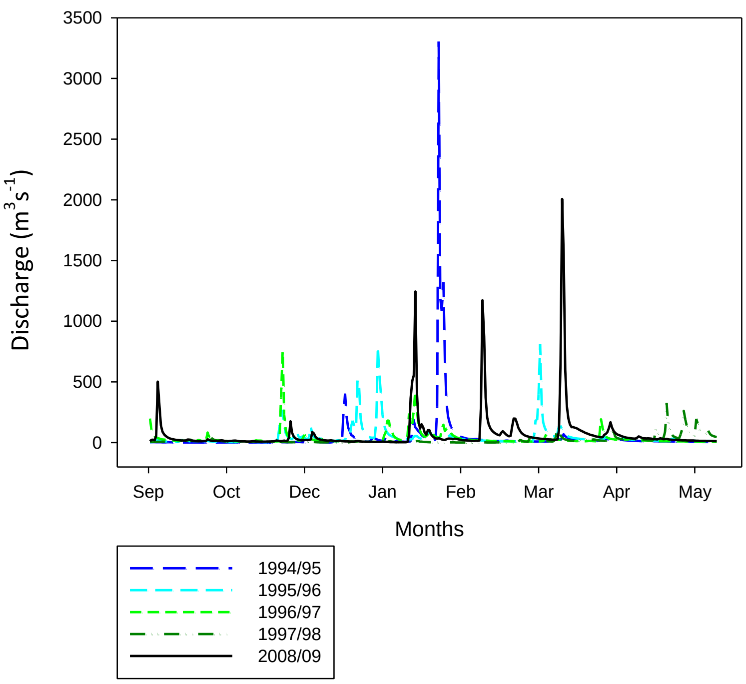


Figure 3.20 Manning River discharge at Killawarra gauge (208004) during non-continuous sampling periods (1994-1998 and 2008-2009) Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au)

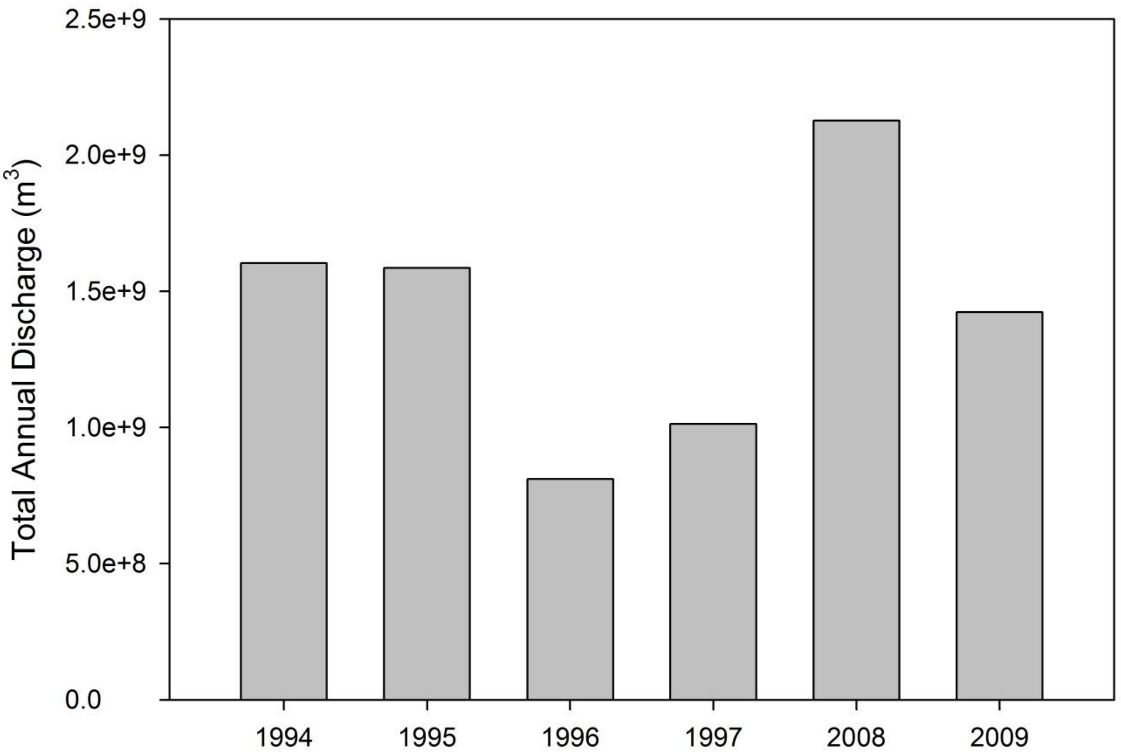


Figure 3.21 Total annual discharge at Killawarra Gauge (208004) during non-continuous sampling periods 1994-97, 2008-09 Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au).

When comparing EC data collected in the 1990s to that collected in 2008/09, there is a decline at all sites, with the greatest declines found at Caparra Creek and Lansdowne River (Fig. 3.22). ANOVA results showed significant differences between sites and times and a significant interaction between sites and times (Table 3.6). Long-term EC levels were significantly different in the mid-catchment site of Rowleys River compared to the lowland Lansdowne River (Tukey's test $p<0.0001$).

Table 3.6 Results of ANOVA main test for significant differences in electrical conductivity over time.

Source of Variation	df	MS	F	SS	P-value
Time	1	0.18	70.9	12.81	**<0.0001**
Site	4	0.53	8.76	18.53	**<0.0001**
Time*Site	4	0.53	10.3	21.76	**<0.0001**

Note: Significant P values are shown in bold

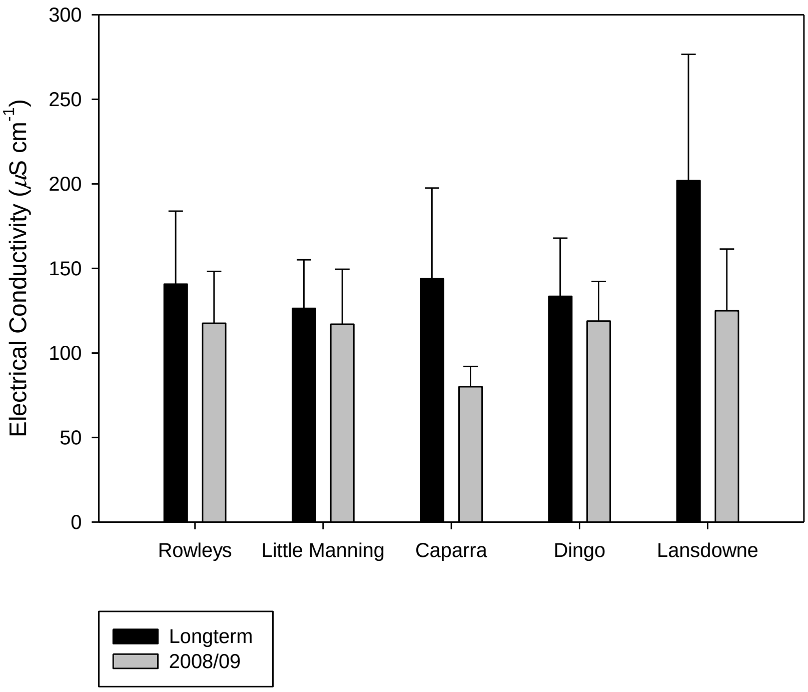


Figure 3.22 Comparison of historical electrical conductivity to 2008/09 data for selected Manning catchment reference sites using mean and standard error

Oxidised nitrogen concentrations measured at reference sites are lower in 2008/09 data when compared to the historical data, with the exception of Dingo Creek (Fig. 3.23). These differences were significantly different between times (Table 3.7). Pairwise comparisons found significant differences between Rowleys River and Lansdowne River (Tukey's test $p<0.0281$), and Dingo Creek and Lansdowne River (Tukey's test $p<0.0355$).

The long-term sampling site located on Dingo Creek is upstream of an area where abattoir (or slaughterhouse) effluent is sprayed on agricultural land. A short-term study, undertaken on behalf of MCW during 2006 and 2007, sampled major tributaries within the Manning catchment. This study indicated that the downstream section of Dingo Creek, located adjacent to the effluent discharge area, had elevated oxidised nitrogen (NO_x) concentrations (Fig. 3.24) (Thurtell 2008).

Table 3.7 Results of ANOVA main test for significant differences in oxidised nitrogen among sites and times.

Source of Variation	df	MS	F	SS	P-value
Time	1	0.76	33.2	15.36	**<0.0001**
Site	4	0.83	1.75	18.53	<0.1464
Time*Site	4	0.83	0.551	21.76	<0.6987

Note: Significant P values are shown in bold

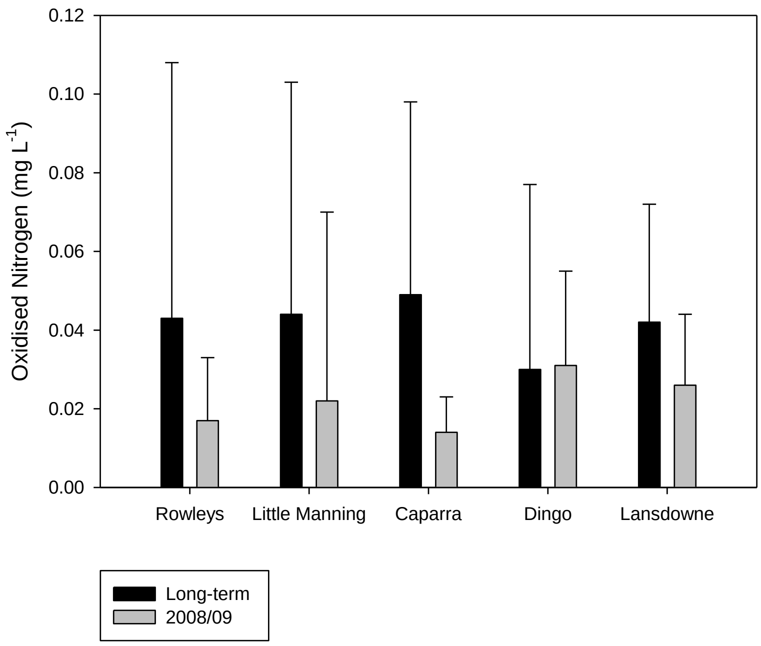


Figure 3.23 Comparison of historical oxidised nitrogen to 2008/09 data for selected Manning catchment reference sites using mean and standard error

Unlike NO_x and EC, TP concentrations did not vary greatly over the two sampling periods, with little difference between historical and more recent concentrations, indicating no major shifts as a result of hydrological influences (Fig. 3.24). TP concentrations significantly varied among sites (Table 3.8). Rowleys River located in the mid-catchment varied significantly from Dingo Creek (Tukey's test p<0.0168).

Table 3.8 Results of ANOVA main test for significant differences in total phosphorus between times and sites.

Source of Variation	df	MS	F	SS	P-value
Time	1	0.65	2.68	1.73	<0.1173
Site	4	0.60	11.7	28.39	**<0.0001**
Time*Site	4	0.60	3.12	7.56	**<0.0193**

Note: Significant P values are shown in bold

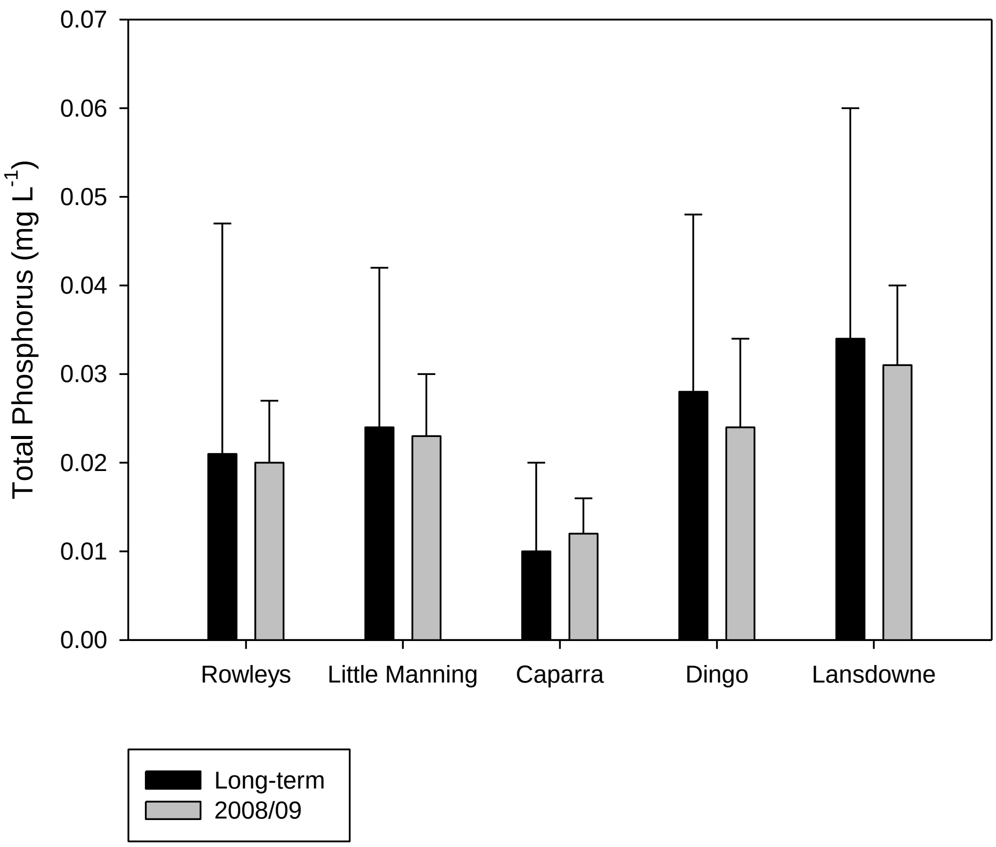


Figure 3.24 Comparison of historical total phosphorus to 2008/09 data for selected Manning catchment reference sites using mean and standard error

Catchment influences can be further described using long-term data from two sites (Manning River at Killawarra and Charity Creek Bridge) located within the lower Manning River to compare nutrient concentrations with discharge between 2002 and 2007 (Figs. 3.25 and 3.26). By determining the extent of the relationship between discharge and total nutrients, the influence of runoff and low flows can be assessed. The relationship between discharge and total nutrients shows a trend towards increased TN and TP concentrations in the lower Manning when discharge is high, supporting the generally accepted paradigm of the greater influence of non-point sources of pollution on waterways (Figs. 3.25 and 3.26). This relationship between increased nutrient concentrations and runoff demonstrates the importance of land use on water quality and reliant aquatic communities.

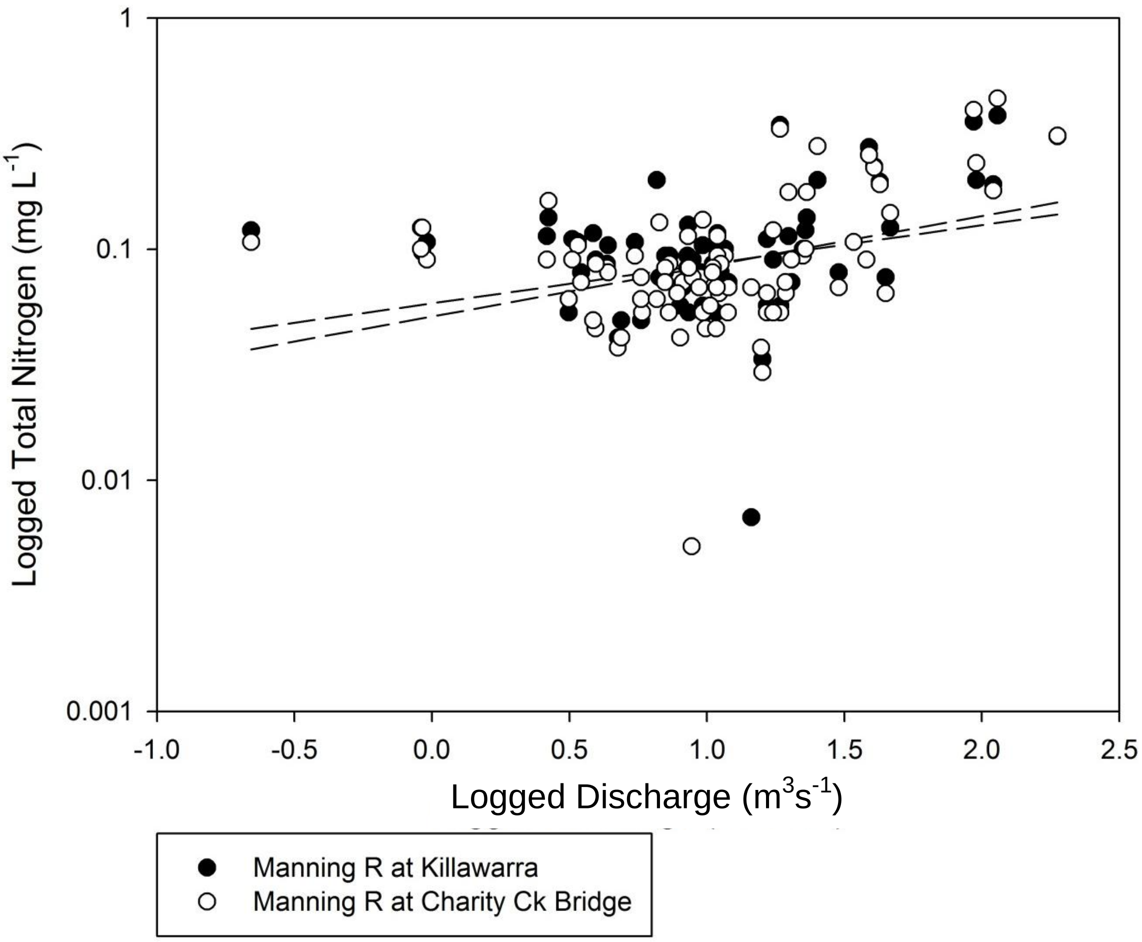


Figure 3.25 Relationship between total nitrogen and discharge in the Manning River at Charity Creek Bridge and Killawarra, 2002 to 2007. (r^2 = 0.2310; P<0.001). Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au).

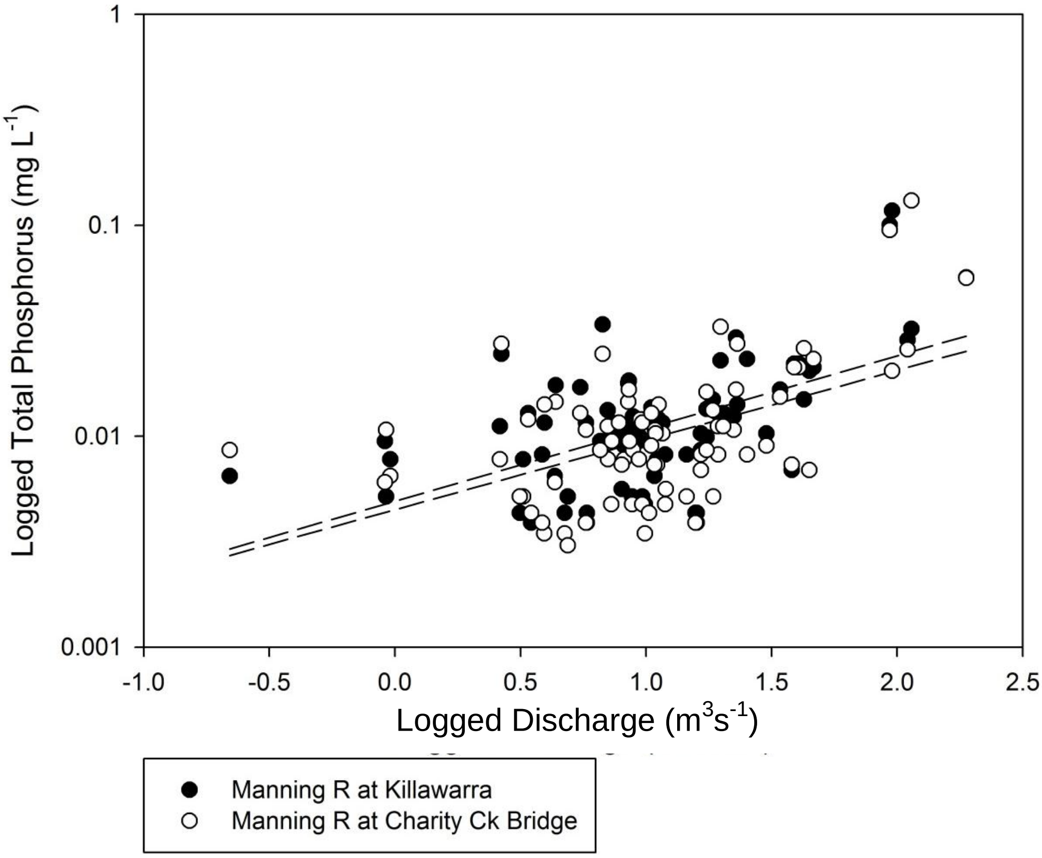


Figure 3.26 Relationship between total phosphorus data and discharge in the Manning River at Charity Creek Bridge and Killawarra, 2002 to 2007. ($r^2 = 0.2540$; P<0.001). Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au).

3.4.2 Reference sites

Reference pH values are within the acceptable range for the protection of upland and coastal freshwater aquatic ecosystems located in south-east Australia (ANZECC and ARMCANZ 2000) (Fig. 3.27).

Higher pH levels in the Little Manning River correspond with low flows (below 90th percentile) which may reflect increased primary productivity, reduced scouring of periphyton and increased groundwater influences from the underlying basalt geology (Figs. 3.27, 3.28 and 3.29). Lower pH levels under high flow conditions may reflect lower pH of rain water, which would dilute river water during runoff events (Fig. 3.28).

Higher TP levels were also recorded in the Little Manning River when compared to other upland reference sites (Fig. 3.30). The average TP concentrations, which exceed the upland threshold, appear only weakly linked to higher discharges, and therefore catchment runoff indicating geological influences from basalt (Fig. 3.29) may be greater in this catchment. There is no significant relationship between TP concentrations and discharge in the Little Manning River (r^2 = 0.02; p=0.6249).

Lansdowne River, located in the lower Manning catchment also has elevated TP concentrations in comparison to all sites, exceeding the threshold for the protection of coastal river ecosystems (Fig. 3.30).

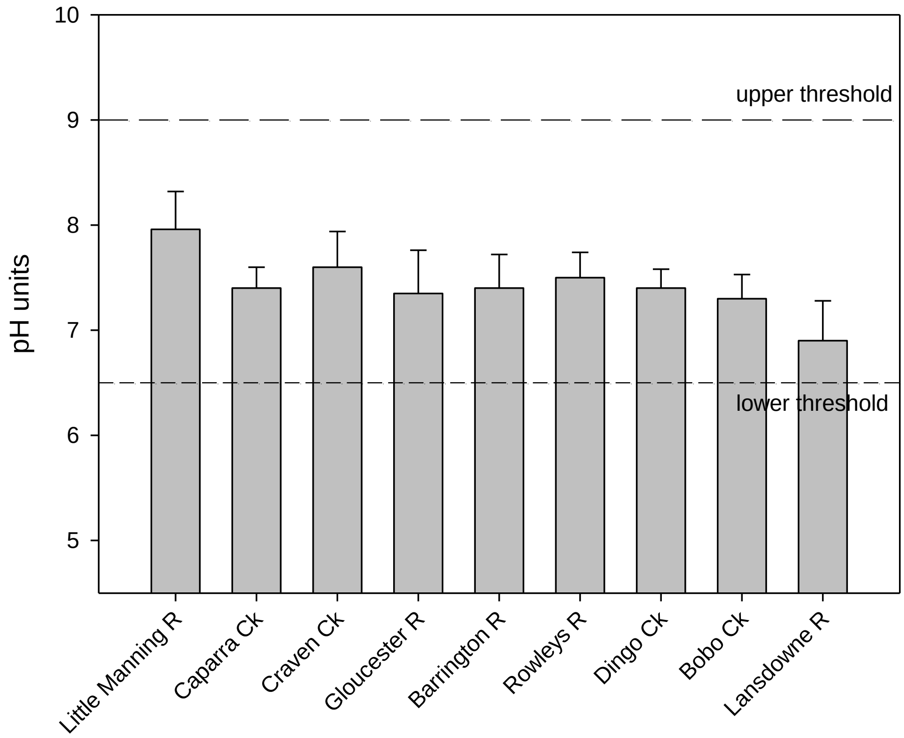


Figure 3.27 pH mean and SE from Manning catchment reference sites, 2008-09 compared to ANZECC/ARMCANZ thresholds

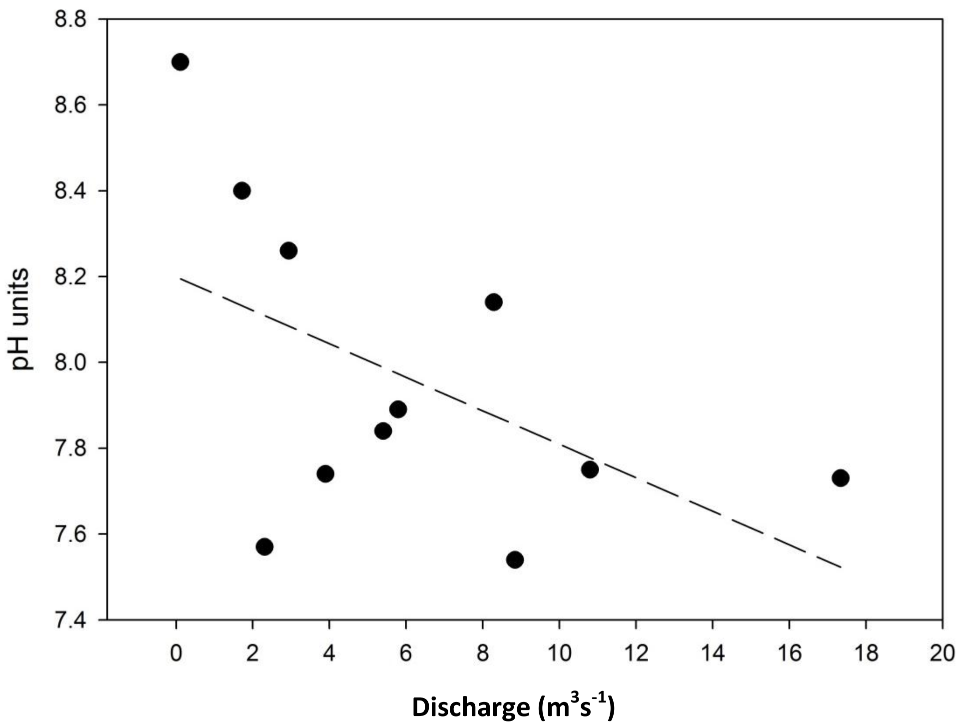


Figure 3.28 pH and discharge relationships for the Little Manning River, 2008-2009 (r^2 = 0.43; p=0.09) Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au)

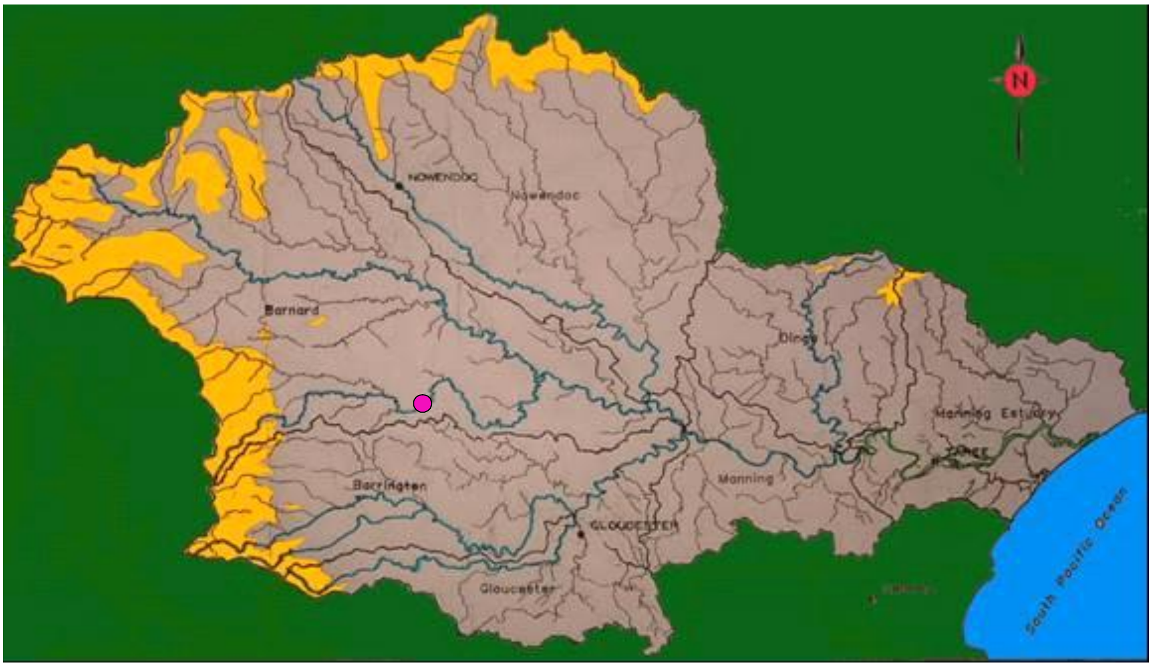


Figure 3.29 Areas of basalt within the Manning catchment (source: DLWC undated)
(Basalt indicated by yellow areas; Little Manning River site indicated by pink dot)

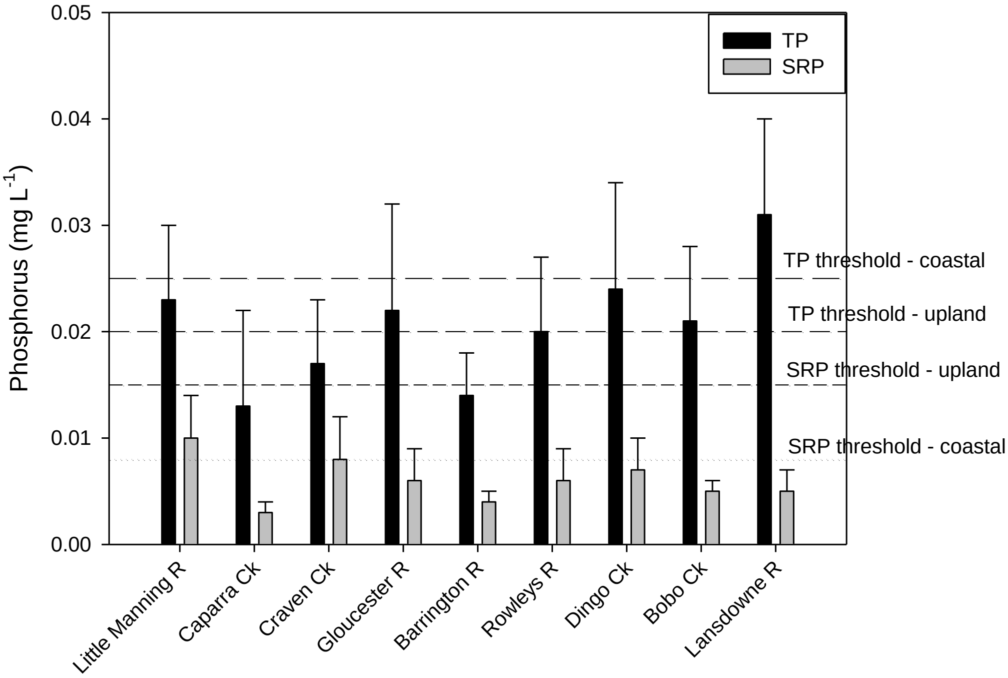


Figure 3.30 Phosphorus concentrations using mean and SE, Manning catchment reference sites, 2008-09 compared to ANZECC/ARMCANZ thresholds

Nitrogen concentrations varied across subcatchments with TN concentrations in the mid to lowland sites within the acceptable threshold of 0.35 mg L^{-1} for coastal rivers (Fig. 3.31). However, an upland waterway, Craven Creek, and a mid-catchment site, Barrington River, had maximum TN levels which were considerably higher than other upper and mid-catchment sites.

The Craven Creek and Barrington River sites are located within well-vegetated riparian areas with minor grazing impacts. Linear regressions using log-transformed data found no significant relationship between elevated TN and discharge at either site (Barrington River - r^2=0.08; p=0.37) (Craven Creek -r^2=0.03; p=0.55). This may be a function of catchment geology, as both are located in basins of mixed sedimentary and crystalline geology.

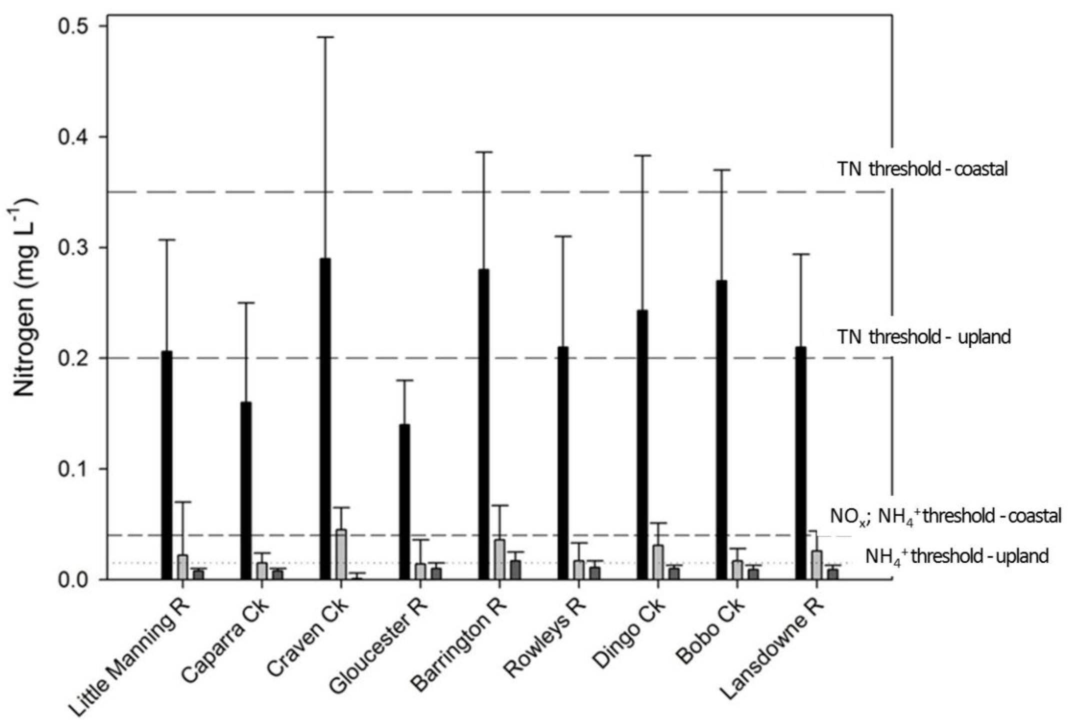


Figure 3.31 Nitrogen (TN, NOx, NH_4^+) concentrations using mean and SE, Manning catchment reference sites, 2008-09 compared to ANZECC/ARMCANZ thresholds

Changes in discharge during the sampling period alters allochthonous inputs, dilution rates, flow velocity and habitat availability. Discharge at reference sites during the sampling period was highly variable, with large SE values indicating the extent of variability within the discharge dataset (Fig. 3.32). This large variability in discharge and the interaction of anthropogenic and natural gradients in the catchment and non-linear responses create difficulties in determining major influences on stream chemistry.

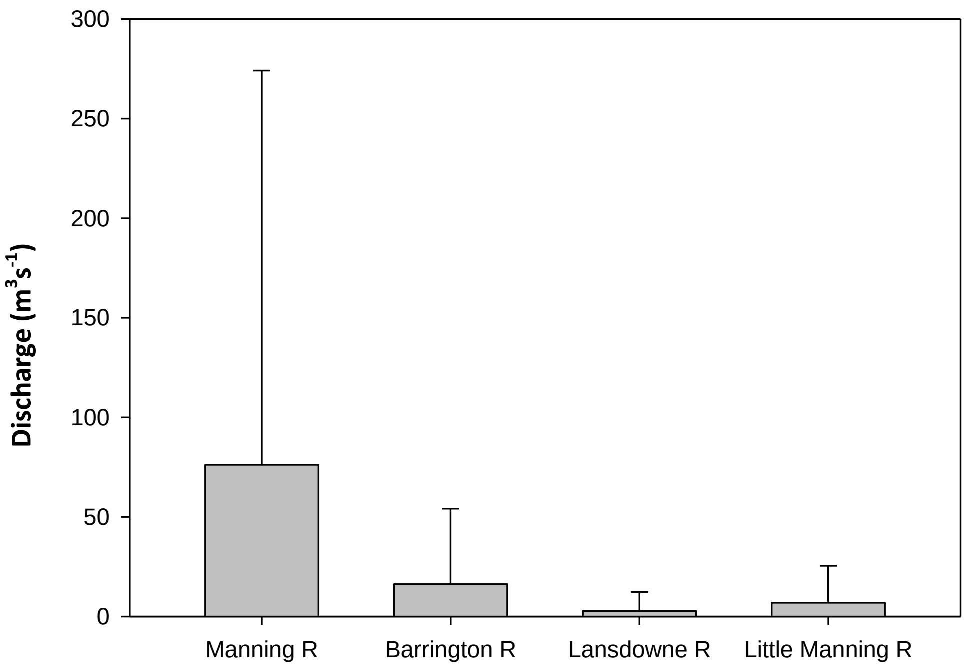


Figure 3.32 Discharge mean and SE across Manning catchment reference sites, 2008-09
Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au)

Results from a PCA combining environmental variables at all reference sites found that the first two axes of the PCA (Fig. 3.33) explained 63.7% of the total variance within the data matrix (9 environmental variables, 9 sites). The third axis (not shown in Fig. 3.33) accounted for a further 12.3%, resulting in a total 75.9% of variability captured by the first three axes. Eigenvector coefficients for declining turbidity and increasing DO contributed the highest to the first axis, while NO_3-N and TN made the highest contribution to the second axis (Fig. 3.33). Barrington River and Caparra were grouped in association with high DO, Little Manning River was characterised by higher pH, while Lansdowne River and Bobo Creek, both lowland sites, were associated with EC and turbidity (Fig. 3.33). Dingo Creek was characterised by an association with higher NO_3-N (Fig. 3.33).

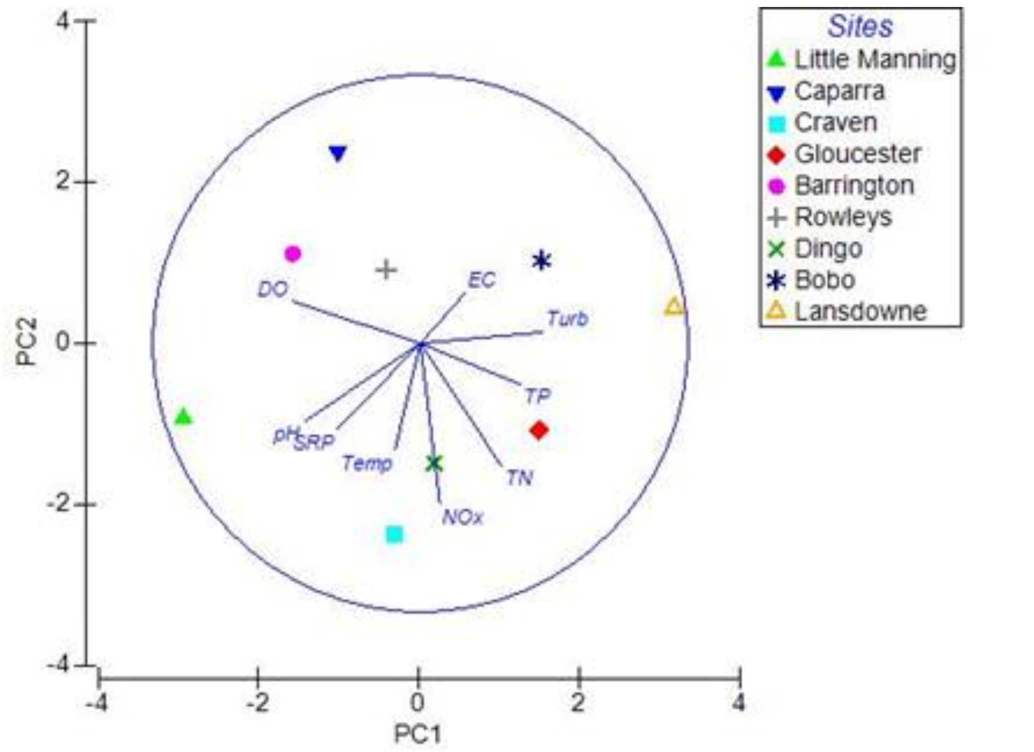


Figure 3.33 Principal Components Analysis of environmental variables at reference sites, vectors showing the contributions of variables to the axes

The vector lengths reflect a variable's contribution to the two axes in relation to all possible axes.

3.4.3 Water quality thresholds

Exceedance curves give the percentage of time that a variable, shown on the horizontal axis, exceeds a given threshold. To identify temporal trends within the catchment, comparisons between the compliance of long-term water quality data and the more recently collected data have been made using exceedance curves for each variable. Suitable data for comparison were available for EC, turbidity and TP.

Using exceedance curves, EC values at most reference sites were within the recommended ANZECC and ARMCANZ threshold of 200-300 µS cm^{-1} for coastal rivers (Fig. 3.34). However, EC in Bobo Creek in 2008-2009 exceeded the guideline in 100% of sampling occasions (Fig. 3.34).

Thresholds for the turbidity of NSW rivers ranges from 2 NTU for upland coastal rivers to 6 NTU for lowland coastal rivers. Figure 3.35 indicates that turbidity levels were low for Craven Creek and Barrington River, both in well-forested catchments. Caparra Creek, though also in a well-forested catchment, exceeded the 2 NTU threshold up to 50% of sampling occasions.

The highest turbidity levels were found in the lower catchment, corresponding with higher discharges (Fig. 3.36), indicating that runoff was a significant contributor to increased turbidity within the lower Manning catchment. There is also an increase in turbidity over time (Fig. 3.36). This result indicates the possible impacts from land use changes, such as riparian clearing on aquatic communities, with the likely result of increasing siltation and a decline in water quality.

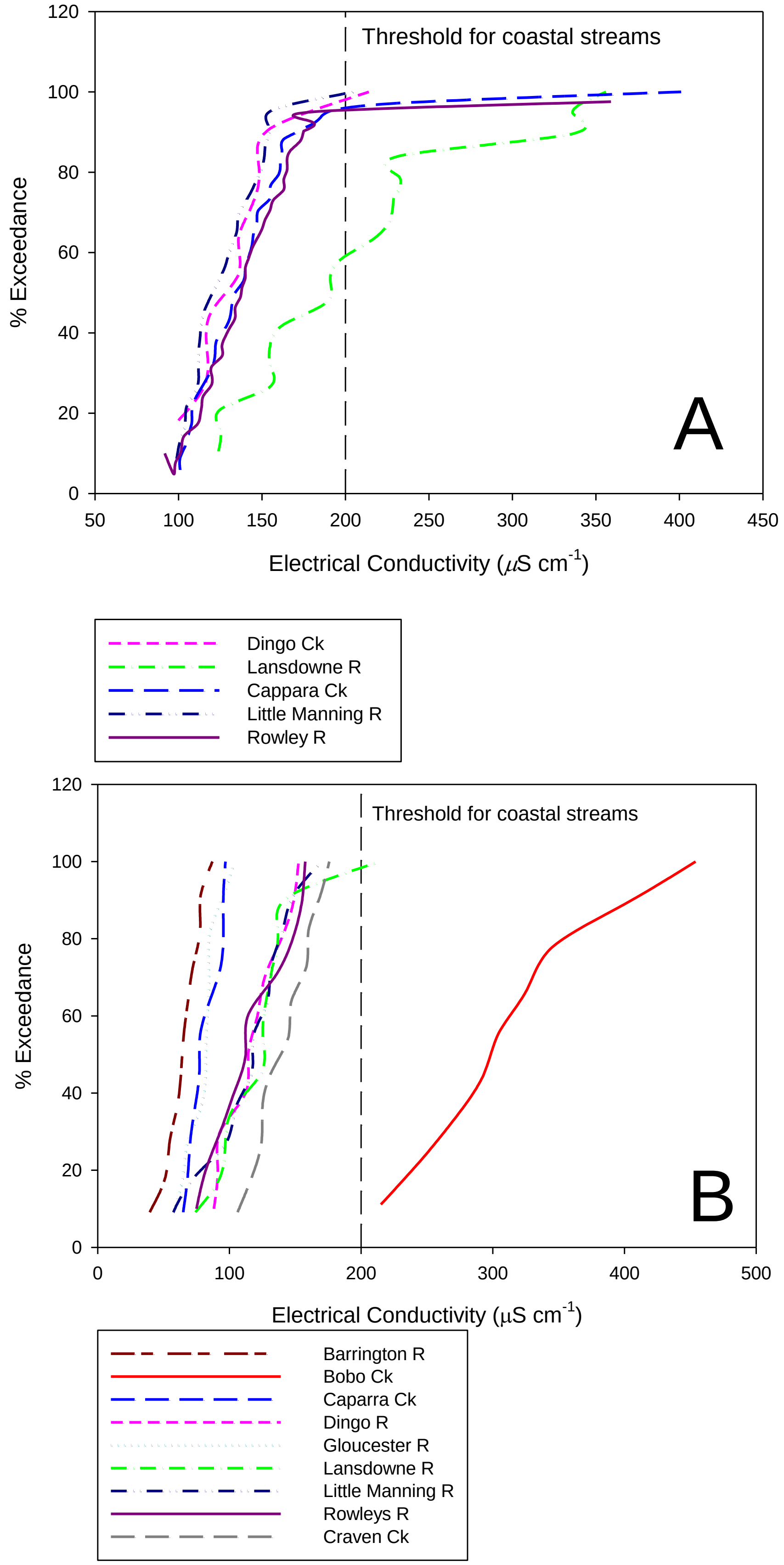


Figure 3.34 Exceedance of upper thresholds for electrical conductivity, Manning catchment reference sites compared to ANZECC/ARMCANZ thresholds. A) Long-term data, B) 2008-2009

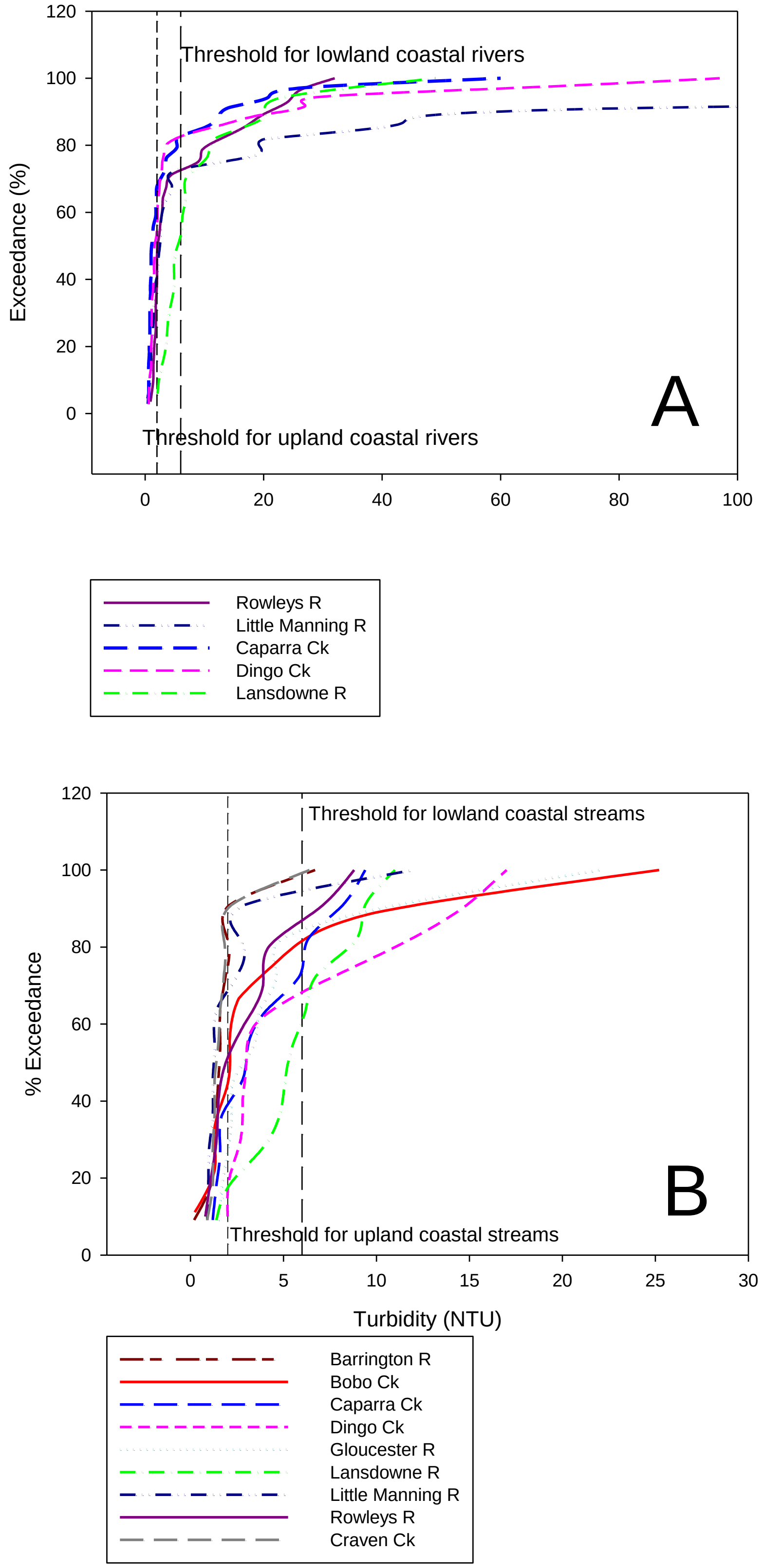


Figure 3.35 Exceedance of upper thresholds for turbidity, Manning catchment reference sites compared to ANZECC/ARMCANZ thresholds. A) Long-term data B) 2008-2009.

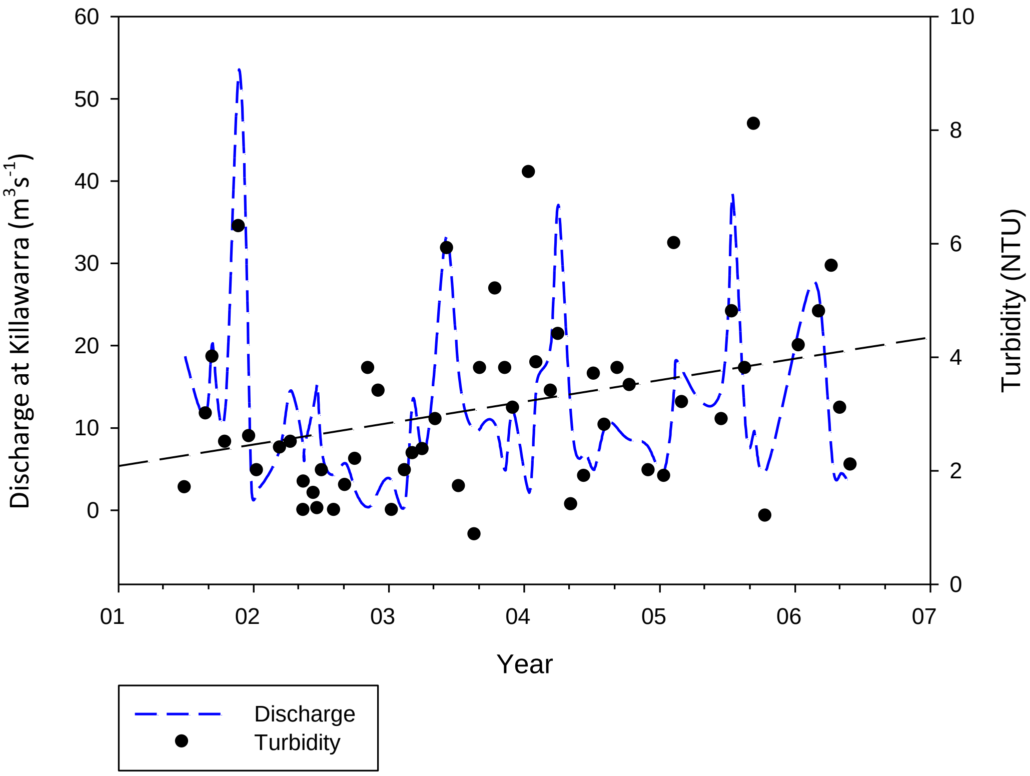


Figure 3.36 Relationship between turbidity and discharge in the Manning River, 2001 to 2007 (r^2=0.16; p=0.0023)

Historical data indicated that the 80th percentile TP threshold was exceeded in the upland site of the Little Manning River and the lowland sites of Dingo Creek and Lansdowne River (Fig. 3.37). More recently collected data indicates Barrington River, Craven Creek and Caparra Creek are the only reference sites within the 80th percentile TP threshold values recommended by ANZECC/ARMCANZ (2000) for upland and coastal streams (Fig. 3.37). The remaining waterways have elevated TP levels compared to the recommended guidelines (Fig. 3.37), with Lansdowne River in particular well outside recommended thresholds. The more recent data also shows that there is an increasing trend for the Lansdowne River when compared to the historical data (Fig. 3.37).

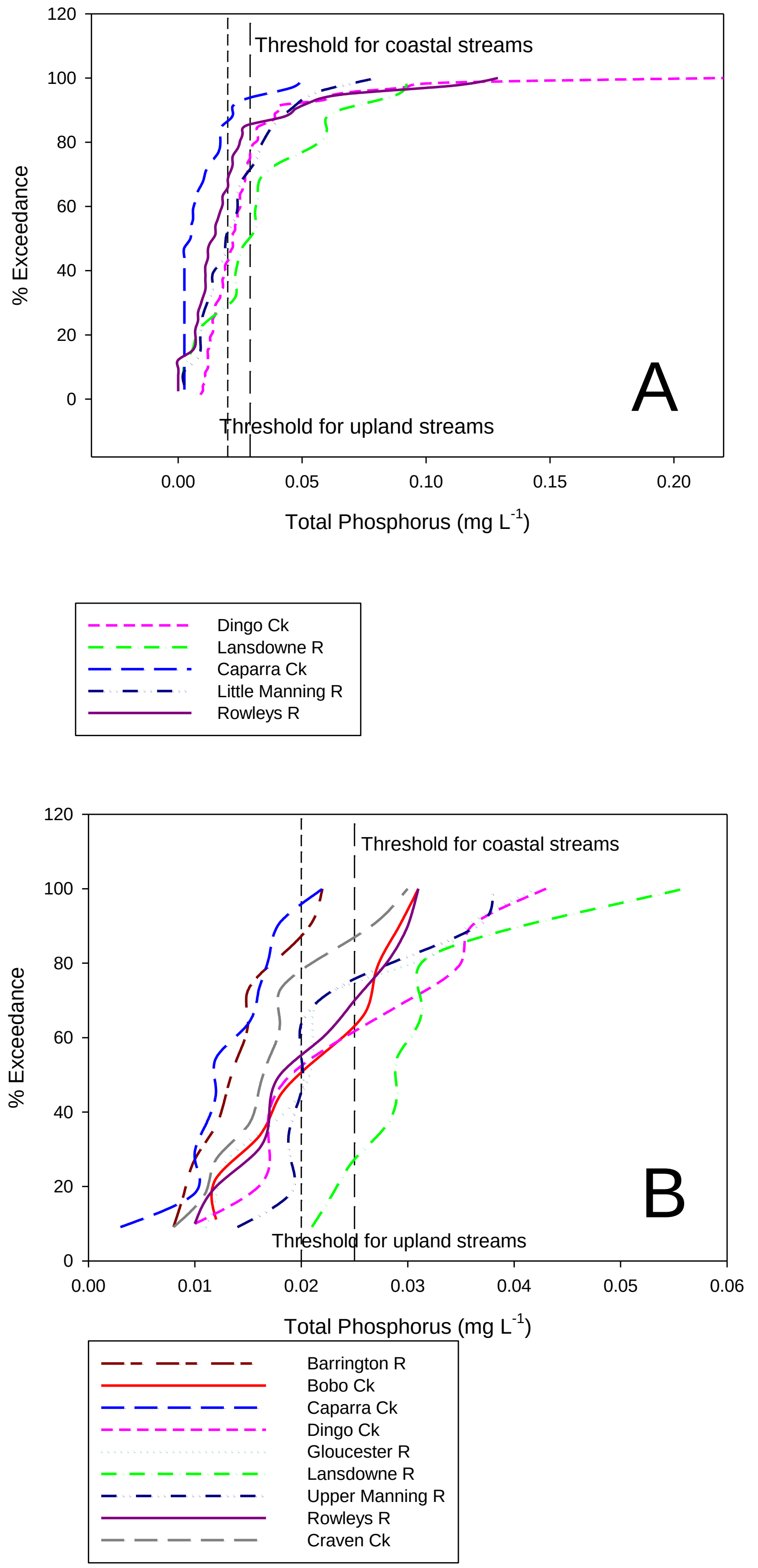


Figure 3.37 Exceedance of upper thresholds for total phosphorus, Manning catchment reference sites compared to ANZECC/ARMCANZ thresholds. A) Long-term data B) 2008-2009.

3.4.3.1 Recent reference site data

Exceedance curves have also been formulated for pH, DO, TN, NOx and SRP to determine the degree to which reference sites meet default guideline threshold values based on data collected during 2008/09.

Little Manning River pH levels are higher than other reference sites within the Manning catchment and this is reflected in the exceedance curves which indicate this site has higher levels than all other sites (Fig. 3.38). DO saturation levels generally met recommended ANZECC/ARMCANZ (2000) guideline values (Fig. 3.39) which is 60-120% for NSW coastal rivers. Two lowland streams, Bobo Creek and Lansdowne River, demonstrated a drop in DO saturation below the recommended 60% around 20% of the time (Fig. 3.39). These lower DO levels occurred during low flows that followed high winter discharge (Fig. 3.40). This decline in DO may indicate increased oxygen demand as a result of biological processing of terrestrial material deposited during the preceding storm event.

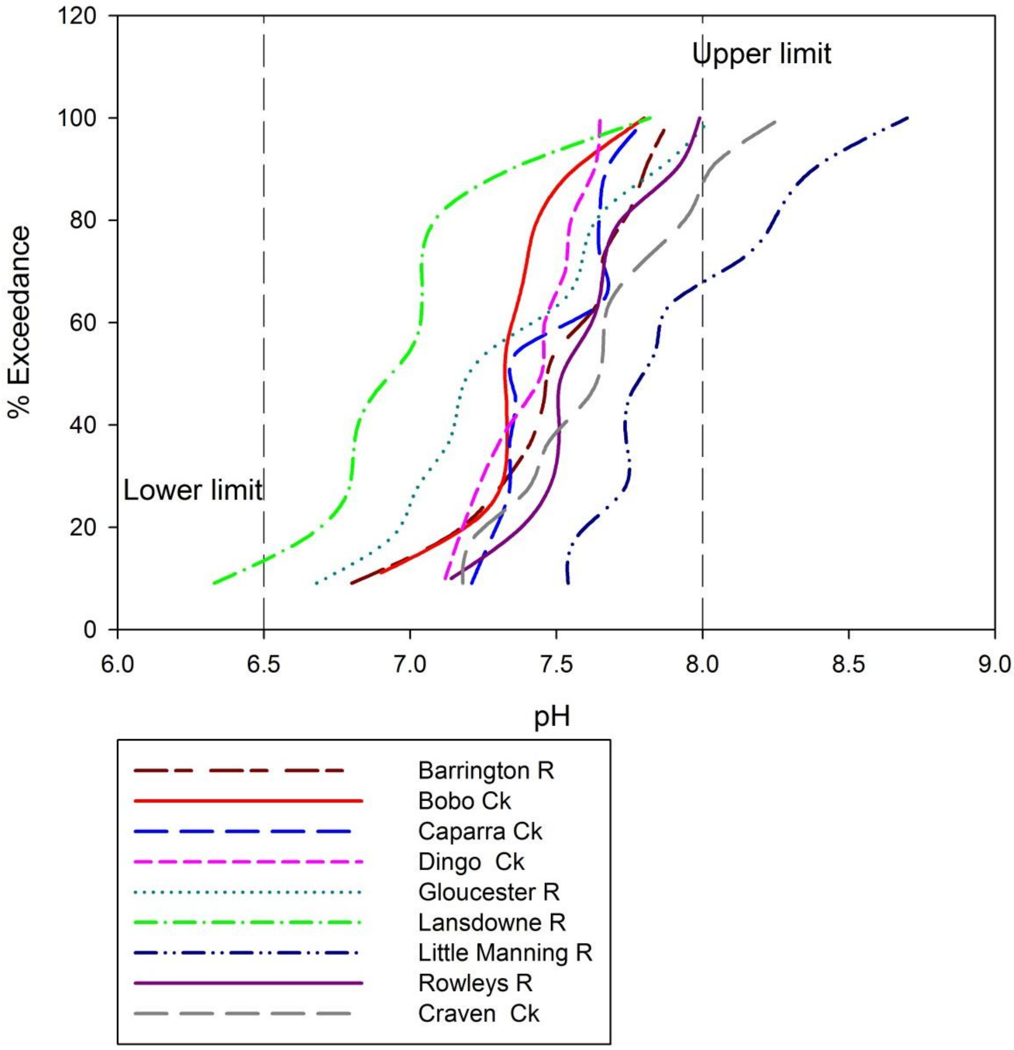


Figure 3.38 Exceedance for upper and lower pH threshold values, Manning catchment reference sites compared to ANZECC/ARMCANZ thresholds

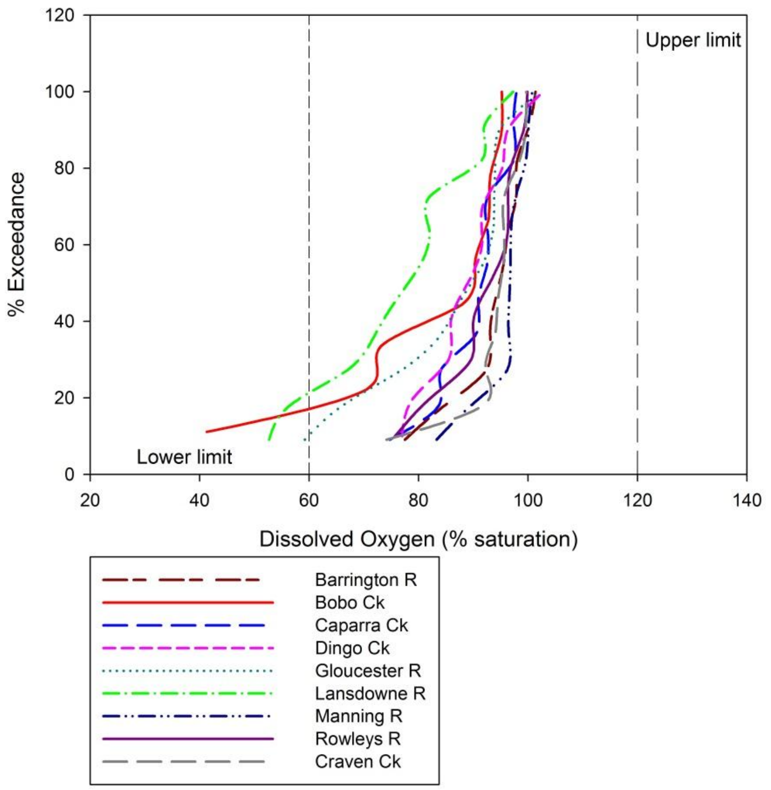


Figure 3.39 Exceedance for upper and lower saturated dissolved oxygen threshold values, Manning catchment reference sites compared to ANZECC/ARMCANZ thresholds

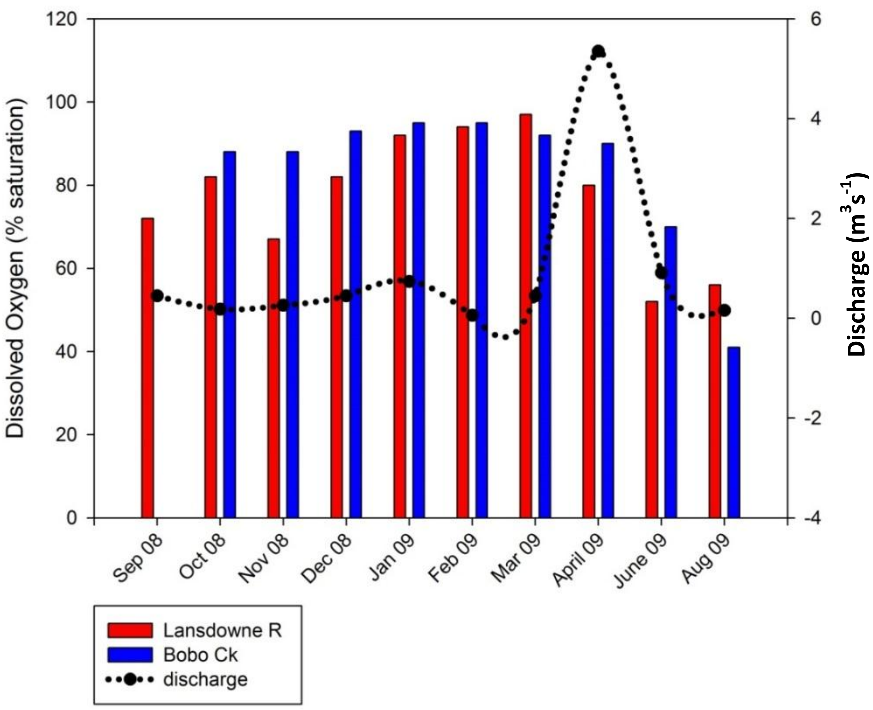


Figure 3.40 Saturated dissolved oxygen for Lansdowne River and Bobo Creek and mean monthly discharge for the Lansdowne River, 2008-09 Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au)

Unlike TP, SRP concentrations at all upland reference sites are within guideline recommendations (Fig. 3.41). The lower threshold for coastal streams is exceeded by the coastal sites of Dingo Creek and Rowleys River (Fig. 3.42) indicating agricultural impacts within those subcatchments.

Two upland sites, Little Manning River and Caparra Creek, have lower and less varied oxidised nitrogen concentrations than the other sites (Fig. 3.42). The biological response to nitrogen concentrations within these creeks is explored further through the nutrient enrichment experiment described in Section 3.4.3.

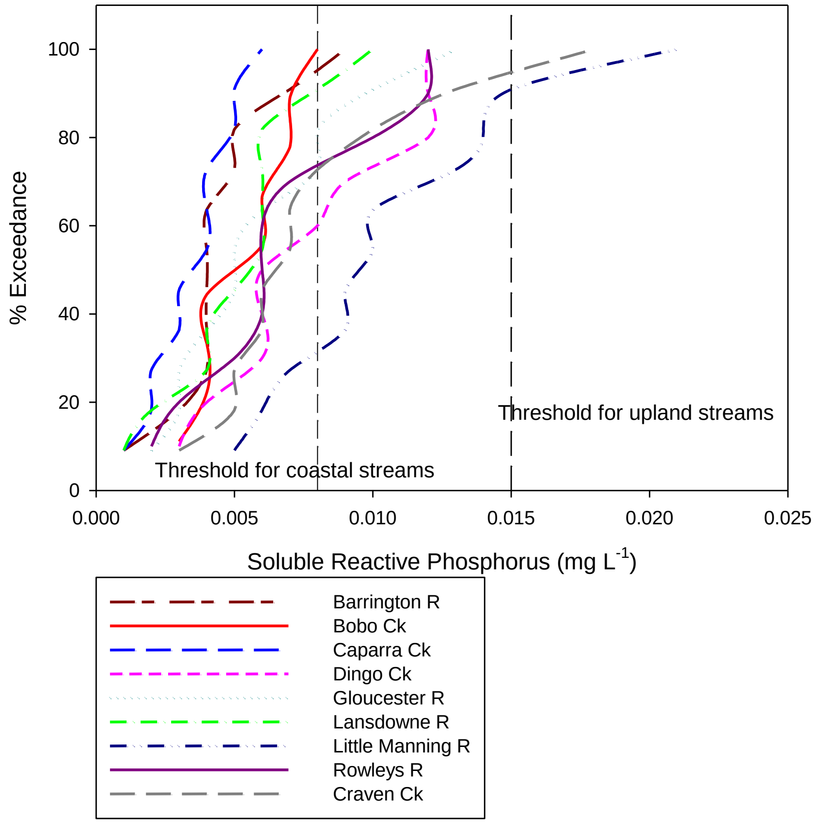


Figure 3.41 Exceedance of 80th percentile thresholds in Manning catchment reference sites for soluble reactive phosphorus compared to ANZECC/ARMCANZ thresholds

As was found in the historical data, Craven Creek, an upland site and Lansdowne River, a lowland site, exceeded the applicable threshold for oxidised nitrogen (Fig. 3.42). Unlike the results from the historical data, Gloucester River also exceeded the recommended oxidised nitrogen concentrations (Fig. 3.42). The Craven Creek and Gloucester River sites are located in areas with low grazing impacts but have the highest oxidised nitrogen concentrations for all the Manning catchment reference sites (Fig. 3.42). Figure 3.43 indicates little relationship between discharge and oxidised nitrogen concentrations at these two sites, indicating something other than flow, and therefore runoff, is having a greater influence on oxidised nitrogen concentrations in these upland rivers.

Lansdowne River exceeds the threshold for coastal rivers 30% of the time (Fig. 3.42) possible relating to land management issues, particularly the removal of riparian vegetation.

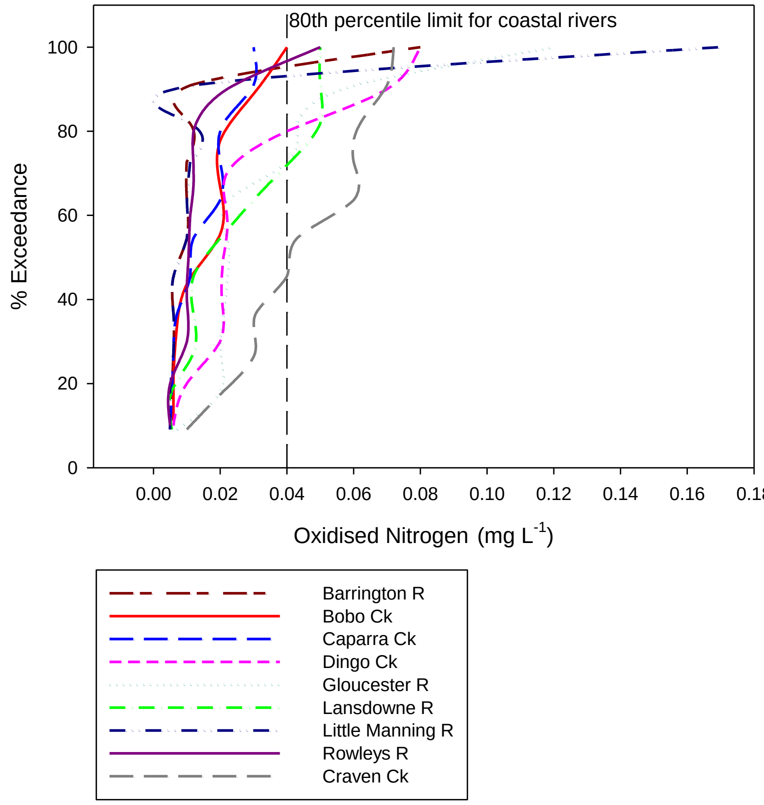


Figure 3.42 Exceedance of 80th percentile thresholds for oxidised nitrogen, Manning catchment reference sites compared to ANZECC/ARMCANZ thresholds

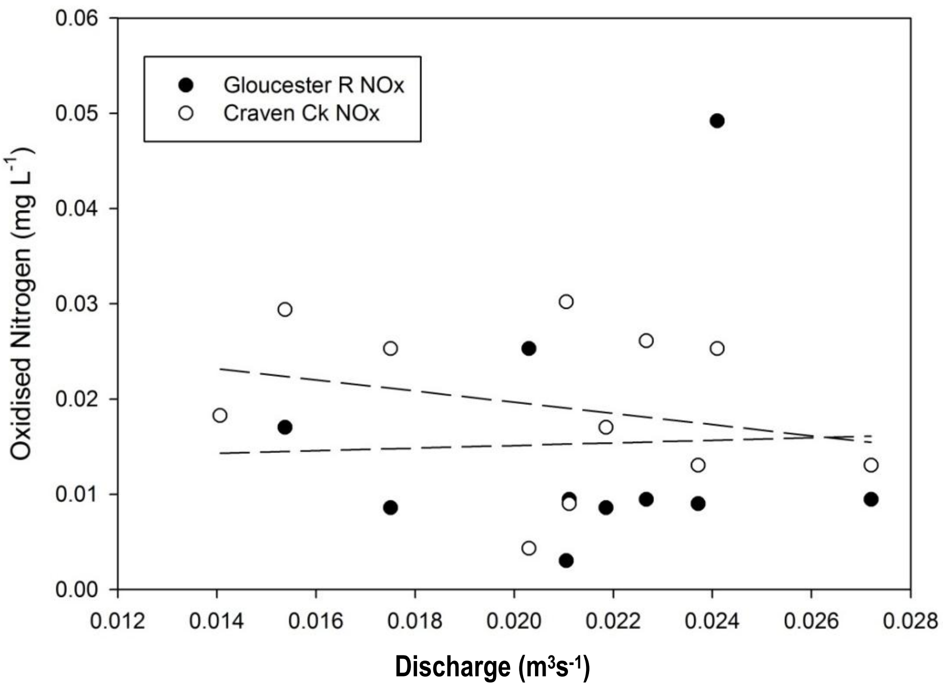


Figure 3.43 Relationship between discharge and oxidised nitrogen in Gloucester River and Craven Creek, 2008 09. (Gloucester R - r^2 = 0.0024, p=0.88; Craven Ck - r^2 = 0.0015, p=0.90)
Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au)

Reference sites were generally within the TN default 80th percentile threshold values recommended by ANZECC/ARMCANZ (2000) for upland streams and coastal rivers (Fig. 3.44). However, the upland site of Craven Creek does not meet the threshold of 0.02 and exceeds the guideline threshold on 70% of sampling occasions (Fig. 3.44).

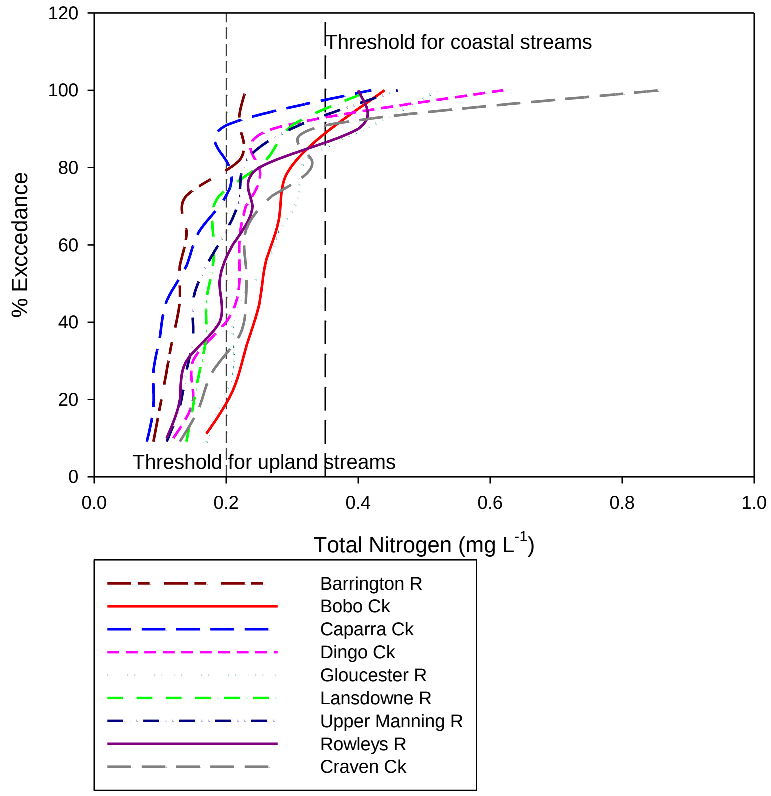


Figure 3.44 Exceedance of 80th percentile thresholds for total nitrogen, Manning catchment reference sites compared to ANZECC/ARMCANZ thresholds

Catchment-derived threshold values were calculated using both the long-term and recently collected data (Table 3.9). By comparing historical datasets and more recently collected water quality data, long-term changes and trends can be identified and comparisons to ANZECC and ARMCANZ (2000) water quality threshold values determined.

The threshold values take into account chemical variables which differ from default 80th percentile values presented in the ANZECC/ARMCANZ (2000) water quality guidelines and variations between subcatchments. Alternate DO, pH, NOx and TP threshold values have been included as a result of data collected from the Manning River reference sites (Table 3.9).

Table 3.9 Catchment-scale low-risk threshold values for upland and lowland streams in the Manning catchment.

Variable	Upland Coastal stream (>150m)	Lowland Coastal stream (<150m)
pH	6.5-8.0[1]	6.5-7.5
EC (µS/cm)	Upper limit 200	Upper limit 550
DO% saturation	85%-110%[2]	75%-110%[2]
Turbidity (NTU)	2-25	6-30
NH_4^+ (mgL^{-1})	80^{th} % = 0.013	80^{th} % = 0.02
NOx (mgL^{-1})	80^{th} % = 0.02[3]	80^{th} % = 0.04
SRP (mgL^{-1})	80^{th} % = 0.015	80^{th} % = 0.02
TP (mgL^{-1})	80^{th} % = 0.025[3]	80^{th} % = 0.03[4]
TN (mgL^{-1})	80^{th} % = 0.25	80^{th} % = 0.35

[1] based on pH values measured in Little Manning River and Caparra Creek
[2] based on 20^{th} and 80^{th} percentile values measured from the upland and lowland reference sites
[3] based on 80^{th} percentile values measured from the upland reference site, Caparra Creek
[4] based on 80^{th} percentile values measured from the lowland reference sites

3.4.4 Validation of catchment scale threshold values

To ascertain the extent to which non-reference sites meet the regionally- derived thresholds, a number of sites have been chosen for comparison. These include one upland site, Barnard River, two mid-catchment sites, Avon and Bowman Rivers, and two lowland sites, Bakers Creek and the Manning River at Killawarra (Fig. 3.45). Exceedance curves have been constructed for nutrients and EC at these sites. Insufficient data were available to complete exceedance curves for turbidity, pH or DO.

Bakers Creek, a floodplain tributary of the lower Manning River, exceeded the regionally developed threshold for EC on 50% of sampling occasions (Fig. 3.45). The highest EC levels were significantly related to low flow conditions, as measured in the Manning River at a nearby site (Fig. 3.46). The relationship with low flow indicates a greater groundwater influence at this site.

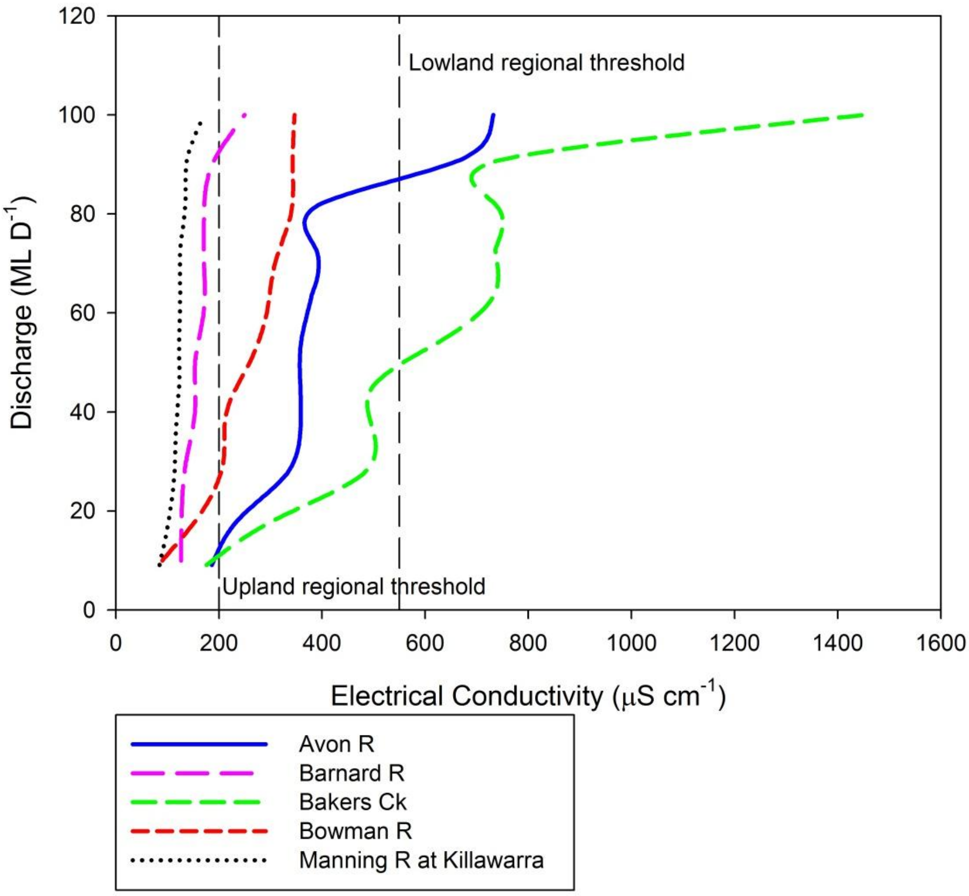


Figure 3.45 Exceedance of 80th percentile thresholds for electrical conductivity at non-reference sites compared to regionally-derived thresholds

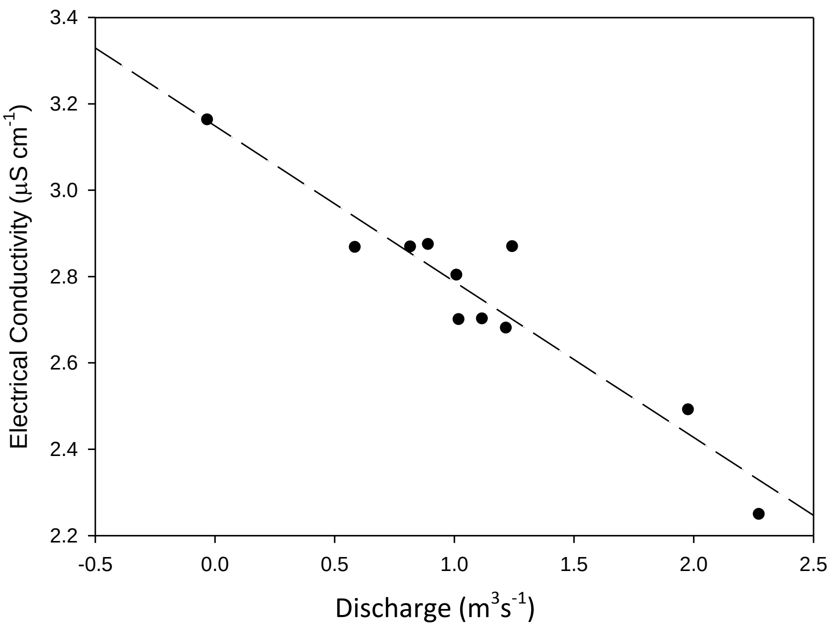


Figure 3.46 Relationship between discharge at Killawarra and electrical conductivity in Bakers Creek, 2007 (r^2 = 0.90; p=<0.0001)

Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au).

A number of exceedances occurred when different forms of N were assessed (Figs. 3.47-3.49). The greatest exceedances were from the Avon River, a tributary of the Gloucester River, which has an open-cut coal mine located in its upper catchment. There is no relationship between high flows and nutrients in the Avon River from the limited data available for comparison (Fig. 3.50).

The Avon River downstream of the Stratford coal mine has a much higher discharge than the neighbouring catchment of Gloucester River (Fig. 3.51). The gauging sites have similar sized catchments with Avon River being smaller at 225km^2 as opposed to 253km^2 catchment size for the Gloucester River at Gloucester. Both also have similar agricultural land uses, however the Gloucester subcatchment did not support open-cut coal mining during this reporting period.

The Manning River at Killawarra is the only lowland site to meet regionally-derived TN thresholds (Figs. 3.47-3.49). Other sites do not meet regionally derived nutrient thresholds, but to a lesser degree than that found in the Avon River (Figs. 3.47-3.49). With the exception of oxidised nitrogen, the Barnard River does not meet the threshold for any other nutrient (Figs. 3.47 and 3.49). The Barnard River is only within the threshold for both TN and TP approximately 20% of sample occasions. Agriculture is the dominant land use within this subcatchment with geology in the upper catchment dominated by basalt. The Bowman River, a mid-catchment site, also appears to be N-enriched (Figs. 3.47-3.49). A major land use in this sub-catchment is dairy farming, with milking shed effluent spread on paddocks and dairy cattle frequently accessing the river.

Bakers Creek also exceeds the regionally-derived TN threshold on over 80% of sampling occasions and, as discussed previously in relation to EC results, this lowland subcatchment is subject to clearing and grazing impacts as well as possible point sources and increased groundwater influences (Fig. 3.49).

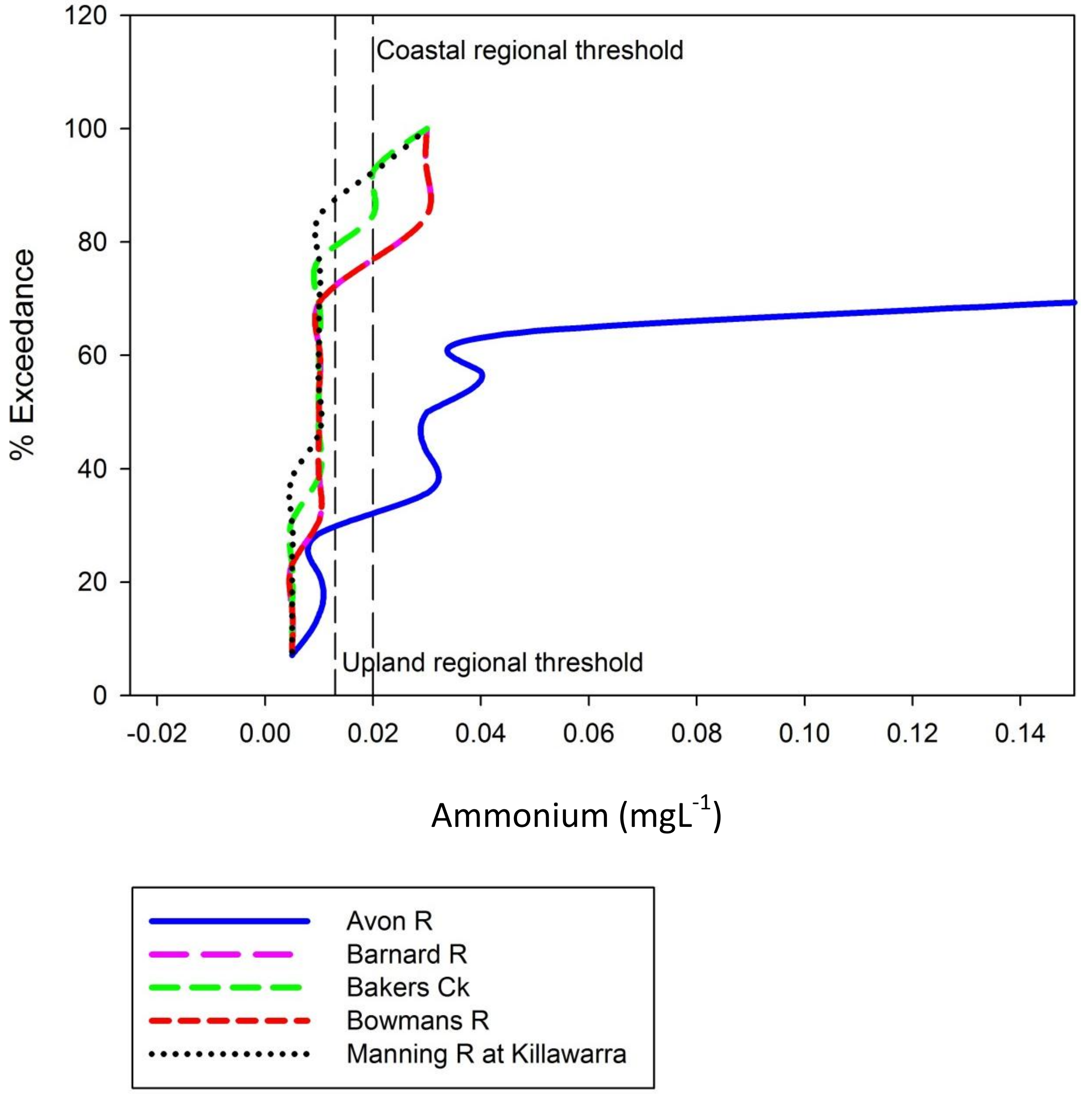


Figure 3.47 Exceedance of 80th percentile thresholds for ammonium at non-reference sites compared to regionally-derived thresholds

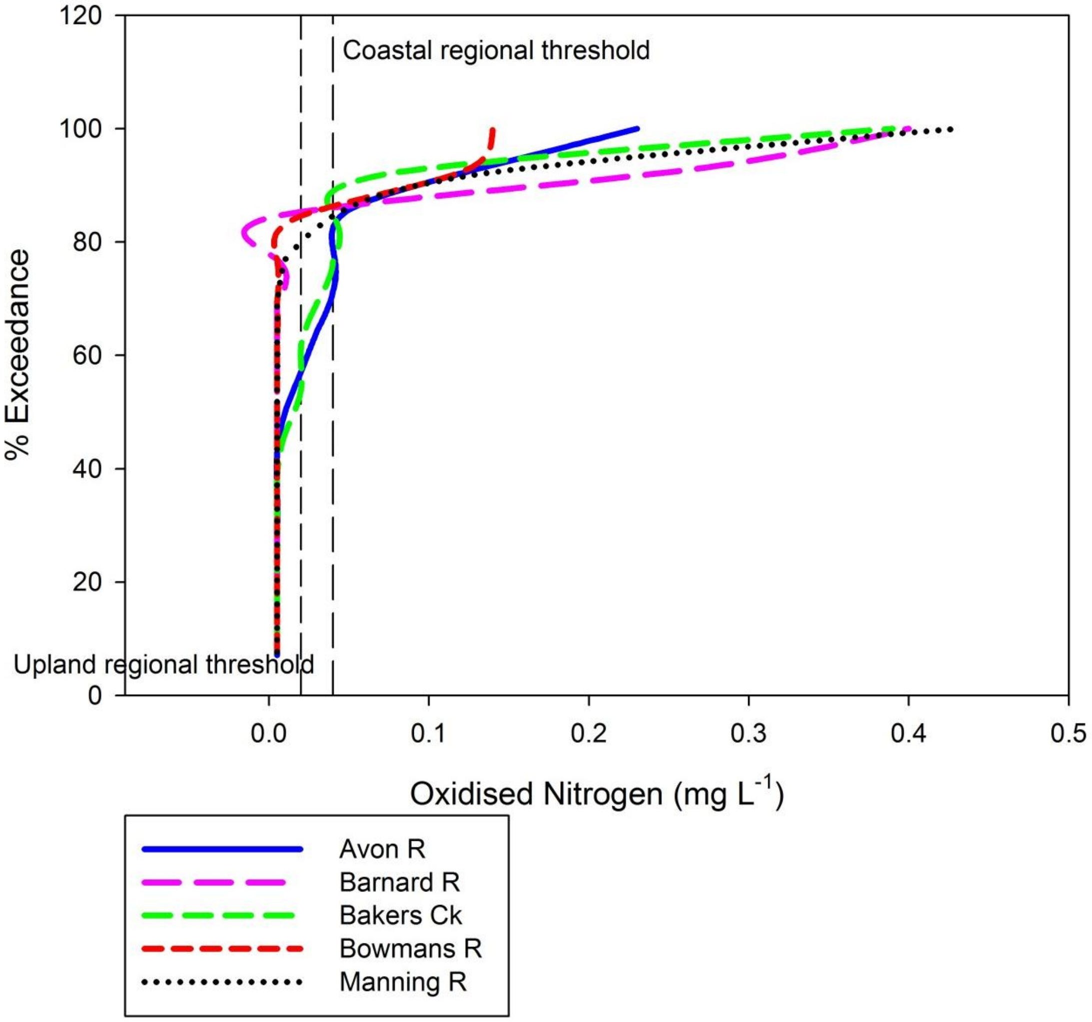


Figure 3.48 Exceedance of 80th percentile thresholds for oxidised nitrogen at non-reference sites compared to regionally-derived thresholds

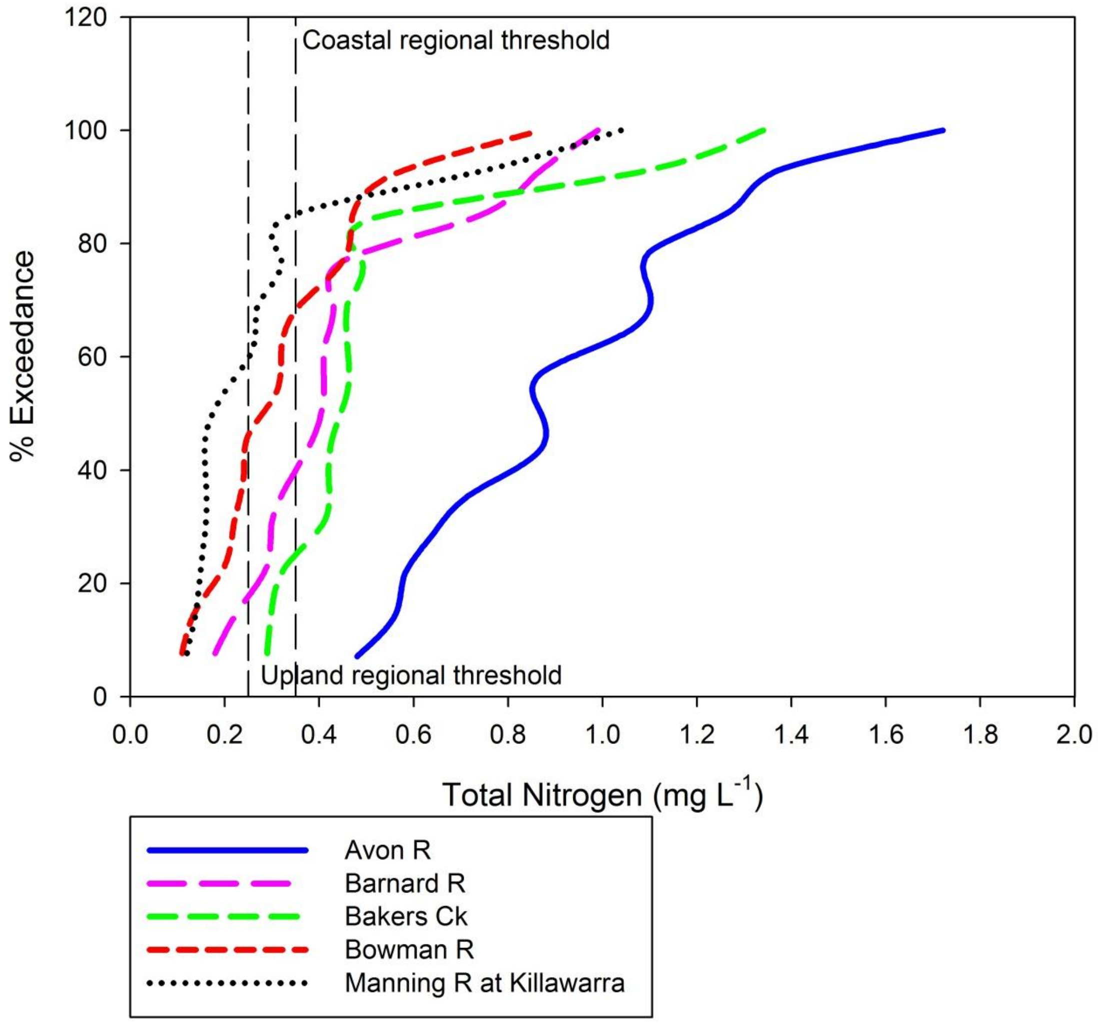
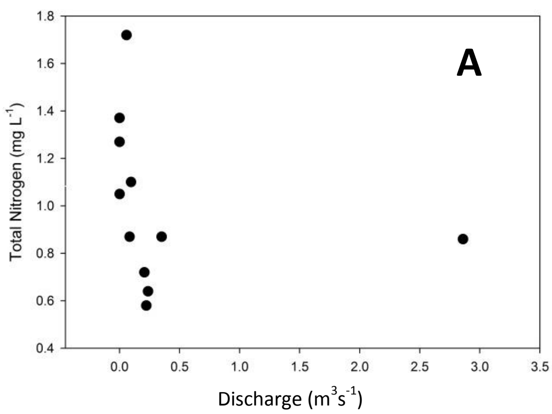


Figure 3.49 Exceedance of 80th percentile thresholds for total nitrogen at non-reference sites compared to regionally-derived thresholds



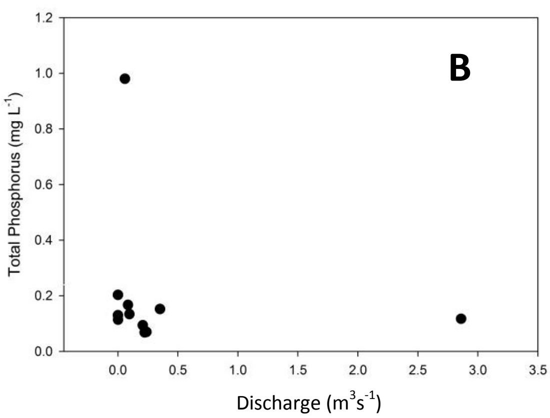


Figure 3.50 Relationship between discharge at Waukory in the Avon River and A) total nitrogen; B) total phosphorus, 2007

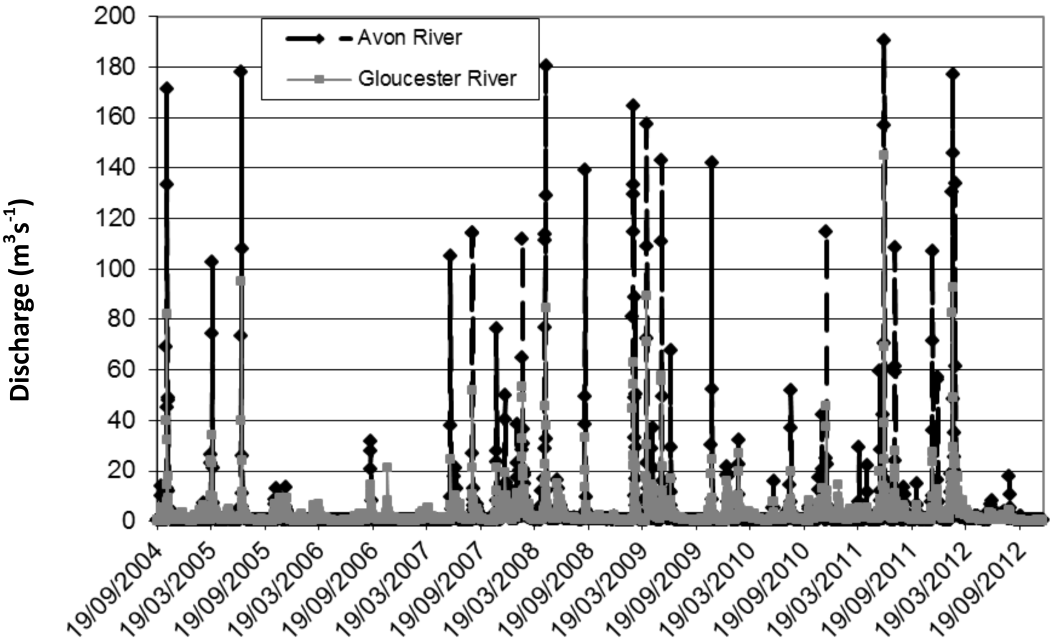


Figure 3.51 Discharge measured in the Avon River at Waukivory and the Gloucester River at Gloucester, 2004 to 2012

Phosphorus concentrations also reflect the possible impact of coal mining within the Avon catchment (Figs. 3.52–3.53). Concentrations in the Avon were outside regionally-derived thresholds for TP for the entire sampling period and, similarly to TN, these concentrations were not related to discharge (Fig. 3.50B). The Avon River also exceeded the SRP threshold over 40% of sampling occasions (Fig. 3.53).

All other sites exceeded the 80th percentile threshold for both TP and SRP, with the exception of the Bowman River, in the mid-catchment (Figs. 3.52-3.53).

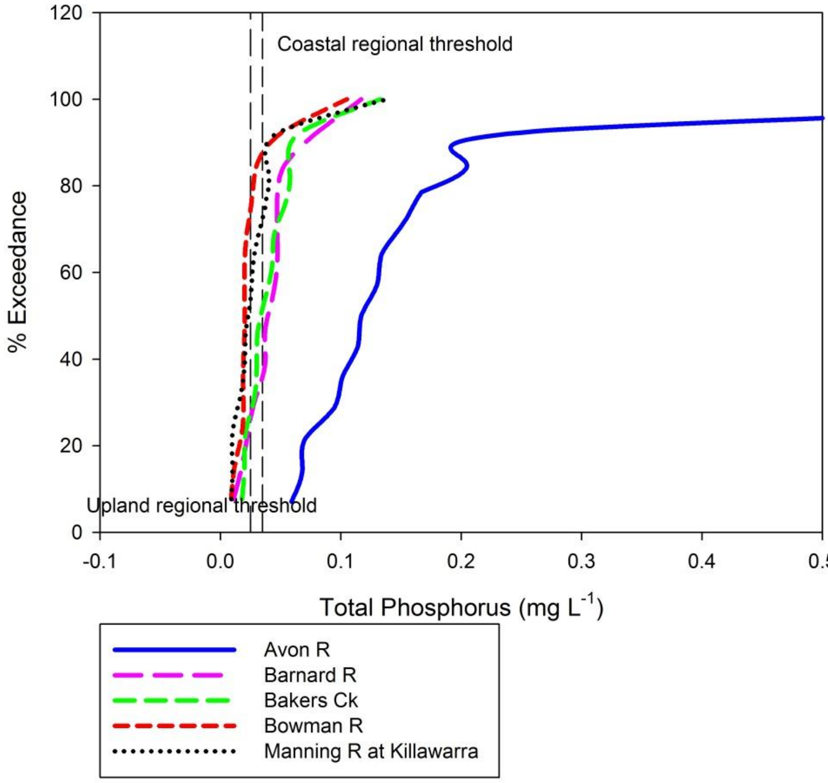


Figure 3.52 Exceedance of 80th percentile thresholds for total phosphorus at non-reference sites compared to regionally-derived thresholds

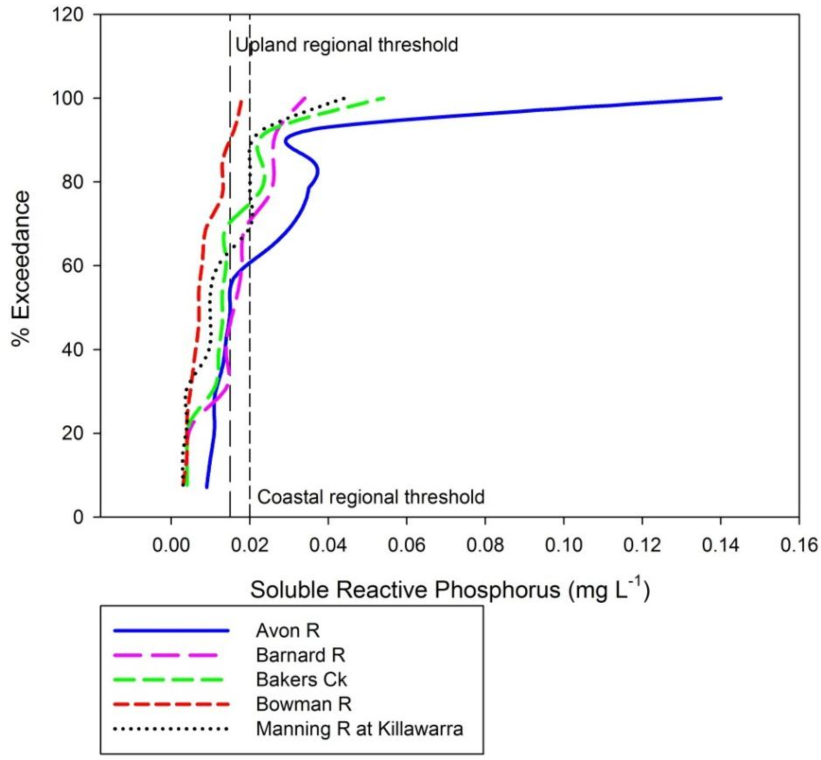


Figure 3.53 Exceedance of 80th percentile thresholds for soluble reactive phosphorus at non-reference sites compared to regionally-derived thresholds

3.4.5 NDS experimental results

When chlorophyll-a was measured, N-related treatments consistently accumulated the highest mean chlorophyll-a mass within Caparra Creek (Fig. 3.54A). While there were larger variations between sites and treatments, there is an indication that autotrophic growth may have been limited by N, regardless of hydrological conditions, which were variable during the incubation period at this site (Fig 3.55). The response to all nutrient treatments within the Little Manning River were highly variable, with site 1 demonstrating a greater response to all treatments than other Little Manning River sites to both N and P related treatments (Fig. 3.4B).

Both Caparra Creek and Little Manning River sites showed a reduced response to the C treatment (Fig. 3.4AB). The C treatment, when compared to other nutrient treatments, appeared to reduce periphyton growth, with the lowest mass recorded from C treatments or C related treatments (Fig. 3.54AB), which may be a function of microbial biofilms out-competing periphyton.

The consistently reduced response to all treatments displayed by Little Manning River site 5 indicates that a physical characteristic of this site may have had a greater influence on periphyton growth rather than nutrients or other water quality parameters (Fig. 3.54B).

TP during the experimental period was higher when compared to long-term averages, particularly in Caparra Creek, while oxidised nitrogen was also higher than long term averages at all sites in Caparra Creek (Table 3.10). TN in the Little Manning River during the experimental period was almost half the long-term average concentrations (Table 3.10). Water quality data collected in 2012 indicated the highest TN concentrations were at site 3, Caparra Creek (Table 3.10). This site also had the highest chlorophyll-a biomass of any of the experimental sites for N-related treatments (Fig. 3.54).

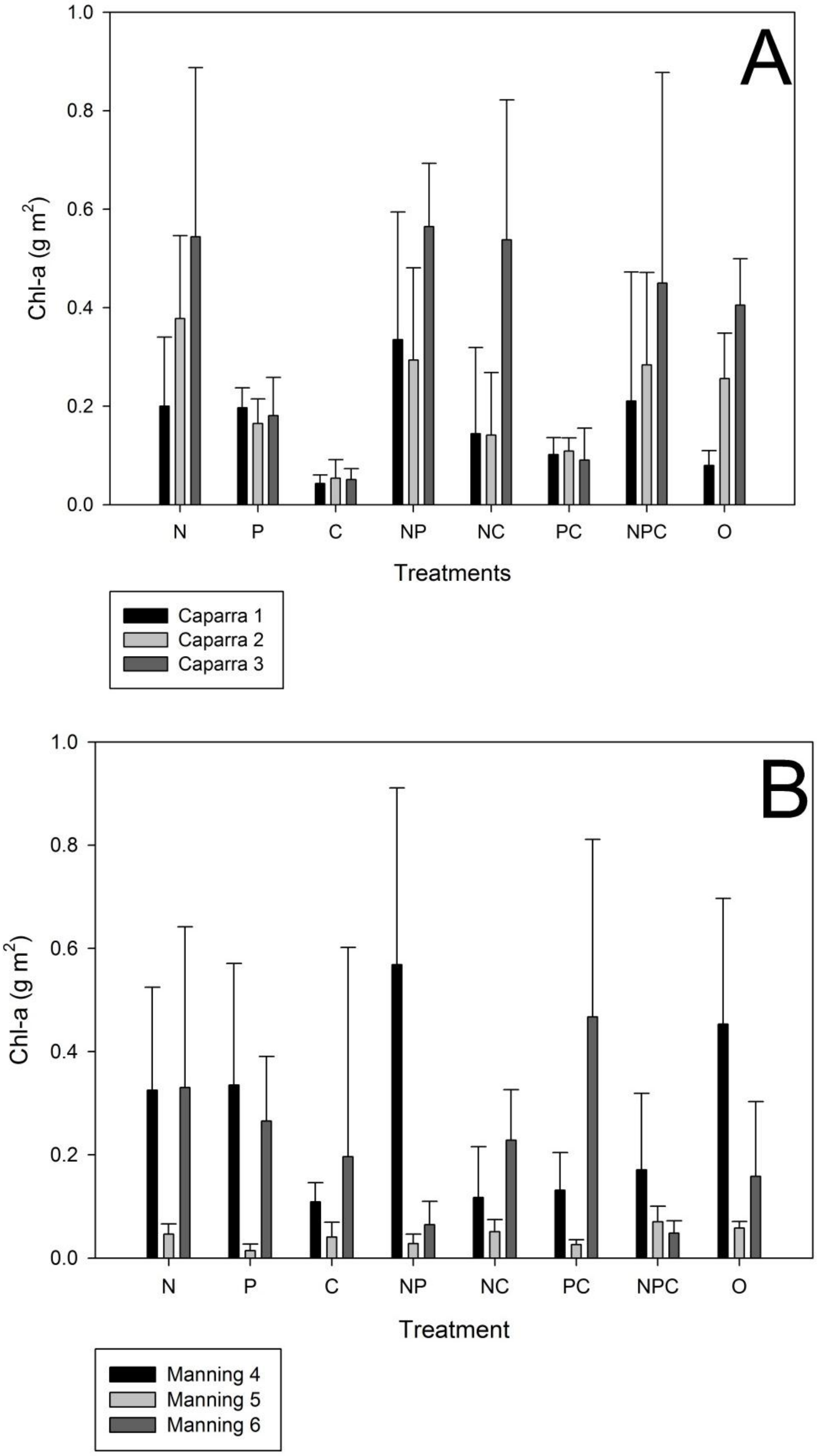


Figure 3.54 Mean chlorophyll-a mass (g m^{-2}) recovered from each of the eight nutrient treated agar pots at (A) Caparra Creek and (B) the Little Manning River, February 2012 Columns correspond to the six sites samples (see legend). The standard error bars represent the standard error of the sample mean (n=8)

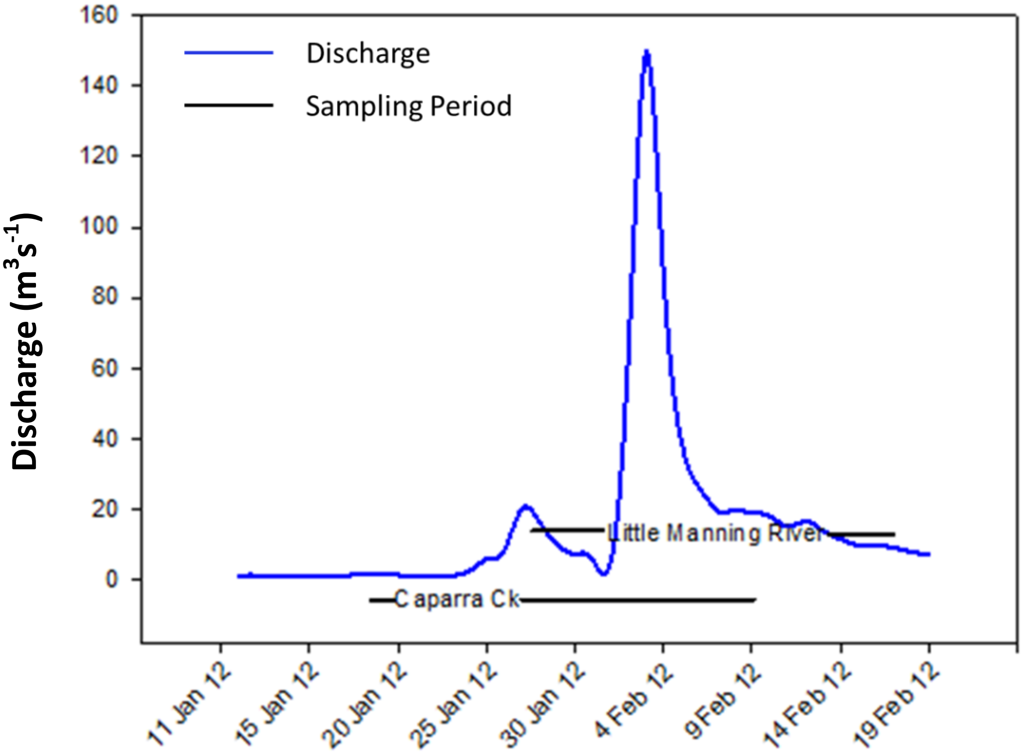


Figure 3.55 Discharge in upper Manning River during incubation period at Caparra Creek and Little Manning River
Discharge data accessed from NSW Water Information website (www.waterinfo.nsw.gov.au).

Table 3.10 Caparra Creek and Little Manning River nutrient summary

Stream		TP (mgL^{-1})	SRP (mgL^{-1})	TN (mgL^{-1})	NOx (mgL^{-1})	TOC (mgL^{-1})*
Caparra	**Long-term average**	**0.013**	**0.003**	**0.16**	**0.015**	**NA**
	Site 1	0.022	0.004	0.16	0.06	
	Site 2	0.021	0.004	0.12	0.04	
	Site 3	0.029	0.005	0.20	0.05	
Little Manning	**Long-term average**	**0.023**	**0.01**	**0.206**	**0.022**	**Mean range: 3.2-7.25**
	Site 4	0.028	0.014	0.16	0.02	
	Site 5	0.028	0.015	0.18	0.02	
	Site 6	0.027	0.014	0.17	0.02	

*TOC data accessed from MCW – using a number of sites downstream of study areas

ANOVA results comparing treatment and sites showed a significant difference between treatments (Table 3.11). Pairwise comparisons indicated significant differences between N and P treatments (Tukey's test $p<0.0125$), P and C treatments (Tukey's test $p<0.02$) and NP and C treatments (Tukey's test $p<0.04$).

Table 3.11 Results of ANOVA main test for significant differences in chlorophyll-a mass (g m^{-2}) between treatment and streams and their significant interactions

Source	df	SS	MS	F	P-value	F-Crit
Treatment	5	0.442	0.088	5.432	**0.0008**	2.485
Site	7	0.234	0.033	2.054	0.0754	2.285
Error	35	0.570	0.016			
Total	47	1.248				

Note: Significant P values are shown in bold

Results from comparisons of biomass from each treatment at each site found that the first two axes of the PCA (Fig. 3.56) explained 83.5% of the total variance within the data matrix (8 treatments, 6 sites). The third axis (not shown in Fig. 3.56) accounted for a further 12.3%, resulting in a total 95.8% of variability captured by the first three axes. Eigenvector coefficients for N, NP and O had a strong negative influence on the first axis (Fig. 3.56). Eigenvector coefficients for C, PC and P had a strong positive influence on the second axis (Fig. 3.56).

The downstream site for the Little Manning River had a high score for PC2 but low for PC1, whereas the most downstream site on Caparra Creek sites had a high score for PC2 but low for PC1 (Fig. 3.56). Sites 2, 3 and 5 had higher scores for both PC1 and PC2 when compared to the other three sites (Fig. 3.56). These differences indicate that individual characteristics at each site may influence nutrient uptake rates by periphyton.

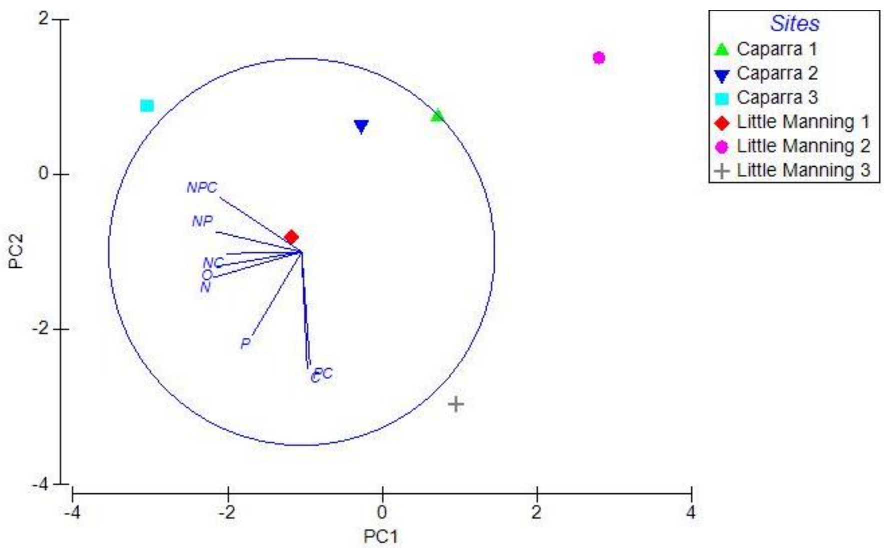


Figure 3.56 Principal Components Analysis of chlorophyll-a mass (g m^{-2}) for treatments at Caparra Creek and Little Manning River with vectors showing the contributions of variables to the axes

The vector lengths reflect a variable's contribution to the two axes in relation to all possible axes.

3.5 Discussion

3.5.1 Regionally-derived water quality thresholds

The aim of water quality standards is to guide the protection and restoration of natural regimes in aquatic systems (Poff et al. 1997, Poole et al. 2004). Current ANZECC water quality standards are poorly suited in meeting this management goal as they are homogenised across regions and cannot account for natural temporal and spatial variability. The inherent variations in water quality under natural conditions confound the identification of threshold values and makes it difficult to distinguish between natural ecosystem dynamics and unacceptable human interference (Poole et al. 2004). Regionally-relevant threshold values take into account the variability of the particular ecosystem or environment, soil type, rainfall and level of exposure to contaminants. These threshold values, if exceeded, indicate a potential environmental problem, and so can initiate a management response.

The smaller scale at which regionally-derived water quality thresholds are determined in comparison to the larger geographic scale used to develop ANZECC/ARMCANZ (2000) guidelines, allows thresholds to be established for the upper tributaries of the Manning catchment. This approach takes into consideration the very different characteristics of these catchments compared to the larger coastal river systems located on the floodplain. Ecological requirements for these two types of systems differ, as many upland species are more sensitive to impacts such as eutrophication, temperature and sedimentation in comparison to many lowland species (Durance and Ormerod 2007). The lower thresholds developed for upland tributary sites using reference water quality data when compared to the lowland thresholds supports the need for spatially-explicit water quality guidelines.

Reference sites were consistent with ANZECC/ARMCANZ (2000) water quality thresholds for EC, TN, SRP, NH^{+}_{4} and turbidity. An alternate threshold was presented for DO with an increase to the 20^{th} percentiles and a decrease in 80^{th} percentiles as a result of DO measurements collected across all reference sites. Other changes to regionally-derived thresholds from the ANZECC/ARMCANZ (2000) guidelines includes a decrease in upland 80^{th} percentiles for pH, an increase in NOx 80^{th} percentile for upland streams and an increase of TP 80^{th} percentiles for upland streams and lowland coastal rivers.

The changes made to DO percentiles reflect the reduced DO variability exhibited within reference sites under a variety of flow conditions, compared to those represented in the ANZECC/ARMCANZ (2000) guidelines. This reduced variability indicates the reference streams are not subject to large increases in biological oxygen demand (BOD) under low flow conditions often experienced in other streams (Rolls et al. 2012). Autochthonous heterotrophic processes, stimulated by nutrient loading, particularly P, have been found to be major drivers of BOD in urban and agricultural streams (Mallin et al. 2006). By limiting nutrient inputs and thereby reducing oxygen-demanding materials, incidences of low DO saturation will be reduced (Mallin et al. 2006). The mostly intact riparian corridors associated with the selected reference sites are likely to reduce nutrient inputs to these areas, thereby reducing BOD.

Increases in the NOx 80th percentile threshold in upland reference sites appears to relate to geological influences rather than discharge, with increased discharge at Craven Creek and Gloucester River reference sites providing no correlation to N concentrations. These sites are located in basins of mixed sedimentary and crystalline geology which has been found to influence N concentrations in rivers, particularly meta-sedimentary rocks such as schist (Montross et al. 2013). Montross et al. (2013) found that elevated NO_3^--N concentrations in a headwater stream were not the result of human activity, but were generated from mineral weathering reactions with sedimentary and metasedimentary rocks. Similarly, Blanco et al. (2010) found that the spatial distribution of N concentrations reflected the carbonate bedrock of a coastal, agricultural watershed. The importance of groundwater discharge was demonstrated by increasing NO_3^--N concentrations under base flow conditions (Blanco et al. 2010).

The increase in TP 80th percentile thresholds for upland and lowland reference sites indicates the Manning catchment has consistently higher concentrations of TP when compared to reference sites across south-east Australia. Baseline information from the Little Manning River, an upland reference site, indicated the underlying geology and its associated soil type and composition may influence the nutrient status of waters draining the landscape. Volcanic rocks (e.g. basalts) are richer in phosphorus than granitic rocks and this factor is often evident in P concentrations in areas dominated by these rock types (Eyre and Pepperell 1999). The weak relationship between P concentrations and discharge and a relatively high concentration of P in comparison to other minimally disturbed upland sites indicates increased input of P is generated from basalt-dominated geology under baseflow conditions.

Other reference sites across the catchment did not meet ANZECC/ARMCANZ (2000) TP thresholds, resulting in a higher regionally-derived TP threshold. The exceedance of the TP threshold by mid-catchment sites Gloucester and Rowleys rivers and all lowland reference sites, indicate higher background concentrations of TP at sites across all subcatchments, despite the relatively intact riparian zones found at each site. This result flags an important consideration when using reference condition for comparison with non-reference sites, as reference condition itself may embody an appreciable and poorly defined degree of human-impact (Chessman and Royal 2004).

Williard et al. (2005) found that the primary source of solutes to streams is catchment soils. On a local scale this results in different water chemistry within different watersheds containing varying bedrock type. On a larger scale, the influence of soils and therefore geology may be masked by land use (Dow et al. 2006), and though the importance of landscape in regulating stream water chemistry has been well established, the role of various landscape factors (e.g. land cover, climate, geology) is highly variable and difficult to determine (Chuman et al. 2012). This is also the case for temporal changes in nutrients, as the biological processes that influence primary productivity and the effect of land use are often hidden by stream heterogeneity (Ramos-Escobedo and Vazquez 2001).

As a result of the deviation of reference sites from ANZECC/ARMCANZ (2000) water guidelines, more regionally suitable thresholds were developed to assist managers to protect aquatic ecological values within the Manning catchment (Table 3.9, Section 3.4.1.3). The use of regionally-derived water quality thresholds provide a tool for easier identification of nutrient hotspots and relationships to adjacent landuse, with the potential to impact on aquatic ecosystems. While there remains uncertainty in management outcomes that attempt to improve water quality for the protection of aquatic ecosystems, improved information tools such as regionally-relevant nutrient information can result in more effective management strategies (Poole et al. 2004, Page et al. 2012).

3.5.2 Deviation of non-reference sites from water quality thresholds

Water quality information collected throughout the Manning indicated non-reference sites spread across upland, mid and lowlands, do not meet the regionally-derived thresholds for the protection of aquatic ecosystems for moderately disturbed NSW coastal systems. The degree to which thresholds were exceeded throughout the non-reference sites was influenced by the magnitude and extent of disturbance within the sub-catchment as the multitude of agricultural impacts, urban development and mining pursuits can alter baseline concentrations of nutrients.

In particular, TP results highlight the influence of landuse, regardless of catchment location on nutrient concentrations in non-reference sites, with higher levels found at all non-reference sites with the exception of Bowman River in the upper catchment. The Barnard River, also located in the upper catchment, exceeded thresholds for all variables with the exception of NOx, demonstrating the influence of riparian clearing and grazing pressures even in the headwaters of a catchment. Bakers Creek, a tributary of the lower Manning, exceeded EC and TN. This exceedance was hydrologically influenced and will be discussed further in Section 3.5.3.

Unlike other sites included in this study, the Avon River not only has agricultural impacts but is subject to open-cut coal mining. Historically, land use impacts to most NSW coastal streams have been attributed to the influence of broader-scale agriculture and urban development, however the advent of mining, particularly coal and coal seam gas extraction, has resulted in major impacts to both water quality and quantity in other areas (Minear and Tschantz 1976, Bonta et al. 1997, Bonta and Dicks 2003, Muschal 2006, Wright and Burgin 2009). These impacts have included changes in water chemistry, including increases in heavy metals and increases in salinity due to landscape modification (Minear and Tschantz 1976, Bonta and Dicks 2003, Muschal 2006, Wright and Burgin 2009).

The impacts of open-cut coal mining extend to changes in baseflow, runoff behaviour and groundwater levels as a result of changing drainage lines and the interception of water by mining spoil (Minear and Tschantz 1978, Dickens et al. 1989, Bonta et al. 1997). Bonta et al. (1997) found mining and reclamation activities caused slightly more frequent higher daily flows, a reduction in seasonal variability, with runoff potential also increasing. My study found that the Avon River has a higher discharge volume when compared with a larger neighbouring sub-catchment. Changes in streamflow volume from watersheds disturbed by open-cut mines also appear to continue post-mining as a result of the unconsolidated mining spoil (Dickens et al. 1989, Bonta et al. 1997), and may be responsible for hydrological changes in the Avon. Apart from the obvious hydrological impacts, geomorphic characteristics of the stream may be irreversibly altered and changes in the biological community is likely to result (Dickens et al. 1989).

Despite land use impacts, the Manning catchment has lower nutrient levels in comparison to neighbouring southern catchments such as the Karuah and Hunter (Table 3.12). The higher TN and TP concentrations found in neighbouring catchments to the south, particularly the Hunter, reflect the greater development and land use changes including mining and more intensive agriculture (Table 3.13) (ANRA 1997). The dominant land use in the Hunter is livestock grazing, which covers over 50% of the catchment, while the dominant land uses in the Hastings is nature conservation (23.6%) and minimal human use (27.7%) which makes up over 50% of the catchment (Table 3.13) (ANRA 1997). Coal mining has not been included as a land use but is particularly prevalent in the Hunter catchment with at least 17 mines present. The Karuah and Manning catchments have similar land use distributions, including one coal mine in each of their upper catchments, while the Hastings catchment does not support coal mines (ANRA 1997).

There are revegetated or rehabilitated programs underway in all of these catchments with the desired outcome of improving water quality (MCW 2011, NRCMA 2011, HCRCMA 2012). Since 2006, over 750 km of riparian vegetation has been protected, 500 km of riparian vegetation regenerated and 80 km of degraded stream channel improved throughout the Hunter, Karuah and Manning catchments (HCRCMA 2012). Riparian and streambank erosion remain major issues in the Manning catchment (Fig. 3.57) and, while some rehabilitation has been undertaken, quantitative information is unavailable.

Table 3.12 Mean nutrient concentrations for mid-north coast catchments, NSW

Catchment	Location	Mean TN (mg L^{-1})	Mean TP (mg L^{-1})	Period	Reference
Hunter	Upland (>150m)	0.30	0.030	2006	DLWC (2006)
	Lowland (<150m)	0.36	0.050	1995-1999	DLWC (n.d.)
Karuah	Upland (>150m)	N/A			
	Lowland (<150m)	0.51	0.045	1995-1999; 2011-2012	DLWC (n.d.); OEH (n.d)
Hastings	Upland (>150m)	0.10	0.060	2011	Ryder et al. (2012)
	Lowland (<150m)	0.26	0.14	2011	Ryder et al. (2012)
Manning	Upland (>150m)	0.21	0.018	1992-1997 2007-2008	MCW; DLWC; Thurtell
	Lowland (<150m)	0.30	0.035		

Table 3.13 Area of land use in mid-north coast catchments 1996/97 (Source: ANRA)

Land Use	Hunter Catchment Total Extent (%)	Karuah Catchment Total Extent (%)	Hastings Catchment Total Extent (%)	Manning Catchment Total Extent (%)
Nature Conservation	20.2	17.3	23.6	12.5
Minimal use	13.3	34.7	27.7	33.5
Livestock Grazing	54.8	27.8	24.2	35.6
Forestry	3.4	13.9	22.0	15.8
Dryland Agriculture	5.5	3.1	1.0	1.7
Irrigated Agriculture	1.4	0.2	0.5	0.6
Built Environment	1.1	0.2	0.6	0.2
Waterbodies	0.3	2.6	0.4	0.1

Figure 3.57 Riparian impacts in the Manning Catchment. A) Cattle accessing the lower Gloucester B) Streambank erosion along the Manning River

3.5.3 Hydrologic influences on water quality

Summer low flow conditions resulted in increases in measured water quality variables at some reference sites, such as the Little Manning River, in the upper catchment areas. This may be explained by geological or groundwater influences that become more evident under dry conditions (Sear et al. 1999, Williard et al. 2003, Olsen and Hawkin 2012) or recycling of internal nutrient loads (Essington and Carpenter 2000). Conversely, increases in variable concentrations at other sites, were associated with run-off events, reflecting the surrounding land-use. These results indicate that hydrological effects, particularly relating to extreme events such as drought or floods have major consequences to water quality through evaporation, dilution or runoff impacts (Poole et al. 2004, Johnson et al. 2007, Klose et al. 2012).

Higher pH levels in the Little Manning River corresponded with low flows (below 90th percentile) which would reduce scouring of periphyton and increase both biomass and groundwater influences (White et al. 2012). There is the possibility that higher pH levels found within the Little Manning River relates to the underlying basalt geology found in its upper catchment, which can influence stream chemistry by increasing phosphorus and buffering changes in pH. The higher pH levels may also be a reflection of greater primary productivity, supported by higher TP levels at this site when compared to other upland reference sites.

As found in other studies, the relationship between nutrients and discharge suggests that even in moderately disturbed catchments, land use factors are likely to be a greater influence on nutrient composition than geological characteristics (Likens and Bormann 1974, Johnson et al. 1997, King et al. 2005). Less modified upper catchments such as the upper tributaries of the Manning catchment reflect local geology, soil type and composition more closely than the more disturbed catchments, while in areas which have a greater extent of land use change, as found in the lower Manning, reflect the greater anthropogenic influences (Killham 1990, Ramos-Escobedo and Vazquez 2001).

High N concentrations were evident under all flow conditions at Craven Creek, an upland site, and the mid-catchment site of Gloucester River. While these subcatchments are subjected to grazing pressure, the areas upstream of the sampling sites are well-vegetated. Groundwater is known to be an important vector for N export from floodplains (Lamontagne 2002, Lamontagne et al. 2005). A study undertaken by Lamontagne et al. (2005) on a large lowland Australian river found that a large fraction of the dissolved N pool was located within the alluvial aquifer and the distribution and form of N varied throughout the floodplain and riparian zone, resulting in plumes at various points. The study also indicated that the riparian zone may be an important source of N, with net nitrification rates highest in these areas as opposed to the unvegetated floodplain (Lamontagne et al. 2005). Under low flow conditions, when surface water becomes disconnected, groundwater can also be a source of N to isolated pools, particularly in reaches with porous bed substrates where the rate of exchange between surface and sub-surface habitats can be enhanced (Boulton et al. 1998). Given that the substrates associated with the pool areas of both Craven Creek and the Gloucester River are predominantly sandy, there is an increased possibility that oxidised nitrogen contributed by groundwater under lower flow conditions may result. The increased oxidised nitrogen concentrations under these conditions may be attributed to increased sub-surface input and a related increase in nutrient regeneration processes.

In the lower reaches of the Manning River, TP and TN concentrations were highest during the high flow periods. This may be explained through the increased runoff from the mostly agricultural landscape. The agricultural pursuits are known to have caused major changes within landscapes (Bullard 1966), resulting in changed hydrology, increased sedimentation and nutrients to streams (Fernandez et al. 2002, Johnson et al. 2007, Klose et al. 2012). The manifestation of these changes is greatest in the Manning under high flow conditions at lowland sites where the mostly cleared floodplain contributes high particulate loads to the river.

Another impact resulting from these hydrological changes is the frequent exceedance of water quality thresholds occurring in conjunction with rainfall and runoff events (Minear and Tschantz 1978). In the case of the Avon River, the limited data indicates that high flows may in fact dilute the high N concentrations found in moderate to low flows. The source of the nutrients is likely to be from seepage or groundwater contributions. Changes in surface and subsurface flow paths have been found to result in significant changes in surface water chemistry as fractured geologic material are exposed to increased weathering processes, resulting in increased concentrations and loads (Bonta and Dick 2003).

Declines in oxidised nitrogen over time at most reference sites reflect dilution effects of the generally wetter conditions experienced in 2008/09 when compared to the later part of the historical sampling period, as increased flows can dilute groundwater sources. An exception to decreased NO_3-N is the long-term sampling site located on Dingo Creek. This site is upstream of an area where abattoir effluent is sprayed on agricultural land. A short-term study, undertaken on behalf of MCW during 2006 and 2007, which sampled major tributaries within the Manning catchment, indicated that the downstream section of Dingo Creek, located adjacent to the effluent discharge area, had elevated NO_3-N concentrations (Fig. 3.58). The application of effluent may have resulted in an increase in NO_3-N within groundwaters, particularly in shallow groundwater systems, thus resulting in contamination of nearby waterways (Magesan et al. 1998).

Comparisons between historical and more recent data showed EC levels reduced over time at reference sites. As found with oxidised nitrogen, declines in EC over time at these sites may be reflecting dilution effects of the generally wetter conditions. An increase in surface water runoff can reduce EC under most circumstances as result of the diluting effect of freshwater inputs decreasing groundwater contributions. The high EC levels in Bakers Creek under low flow conditions indicate ground water influences at this site or an undiluted point source which has not been investigated as part of this study. The increase in EC under low flow conditions may result in added impacts to biota under low flow conditions, with salt-tolerant species being favoured (Lind et al. 2007). Electrical conductivity levels approached 1,500 $\mu S\ cm^{-1}$ in Bakers Creek under low flow conditions which Nielsen et al. (2003) suggest may adversely affect aquatic biota.

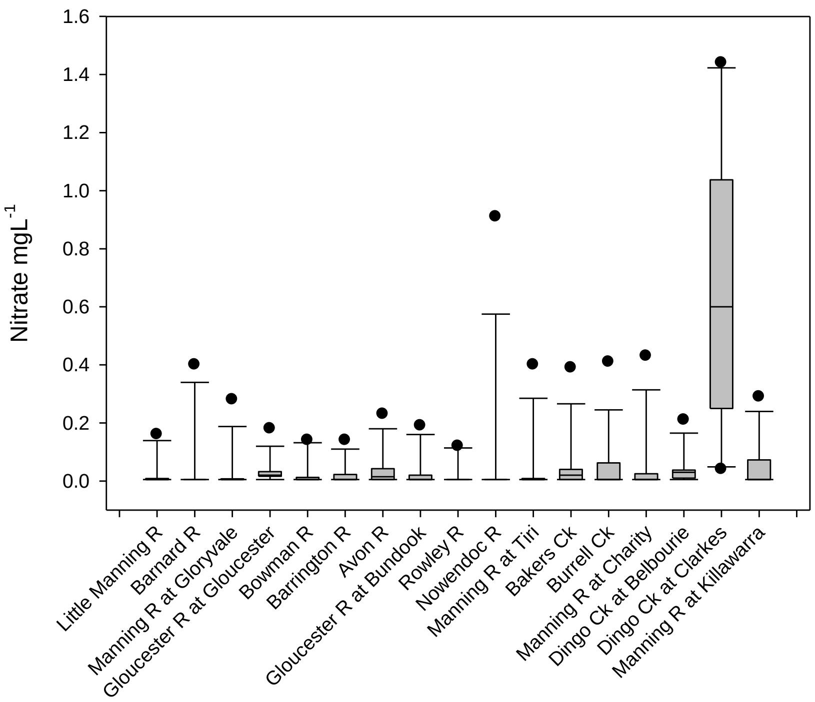


Figure 3.58 Box-whisker plot comparing nitrate concentrations in Manning River Catchment, 2006/07 (data source: MCW)
The centre horizontal line in the box is the median; the top and bottom of the box are the 25th and 75th percentiles (quartiles), and the ends of the whiskers are the 5th and 95th percentiles. ● denotes minimum and maximum values.

The impacts of land use may be exacerbated under predicted climate change impacts, as warmer, drier conditions are likely to result in longer periods of low flows and increased algal growth (Arheimer et al. 2005, CSIRO 2007b). It is likely that lowland coastal streams may be more susceptible to climate change influences due to their location on coastal floodplains. Modelling undertaken by CSIRO (2007a) indicated that the future climate of the Hunter-Central Rivers catchment, which includes the Manning catchment, will be warmer and drier due to an increase in evaporation. These changes are likely to increase heat waves, extreme winds and fire risk (CSIRO 2007b). Despite this trend toward drier conditions, there is a potential for seasonal increases in extreme rainfall events.

A number of studies have attempted to predict the impacts of increased hydrologic variability and warmer temperatures on aquatic ecosystems under various climate change models (Murdoch et al. 2000, Arheimer et al. 2005, Clarke 2009, Xia et al. 2012). The susceptibility of coastal streams to climate change impacts through sea level rise and extreme weather is well-supported by such predictive models, with implications for increased algal growth and the greater likelihood of drought reducing biodiversity (CSIRO 2007b). Modelling studies conducted elsewhere also predict increased low flows and algal growth (Xia et al. 2012), which in terms of the Manning catchment is likely to result in a loss of habitat variability and a decline in sensitive invertebrate taxa (Mulholland et al. 1997).

Using data from long-term ecosystem monitoring, Murdoch et al. (2000) found that continued climate stress would increase the frequency with which ecological thresholds are exceeded and lead to chronic water quality changes. The authors go onto suggest that management strategies would need to be based on local ecological thresholds rather than annual median condition (Murdoch et al. 2000). In the light of possible climate change impacts and the need for local thresholds, longer term historical water quality information can shed light on catchment trends and provide guidance on appropriate ecological thresholds.

This study has found inconsistencies in water quality response over time, with some variables such as EC and NOx improving at some sites in recent times, while TP remains relatively stable across the catchment. A broad-scale study such as this one cannot differentiate factors that may be key in improving water quality response as climatic and land use changes are likely to hinder any interpretation. However, an assessment of changes in land use such as riparian vegetation condition may assist in determining likely factors in water quality improvements.

3.5.4 CNP ratios influence on primary productivity

During summer, under base flow conditions, there was a large amount of variation in the dominant source(s) of nutrient limitation between treatments but not between sites. There were significant differences found among periphyton responses to N, P and C, with treatments containing N generally supporting higher biomass, suggesting that autotrophic growth in the upland streams of the Manning Catchment may be N-limited.

Previous studies have indicated that both N and P can be limiting factors in primary production in aquatic systems (Fairchild et al. 1985, Winterbourn 1990, Winter and Duthie 2000). Resource ratio theory suggests changes in environmental ratios for N and P will cause changes in algal community structure due to exploitive competition among taxa with different optimal nutrient ratios (Rhee and Gotham 1980, Tilman 1981). Predictions made regarding nutrient limitation often use N:P >16:1, based on the Redfield ratio determined for oceanic seston, to indicate P as a limiting nutrient in algal growth, dependent on total nutrient concentrations (Redfield et al. 1963, Bothwell 1985). The two streams in this study have N:P ratios less than 16:1, with Caparra Creek having an N:P ratio of 12:1 and the Little Manning River having a ratio of 8:1.

Recent studies in New Zealand gravel bed stream and experimental stream settings have found N:P ratios to be of little value in predicting nutrient limitation, whereas ambient levels of N, particularly dissolved N, was a better indicator of possible N limitation (Francoeur et al. 1999, Stelzer and Lamberti 2001). Francoeur et al. (1999) found that seasonal changes altered the degree to which nutrient limitation impacted on benthic algal growth, with the greatest impacts experienced under higher water temperatures. As this study was only undertaken during summer, it is likely that results are reflective of the greatest levels of nutrient limitation experienced in the streams, given that temperature and metabolism rates were at their highest.

Francoeur et al. (1999) found that seasonal changes were strongest in streams with low dissolved N and likely to be nutrient limited, which suggested that benthic algae had the potential to impose a seasonal pattern on nutrient export and therefore impact on nutrient availability by influencing nutrient spiralling lengths (Francoeur et al. 1999). With relatively low instream dissolved N concentrations and N treatments appearing to be favoured for autotrophic growth on the artificial substrates placed in the two streams, it appears that N was the limiting nutrient in periphytic growth under summer conditions.

Implications of N limitation through its determination of algal productivity and community structure is an important aspect of stream ecosystem dynamics (Chessman et al. 1992, Wold and Hershey 1999). Nutrient cycling in headwater streams controls N transport to downstream systems largely due to a larger benthic surface area relative to overlying water volume leading to greater exchange of water and N within the hyporheic zone (Peterson et al. 2001, Dodds et al. 2004). Seasonal variability of N export from upland streams, where N has been found to be more limited over summer, may increase N cycling rates in the downstream reaches, compensating for any longitudinal declines (Mulholland 1992, Mulholland et al. 1995). Muholland et al. (1995) found that nutrient cycling and algal community composition demonstrated the strongest links to longitudinal change in periphyton-dominated streams, with increasing importance of cyanobacteria with distance downstream.

My study found a negative periphyton biomass response to C infused artificial substrates when compared to the control substrates, indicating C may suppress periphyton growth. This response coupled with the response to N-infused artificial substrates suggests C may be playing a role in N retention in these streams. Other studies, undertaken in desert and prairie streams in the U.S., have found a negative relationship between C:N ratio of ecosystem compartments, such as detritus and periphyton, and the uptake of N in those various compartments (Dodds et al. 2000). C:N ratios can influence N cycling rates as it controls the relative assimilation against the release of N in organic matter being degraded by bacteria and fungi (Fenchel et al. 1998, Dodds et al. 2004). For substrates rich in C, with little available N in the water column, microbial activity will be limited by this lack of available N resulting in reduced N cycling rates as microbes conserve N (Goldman et al. 1987, Dodds et al. 2004).

The results from these studies that suggest the presence of high C:N ratio in materials can lead to greater N retention (Dodds et al. 2004) may also be applicable to the upper Manning streams. While C-rich substrate is likely to be plentiful in the forested upper catchments of the Manning, factors such as channelization, reduction in riparian vegetation and scouring in the lower Manning may remove large particulate matter and other C-rich material, resulting in a decrease of N retention in the ecosystem (Dodds et al. 2004).

Not only riparian zones influence nutrient cycling, nutrient ratios also determine N cycling rates through controlling the relative assimilation of nutrients against the release from organic matter (Fenchel et al. 1998, Dodds et al. 2004). As was found in this study, the lack of available N, or stoichiometric ratios may be limiting factors for periphyton growth in upland streams. The relationship between nutrient ratios and periphyton growth may be a useful tool in developing nutrient criteria or assist in the prioritisation of streams for riparian restoration or protection (Ludwig et al. 2012).

The combination of nutrient and physical factors such as temperature and light can mask the influence catchment land use on stream benthic metabolism. In a study by Bunn et al. (1999), the percentage of the catchment cleared for crops and pasture explained 14% of spatial variation in benthic metabolism. In contrast, Chessman et al. (1992) found that N was the dominant nutrient limiting periphyton biomass in Victorian streams, regardless of catchment type. Nutrient limitation not only occurred in forested streams but also in agricultural and urban streams which had elevated nutrients (Chessman et al. 1992). However, Chessman et al. (1992) also found spatial and temporal shifts in nutrient limitation behaviour across all watersheds regardless of land use. The spatial and temporal variability exhibited in regions, in spite of similarities in geology and land use, suggests that regional-scale extrapolation of nutrient limitation cannot be undertaken with any confidence (Wold and Hershey 1999).

3.5.5 Conclusion

The catchment water quality information used to modify default guideline threshold values into regional thresholds accounts for factors such as the variability of the particular ecosystem or environment, geology, rainfall and level of exposure to contaminants. These thresholds, if continually exceeded, may result in acute ecological impacts including a loss of sensitive species, and therefore threshold exceedances should prompt an appropriate management response. The results of my study indicated that upland nutrient thresholds, based on reference site information, are lower than those for the lowland catchment. These lower thresholds are required to protect the sensitive species frequently associated with upland riverine ecosystems.

The exceedance of the regionally-derived thresholds by non-reference sites demonstrates land-use influences and associated impacts on aquatic communities. These impacts may be alleviated through the protection of low flows and the maintenance and enhancement of riparian zones. Ecological responses to low flows have been found to be affected by water quality, with the greatest impacts to community structure occurring under increased nutrients, EC and temperature (Lancaster et al. 2009, Rolls et al. 2012). The protection of riparian zones provide a buffer against land use impacts and, in the case of smaller streams, increase shading and reduce temperature increases (von Schiller et al. 2007).

The monitoring of water quality responses to changes in climate can guide appropriate actions and is an important component for the long-term protection of the aquatic health of the system. The development of catchment-relevant thresholds allows managers to compare overall catchment water quality performance over time. The resulting comparisons could then be used to inform catchment and water management within the Manning system through the identification of on-ground restoration priorities and water extraction thresholds. On-ground actions to improve water quality and reduce possible climate change impacts should address activities that are likely to increase nutrients or alter hydrology, particularly impacts that are exacerbated under extreme flow conditions or may increase the likelihood of low flow or no flow conditions.