

**EVENT-BASED WATER QUALITY MONITORING
OF THE ROSS AND BLACK RIVER BASINS
DURING THE 2006/07 WET SEASON.**

Volume 1 - Main Report

Report No. 07/09

for the Creek to Coral Ross Black WQIP

October 2007

Event-based water quality monitoring of the Ross and Black River Basins during the 2006/07 wet season.

Volume 1 - Main Report

for the Creek to Coral Ross Black Water Quality Improvement Plan



ACTFR Report No. 07/09

**Prepared by Laurence Liessmann, Stephen Lewis, Zoe Bainbridge, Barry Butler
Jon Brodie, John Faithful and Mirjam Maughan.**



Australian Centre for Tropical Freshwater Research
James Cook University, Qld, 4811
Phone: (07) 47814262
Fax: (07) 47815589
Email: actfr@jcu.edu.au

EXECUTIVE SUMMARY

Twenty sites within the Townsville Thuringowa Region were monitored for water quality parameters in event flow conditions during the 2007 wet season, as part of the Townsville Thuringowa Creek to Coral Water Quality Improvement Plan. Significant rainfall occurred in January and February 2007, which triggered two separate flow events in the region. High flow events transport the highest flux of terrestrial pollutants (e.g. suspended sediments, nutrients and pesticides) in waterways to downstream receiving waters, such as coastal wetlands and the Great Barrier Reef lagoon. In this study we established water quality monitoring sites on the major watercourses (e.g. Black River, Bohle River, Ross River, Bluewater Creek, Stuart Creek and Alligator Creek) as well as other smaller waterways which drain dominant land uses within the region. For analysis purposes, these land uses were then grouped into five main categories including natural, mixed (natural, grazing and minimal use), rural residential, urban (including two developing urban sites) and industrial.

Freshwater plumes in Cleveland and Halifax Bays that resulted from the significant flow events were also monitored for selected water quality parameters. As the Townsville Thuringowa Region is the largest urban and industrial centre within the Great Barrier Reef (GBR) catchment area, the urban and industrial land uses form a major component of this study. Most of the water quality parameters that are generally considered to be of potential concern to the GBR were monitored in this study, including suspended sediments, nutrients, pesticides, trace metals, and oil and grease residues.

The study focused on examining contaminant exports to the marine environment and was not aimed at assessing ambient water quality or the health of aquatic ecosystems within the catchment. Accordingly, some key ambient water quality indicators such as dissolved oxygen and BOD were not included.

The specific objectives of this project were to:

- Obtain data that will aid the identification of subcatchments and land uses responsible for the fluvial exportation of sediments, nutrients, pesticides and trace metals from the Townsville Thuringowa Region to the GBR lagoon;
- Augment the baseline data that will be needed to support regional and local target-setting, and the Townsville Thuringowa Creek to Coral Water Quality Improvement Plan;
- Improve the ability to predict loads and concentrations of sediments, nutrients and pesticides being exported to the GBR lagoon; and
- Increase awareness of water quality and aquatic ecosystem issues within the Townsville Thuringowa Region.

Summary of Findings

This was a short term study that utilised only a few sites per catchment. A low resolution monitoring program of this kind does not provide a definitive basis for assessing risks, especially within complex urban subcatchments that contain a diversity of potential pollutant sources. Nevertheless, it proved possible to identify some key differences in the amounts and concentrations of contaminants that were transported from subcatchments with different dominant land uses.

The results indicate that there are five combinations of contaminant and land use type that stand out as potential issues in the context of this project:

- TSS concentrations in developing urban landscapes;
- Filterable Reactive Phosphorus in the urban and industrial land uses;
- Insecticides (endosulfan and malathion) in the rural residential and urban land use categories;
- Diuron residues in urban and industrial land uses, and;
- Trace metals in urban and industrial land uses.

Suspended sediments

Total suspended solids (TSS) concentrations were relatively low throughout the Townsville Thuringowa Region with the exception of the two developing urban sites (medians of 278 and 351 mg/L). Opportunistic sampling from an additional developing urban sites yielded peak TSS concentrations in excess of 30,000 mg/L, the highest known concentrations recorded for any study within the GBR catchment area. While runoff from developing urban sites is likely to produce only small TSS loads due to the relatively small catchment areas, the high TSS concentrations generated create extremely turbid environments and may have significant implications for downstream aquatic ecosystems. The larger grazing catchments in this region also produced higher TSS concentrations than the other land uses, although these results are consistent or lower than other grazed catchments within the GBR region.

Nutrients

Concentrations of particulate nitrogen (PN) and phosphorus (PP) were also relatively low across the Townsville Thuringowa Region. PN and PP concentrations generally mirrored trends in TSS concentrations; however, the two developing urban sites had low PN and PP concentrations and high TSS levels. These results suggest that the top soils (which are usually nutrient enriched) have already been removed from these sites and sediment is now sourced from the underlying nutrient poor soils. Dissolved organic nitrogen and phosphorus concentrations were consistent with other studies in the GBR catchment area, and are considered of low concern in the Townsville Thuringowa Region. Nitrate + nitrite concentrations (NO_x) were slightly elevated in all land use groupings (~100 µg N/L) compared to the natural sites (~50 µg N/L). The source of this extra NO_x is unknown, however these concentrations are considerably lower than intensive agricultural land use areas (eg. sugarcane, horticulture) of the Great Barrier Reef catchment area. Ammonia concentrations were highest in the urban land use (median of 36 µg N/L) compared to the other categories (< 10 µg N/L) within the region. The probable sources of ammonia in the region include sewage effluent, animal excreta (e.g. dogs) and fertiliser runoff. Filterable reactive phosphorus (FRP) concentrations were considerably higher in urban and industrial sites compared to the other land use categories. These elevated concentrations were comparable to the urban catchments in the Mackay Whitsunday Region. Possible sources for elevated FRP concentrations include fertilisers, detergents, wastewater, industrial effluent and animal excreta. More specific sources need to be identified in the region to assist in managing the high FRP levels obtained from the urban and industrial land uses.

Herbicides

Five herbicide residues (diuron, atrazine, simazine, bromacil and hexazinone) were detected in the waterways of the Townsville Thuringowa Region, particularly in urban and industrial land uses. Of these herbicides, diuron was the most commonly detected and one sample (0.3 µg/L) exceeded the ANZECC and ARMCANZ (2000) low reliability guideline (0.2 µg/L). The proposed revised guideline for diuron (1 µg/L) is higher than any concentration from samples collected in the monitoring program, although further investigations are required to ensure that diuron concentrations remain below the accepted guidelines. The other herbicides detected were at very low concentrations, and were well below guideline values. Two insecticide residues (endosulfan, malathion) were detected in the urban and rural residential land use categories. While the residues were only detected in limited samples from individual sites (endosulfan at Alligator Creek (D/S) and Captain Creek Drain; malathion at Louisa Creek), the concentrations were above the recommended 95% ANZECC and ARMCANZ (2000) ecological protection guidelines. The overall toxicity of these residues is relatively unknown due to their relatively short exposure times (within 24 hours) in the monitored waterways. Some organisms may have the capacity to tolerate high concentrations of these insecticides over short time frames, however research results concerning toxicity of species endemic to the north Queensland Region is currently limited. Further monitoring of these residues is required to determine the specific sources, the uses and the exposure times of endosulfan and malathion in this region. Monitoring of pesticide residues in ambient conditions is required as some residues have the potential to accumulate in waters and sediments over time and thus may be at higher concentrations. In particular, this monitoring should target the horticultural and urban land uses where these residues were detected.

Trace Metals

The concentrations of trace metals reported in some of the urban water samples were high enough to suggest the potential for impacts on ecosystems that lie within close proximity to the sampling sites. In particular, the concentrations of zinc, copper and aluminium observed in Gordon Creek (21/01/07), the silver and copper levels recorded in Stuart Ck, and to a lesser extent, the copper and zinc levels in Kern and Woolcock Street drains, all deserve closer investigation. Specifically, further monitoring of filterable trace metals under both high and low flow conditions, is strongly recommended, especially for Stuart and Gordon Creeks. If elevated metal concentrations prove to be recurrent or persistent problem it would be considered advisable to implement biological monitoring to determine if there are detectable impacts.

Oil and Grease

Oil and grease residues were detected in developing urban sites and from one sample in the natural land use category. Oil and grease analysis was included in this program mainly to determine if there was any evidence of highly anomalous concentrations, and the analytical method employed is only suitable for coarse screening purposes. Since oil and grease were detected within developing urban land areas some closer investigation may be warranted. It would be wise to adopt more accurate hydrocarbon analyses for both sediment and water in the future. However, the results to date provide no evidence of any serious problems or an urgent need to devote a significant proportion of the available monitoring budget to this parameter.

Sediment and nutrient loads

The sediment and nutrient loads for the Townsville Thuringowa Region are typically lower than those measured for other catchments of the Great Barrier Reef such as in the Burdekin (Bainbridge *et al.* 2006a; 2006b) and Mackay Whitsunday (Rohde *et al.* 2006) Region. When the event mean concentration (EMC) is applied to normalise the data for discharge, the concentrations of nutrients and sediments are comparable to several coastal catchments within the Burdekin Dry Tropics (between the Haughton River and Don River). Higher resolution input data may be required before SedNet and ANNEX models can provide reliable predictions of sediment and nutrient loads in the region.

Flood plumes in Halifax and Cleveland Bays

The freshwater plumes generated by the Black, Bohle and Ross Rivers impinged on a small number of coral reefs (e.g. middle Reef) within Cleveland and Halifax Bays. TSS concentrations decreased away from the river mouths and were typically less than 20 mg/L by the 10-15 ppt salinity zone (<4 km from river mouths). Most nutrient species also decreased along the salinity gradient. Concentrations of FRP were relatively high compared to other studies of freshwater plumes in the GBR lagoon (Devlin *et al.* 2001). Three herbicides residues (diuron, atrazine and hexazinone) were detected in the Ross River and Sandfly Creek plumes at concentrations (<0.02 µg/L) well below ANZECC and ARMCANZ (2000) ecological protection guidelines. No pesticide residues were detected in the Black and Bohle River plumes. Trace metal concentrations and oil and grease residues were below detection limits in the freshwater plumes.

Table of Contents

Volume 1

EXECUTIVE SUMMARY.....	i
ACKNOWLEDGEMENTS.....	vi
1. INTRODUCTION	1
1.1. Overview.....	1
1.2. Study Objectives	1
1.3. Study Description.....	2
1.4. Ambient Monitoring Requirements	2
2. BACKGROUND	5
3. 2006/07 FLOW EVENTS AND SAMPLING TIMING	8
4. METHODS.....	14
4.1. Site Selection	14
4.2. Sampling Methods	21
4.2.1. <i>Freshwater sampling</i>	21
4.2.2. <i>Marine Sampling</i>	22
4.3. Analytical Methods.....	23
4.3.3. <i>Electrical Conductivity and Salinity</i>	23
4.3.4. <i>Total suspended solids</i>	23
4.3.5. <i>Nutrients</i>	23
4.3.6. <i>Chlorophyll a and Phaeophytin</i>	24
4.3.7. <i>Pesticides</i>	24
4.3.8. <i>Trace metals</i>	24
4.3.9. <i>Oil and Grease</i>	24
4.4. Statistical Analysis.....	24
4.5. Load calculations	25
5. RESULTS.....	26
5.1. Freshwater Sampling	26
5.1.1. <i>Electrical Conductivity (EC)</i>	26
5.1.2. <i>Total Suspended Solids</i>	27
5.1.3. <i>Nutrients</i>	36
5.1.4. <i>Pesticides</i>	44
5.1.5. <i>Trace metals</i>	47
5.1.6. <i>Oil and Grease</i>	51
5.2. Marine Sampling.....	51
6. DISCUSSION.....	58
6.1. Conductivity.....	58
6.2. Suspended sediments	58
6.3. Nutrients.....	60
6.4. Pesticides	62
6.5. Trace metals	63
6.6. Oil and Grease.....	63
6.7. Flood plumes in Cleveland and Halifax Bays.....	64
7. CONCLUSIONS	66
8. REFERENCES	68
APPENDICES.....	Volume 2

ACKNOWLEDGMENTS

We greatly appreciate the considerable efforts of the community volunteers for sampling during the ‘big wet’ of 2006/07, including Ron Gordon and the Bluewater Landcare Group members (Karen Brereton and Barb Hancock), Rick Willis, Matt Bartell, Glen Morgan, Damien Burrows, Andrea Sorbello, Mitchell Brewer and Bruce Shirley. A special mention is extended to Merilyn Thomas who displayed outstanding enthusiasm throughout the intense sampling period. Appreciation is given to the NR&W Ayr hydrographers and Bureau of Meteorology for access to stream flow and rainfall gauging station data. Appreciation is also expressed to the ACTFR Laboratory Services staff for analysing samples, and the ACTFR casual field staff for sampling during the wet season. This field team included Shane Blowes, Angus Cunningham, Chris Cvitanovic, Jaime Kay, Jana Guenther and Alice Ryder. We thank Captain Paul Crocombe from Adrenalin Dive for providing his expertise and charter vessel for marine sampling in Halifax and Cleveland Bays. We are grateful for the reviews conducted by Lionel Glendenning (ACTFR) and Andrew Moss (EPA, Brisbane) which helped to improve the final document.

1. INTRODUCTION

1.1. Overview

The Australian Centre for Tropical Freshwater Research (ACTFR) was appointed to carry out an event-based water quality monitoring program to assist the development of longer term monitoring strategies for the Townsville and Thuringowa City Council's Creek to Coral Coastal Catchment Initiative. The primary aim of the sampling program was to obtain data indicative of the quantities and types of contaminants being exported to the marine environment from the region's major waterways during high flow events, and of the quality of the flood plumes that form outside the river mouths when fluvial discharge rates are high. The vast majority of the terrestrial contaminants that reach offshore marine environments in the Great Barrier Reef (GBR) lagoon are carried there by floods associated with tropical cyclones and/or monsoonal rain depressions (Devlin *et al.* 2001). The data collected in this study will aid in determining which subcatchments, land uses and potential pollutants are of greatest concern for the Cleveland and Halifax Bay sections of the GBR lagoon.

Catchment conditions, human activities and the intensity, duration and timing of events can all vary significantly over time. This study had limited capacity to investigate the effects of such variations as monitoring has only been conducted for a short time and has encompassed only a few flow events. Nonetheless, by comparing the results to expected values, modelled predictions and the findings of studies conducted in other GBR catchments, it is possible to gain some valuable insights into the behaviour of the study catchments.

The monitoring parameters and sampling tactics employed in this study were specifically selected to aid the prediction of impacts on marine environments located well downstream of the riverine and estuarine sampling sites. As will be discussed in section 1.4, high flow events are a time of major disruption for the rivers and estuaries, and although water quality may play some part in these disturbances, it is rarely a major determinant of outcomes for the ecosystems. For aquatic habitats located within the drainage system, water quality becomes a much more significant issue when flows are low or absent, and the key contaminants and processes involved are quite different to those that are of concern during floods. Accordingly, the data collected in this study are not designed to be used for assessing the health of the freshwater and estuarine sites where samples were collected.

1.2. Study Objectives

The specific objectives of this project were to:

- Obtain data that will aid the identification of subcatchments and land uses responsible for the fluvial exportation of sediments, nutrients, pesticides and trace metals from the Townsville Thuringowa Region;
- Augment the baseline data that will be needed to support regional and local target-setting, and the Townsville Thuringowa Creek to Coral Water Quality Improvement Plan;
- Improve the ability to predict loads and concentrations of sediments, nutrients and pesticides being exported to the GBR lagoon; and
- Increase awareness of water quality and aquatic ecosystem issues within the Townsville Thuringowa Region.

1.3. Study Description

The study area includes drainage basin numbers 118 (Ross) and 117 (Black), as assigned by the Australian Water Resources Council. The Ross Basin ($1,707 \text{ km}^2$) extends south to Alligator Creek and north to the Bohle River, while the Black Basin ($1,057 \text{ km}^2$) extends from Crystal Creek south to Black River (Fig 5). In this report, the Ross and Black Basins will be referred to as the Townsville Thuringowa Region. Six key catchment sites were established and monitored during the 2005/06 wet season, under the Burdekin Dry Tropics NRM Community Event Monitoring Project (Bainbridge *et al.* 2006b).

An additional 14 monitoring sites were established for the 2006/07 wet season. These were strategically located within major waterways and urban stormwater drains in order to intercept runoff from subcatchments with distinctive land use types. These included catchment areas that were predominantly natural, as well as areas dominated by grazing, rural residential, urban (existing and developing) and industrial land uses, and some small areas of sugarcane and horticulture located on the northern boundary of the region.

There were only two significant periods of storm flow in the catchment during the 2006-2007 wet season; a moderate “first flush” event associated with 100 to 300 mm rain that fell between the 20th to the 24th of January 2007, and a larger set of spates generated by 300 to 700 mm of rainfall between the 28th of January and the 3rd of February. Sampling was carried out at catchment monitoring sites during the early, middle and late stages of both of these flow events. Routine samples were analysed for conductivity/salinity, total suspended solids and total and dissolved nitrogen and phosphorus species. Selected samples were analysed for pesticides, trace metals (total and filterable) and oil and grease residues.

The larger of the two events generated flood plumes outside the mouths of the Black River, Ross River and adjacent coastal streams. The plumes from the Black River, Bohle River, Ross River and Sandfly Creek were sampled on the 2nd of February. The areal extent of the plumes was estimated from visual observations and the subsequent movements of the Ross River plume were observed on the 3rd, 6th and 7th February.

1.4. Ambient Monitoring Requirements

As mentioned above, this study focuses mainly on contaminant export events and the issue of potential impacts on the marine environment. It does not deal with ambient water quality issues or attempt to assess the ecological health of the streams and estuaries that were sampled during the study. Since these are also essential aspects to consider in a water quality improvement plan, the following discussion has been included in this report. It briefly explains the need to employ different methods for ambient assessments and lists some of the factors that need to be taken into consideration when designing monitoring programs.

The swift turbulent flows and sudden changes in water depth and salinity that occur during floods can have an enormous impact on rivers and estuaries. These intense physical effects are usually so overwhelming that most of the accompanying water quality changes are of little consequence to instream ecosystems. Freshwater and estuarine habitats are most affected by water quality changes and contaminant inputs that occur at times when flow rates are too low to efficiently dilute and/or wash away contaminants, and it is those conditions that must be targeted in ambient monitoring programs.

There are numerous potential sources of low flow inputs in urban catchments. These include but are by no means limited to, runoff from small scale storm events and domestic water uses,

authorised and accidental releases of wastewater effluents, groundwater seepage, dust, spillages, recreational water use and illegal dumping. The total quantities of contaminants delivered from these low flow sources are often very small, especially compared to the amounts that pass through the system during floods, so impact is often limited mainly to times and places where dilution and dispersion rates are low. However, because rivers in this region rarely flow strongly, these kinds of high risk conditions are the norm for most freshwater ecosystems.

The mean tidal ranges in this region are adequate to ensure that most open estuary waters are efficiently flushed and mixed during spring tide sets. However, dilution and dispersion capacities can fall by orders of magnitude during neap sets (i.e. for almost 2 weeks each month). Moreover, the region contains many partially enclosed estuary sites such as marinas, port facilities, artificial lakes, intertidal wetlands, natural and constructed backwaters, and small mangrove creeks that are poorly flushed even during spring tides.

The duration and physical extent of the impacts associated with each of the individual contaminant sources that influence the quality of low-dilution waters is often quite small, but there are so many potential impact sources in the study area that the cumulative effects can be extensive in terms of both time and space.

The task of assessing these kinds of ambient water quality effects is a major and long term undertaking that fell outside the scope and capabilities of the current study. It is complicated by the following factors:

- Potential contaminant input sources are numerous and diverse.
- The quality of poorly flushed waters can easily deteriorate to the point where conditions become acutely lethal to aquatic life, hence even brief transient episodes can have long lasting impacts on the health of the ecosystem. Events of this kind are easily missed in conventional monitoring programs even though they may be major determinants of ecological health.
- Anthropogenic pressures other than contaminant inputs – removal or modification of riparian vegetation, alterations to flow and depth, invasions by aquatic weeds and other exotic species, and recreational water activities, to name just a few – all have the potential to substantially alter the relationships between water quality and ecosystem health. These effects must be assessed and taken into consideration when designing ambient monitoring programs and/or interpreting monitoring data.
- The parameters and contaminants that most threaten the integrity of poorly flushed waters are quite different to those that are of principle concern to the marine environments further downstream. Dissolved oxygen availability, oxygen demanding substances, pH, water clarity and salinity, are important issues for most such waters, but because impacts are so localised and sources so diverse, different contaminants may need to be monitored at each individual site. For example a waterhole located adjacent to an industrial site may be at risk from a particular chemical that is used nowhere else in the region.
- The waters in question are also very poorly mixed, hence water quality can rarely be confidently assessed by taking grab samples from one point in the water column.

It is impossible to design cost-effective ambient monitoring programs capable of contending with these complications, without first conducting a detailed ecological risk assessment in order to identify precisely what problems are most likely to eventuate, and when and where they are most likely to occur. This is an intellectually challenging job in its own right, as it requires an

intimate understanding not only of contaminant sources and catchment drainage patterns, but also the intrinsic vulnerabilities of individual waterbodies. It is unlikely to be feasible to collect sufficient data to be able to gain the required level of understanding within the foreseeable future. However, a lot of water quality investigations have been conducted in local catchments over the years, and it is likely that much of the data required for a risk analysis actually already exists. Unfortunately this information is the property of the stakeholders who commissioned the work and most of it is not currently accessible to the public. The prospects of achieving an optimal monitoring program design would be greatly enhanced if this problem could be rectified.

In the meantime it may be necessary to rely on adaptive research and monitoring strategies, meaning that the monitoring program will need to be constantly redesigned and allowed to evolve as understanding of the system improves. Under this approach site networks, sampling regimes and monitoring parameters may need to change considerably over time.

Due the complexities involved and existing uncertainties regarding the tolerances of local aquatic species (most of which have never been subjected to toxicological tests), water quality data alone seldom provide a reliable basis for confident management decisions; biological monitoring is an essential and strongly recommended component of any ambient assessment program. It offers the following important benefits:

- Assurance that the ecosystem has not been adversely affected by an unmonitored contaminant or by an undetected event.
- The capacity to develop local water quality guidelines for toxicants based on actual rather than predicted biological responses.
- Improved understanding of the potential susceptibilities of the ecosystem (i.e. knowing what lives there enhances investigator's capacity to predict the ecosystems responses to water quality change).

It should be noted that different water quality parameters and anthropogenic pressures affect different species and processes in different ways. Hence biological monitoring methods must be selected judiciously with due regard to existing risks; no single biological monitoring parameter can be used to cover all possible contingencies. For example fish are generally more sensitive to oxygen deficiency (hypoxia) than macroinvertebrates which are in turn more sensitive than plants. Hence the existence of acceptable invertebrate and plant diversity is not diagnostic of an absence of hypoxia-related impacts.

2. BACKGROUND

Creek to Coral is a communications network and branding which provides a coordinating role for total water cycle management in the Townsville and Thuringowa Local Government Regions. The Townsville Thuringowa Creek to Coral initiative is an adapted version of the South East Queensland (SEQ) Healthy Waterways Program. The initiative emphasises local concerns and issues in an environmental context that is relevant to the Townsville Thuringowa Region, adjacent to the Great Barrier Reef lagoon. The primary objective is to improve the sustainable use and management (environmental, economic and social) of our coastal marine and freshwater resources.

The Townsville Thuringowa Region lies within both the Black and Ross Basins, which consist of a number of waterways between Ingham and Giru (Fig 5). Land use in these catchments varies widely within the region. The upper reaches of most streams are located in rainforest of the Wet Tropics World Heritage Area and Mount Elliot National Park. The lower reaches are dominated by horticulture and sugarcane cultivation in the north, and urban and industrial development in the region's south. Cattle grazing is also an important land use which is practiced throughout the basins. The Townsville Thuringowa Region (population ~160,000) is the only urban based CCI, with the region being the largest urban and industrial centre of the GBR catchment area (ABS, 2007). Major industries within the Townsville Thuringowa Region include Queensland Nickel Pty. Ltd., Xstrata Copper Refinery Pty. Ltd., Sun Metals Pty. Ltd., Australia Meat Holdings Pty. Ltd., Queensland Rail locomotive and rolling stock maintenance facilities, Pacific National's Stuart Rail Freight Facility and the Port of Townsville. Under Queensland's Environmental Protection Policy, most industrial operations in the region are classed as Environmentally Relevant Activities and are subject to regulation by the Queensland EPA. A number of quite large scale monitoring projects have been carried out in connection with these activities but the findings are not a matter of public record, so the impact of industries on the water quality of the region is poorly known in the scientific community.

The majority of the long term monitoring and modelling data available for GBR catchments has been gathered from land uses which are predominantly forest, sugarcane and grazing. Previous investigations have targeted catchments including the Herbert River (Mitchell *et al.* 1997), Johnstone River (Hunter *et al.* 1996), Mackay Whitsunday Region (Mitchell *et al.* 2005; Rohde *et al.* 2006), Burdekin Dry Tropics (Furnas and Mitchell 2001; Bainbridge *et al.* 2006a; 2006b), Tully Murray Region (Faithful and Finlayson, 2004; Faithful *et al.* 2007) and Fitzroy River (Packett, 2007).

This water quality monitoring program is intended to enhance the deficient (event based) dataset relating to industrial and urban land use, and to expand datasets of previous ambient monitoring in the Townsville Thuringowa Region which has been undertaken by various community and local government based groups (e.g. Bluewater Landcare Group, Oak Valley Landcare), as well as research gathered from natural and grazing lands. This dataset will also aid in the calibration and/or further development of existing modelling software packages such as SedNet and ANNEX. SedNet is the set of geographical information system (GIS) programs developed by CSIRO Land and Water to predict sediment and nutrient budgets for large regions using input GIS data layers and a synthesis of hydrological data (Prosser *et al.* 2002). SedNet was initially developed for the Australian National Land and Water Resources Audit in 2000 (“NLWRA” www.nlwra.gov.au). Since completion of the NLWRA project, these models have been further developed and applied to regional case studies using higher resolution input data. The development of the SedNet model is briefly described in Table 1.

Table 1. The development of SedNet models for the GBR catchments (Modified from: Kinsey-Henderson and Sherman, 2007).

Year	Undertaken by	Issues addressed
2001	National Land and Water Resources Audit Prosser <i>et al.</i> (2001)	Original model done as part of the National Land and Water Resources Audit (NLWRA)
2002	Prosser <i>et al.</i> (2002) – CSIRO	First application of model to an individual catchment (Burdekin Region)
2003	Brodie <i>et al.</i> (2003) and McKergow <i>et al.</i> (2005a); McKergow <i>et al.</i> (2005b)– ACTFR and CSIRO	Nutrients (ANNEX) added , Landuse improved
2006	Cogle <i>et al.</i> (2006)– QNRM&E and CSIRO – Short Term Modelling Project	Erosivity, dissolved nutrient data, landuse, bank erosion, plus port to the Toolkit version (not ANNEX)
2007	Kinsey-Henderson and Sherman (2007) – Improved SedNet Modelling of Grazing Lands in the Burdekin Catchment	Higher resolution land cover inputs
2007	Kinsey-Henderson (in prep)	Improved c factors for rainforest lands Improved modelling of coastal plains

Estimations of sediment and nutrient exports derived from modelling and monitoring data for the Townsville Thuringowa Region, namely the Black and Ross Basins are highly variable (Table 2). Estimated suspended sediment loads within the Black and Ross Basins range from 42 t/y (CSIRO 2007) to 250 t/y (Belperio 1983) and 60 t/y (NLWRA 2001) to 250 t/y (Belperio, 1983) respectively. Total nitrogen and phosphorus loads in the Black River Basin range from 319 t/y (Furnas, 2003) to 570 t/y (Brodie *et al.* 2003) and 63 t/y (Furnas 2003) to 99 (Brodie *et al.* 2003) respectively. Total nitrogen and phosphorus for the Ross River Basin ranged from 307 t/y (Brodie *et al.* 2003) to 411 t/y (Furnas, 2003) and 44 t/y (Brodie *et al.* 2003) to 80 t/y (Furnas 2003) respectively (Table 2).

The models have also been applied to predict the change in sediment and nutrient loads to the GBR lagoon since European Settlement (~ 1860). The model of Brodie *et al.* (2003) predicts that sediment loads have increased by 4 to 5 fold and TN and TP loads have increased by 8 and 9 fold respectively in the Black and Ross Basins (Table 2). A similar increase has been predicted for these basins by Furnas (2003).

These predictive models of sediment and nutrient export are based on data from other catchments in Australia and are not based on water quality data from the Townsville Thuringowa Region. Indeed, there is limited water quality data available for this region during event flows when the majority of materials are transported. In addition, low resolution input data are available for the Townsville Thuringowa Region to satisfy reasonable SedNet and ANNEX outputs. Bainbridge *et al.* (2006b) monitored four locations within the Townsville Thuringowa Region in the 2006 wet season; however, the study was limited to the parameters of suspended solids and nutrients.

This monitoring program will expand the number of sites monitored by Bainbridge *et al.* (2006b), as well as investigate additional water quality parameters which may be of concern in the Townsville Thuringowa Region. The study will provide estimates of sediment and nutrient loads to compare with current predictions, as well as expand our current dataset on water quality throughout the Townsville Thuringowa Region.

Table 2. Modelling and monitoring water quality data for the Black and Ross River Basins.

Basin		Black River							Ross River						
		AWRC Basin 117							AWRC Basin 118						
Reference		Furnas (2003)	Belperio (1983)	Horn <i>et al.</i> (1998)	NLWRA (2001)	Brodie <i>et al.</i> (2003)	Fentie <i>et al.</i> (2006)	Kinsey-Henderson and Sherman (2007)	Furnas (2003)	Belperio (1983)	NLWRA (2001)	Brodie <i>et al.</i> (2003)	Fentie <i>et al.</i> (2006)	Kinsey-Henderson and Sherman (2007)	
Sediment (kt/y)	Natural (total)	-	-	-	-	30	-	-	-	-	-	-	20	-	-
	Current bed load	-	-	-	-	-	-	12	-	-	-	-	-	-	26
	Current wash-load	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Current total export	140	250	67	80	161	182	42	180	250	60	80	186	79	
Dissolved Inorganic Nitrogen (t/y)	Current	75	-	-	-	53	-	1076	97	-	-	63	-	-	159
	Natural	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Dissolved Organic Nitrogen (t/y)	Current	53	-	-	-	65	-	21	68	-	-	32	-	-	50
	Natural	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Particulate Nitrogen (t/y)	Current	191	-	-	-	452	-	202	246	-	-	212	-	-	343
	Natural	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total Nitrogen (t/y)	Current	319	-	-	-	570	-	-	411	-	-	307	-	-	-
	Natural	-	-	-	-	77	-	-	-	-	-	39	-	-	-
Dissolved Organic Phosphorus (t/y)	Current	3	-	-	-	4	-	1	-	-	-	5	-	-	2
	Natural	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Filterable Reactive Phosphorus (t/y)	Current	10	-	-	-	3	-	4	-	-	-	1	-	-	40
	Natural	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Particulate Phosphorus (t/y)	Current	49	-	-	-	92	-	37	-	-	-	38	-	-	60
	Natural	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total Phosphorus (t/y)	Current	62	-	-	-	99	-	-	80	-	-	44	-	-	-
	Natural	-	-	-	-	11	-	-	-	-	-	5	-	-	-

3. 2006/07 FLOW EVENTS AND SAMPLING TIMING

Two separate rainfall events in January–February 2007 triggered two flow events within the Townsville Thuringowa Region. No significant rain fell in the catchment during the beginning of the wet season (i.e. <30 mm from September 2006) before this period. The smaller event of the two occurred from the 20th to the 24th of January, which is considered the first flush event of the season (Fig 1). Between 100 and 300 mm of rain fell in the catchment area in the five day period from the 20th to the 24th January which was linked to a trough stretching along the east coast of Australia (Fig 1). A considerably larger rainfall event occurred from the 28th of January to the 3rd of February where 300 to 700 mm fell within the catchment area (Fig 2). The southward excursion of the monsoon trough caused this heavy rainfall event (Fig 2). This event created high flows within the region and caused localised flooding throughout the Townsville Thuringowa Region. The flow hydrographs at the major waterway sites (Black River, Bohle River, Alligator Creek and Bluewater Creek) highlight these two distinct high flow events (Fig 3).

These events were sampled on the rise, peak and fall of the hydrographs so loads and concentration ranges could be estimated. The combined discharge of these two events is considerable when compared to historical flow records (NRW Watershed). Stream discharge volume recorded at Black River (NRW gauge 117002A) of 135,000 ML was the 7th largest flow event (of 33 records) since the commencement of gauged records in 1973. Stream discharge for Alligator (gauge no. 118106A: 41,500 ML) and Bluewater (gauge no. 117003A: 63,500 ML) Creeks in 2007 were ranked the 12th and 11th largest flow events of the 33 record period, respectively. Stream discharge for the Bohle River was only available approximately 8 km upstream of the sampling site (118003A: Bohle River at Hervey Range Road). The 147,000 ML discharge at this gauge for 2007 was the 3rd largest flow event for the 21 year gauged record. This discharge may have been the second largest event on record at the end of catchment site of 29 records (comparing the discharge to the decommissioned gauge at the Bohle River at Mt Bohle: Appendix A).

The larger of the two rainfall events which occurred in late January produced a flood plume from the Black River, Ross River and adjacent coastal streams. The plumes from the Black River, Bohle River, Ross River and Sandfly Creek were sampled on the 2nd of February and mapped using observations from the sampling vessel as well as some GPS coordinates. The plume was observable as a turbid brown water mass contrasted very distinctly against the clearer seawater. The visible edge was periodically plotted from the sampling vessel (Adrenaline Dive) by GPS. The areal extent of the flood plumes were estimated from these records and the subsequent movements of the Ross River plume were observed on the 3rd, 6th and 7th February (Ross River only) (Fig 4).

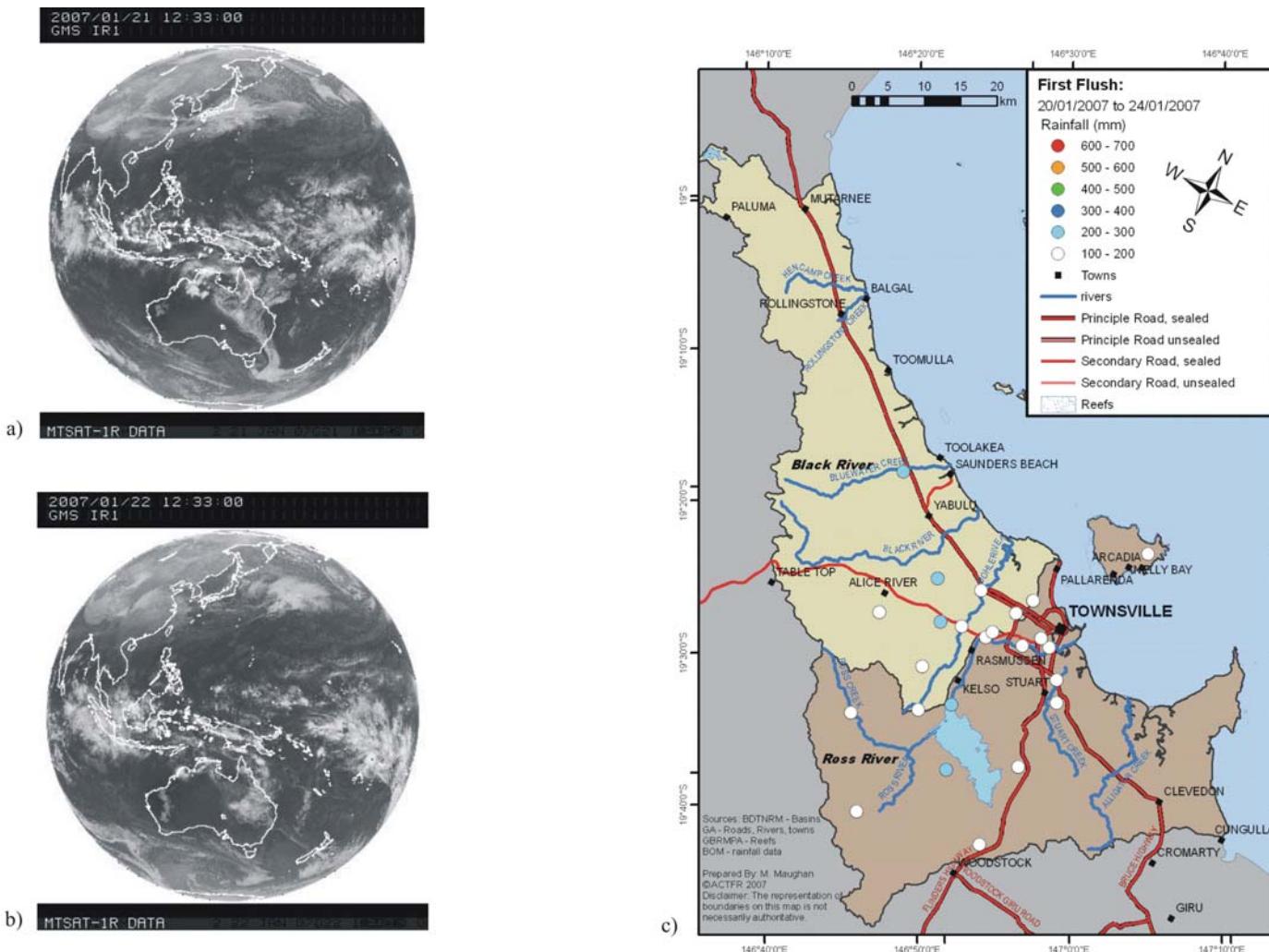


Figure 1. January 21st (a) and 22nd (b) 2007 satellite imagery showing the source of the first rainfall event and corresponding rainfall distribution in the Townsville Thuringowa Region from the 20th – 24th January (c).

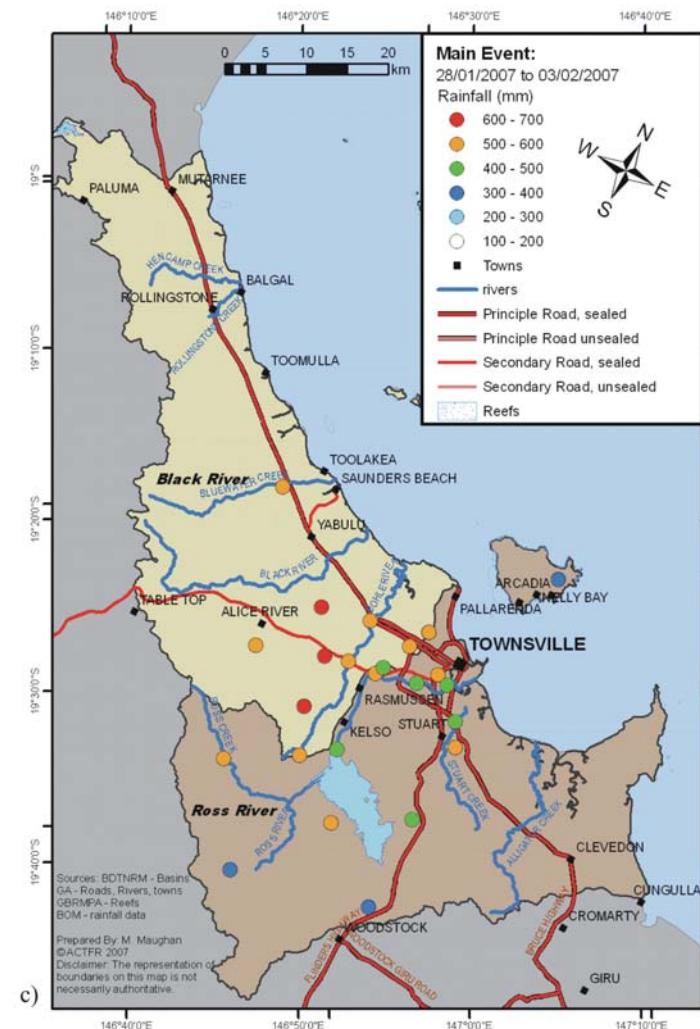
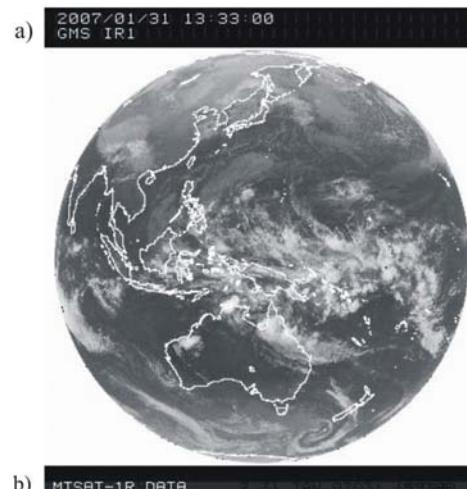


Figure 2. January 28th (a) and 31st (b) 2007 satellite imagery showing the source of the major rainfall event (a) and corresponding rainfall distribution in the Townsville Thuringowa Region from 28th of January to the 3rd February (c).

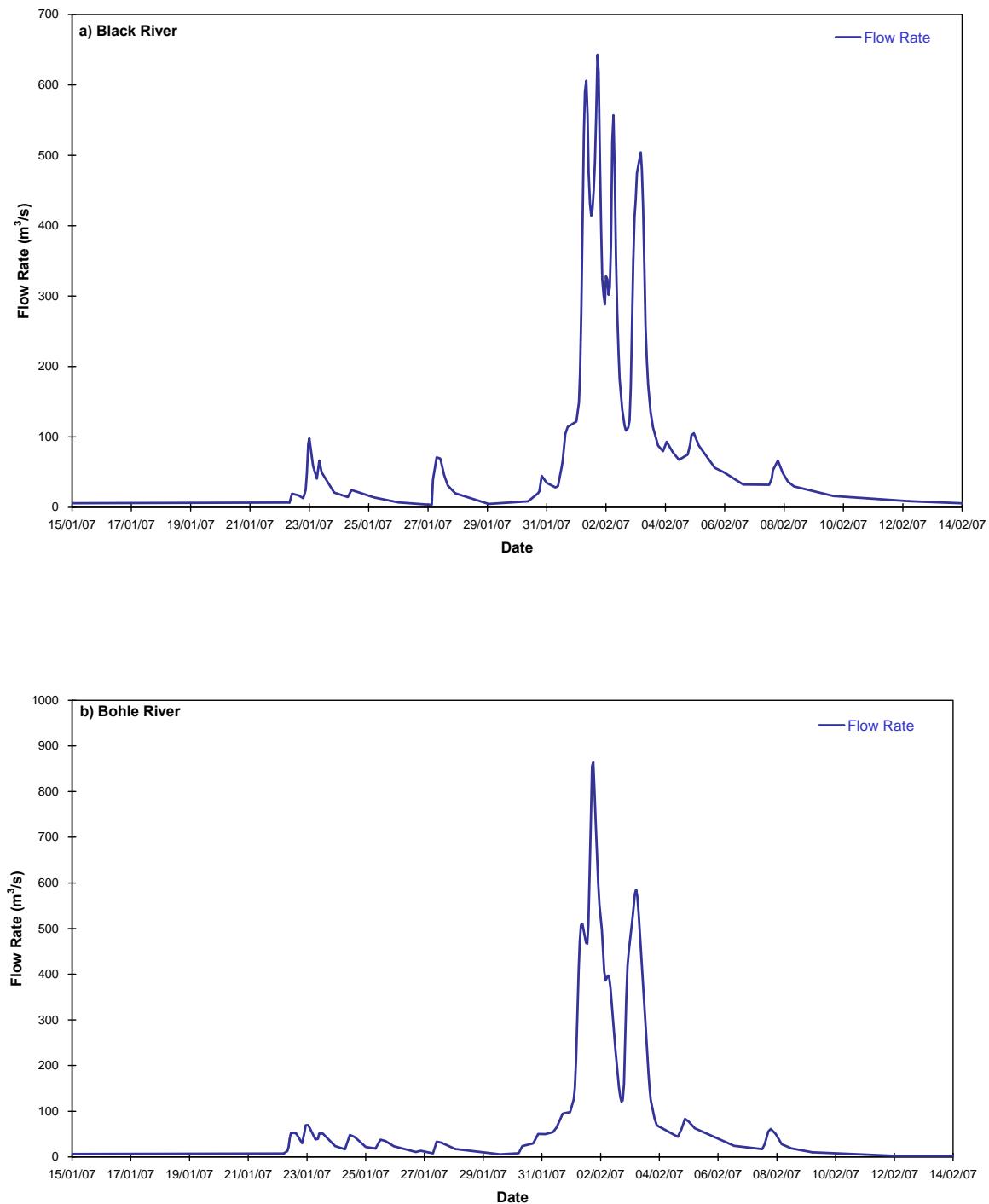


Figure 3. Stream discharge at the Black River (a) and Bohle River (b) gauging stations from the 15th January - 14th February 2007 (Source: NRW Watershed, 2007).

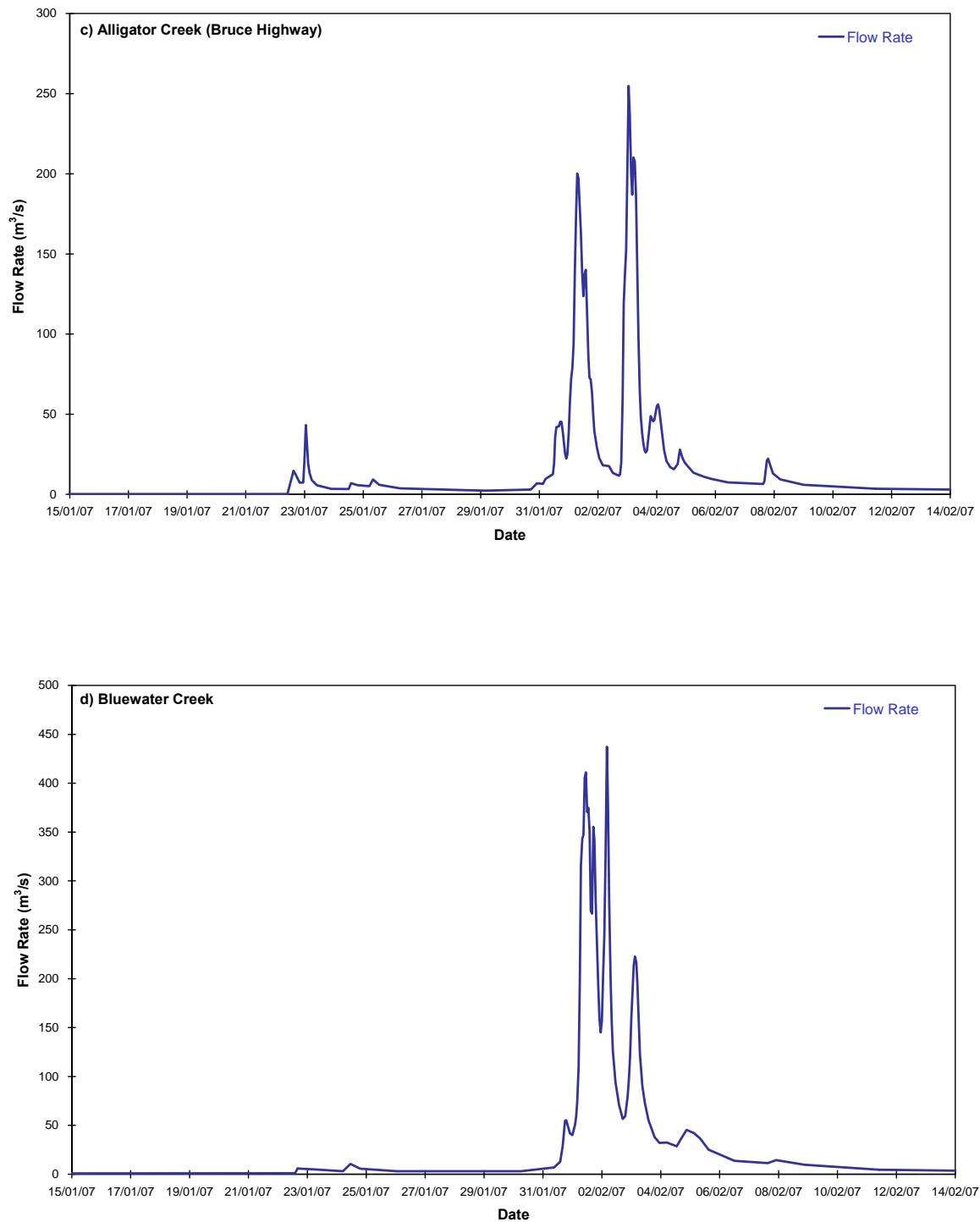


Figure 3. cont. Stream discharge at the Alligator Creek (c) and Bluewater Creek (d) gauging stations from the 15th January - 14th February 2007 (Source: NRW Watershed, 2007).

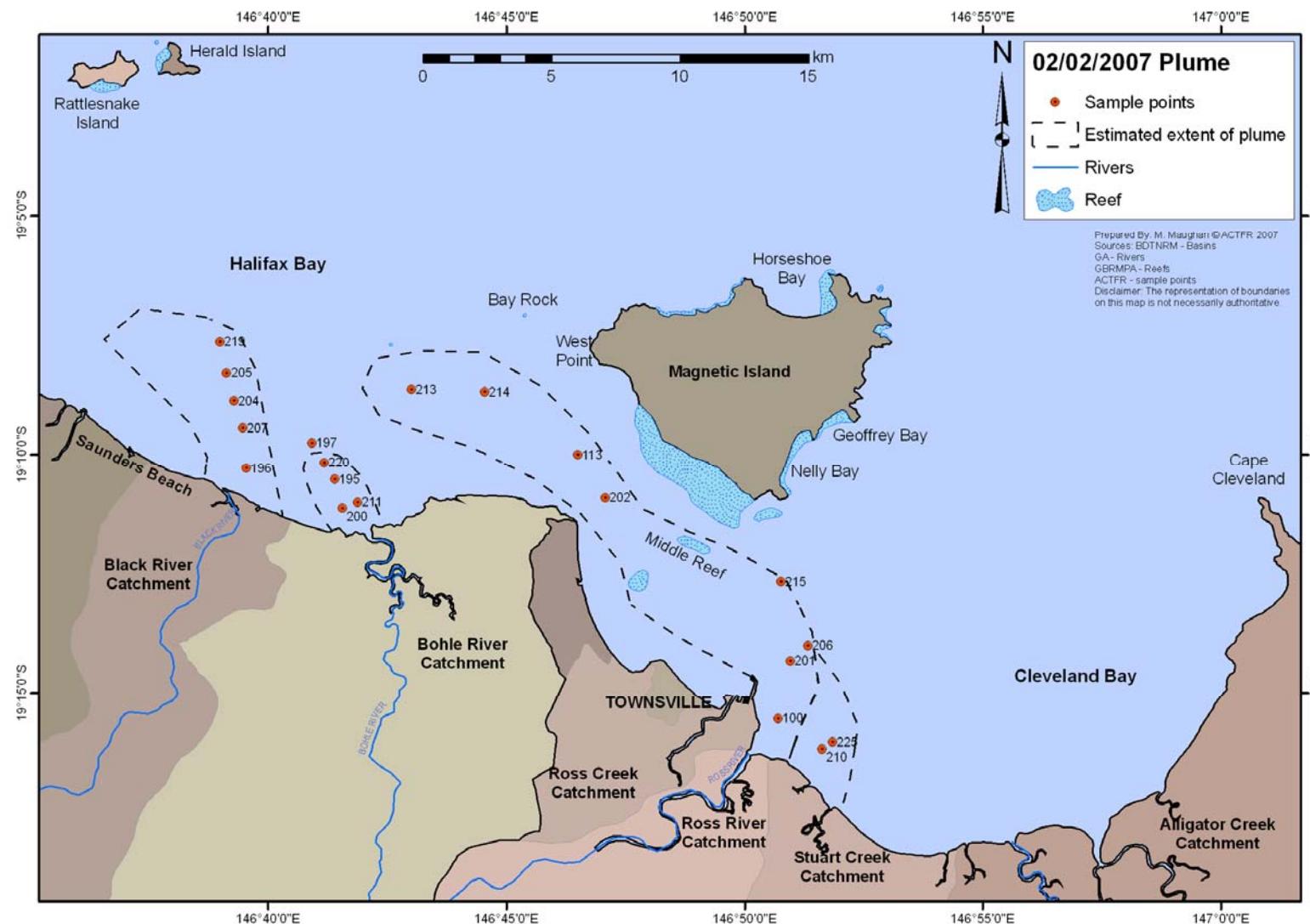


Figure 4. Plume water quality sampling sites within Halifax and Cleveland Bays during the 2006/07 wet season.

Australian Centre for Tropical Freshwater Research

4. METHODS

4.1. Site Selection

To determine which of the selected pollutants are potentially of greatest concern within the region, sites were established within the region's major waterways (e.g. Ross, Black and Bohle Rivers) and urban stormwater drains, and additional sites were also selected to ensure that the runoff from each major land use was intercepted. Upstream and downstream sampling was conducted on some of the larger waterways (Bluewater, Alligator and Stuart Creeks), where the land use in the upper catchment (often natural, or light grazing) differed to that downstream (rural residential, industrial). Five land use categories were developed for a total of 20 sampling sites illustrated in Figure 5. These categories include natural, mixed (natural, grazing or minimal use), rural residential, urban (including developing urban sites) and urban/industrial (Table 3, Fig 6). The mixed land use category includes catchments that are predominately natural pasture grazing (low intensity agriculture) such as the Black, upper Ross and upper Stuart catchments, or a predominately natural catchment (Hen Camp Creek) that has a small area (<3%) of intensive agriculture (horticulture and sugarcane cultivation) on the coastal plain. It should also be noted that “natural” conditions for the wetter catchments such as Alligator Creek, Bluewater and Hen Camp Creek will be different to those of the drier catchments, which are also often influenced by varying levels of cattle stocking. The urban land use category includes 5 urban sites, 2 of which have been classed as “developing” urban, as there is active development and land clearing directly above the sampling sites. Although these two sites have been classed within the urban land use category it is expected that there will be water quality differences in the urban and developing urban sites. Where possible the monitoring sites were located adjacent to NRW stream gauging stations (Table 3) where continuous flow data are recorded. Opportunistic sampling of additional waterways was also conducted where water quality issues (e.g. highly turbid runoff) became evident during the significant rainfall event.

At each site, samples were collected for the analysis of conductivity, total suspended sediments and total and filterable nutrients (nitrogen and phosphorus), while selected sites were also monitored for trace metal concentrations, pesticide residues and oil and grease residues (Table 3).

It was expected that the concentrations of water quality parameters measured at each site would reflect the dominant land use upstream of that specific sub-catchment. For example, grazing and developing urban lands involve significant rates of soil disturbance. Consequently, we expect to measure elevated concentrations of suspended sediment in waters draining these land uses during high rainfall periods. Pesticide residues are also expected to be detected within urban lands, due to the control and eradication of weeds and insects by government divisions and private residents in the region. The horticultural industry uses considerable amounts of fertiliser and pesticide products; we expect to measure elevated concentrations of nitrogen, phosphorus and certain pesticide residues in water draining this land use. We also expect to see a change in the proportion of nutrient species draining agriculture and urban land uses. For example, in fertilised cropping lands there is a shift from natural nutrient conditions (such as dissolved organic N and P) to a dominance of dissolved inorganic nitrogen (DIN, comprising nitrate, nitrite and ammonia). Hence it is important to measure all forms of nitrogen and phosphorus as the different forms reflect different land uses, sources and processes. Industrial and urban land uses may generate waste or by-products containing elevated levels of trace metals or oil and grease residues. Sources of these pollutants may range from cars, household products and industrial waste.

Table 3. Townsville Thuringowa monitoring site details.

Land Use	Site no	Waterway	Location	GPS Location		Sampler	NRW Gauging Station	Parameters				
				Lat	Long			TSS	Nutrients	Pesticides	Oil and Grease	Metals
Natural	1	Alligator Ck (U/S)	Alligator Ck Drive	-19.44	146.95	Volunteer Bluewater Landcare	-	X	X	X	-	-
	2	Bluewater Ck (U/S)	Blue Hills Pastoral	-19.23	146.50		-	X	X	X	-	-
	3	Campus Ck	JCU Campus- Physics Annex Rd	-19.32	146.76		-	X	X	X	X	X
Mixed (Natural, Grazing or Minimal Use)	4	Stuart Ck (U/S)	Bogangville Rd	-19.37	146.85	ACTFR	-	X	X	X	X	X
	5	Hen Camp Ck (Hwy)	Bruce Hwy	-19.02	146.36	ACTFR Volunteer	-	X	X	X	-	-
	6	Hen Camp Ck (D/S)	D/S below cane	-19.02	146.38	ACTFR Volunteer	-	X	X	X	X	-
	7	Black R	Bruce Hwy	-19.23	146.63	ACTFR	117002A	X	X	X	X	X
	8	Ross River 1 (below dam)	Below dam overflow	-19.40	146.73	ACTFR	NRW*	X	X	X	-	-
Rural Residential	9	Sachs Ck	Benella Rd	-19.42	146.82	Oak Valley Landcare	-	X	X	X	-	-
	10	Alligator Ck (D/S)	near Bruce Hwy	-19.39	146.96		118106A	X	X	X	-	-
	11	Bluewater CK (D/S)	Old Bruce Hwy (footbridge)	-19.17	146.56		117003A	X	X	X	-	-
Urban	12	Woolcock St Drain	Woolcock St (near Hyde Park)	-19.27	146.80	ACTFR	-	X	X	X	X	X
	13	Ross River 2 (Black weir)	Black Weir footbridge	-19.32	146.74	ACTFR	BoM*	X	X	X	X	X
	14	Ross River 3 (Aplins weir)	Aplins Weir footbridge	-19.30	146.78	ACTFR	BoM*	X	X	X	X	X
	15	Gordon Ck	Abbott St	-19.31	146.82	ACTFR	-	X	X	X	X	X
	16	Kern Drain	Dalrymple/Shaws Rd	-19.29	146.71	ACTFR	-	X	X	X	X	X
Urban/Industrial	17	Bohle R	Bruce Hwy	-19.26	146.70	ACTFR	118001B	X	X	X	X	X
	18	Louisa Ck	Woolcock St	-19.27	146.75	ACTFR	BoM (height)	X	X	X	X	X
	19	Stuart Ck (D/S)	Below Bruce Hwy (grazing property)	-19.32	146.84	ACTFR	BoM (height)	X	X	X	X	X
	20	Captains Ck	Melton Black Drive	-19.25	146.78	ACTFR		X	X	X	X	X

* data not currently available or calibrated.

U/S = upstream

D/S = Downstream

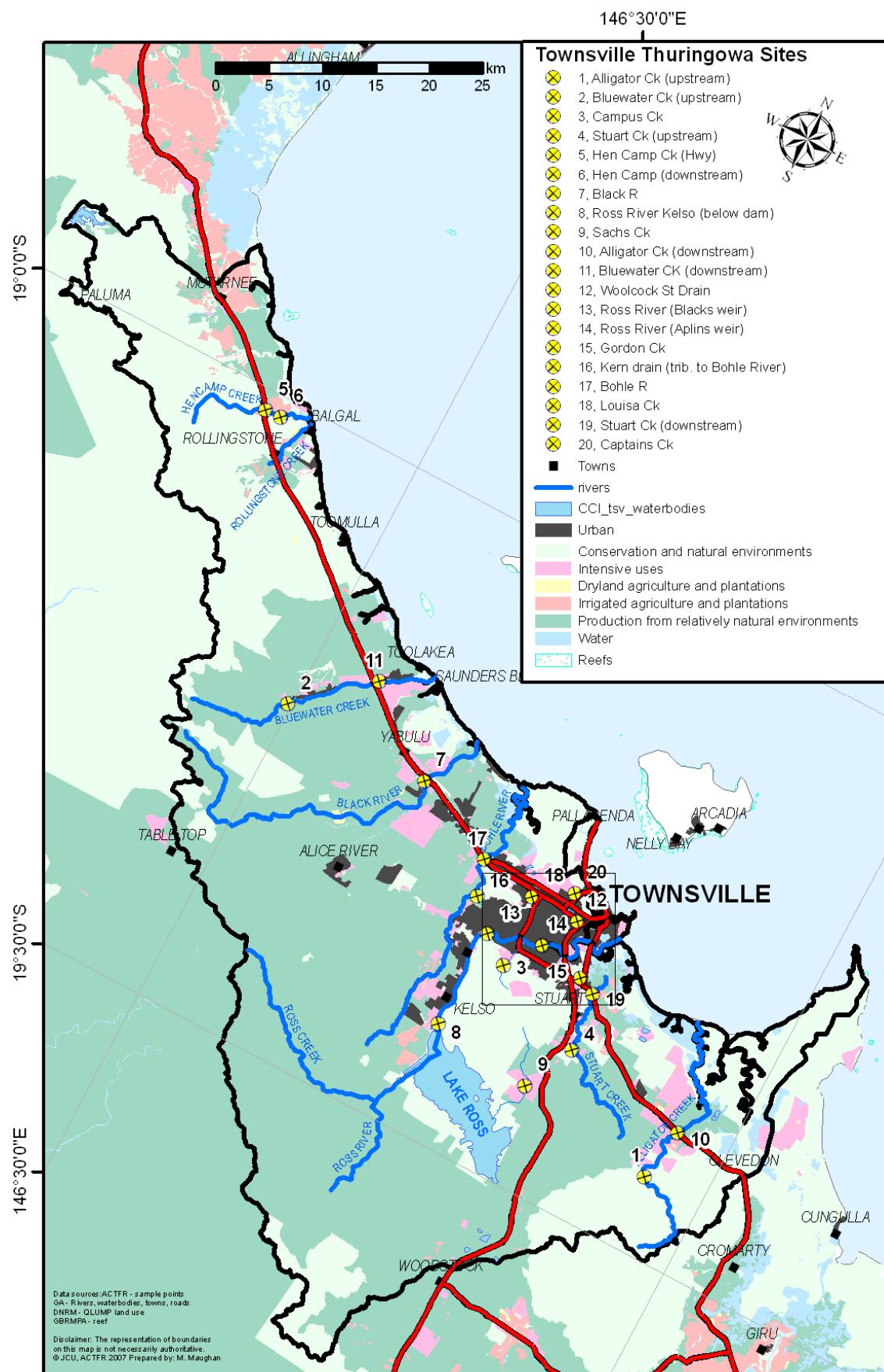


Figure 5. a) A site map of the Townsville Thuringowa Region identifying the location of the water quality sampling sites.

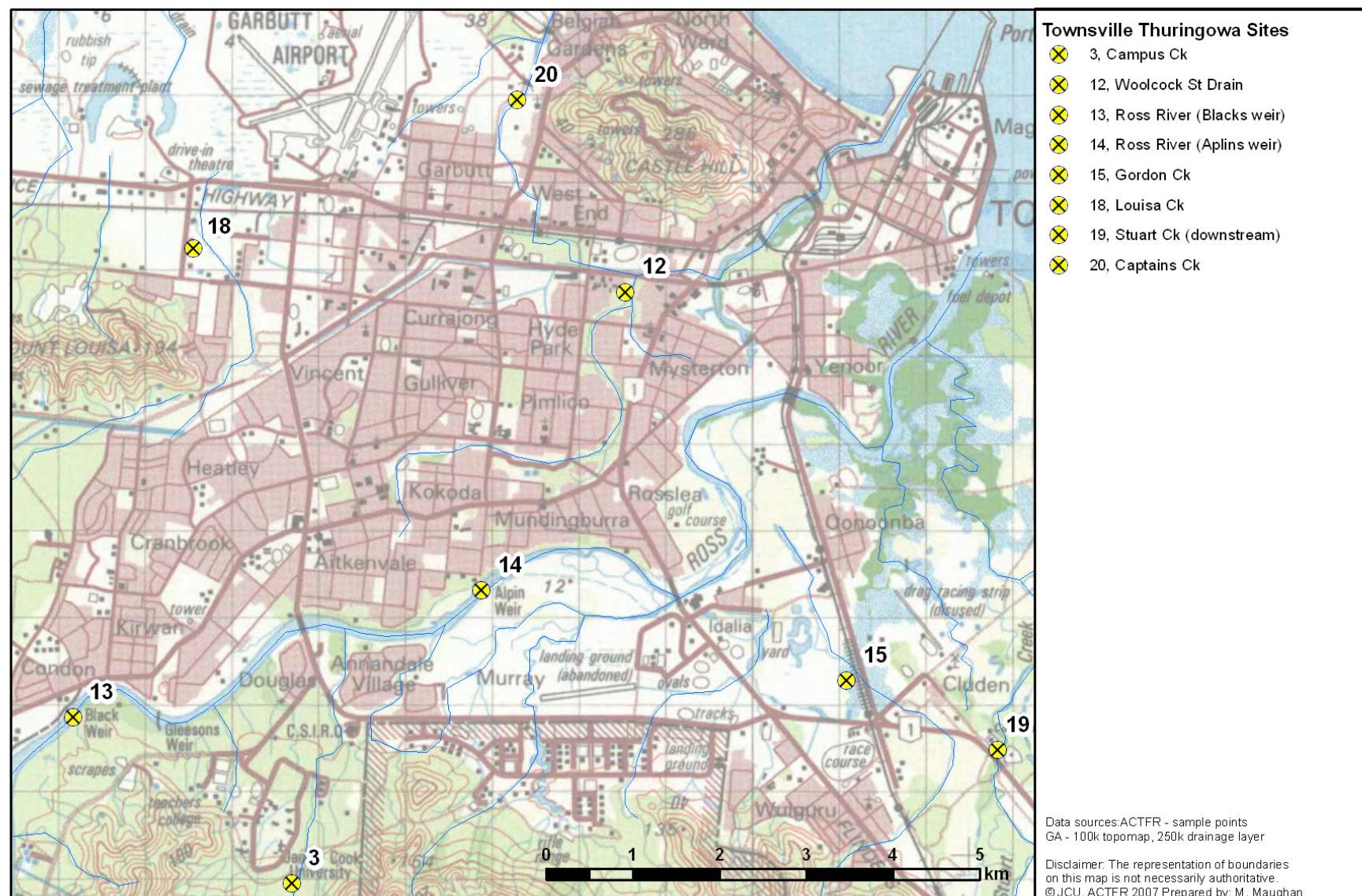


Figure 5 cont. b) A site map of the Townsville Thuringowa Region identifying the location of the water quality sampling sites.

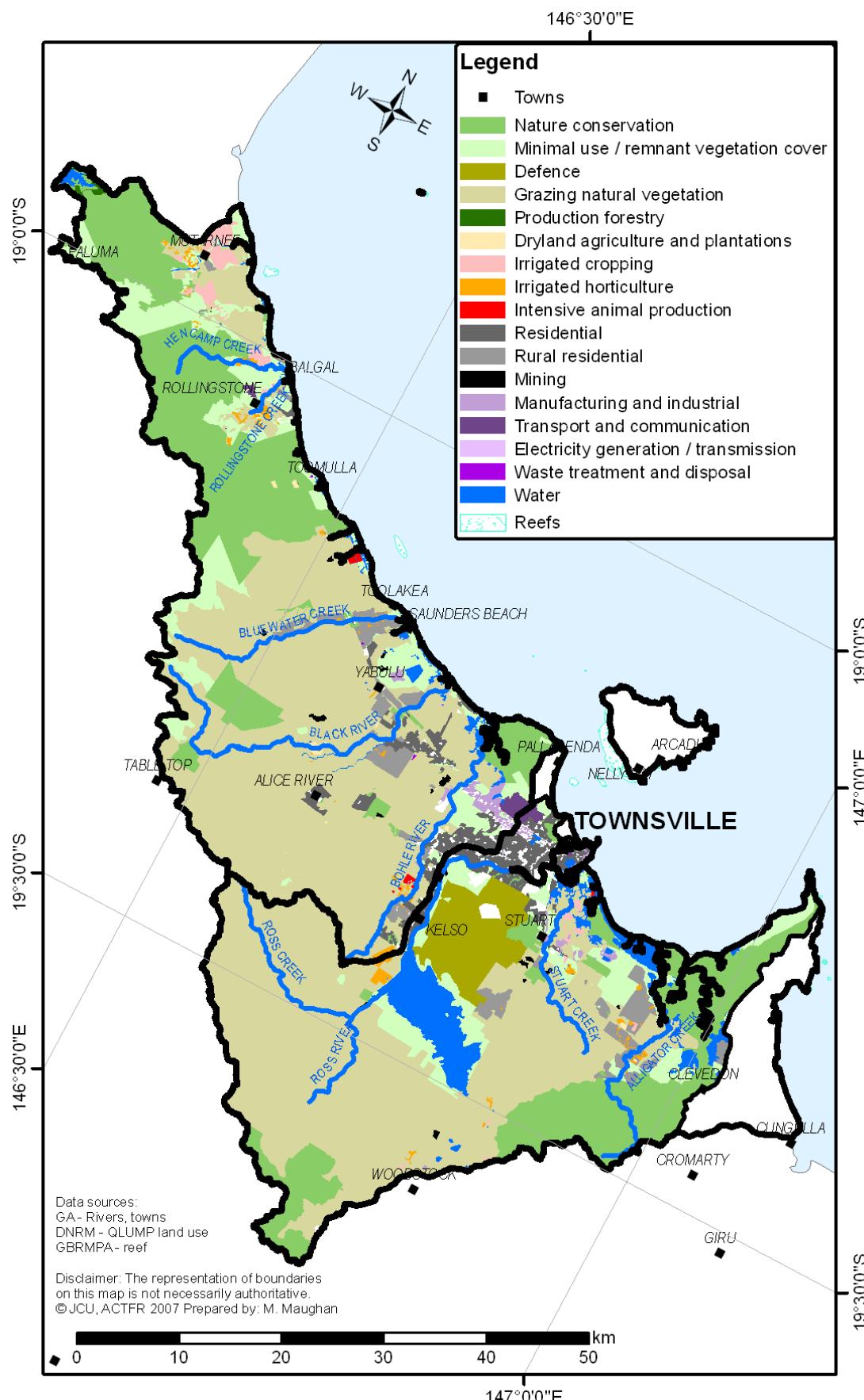


Figure 6. The major land use categories within the Townsville Thuringowa Region.

4.2. Sampling Methods

4.2.1. Freshwater sampling

Freshwater sampling within the Townsville Thuringowa Region was conducted by volunteers and ACTFR project staff. Project staff were trained in the correct sampling and quality assurance procedures. Volunteer samplers were given detailed sampling and storage procedures to follow during both sample collection and storage (Bainbridge *et al.* 2005). A range of stream flow and sampling photographs have been provided in Appendix H.

The freshwater monitoring strategy was to sample throughout the duration of the flow hydrograph at each site, including the rise, peak and falling stages. To compare event sample concentrations to ambient/baseflow conditions, some samples were collected in January at sites where water was present. Surface samples (top 50 cm of the water column) from all sites were collected with a sampling pole where the sample was collected directly into the appropriate container (Fig 7). Where it was not possible to collect the sample using a sampling pole, samples were collected in a bucket which was triple rinsed with water from the corresponding site. The sediment and nutrient samples were then sub-sampled into the appropriate containers. A stirring rod was provided to each volunteer/staff to ensure the sample water collected in the bucket was well mixed during sub-sampling.

Samples were collected from the centre of the channel flow were possible, otherwise samples were collected from the edge of the waterway. Every effort was made to ensure samples were collected from the main flow, away from the backwash at the riverbank. Nutrient samples were filtered at the time of sampling using a 0.45 μm sterile filter cartridge (Sartorius MiniSart) and stored on ice with the unfiltered nutrient samples before being frozen. Total suspended solid (TSS) samples were stored on ice before being refrigerated.

Where flow or stream height data were unavailable for the ACTFR monitored sites, the water depth was measured with a height stick at the time when the water quality samples were collected (sites include: Campus Creek, Kern Drain, Woolcock St Drain, Gordon Creek and Captains Creek). This measurement allowed trends between the water quality data and stream flow stage (i.e. rising, peak, falling) to be investigated. Unfortunately, material loads could not be calculated in these catchments due to the lack of flow speed data, although estimates of the event mean concentrations can be used as model input data.

An automated ISCO sampler was also used to sample water from Stuart Creek (D/S) during the main event (Fig 8). The use of an autosampler to collect water samples allows for reliable sampling of the rising stage of an event, which is often missed in small watershed sampling programs. The autosampler was programmed to collect samples at hourly intervals. The liquid level actuator was set so that samples were collected once flow height exceeded 2.4 m above the creek bed so that only considerable flow events were sampled. Samples collected by the automated ISCO sampler were transported on ice to the ACTFR laboratory and were sub-sampled for appropriate parameters.



Figure 7. ACTFR staff member Shane Blowes collecting a water sample from Sachs Creek.



Figure 8. An example of a trailer-mounted autosampler, which is similar to the one positioned at Stuart Creek (D/S) (Photo: Faithful *et al.* 2007)

4.2.2. Marine Sampling

Samples were collected along transects adjacent to the mouth of the Black River, Bohle River, Ross River and Sandfly Creek both within and outside the visible plume area from the sites shown in Figure 4. Surface samples were collected from the top 0.5 m of the water column. Samples were collected for TSS, nutrients, chlorophyll *a*, pesticide residues, oil and grease and trace metal analyses. Salinity was measured in the field using a hand-held refractometer and YSI probe and also later in the laboratory with an electrical conductivity meter for comparison. The laboratory salinity measurements were used in the plots to investigate the dynamics of the water quality parameters over the salinity gradient. The only exceptions where the laboratory measurements were not used were the 15J350-207 and 15J350-225 samples; sample 207 produced inconsistent salinity measurements between the laboratory and the two field

measurements and a laboratory measurement for sample 225 was not available; the YSI probe reading was used for these samples.

4.3. Analytical Methods

Samples collected for TSS, electrical conductivity, nutrients and chlorophyll *a* were analysed at the Australian Centre for Tropical Freshwater Research (ACTFR) Water Quality Laboratory, James Cook University (JCU), Townsville. Trace metal analysis was performed by the Advanced Analytical Centre (AAC), Townsville. Samples collected for pesticide analyses were analysed at the Queensland Health Scientific Services laboratory, Brisbane. Samples collected for hydrocarbon analysis were analysed at SGS Australia Pty Ltd, Cairns.

4.3.3. Electrical Conductivity and Salinity

Electrical conductivity values were analysed directly using a ATI Orion 130 specific conductivity meter (Analytical Technology, Incorporated, USA), after calibration with reference potassium chloride standards similar to the sample range. Salinities for the marine plume were measured using a number of methods. A YSI 556 MPS multiprobe water quality meter (Yellow Springs Instruments Ltd Pty, Ohio, USA) and a hand held refractometer (Atago Co. Ltd, Tokyo, Japan) were used for measuring salinities *in situ*. Marine samples were also taken back to the laboratory to measure conductivity using a ATI Orion 130 specific conductivity meter (Analytical Technology, Incorporated, USA). Salinity was than derived from an algorithm that permits practical salinity (S) to be determined from the conductivity and temperature measurements as per APHA/AWWA/WEF (2005).

Technically salinity is a unitless quantity (APHA/AWWA/WEF 2005), nevertheless, many practitioners report results in practical salinity units (psu) or parts per thousand (‰ or ppt). The unit ppt is actually the least desirable of these because sometimes it is also used to denote parts per trillion. However, ppt is the unit that has been most widely used in water quality reports throughout this region, and in the interests of consistency that is the unit has been employed in this report.

A total of 228 samples were analysed for conductivity and salinity.

4.3.4. Total suspended solids

Sample that were collected for TSS analysis were filtered through pre-weighed GF/C filter membranes (nominally 1.2µm pore size) and oven dried at 103-105°C for 24 hours before being re-weighed to determine the dry TSS weight. A total of 229 samples were collected and analysed for TSS throughout the 2006/07 wet season. 10 % of all TSS samples were duplicated to assess the repeatability of the analysis. Duplicate determinations were, on average, within 10 % of each other.

4.3.5. Nutrients

Samples were analysed for total nitrogen (TN) and phosphorus (TP), total filterable nitrogen (TFN) and phosphorus (TFP, ammonia, NO_x (nitrate and nitrite) and filterable reactive phosphorus (FRP). Samples for TN and TP, and TFN and TFP were digested in an autoclave using an alkaline persulfate technique (modified from Hosomi and Sudo 1987) and the resulting solution simultaneously analysed for NO_x and FRP by segmented flow auto-analysis using an ALPKEM Flow Solution II (Alpkem Corporation, Wilsonville, Oregon, USA). The analyses of NO_x, ammonia and FRP were also conducted using standard segmented flow auto-analysis techniques following standard methods (APHA, AWWA and WEF 2005). Particulate nutrient

concentrations were calculated by subtracting the total filterable nutrient concentrations from the total nutrient concentrations. Similarly, filterable organic nitrogen or phosphorus (referred to in this report as DON or DOP) was calculated by subtracting of NO_x plus ammonia (for nitrogen) or FRP (for phosphorus) from the TFN or TFP concentration.

4.3.6. Chlorophyll a and Phaeophytin

Chlorophyll *a* and its magnesium-free derivative, phaeophytin, (indicators of phytoplankton biomass) were determined using solvent extraction and measured using a UV-visible spectrophotometer (Pharma spec UV-1700, Kyoto, Japan).

4.3.7. Pesticides

The standard suite of PSII herbicides was analysed using liquid chromatography (LC/MS) by QHSS, Brisbane (Laboratory Reference No. 04EP). Water samples were extracted with dichloromethane, concentrated (initially with rotary evaporation then nitrogen-blowdown) prior to LC/MS analysis. LC/MS is the preferred method for the range of herbicides targeted in this investigation because of the method's lower limit of reporting (LOR) for triazine herbicides (e.g. Atrazine). A total of 89 samples were collected for pesticide analysis. The reporting limits and list of pesticides analysed are outlined in Appendix C.

4.3.8. Trace metals

Two separate acid-washed 100 ml containers were collected for total and dissolved trace metal concentrations. Within 12 hours of sample collection, the samples were acidified with concentrated nitric acid.

All trace elements were measured by a Varian ICPMS 820-MS (Melbourne, Australia). The instrument was calibrated by a series of multi-element standard solutions. Major elements were measured by a Varian Liberty Series II ICPOES (Melbourne, Australia). A series of multi-element standard solutions were used to calibrate the instrument.

Marine water samples are diluted 10-fold, and all elements were measured by Varian ICPMS 820-MS. The CRI technique was used to eliminate polyatomic interferences, H₂ was applied for Fe, Se and As determination, and helium was used for V, Cr, Cu, Ni. The instrument was calibrated by a series of multi-element standard solutions.

4.3.9. Oil and Grease

Dissolved or emulsified oil and grease is extracted from water by intimate contact with an extracting solvent, followed by solvent evaporation and gravimetric quantitation. The solvent used for extraction was 80% v/v hexane 20% v/v methyl-tertiary-butyl ether mixture. A total of 44 samples were analysed for oil and grease.

4.4. Statistical Analysis

The boxplots were produced using the statistical software package, SPSS 14.0. The box length of the boxplot is the inter-quartile range (25th to 75th inter-quartiles), with the median denoted by the dark line within the box. Outliers (circles) are values that are between 1.5 and 3 box lengths from the upper or lower edge of the box, and extreme cases (stars) are values more than 3 box lengths from the upper or lower edge of the box (Appendix G). Raw data and summary statistics are available in Appendix B and D.

4.5. Load calculations

The continuous time series flow data from the hydrographic gauging stations, and point source water quality data, were entered into the NRW “Brolga database”, and loads were calculated using linear interpolation. Loads were normalised to average annual discharge to directly compare to the latest modelled output (SedNet model: Kinsey-Henderson, in prep; ANNEX model: Kinsey-Henderson and Sherman, 2007).

5. RESULTS

5.1. Freshwater Sampling

For comparison purposes, the water quality data collected for the 20 sites sampled in the Townsville Thuringowa Region have been grouped into the five specific land use categories. The corresponding site number representing each site is listed in Table 4. We present the results for electrical conductivity (EC: section 5.1.1), TSS (section 5.1.2), nutrients (section 5.1.3), pesticides (section 5.1.4), trace metals (section 5.1.5), oil and grease (section 5.1.6). The marine sampling results are presented in section 5.2.

5.1.1. Electrical Conductivity (EC)

Natural, mixed (natural, grazing or minimal use) and rural residential sites had a similar range of EC values (28 to 214 $\mu\text{S}/\text{cm}$) which are typical of freshwater values. The urban catchment site Gordon Creek (site #15) and the urban and industrial site Captain Creek (#20) produced significantly higher EC values with high variability (15 to 6140 $\mu\text{S}/\text{cm}$ and 6 to 392 $\mu\text{S}/\text{cm}$, respectively). However, it should be noted that high conductivity values for Gordon and Captain Creeks are directly attributable to tidal influence (Fig 9; Appendix B). The Bohle River (#17) and Woolcock Street drain (#12) sites also produced outliers that were consistent with some tidal influence.

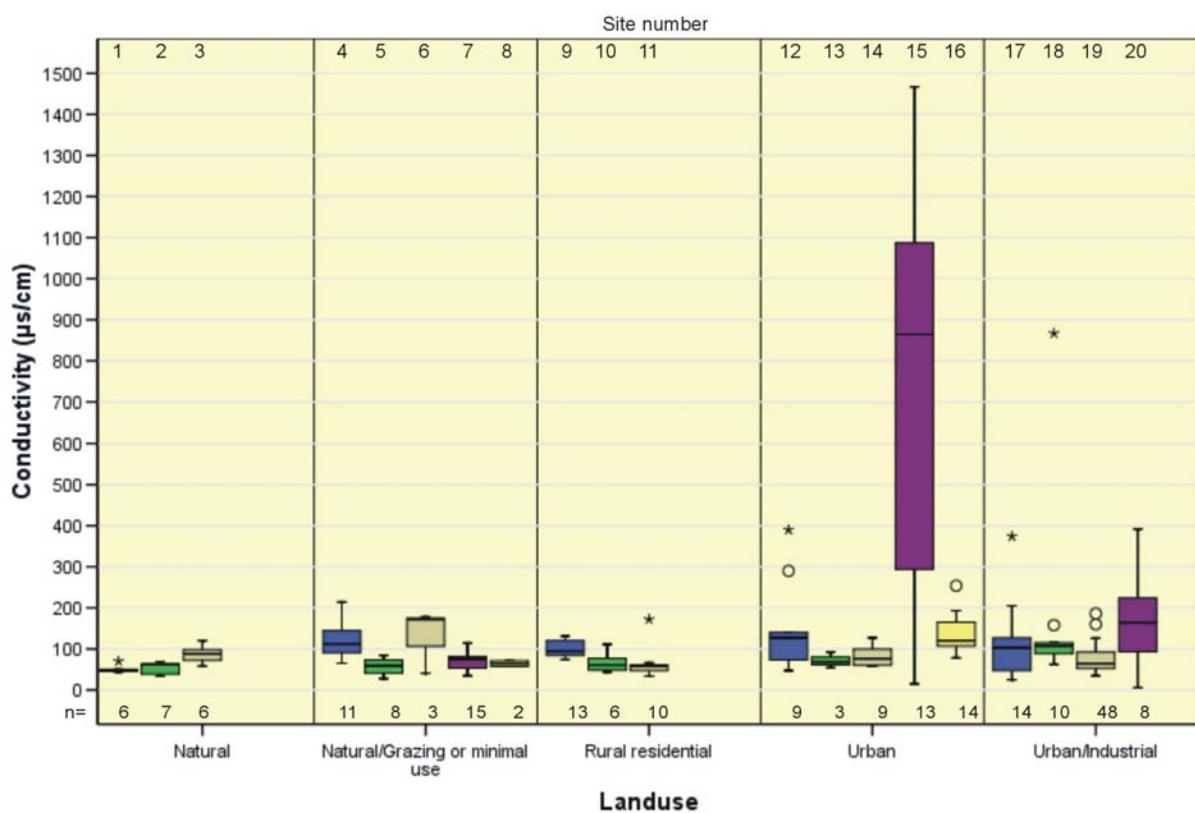


Figure 9. A boxplot summarising the electrical conductivity ($\mu\text{S}/\text{cm}$) data collected in the monitored waterways between December 2006 and March 2007. Individual sites are categorised by land use classes (see section 4.1 for further details), with site numbers displayed at the top of the boxplot listed in Table 4.

5.1.2. Total Suspended Solids

The natural and rural residential land use categories consistently produced the lowest TSS concentrations across the Townsville Thuringowa Region with median values of 9 and 10 mg/L respectively (Fig 10). Values obtained within the mixed (natural, grazing or minimal use) land use category were variable, and ranged from 0.3 to 640 mg/L. Within this category the lowest TSS concentrations were obtained at both Hen Camp Creek sites (Bruce Highway #5 and D/S #6: median values of 5 and 28 mg/L respectively). In comparison, the Black River (#7) and Ross Dam (#8) sites had considerably higher median values of 199 and 316 mg/L, respectively. Sites within the urban land use also displayed considerable variability with median TSS concentrations ranging from 24 mg/L (Woolcock Street Drain #12) to 351 mg/L (Gordon Creek #15). Indeed, the developing urban sites (Gordon Creek and Kern Drain #16) had consistently higher TSS concentrations (ranges from 85 to 1600 mg/L and 59 to 1120 mg/L respectively). Sites within the urban and industrial land use had differing TSS values where the Bohle River and Stuart Creek (D/S #19) produced the highest median values (155 and 200 mg/L respectively), compared to Louisa Creek (#18) and Captain Creek Drain (#20) which both had a median concentration of 12 mg/L (Table 4, Fig 10).

The only waterway to have a considerably higher TSS concentration downstream was Stuart Creek which increased from a median concentration of 63 mg/L (U/S #4) to 200 mg/L (D/S #19). There were only minor increases at downstream sites of both Alligator and Hen Camp Creeks and no discernable difference existed between upstream and downstream stratified sampling sites at Bluewater Creek (Table 4, Fig 10).

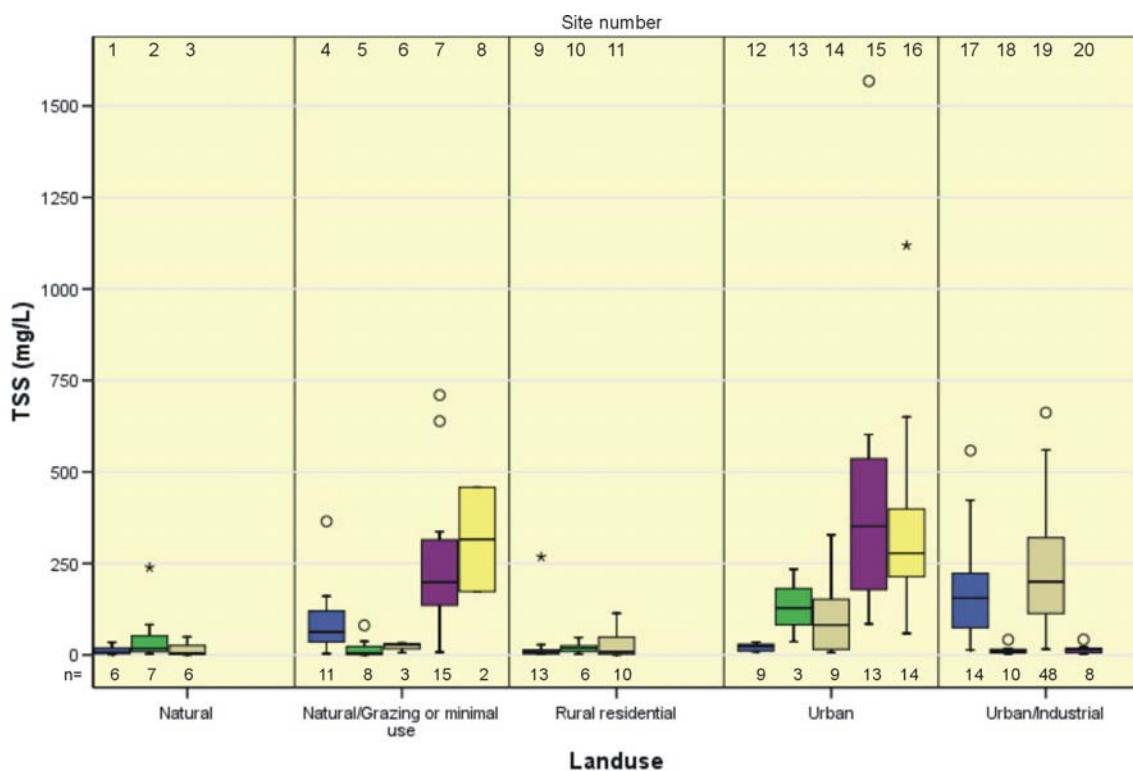


Figure 10. A boxplot summarising the total suspended solids (mg/L) data collected in the monitored waterways between December 2006 and March 2007.

Table 4. Median and range TSS concentrations (mg/L) for the land use categories and individual sampling sites.

Land Use	Site no	Waterway	Site		Land use	
			Median	Range	Median	Range
Natural	1	Alligator Ck (U/S)	7	1-34	9	0.2-240
	2	Bluewater Ck (U/S)	18	3-240		
	3	Campus Ck	3	0.2-50		
Mixed (Natural, Grazing or Minimal Uses)	4	Stuart Ck (U/S)	63	4-370	81	0.3-640
	5	Hen Camp Ck (Hwy)	5	0.3-80		
	6	Hen Camp Ck (D/S)	28	6-33		
	7	Black R	199	8-710		
Rural Residential	8	Ross River 1 (below dam)	316	180-460	10	0.5-270
	9	Sachs Ck	7	1-270		
	10	Alligator Ck (D/S)	19	3-48		
Urban	11	Bluewater CK (D/S)	20	0.5-110	152	7-1600
	12	Woolcock St Drain	24	9-35		
	13	Ross River 2 (Black weir)	128	36-230		
	14	Ross River 3 (Aplins weir)	82	7-330		
	15	Gordon Ck	351	85-1600		
Urban/ Industrial	16	Kern Drain	278	59-1120	143	3-660
	17	Bohle R	155	14-560		
	18	Louisa Ck	12	3-42		
	19	Stuart Ck (D/S)	200	16-660		
	20	Captain Ck	12	3-42		

The flow hydrographs for the major sub-catchments in the Townsville Thuringowa Region (Black River, Bohle River, Alligator Creek and Bluewater Creek – note that no flow data was available for the Ross River sub-catchment) show that the two major flow events in 2007 were well sampled over the rising, peak and falling stages (Fig 11). During the first flush event on the 23rd to the 24th of January, peak TSS concentrations generally coincided with the rise to peak stages of the hydrograph. At the Black River site (Fig 11a), TSS concentrations (710 mg/L) peaked on the highest flow of the hydrograph on the 1st February. Within five hours of this peak, TSS concentrations fell considerably to 240 mg/L and continued to fall throughout the remainder of the hydrograph. At the Bohle River site (Fig 11b), the highest TSS concentration (558 mg/L) recorded coincided with peak flow during the first flush event on the 22nd January. Concentrations then fell considerably to 168 mg/L on the 23rd January, approximately 20 hours later. TSS concentrations in the second event peaked (423 mg/L) on the early rise of the hydrograph on the 30th January before falling to 93 mg/L on the 1st February. Within four hours, TSS concentrations rose again (220 mg/L) which coincided with the highest flow on the 1st February, before decreasing again on the falling stage of the hydrograph (Fig 11b). Only two samples were collected during the major flow event at Alligator Creek (D/S) due to the flashiness of hydrograph, where two separate pulses of flow were recorded from the 1st to the 3rd February (Fig 11c). The durations of these two pulses were 19 hours and 15 hours respectively. While the samples were collected on the falling stages of both pulses, the TSS concentrations during this larger event (23 and 25 mg/L) were higher compared to the smaller first flush event. An anomalous TSS concentration (48 mg/L) was recorded at Alligator Creek (D/S) which corresponded with a small flow on the 25th January, two days after the first flush event (Fig 11c). At the Bluewater Creek sampling site, TSS concentrations taken during the first flow event on the 24th January peaked at a concentration of 28 mg/L before falling to 0.5 mg/L (Fig 11d). The

highest TSS concentration (114 mg/L) occurred on the 2nd February coinciding with the first pulse of the main event. TSS concentrations (59 mg/L) dropped considerably on the fall of the first pulse. No samples were taken during the rise and peak of the second pulse of the main event which was the slightly larger of the two (Fig 11d).

The smaller waterways in the Townsville Thuringowa Region displayed similar trends in TSS concentrations throughout the two flow events in 2007, with the highest concentrations coinciding with the rise/peak of the flow. Interestingly, the peak TSS concentration during the smaller first flush event (21st to 24th of January 2007) was more than double the peak concentration in the larger second event in these smaller waterways (Figs 12 and 13). Peak TSS concentrations between the developing (Gordon Creek: 1,600 mg/L and Kern Drain: 1,100 mg/L) and established (Woolcock Street Drain: 35 mg/L and Captains Creek: 40 mg/L) urban sites were highly variable (Fig 13).

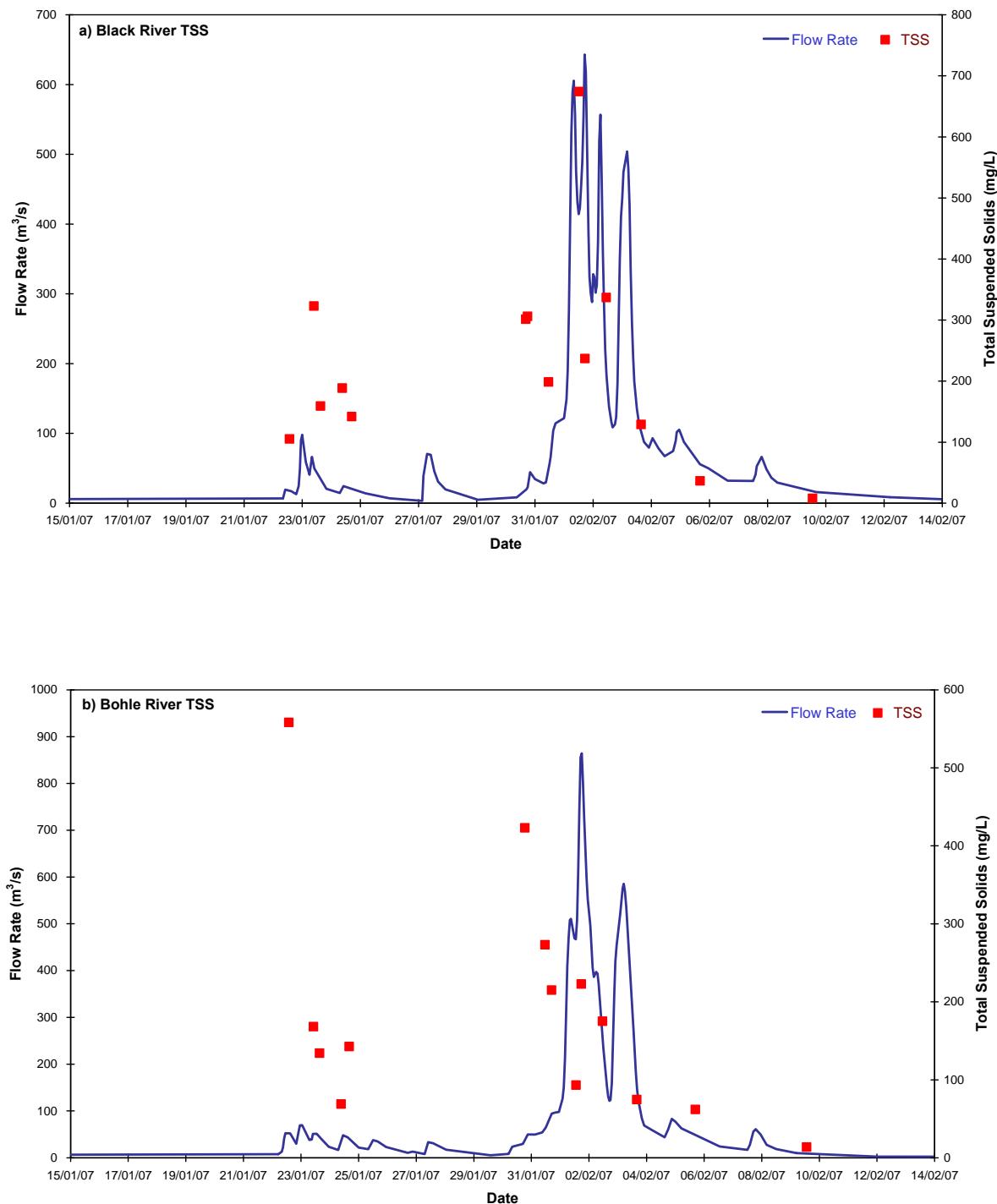


Figure 11. Stream discharge and TSS concentrations (mg/L) for the Black River (a) and Bohle River (b) from the 15th January - 14th February 2007 (Source: NRW Watershed, 2007).

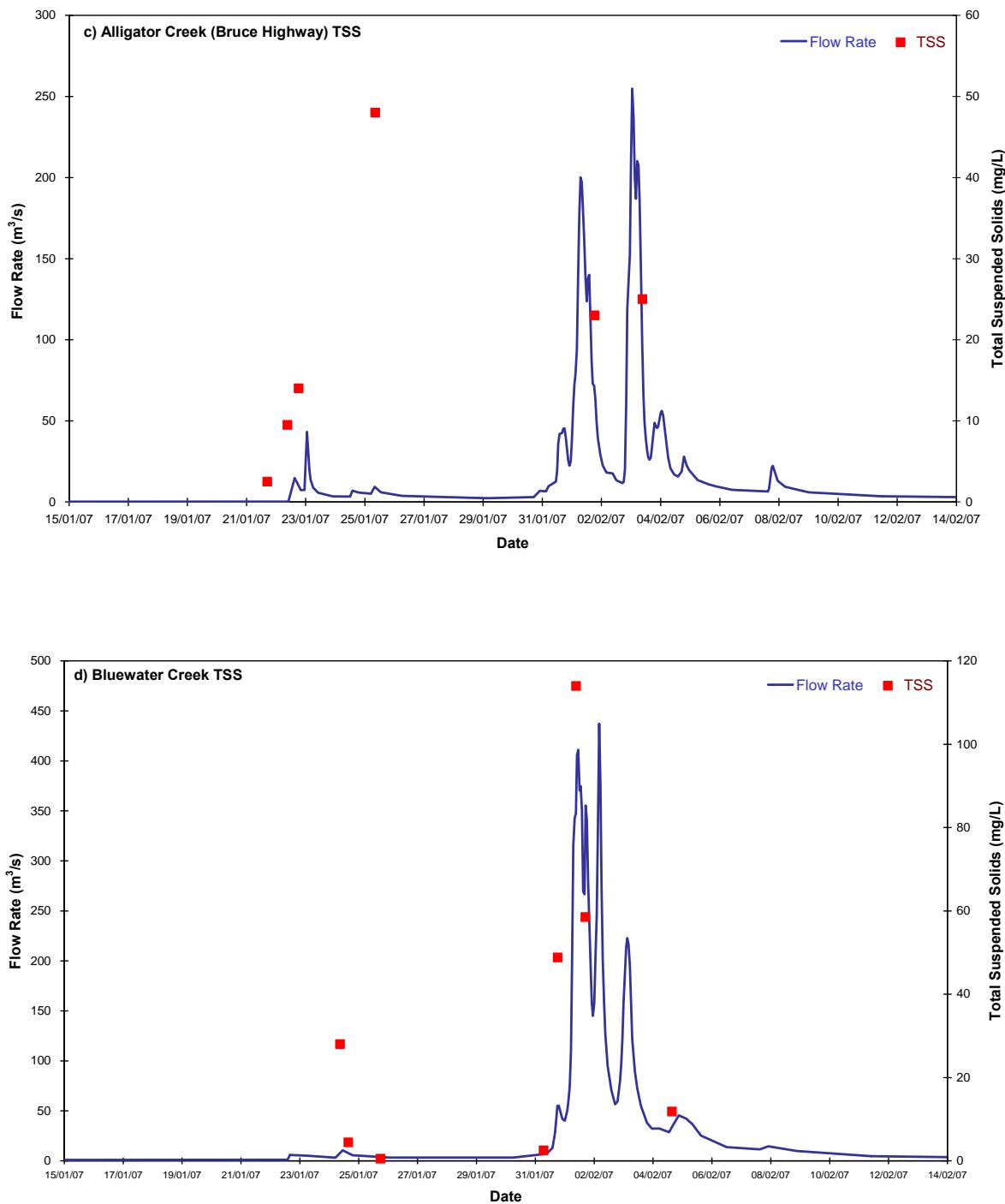


Figure 11 cont. Stream discharge and TSS concentrations (mg/L) for Alligator Creek (c) and Bluewater Creek (d) from the 15th January - 14th February 2007 (Source: NRW Watershed, 2007).

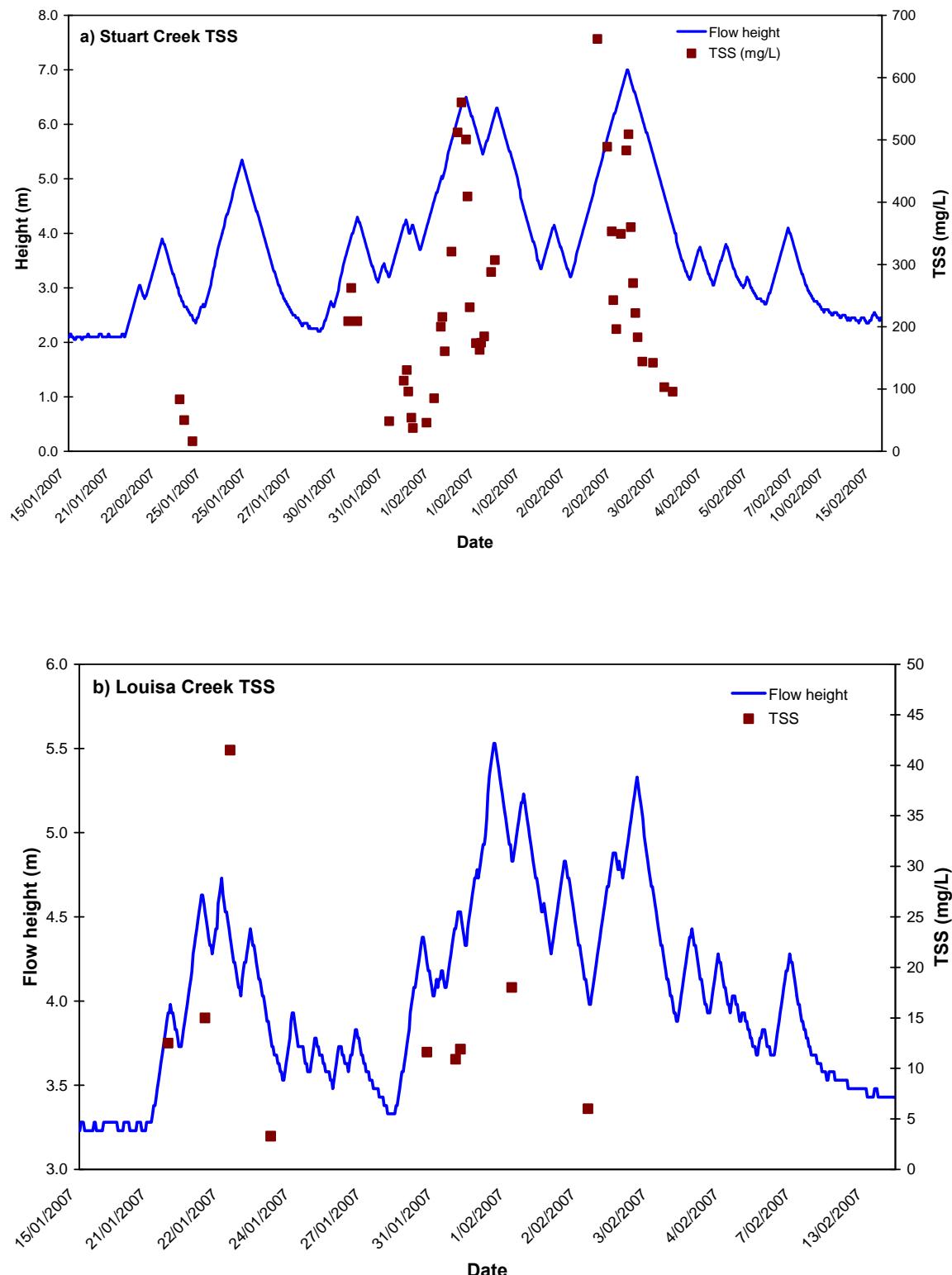


Figure 12. Creek heights and corresponding TSS concentrations (mg/L) for Stuart Creek (D/S) (a) and Louisa Creek (b) between 2nd January- 2nd February 2007. (Source: BoM, 2007).

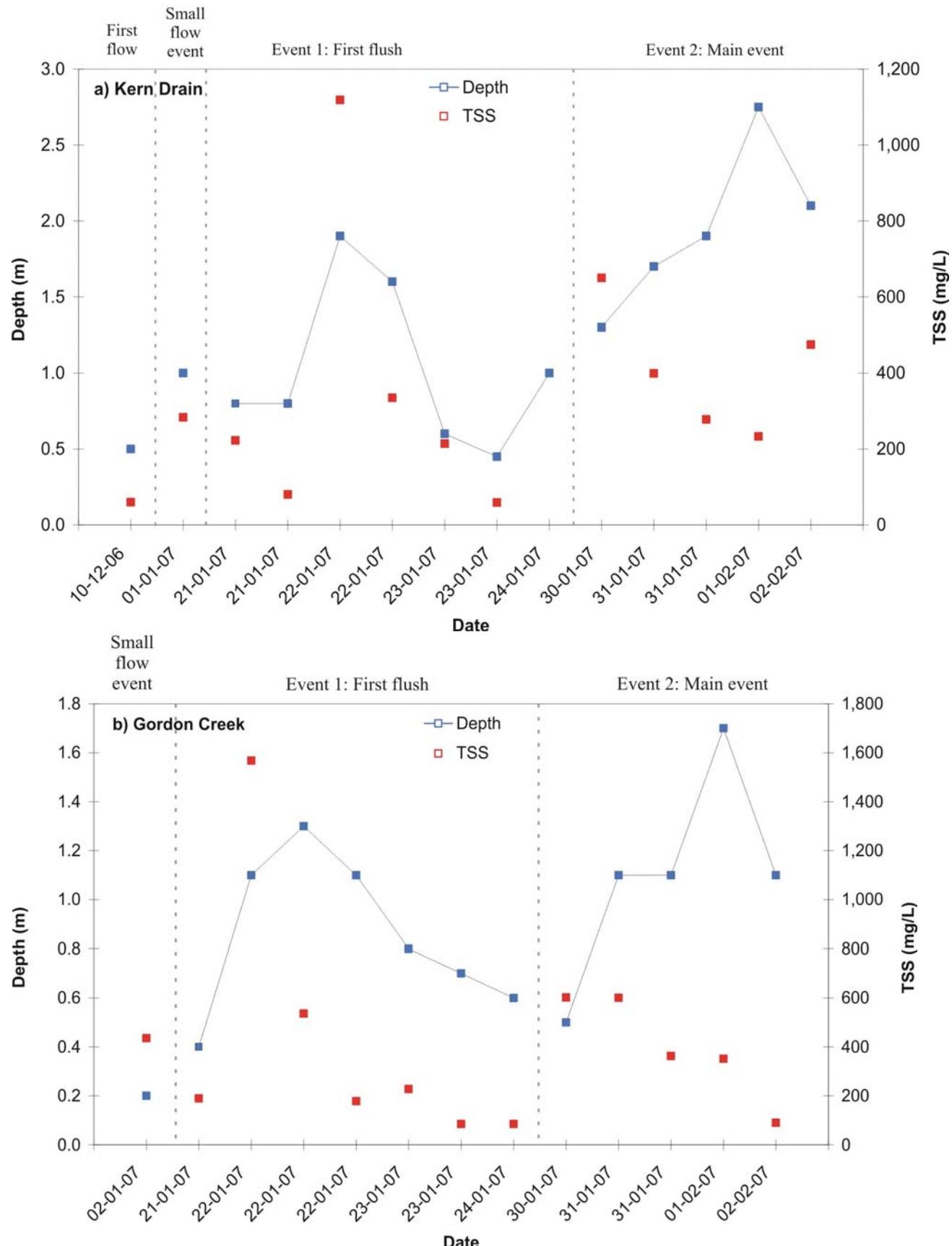


Figure 13. Depths and TSS concentrations (mg/L) for Kern Drain (a) and Gordon Creek (b) between 2nd January-2nd February 2007.

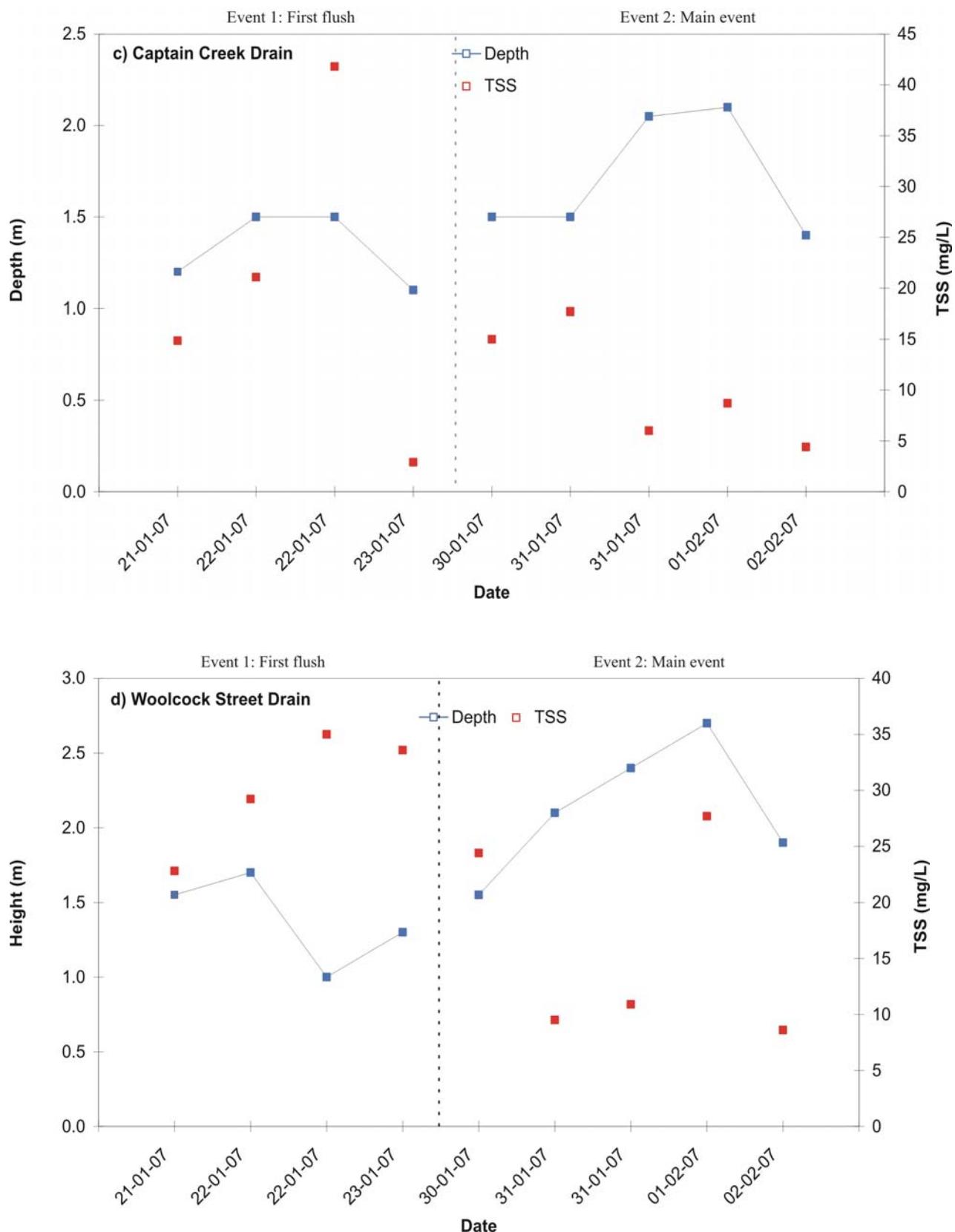


Figure 13 cont. Depths and TSS concentrations (mg/L) for Captain Creek Drain (c) and Woolcock Street Drain (d) between 21st January- 2nd February 2007.

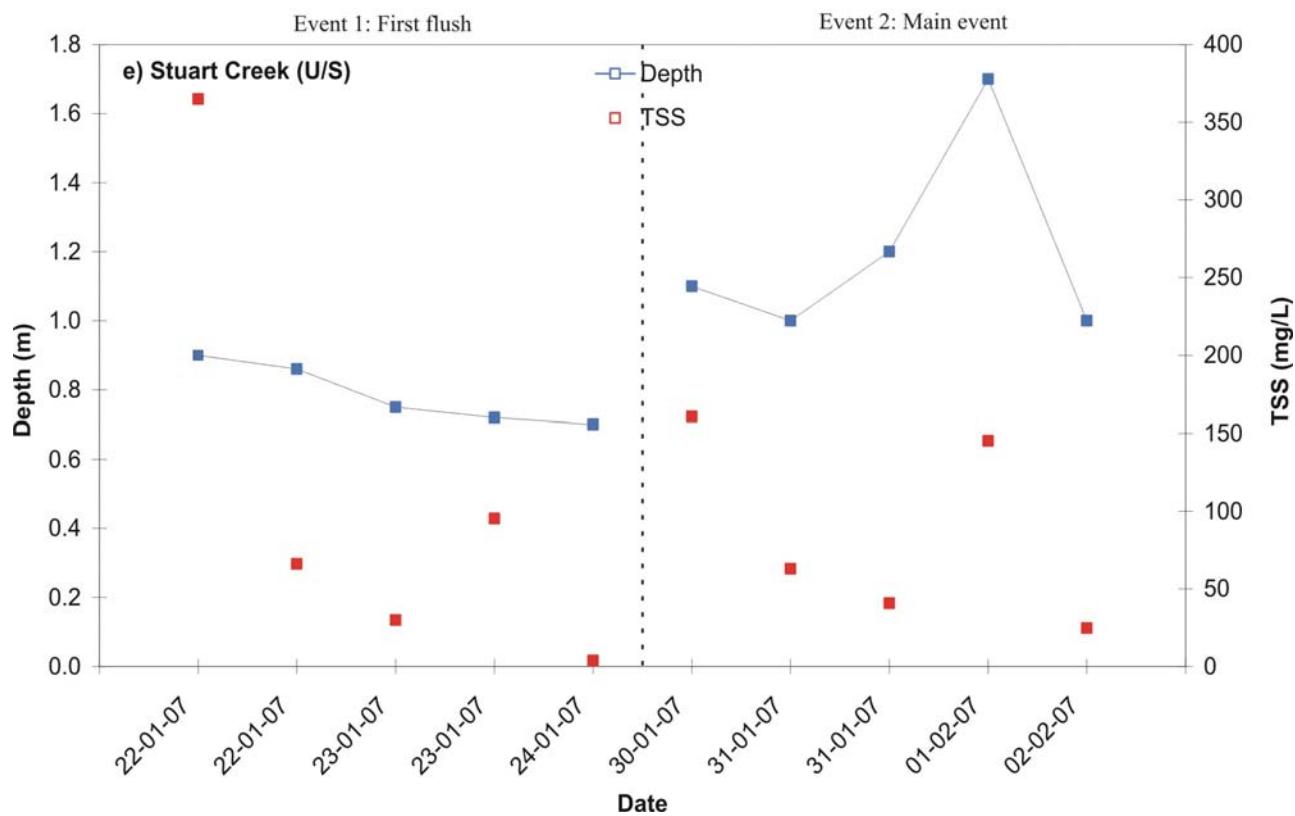


Figure 13 cont. Depths and TSS concentrations (mg/L) for Stuart Creek (U/S) (e) between 22nd January-2nd February 2007.

Sediment loads for the major waterways within the Townsville Thuringowa Region were highest in the Black River (33,000 tonnes) followed by Bohle River (22,000 tonnes), Bluewater Creek (2,700 tonnes) and Alligator Creek (600 tonnes) (Table 5). Unfortunately no flow data were available to calculate loads for the Ross River. The event mean concentrations (EMC) for these waterways ranged between 15 mg/L (Alligator Creek) to 240 mg/L (Black River). With the exception of the Black River, the comparisons of flow-adjusted annual loads with the latest SedNet model were poor (Table 5).

Table 5. Comparison of monitored (flow adjusted) and modelled loads of TSS for the major sub-catchments within the Townsville Thuringowa Region.

Catchment	Sediment load 2007 (tonnes)	Total flow volume (ML)	EMC (mg/L)	Flow adjusted to MLA model (tonnes)	Kinsey Henderson, in prep. (tonnes)
Alligator Creek	600	41,500	15	530	8,800
Black River	33,000	135,000	240	18,000	21,000
Bluewater Ck	2,700	63,500	40	1,500	12,800
Bohle River	22,000	147,000	150	31,000	63,900

5.1.3. Nutrients

Similarly to TSS, total nitrogen (TN) across the natural (median of 327 µg N/L) and rural residential (median of 452 µg N/L) land uses contained consistently lower concentrations than the other land use categories. The urban (median of 639 µg N/L) and urban and industrial (median of 624 µg N/L) land uses had higher TN concentrations compared to natural sites. There was considerable variability within the mixed (natural, grazing or minimal use) category. Three of the sites within the mixed land use contained similar TN concentrations to the natural and rural residential sites, while Black River (median of 793 µg N/L, #7) and Ross River (median of 809 µg N/L, #8) contained the highest median concentrations throughout the region (Fig 14). The Black and Ross River sites also had high PN (that coincided with higher TSS concentrations) than the other sites within the mixed land use (Fig 15). This trend between TSS and PN concentrations is also evident within the urban and industrial land use, with Stuart Creek (D/S #19) containing the highest median TSS and PN concentrations in this category. While the developing urban sites (Gordon Creek #15 and Kern Drain #16) had the highest median TSS concentrations within the urban land use (Fig 10) these sites had relatively low median PN concentrations which were similar to the other urban sites.

There was little variability in dissolved organic nitrogen (DON) concentrations across the natural (median of 191 µg N/L) and rural residential (median of 223 µg N/L) land uses (Fig 16). The other land use categories in comparison had higher variability between sites, with the urban (median of 388 µg N/L) and urban industrial (median of 350 µg N/L) sites displaying the highest concentrations in the region (Fig 16). Oxidised nitrogen (NO_x : nitrate + nitrite) concentrations were relatively consistent across most land use categories (Fig 17). Compared to the natural (median of 50 µg N/L) land use, slightly higher NO_x concentrations were obtained across all other land use categories (median range of 94 to 140 µg N/L). The proportion of $\text{NO}_x:\text{TN}$ was similar across the land use categories (15-20%) with the exception of the rural residential land use which had a higher proportion of NO_x (30%).

Ammonia (NH_3) concentrations were consistently low within the natural and rural residential land uses, with both categories containing medians of 2 µg N/L (Fig 18). Ammonia concentrations were variable between individual sites in the mixed and urban and industrial categories, however, the median for these two classes were also low (< 5 µg N/L). The urban land use contained higher ammonia concentrations than all other land use categories with a median of 36 µg N/L (Fig 18).

Total phosphorus (TP) concentrations were consistently low across the natural (median of 54 µg P/L) and rural residential (median of 41 µg P/L) land uses (Fig 19). Considerably higher TP concentrations were found within the urban (median of 258 µg P/L) and urban and industrial (median of 191 µg P/L) land uses while concentrations within the mixed (median range of 21 to 156 µg P/L) land use were variable. Variability was also found within the urban land use (median range of 67 to 340 µg P/L).

Median particulate phosphorus (PP) concentrations were slightly higher in the urban (median of 84 µg P/L), urban and industrial (median of 57 µg P/L) and mixed (median of 55 µg P/L) land uses compared to natural (median of 21 µg P/L) and rural residential (median of 18 µg P/L) categories (Fig 20). In general, the PP:TP proportion was considerably lower in the urban and urban industrial land uses (~30%) compared to the other categories (40 to 45 %).

Dissolved organic phosphorus (DOP) concentrations were consistently low throughout the Townsville Thuringowa Region. Median DOP concentrations in the urban (median of 11 µg

P/L) and urban and industrial (median of 15 µg P/L) land uses were slightly higher than the other land use categories (median range between 5 and 8 µg P/L) (Fig 21). Filterable reactive phosphorus (FRP) concentrations were considerably higher in the urban (median of 131 µg P/L) and urban and industrial (median of 99 µg P/L) categories compared to the other land uses (median range between 12 and 35 µg P/L) in the region (Fig 22). The proportion of FRP:TP was also higher in these two land use categories, where FRP comprised of 50% of the total phosphorus concentrations. In the other land use categories the FRP:TP proportion was between 34 and 43%.

All nutrient species were consistently higher at the downstream sites for Alligator and Hen Camp Creeks compared to their upstream counterparts (Figs 14-22). Nutrient species at Stuart Creek were highly variable, with lower DON and NO_x and higher PN, TP, PP and FRP concentrations at the downstream urban and industrial influenced site. Concentrations of DOP and TN were similar at both sites. Bluewater Creek had lower TN, PN, TP, PP concentrations at the downstream site, while concentrations of NO_x were higher downstream. Comparisons were not drawn between the Ross River stratified sites as limited sampling was conducted at the upstream sites.

For the nitrogen speciation, both DON and NO_x displayed higher concentrations on the rising and peak limbs of the hydrograph (appendix) at the main waterway sites. PN concentrations were generally low throughout the hydrographs but displayed some first flush characteristics. Overall DON and NO_x contributed the highest proportion of TN. Similarly to the N species, FRP and PP both had elevated concentrations during the first flush, while DOP concentrations were generally low and displayed no apparent response to changing hydrological conditions. An anomalously high PP concentration was obtained from the Black and Bohle River sites towards the end of the first flush event (Appendix E). The smaller catchment sites also displayed similar first flush characteristics to those of the major waterways (Appendix E).

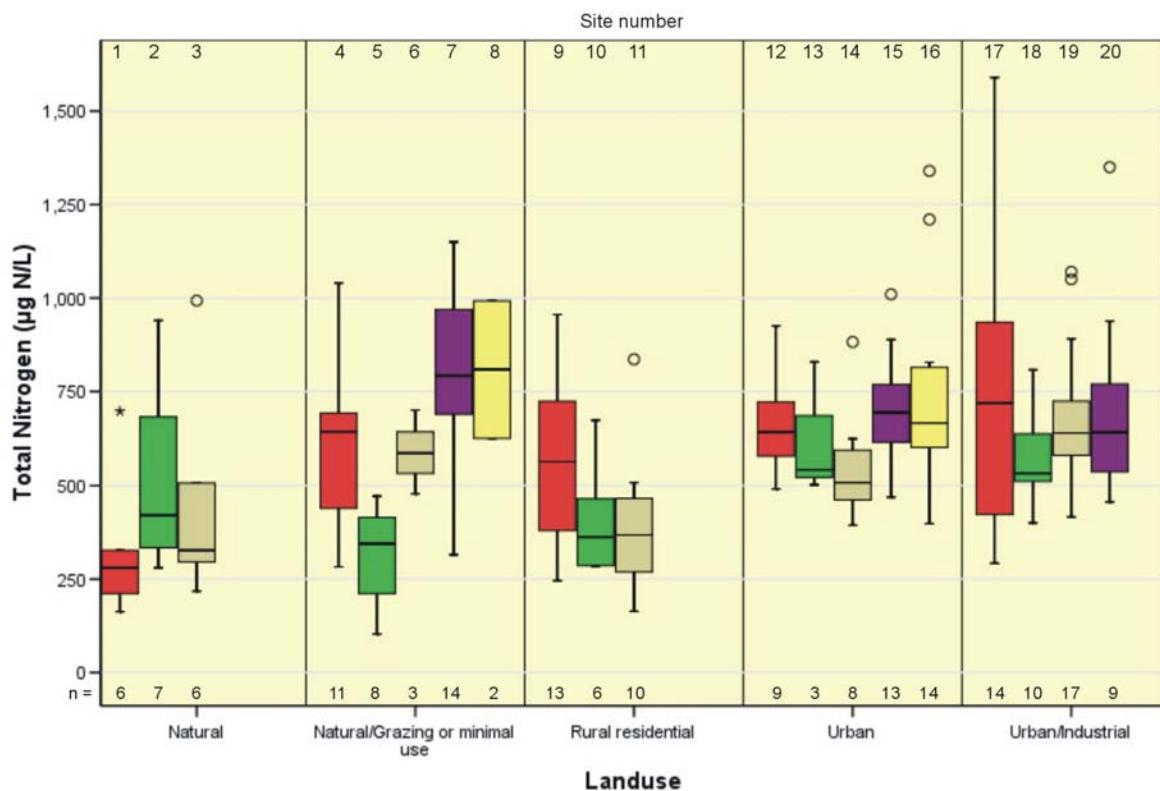


Figure 14. A boxplot summarising the total nitrogen ($\mu\text{g N/L}$) data collected in the monitored waterways between December 2006 and March 2007.

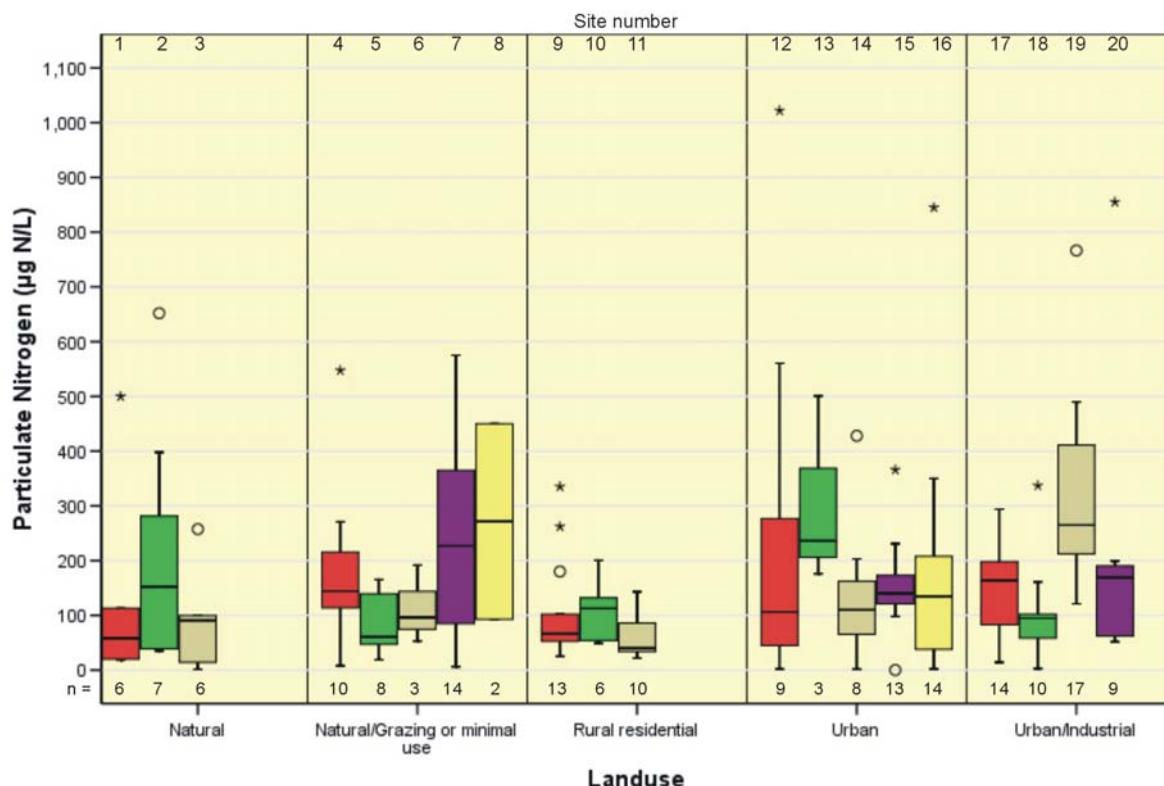


Figure 15. A boxplot summarising the particulate nitrogen ($\mu\text{g N/L}$) data collected in the monitored waterways between December 2006 and March 2007.

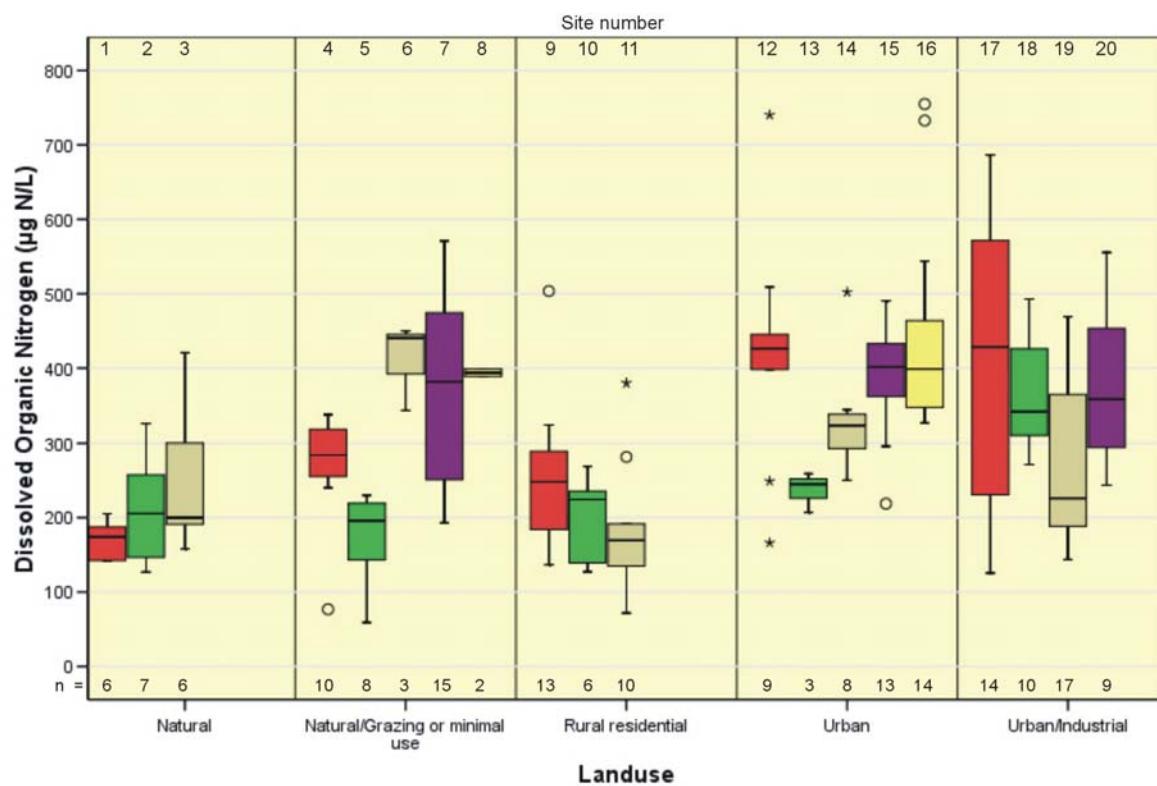


Figure 16. A boxplot summarising the dissolved organic nitrogen ($\mu\text{g N/L}$) data collected in the monitored waterways between December 2006 and March 2007.

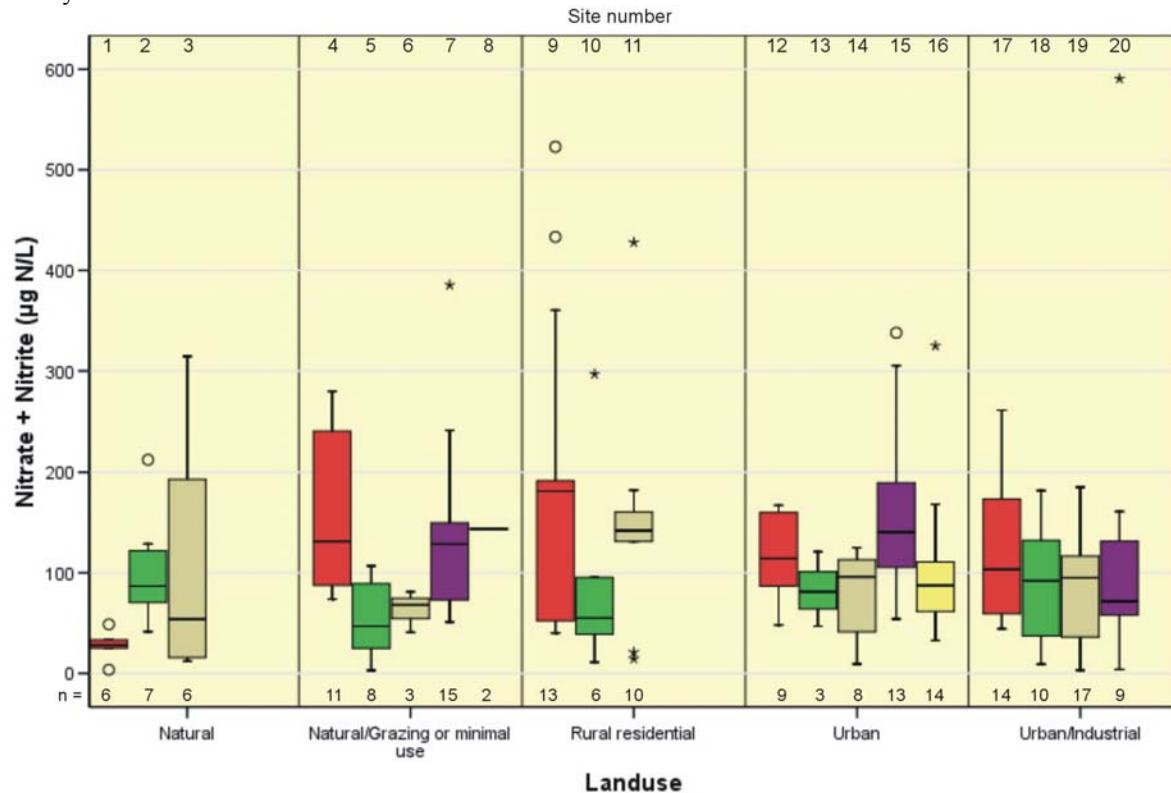


Figure 17. A boxplot summarising the nitrate + nitrite (NO_x) ($\mu\text{g N/L}$) data collected in the monitored waterways between December 2006 and March 2007.

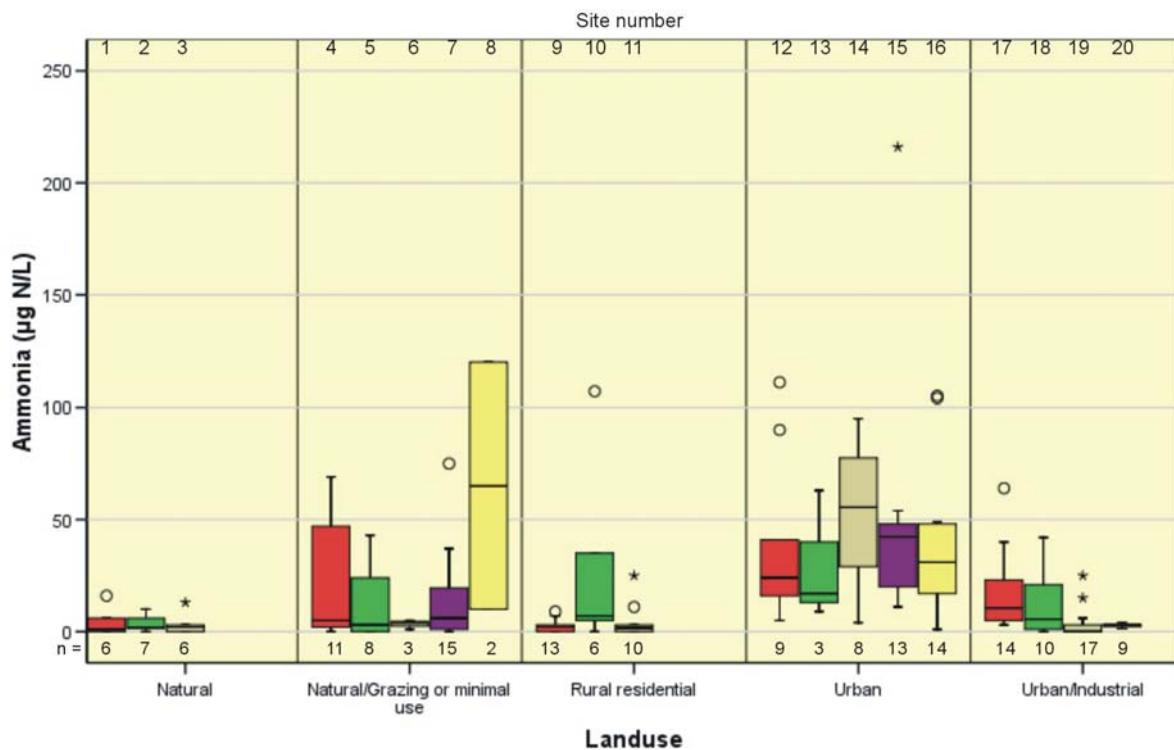


Figure 18. A boxplot summarising the ammonia ($\mu\text{g N/L}$) data collected in the monitored waterways between December 2006 and March 2007.

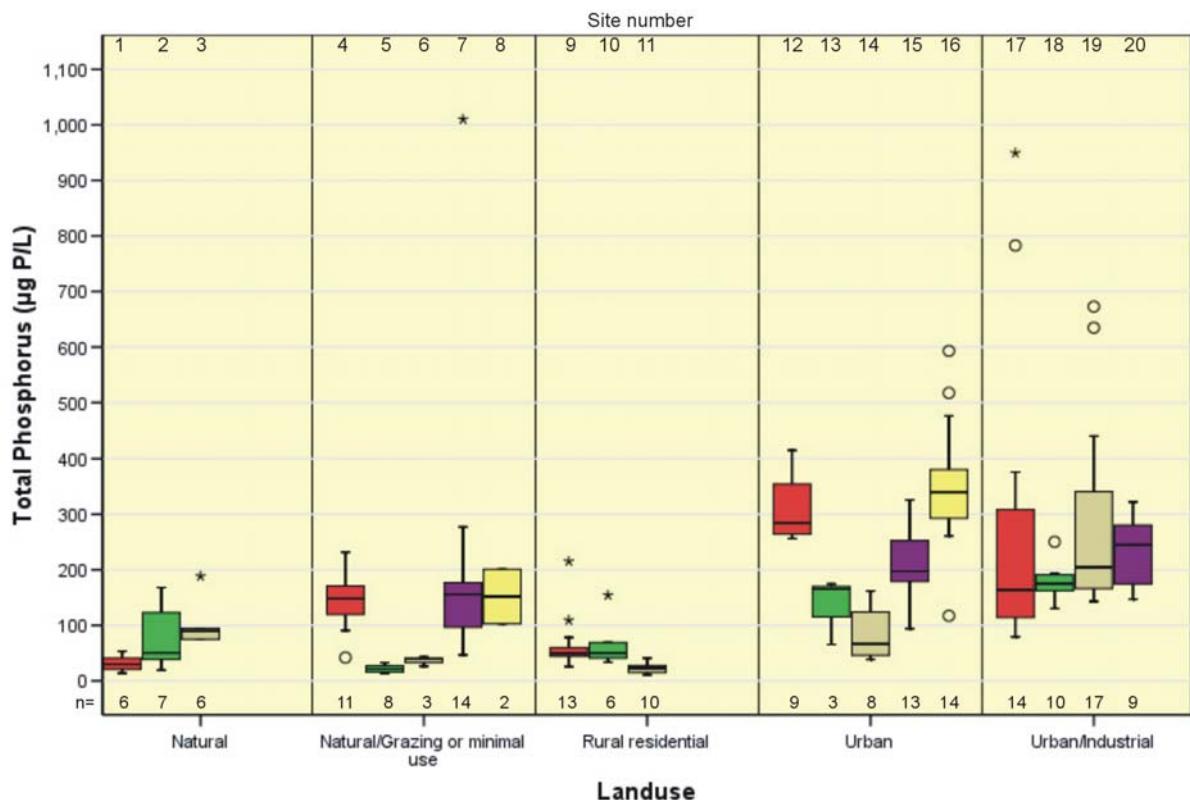


Figure 19. A boxplot summarising the total phosphorus ($\mu\text{g P/L}$) data collected in the monitored waterways between December 2006 and March 2007.

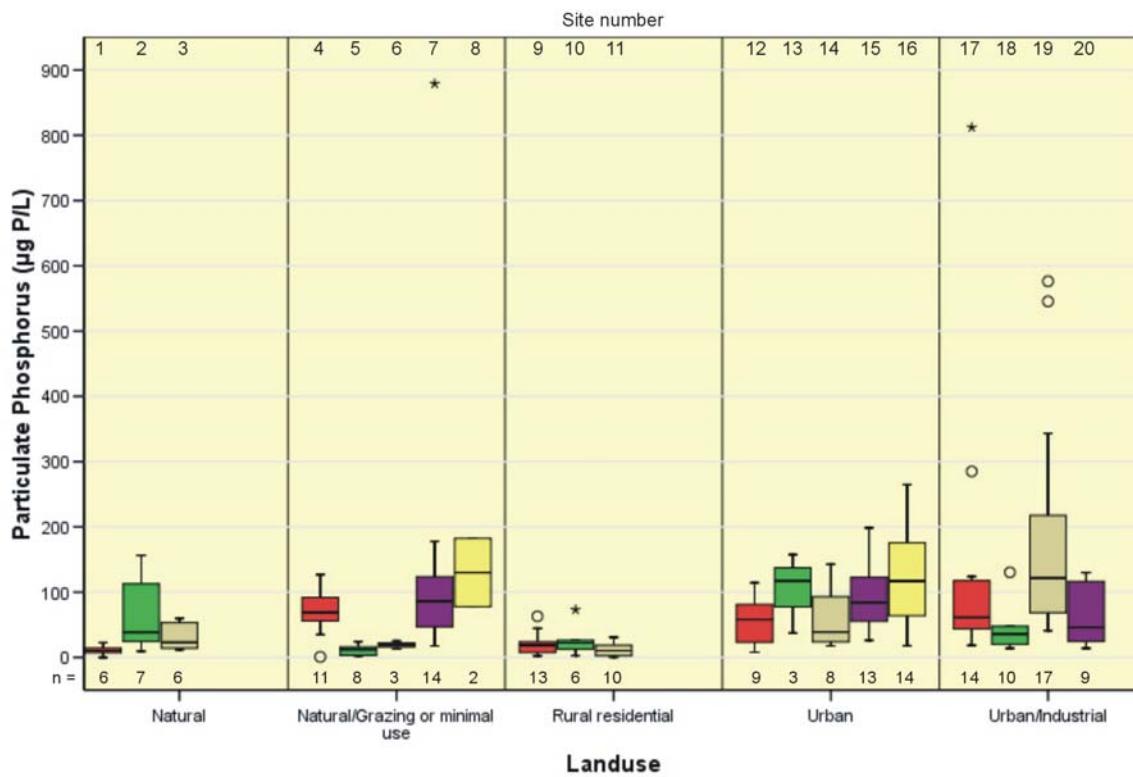


Figure 20. A boxplot summarising the particulate phosphorus ($\mu\text{g P/L}$) data collected in the monitored waterways between December 2006 and March 2007.

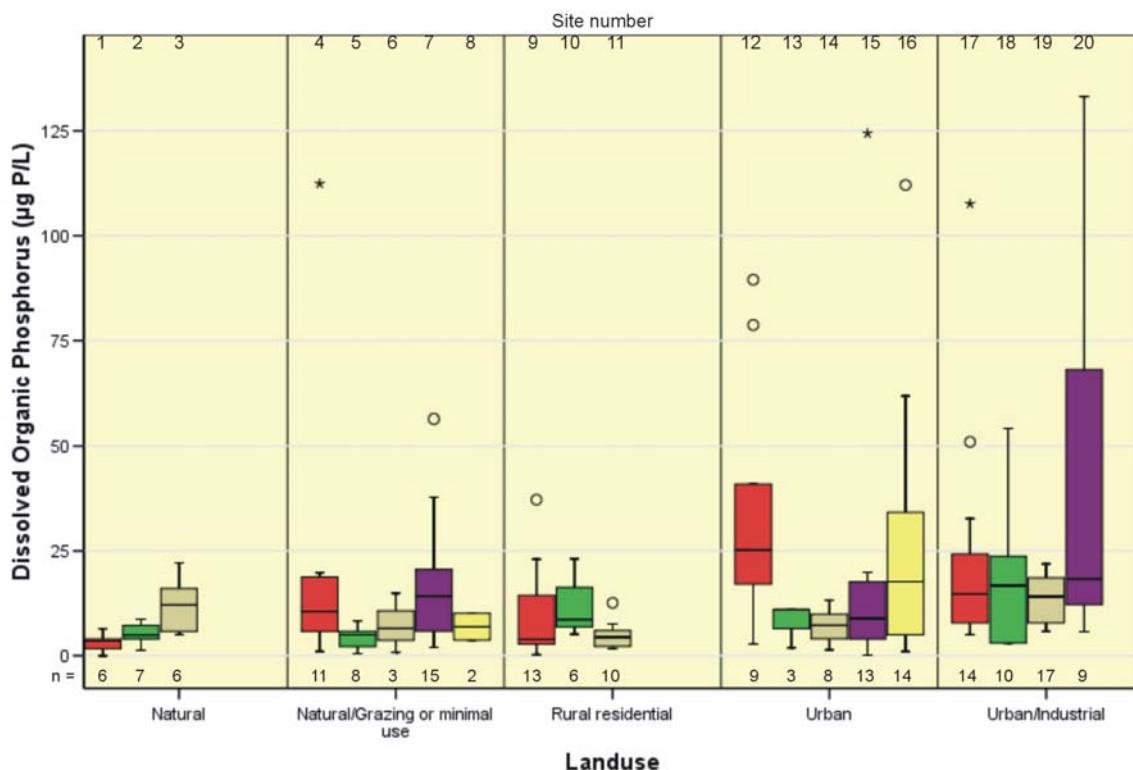


Figure 21. A boxplot summarising the dissolved organic phosphorus ($\mu\text{g P/L}$) data collected in the monitored waterways between December 2006 and March 2007.

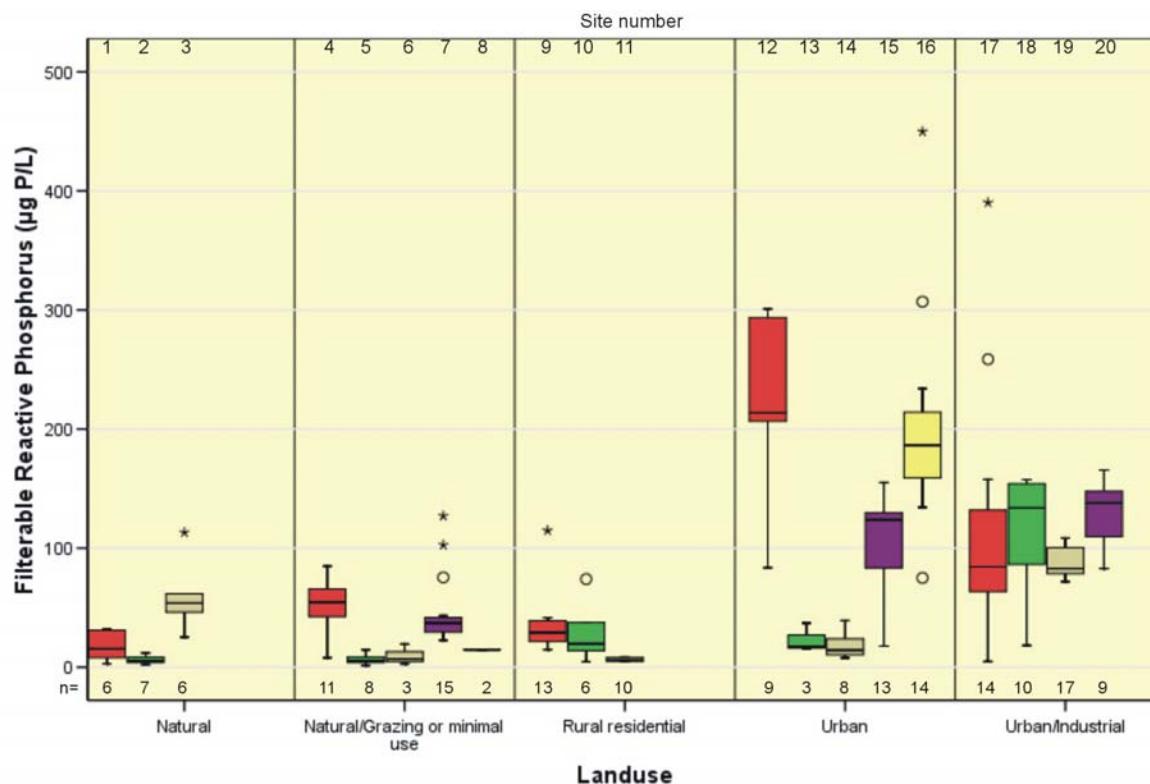


Figure 22. A boxplot summarising the filterable reactive phosphorus ($\mu\text{g P/L}$) data collected in the monitored waterways between December 2006 and March 2007.

The model PN and PP loads for the major waterways of the region were considerably overestimated (in most cases by over an order of magnitude) compared to the flow adjusted loads calculated for the 2007 water year (Table 6). Comparisons between the modelled (Kinsey-Henderson and Sherman 2007) and monitored loads for DON and DOP were reasonable with the exception of DON loads for the two larger catchments (Black and Bohle Rivers) which appear to have been underestimated. Modelled loads for NO_x and FRP were considerably higher than the flow adjusted loads calculated for the 2007 water year.

Table 6a. Comparison of monitored (flow adjusted) and modelled loads of PN for the major sub-catchments within the Townsville Thuringowa Region.

Catchment	PN load 2007 (kg)	Total flow volume (ML)	EMC ($\mu\text{g/L}$)	Flow adjusted to MLA model (kg)	Kinsey- Henderson and Sherman, 2007 (kg)
Alligator Creek	2,220	41,500	53	2,000	37,200
Black River	3,000	135,000	22	1,640	124,400
Bluewater Creek	2,570	63,500	40	1,500	77,800
Bohle River	19,700	147,000	134	27,400	288,300

Table 6b. Comparison of monitored (flow adjusted) and modelled loads of DON for the major sub-catchments within the Townsville Thuringowa Region.

Catchment	DON load 2007 (kg)	Total flow volume (ML)	EMC (ug/L)	Flow adjusted to MLA model (kg)	Kinsey- Henderson and Sherman, 2007 (kg)
Alligator Creek	4,850	41,500	117	4,300	5,400
Black River	40,900	135,000	303	22,300	14,500
Bluewater Creek	7,730	63,500	122	4,500	6,700
Bohle River	39,000	147,000	265	54,200	37,700

Table 6c. Comparison of monitored (flow adjusted) and modelled loads of NO_x for the major sub-catchments within the Townsville Thuringowa Region.

Catchment	NO _x load 2007 (kg)	Total flow volume (ML)	EMC (ug/L)	Flow adjusted to MLA model (kg)	Kinsey- Henderson and Sherman, 2007 (kg)
Alligator Creek	2,150	41,500	52	1,900	4,100
Black River	13,900	135,000	103	7,600	1,070,700
Bluewater Creek	7,000	63,500	110	4,050	5,200
Bohle River	10,700	147,000	73	14,900	149,700

Table 6d. Comparison of monitored (flow adjusted) and modelled loads of PP for the major sub-catchments within the Townsville Thuringowa Region.

Catchment	PP load 2007 (kg)	Total flow volume (ML)	EMC (ug/L)	Flow adjusted to MLA model (kg)	Kinsey- Henderson and Sherman, 2007 (kg)
Alligator Creek	410	41,500	10	360	10,600
Black River	9,200	135,000	68	5,000	19,900
Bluewater Creek	800	63,500	13	460	16,900
Bohle River	12,600	147,000	86	17,500	46,200

Table 6e. Comparison of monitored (flow adjusted) and modelled loads of DOP for the major sub-catchments within the Townsville Thuringowa Region.

Catchment	DOP load 2007 (kg)	Total flow volume (ML)	EMC (ug/L)	Flow adjusted to MLA model (kg)	Kinsey- Henderson and Sherman, 2007 (kg)
Alligator Creek	360	41,500	9	320	300
Black River	1,800	135,000	13	980	700
Bluewater Creek	140	63,500	2	81	300
Bohle River	2,100	147,000	14	2,920	1,800

Table 6f. Comparison of monitored (flow adjusted) and modelled loads of FRP for the major sub-catchments within the Townsville Thuringowa Region.

Catchment	FRP load 2007 (kg)	Total flow volume (ML)	EMC (ug/L)	Flow adjusted to MLA model (kg)	Kinsey- Henderson and Sherman, 2007 (kg)
Alligator Creek	770	41,500	19	680	1,300
Black River	4,200	135,000	31	2,300	2,900
Bluewater Creek	300	63,500	5	170	900
Bohle River	8,300	147,000	56	11,500	34,900

5.1.4. Pesticides

Seven pesticide residues were detected in the Townsville Thuringowa Region including diuron (8 of the 20 sampling sites), atrazine (3 sites), simazine (4 sites), bromacil (4 sites), hexazinone (2 sites), malathion (1 site) and endosulfan (2 sites). These pesticides were mainly associated with urban and urban and industrial land uses. No pesticide residues were detected within the natural land use sites. The pesticides analysed in this study are listed in Appendix C. The detection limits for all pesticides analysed are also included in this appendix.

The majority of pesticides detected were herbicides: diuron, atrazine, simazine, bromacil and hexazinone. Diuron residues (ranged from 0.01 to 0.30 µg/L) were detected in 40 of 54 samples collected from the 8 sites which included the urban, urban and industrial and mixed lands uses. The highest diuron concentration (0.30 µg/L) was from the Woolcock Street Drain (#12). This was the only sample to exceed the ANZECC and ARMCANZ (2000) low reliability guideline (Fig 23). Diuron and hexazinone were also detected (0.1 µg/L and 0.01 µg/L, respectively) in an opportunistic sample collected at Ross Creek on the 1st February (Appendix B). The other herbicides were all well below ANZECC and ARMCANZ (2000) ecological guidelines. Atrazine residues (ranged from 0.01 to 0.02 µg/L) were only detected in four samples from rural residential, urban and urban and industrial land uses (Fig 24). Residues of the breakdown products of atrazine (desethyl and desisopropyl atrazine) were not detected at any of the sites. Simazine residues (ranged from 0.01 to 0.04 µg/L) were detected in twelve samples only in the urban and urban and industrial land uses (Fig 25). Simazine was commonly detected in Kern Drain (#16) in 6 of the 10 samples taken at this site. Bromacil residues (ranged from 0.01 to 2.10 µg/L) were detected in 10 samples from the urban (Woolcock Street Drain), urban and industrial (Stuart Creek D/S #19) and mixed (Hen Camp Creek D/S #6) land uses (Fig 26). Hexazinone residues (ranged from 0.01 to 0.02 µg/L) were only detected within the urban land use (Appendix B).

The two insecticides detected in the Townsville Thuringowa Region were malathion (1 of 20 sites) and endosulfan (2 sites). Malathion residues were only detected once throughout the entire sampling period at Louisa Creek during the first event on the 23rd January. However, this sample (2.9 µg/L) exceeded the 95% ANZECC and ARMCANZ (2000) ecological protection guideline for freshwater (0.05 µg/L). Endosulfan residues were detected in Alligator Creek (D/S) at a concentration of 0.59 µg/L (α -endosulfan - 0.36 µg/L, β -endosulfan - 0.23 µg/L), which coincided with the first flush event. Endosulfan was also detected at Captains Creek Drain on the rising stage of the major event (0.09 µg/L: β -endosulfan only). These

concentrations exceeded the 99% ANZECC and ARMCANZ (2000) ecological protection guideline for freshwater ($0.03 \mu\text{g/L}$; 95% guideline: $0.2 \mu\text{g/L}$) (Appendix B).

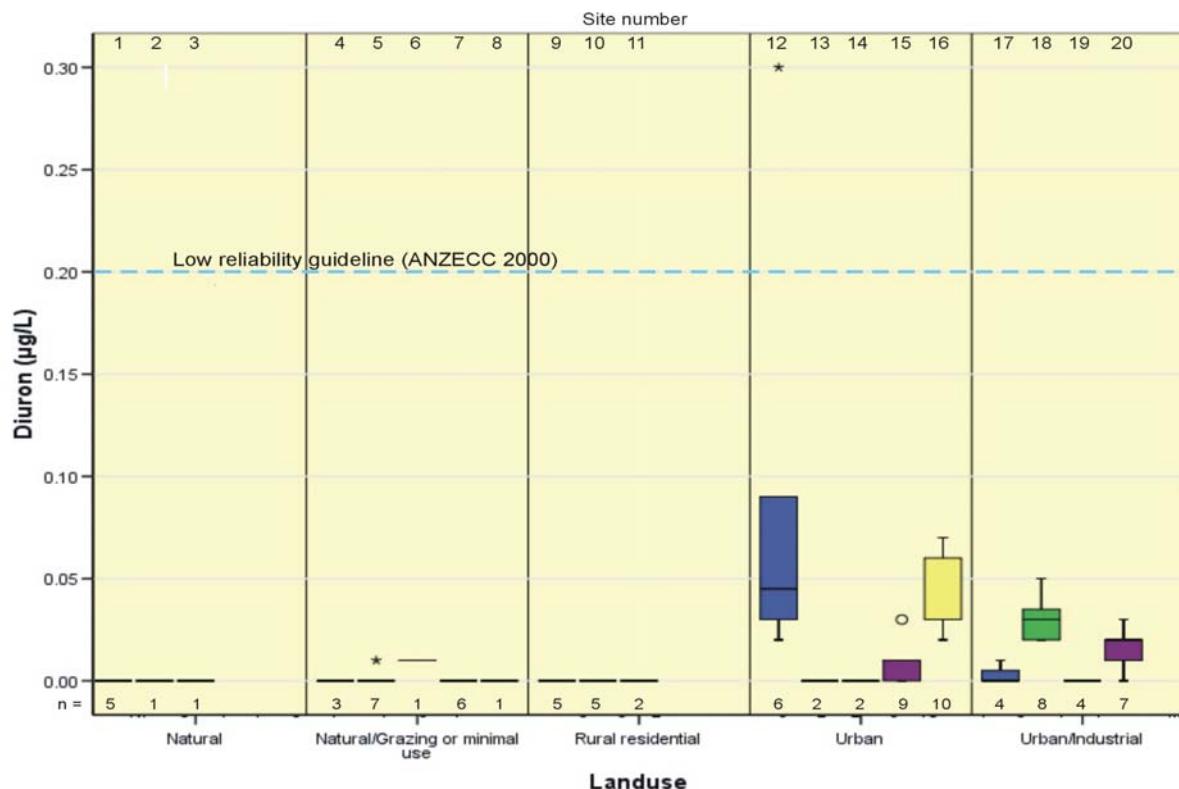


Figure 23. A boxplot summarising the diuron ($\mu\text{g/L}$) data collected in the monitored waterways between December 2006 and March 2007.

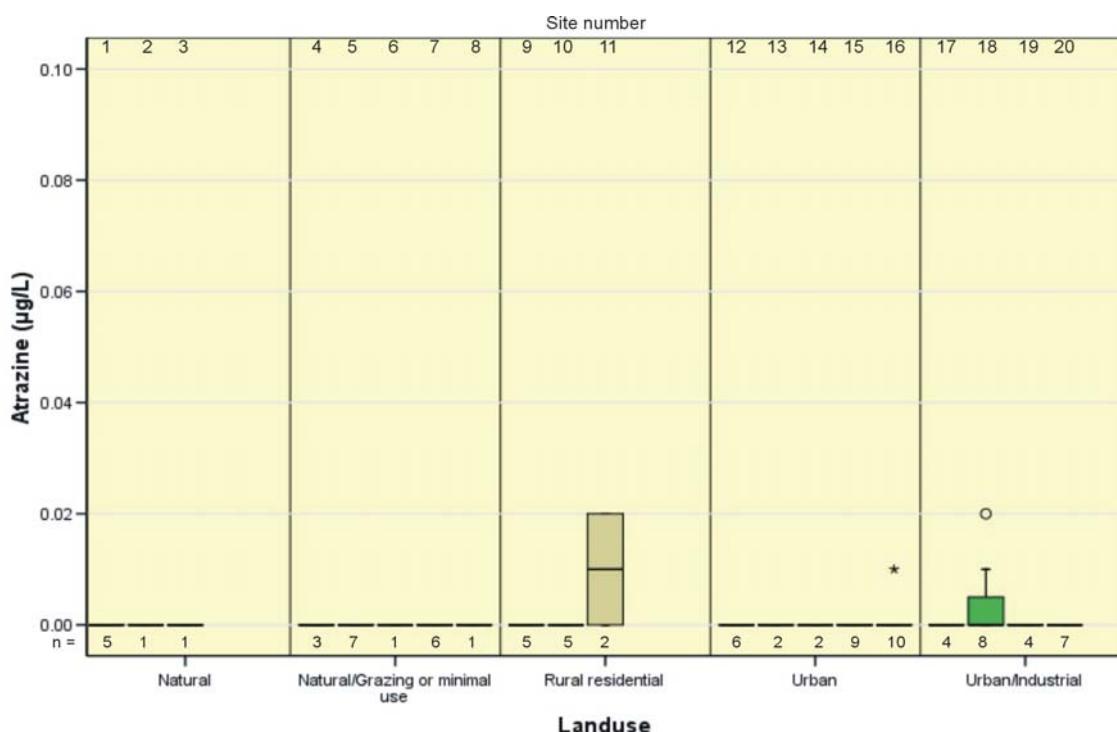


Figure 24. A boxplot summarising the atrazine ($\mu\text{g/L}$) data collected in the monitored waterways between December 2006 and March 2007.

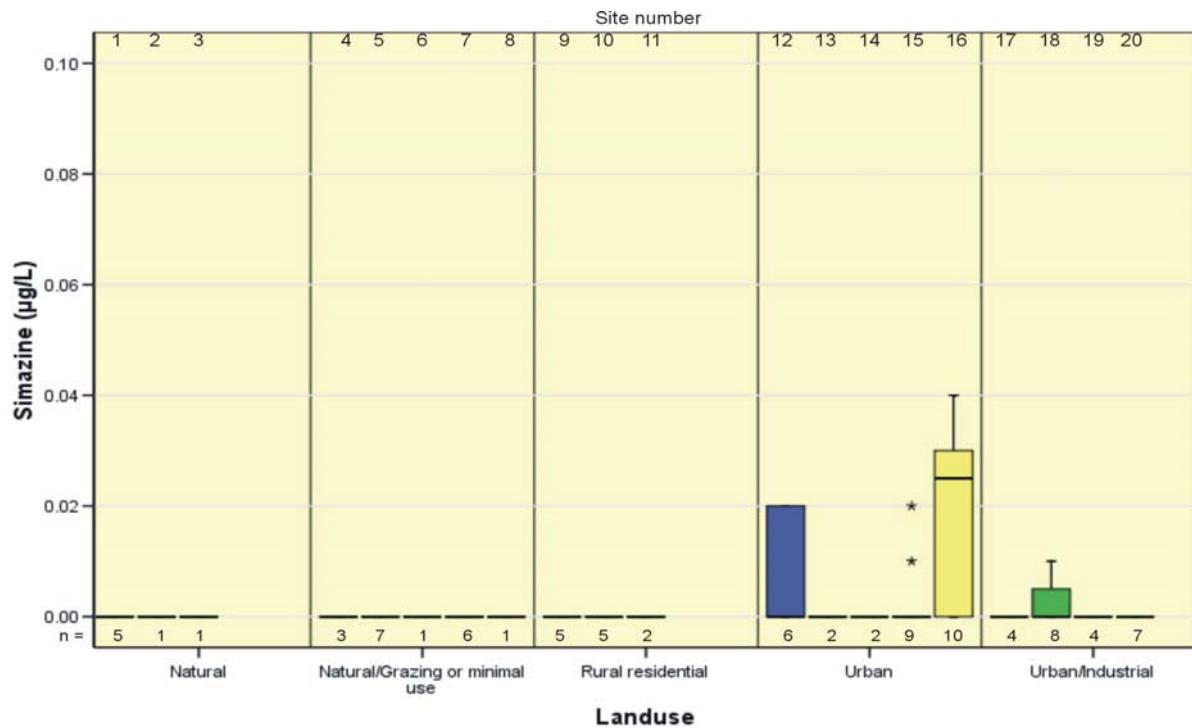


Figure 25. A boxplot summarising the simazine ($\mu\text{g/L}$) data collected in the monitored waterways between December 2006 and March 2007.

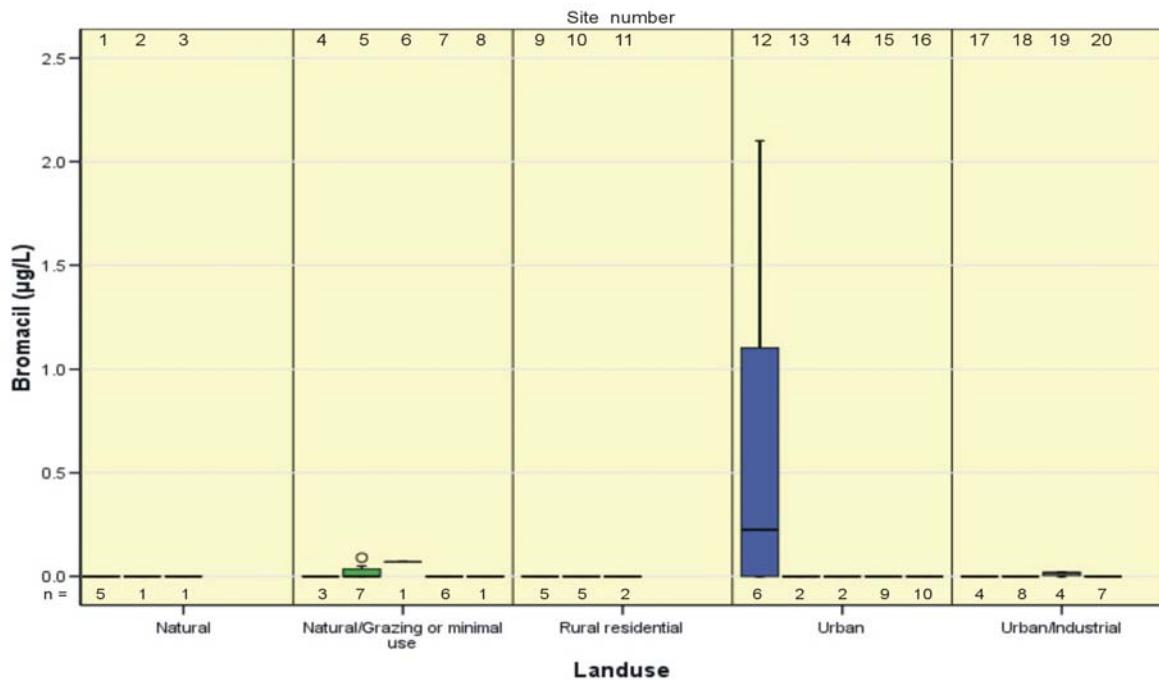


Figure 26. A boxplot summarising the bromacil ($\mu\text{g/L}$) data collected in the monitored waterways between December 2006 and March 2007.

5.1.5. Trace metals

Metals concentration data are normally interpreted with reference to the default trigger values (TVs) provided in ANZECC & ARMCANZ (2000) Australian Water Quality Guidelines (AWQG). It must be stressed, however, that there are currently no authoritative Australian guidelines or water quality criteria that can be used to directly assess the ecological significance of the brief transient fluctuations in water quality that occur in connection with storm events. The AWQG TVs explicitly relate only to long term ambient conditions and are designed to protect against adverse chronic effects (i.e. those that develop gradually over time due to constant or repeated exposure to contaminants). They provide an estimate of the highest “average” concentration that can safely be tolerated by the ecosystem over a prolonged exposure period. In order to assess compliance with the existing TVs it is necessary to determine long term average (or more commonly median) contaminant concentrations by monitoring sites at regular intervals (at least monthly) for a protracted period (usually at least 2 years). The guidelines are breached if the median concentration exceeds the TV – i.e. if concentrations greater than or equal to the TV are maintained for more than 50% of the monitoring period.

There are undoubtedly times and places where some toxicants reach concentrations that are high enough to cause immediate (i.e. acute) harm, however, the relationships between exposure time and toxicant concentration have proven to be so complex that authorities in most countries, including Australia, have been unable to propose scientifically defensible criteria for short duration water quality disturbances of this kind. The USEPA have developed some criteria relating to 24 hour and three day exposure periods (<http://www.epa.gov/waterscience/criteria/wqcriteria.html#cc>), but the authors of the existing version of the AWQG reviewed the available data and determined that these guidelines could not validly be applied in Australia.

The uncertainties involved have recently been illustrated by Raimondo *et al.* (2007) who analysed the acute to chronic ratios (ACR) of 456 species that had been subjected to both acute and chronic toxicological tests (i.e. they divided the acute). They found that ACR values ranged from a minimum of 1.1 (indicating that there was at least one combination of species and toxicant where acute effects were observed at virtually the same concentration as chronic effects) to a maximum of 18,500 (indicative of a case where there was very low risk of acute effects). The median ACR was 8.3, and the 10th and 90th percentile values were 2.5 and 79.5, respectively.

The world literature contains at least some acute toxicity data for most commonly occurring toxicants and these provide some semi-quantitative indications of the kinds of combinations of exposure time and concentration that have proven harmful to at least some species somewhere in the world, albeit usually only under artificial laboratory conditions. However, for most contaminants the data is surprisingly scant, includes few if any local species, covers a very limited range of exposure times, and provides only vague indications of the effects of real-world variations in environmental conditions (which can enormously alter the toxicity of contaminants such as metals).

Accordingly the task of interpreting storm event monitoring data is an intellectually challenging and somewhat speculative undertaking. In order to overcome existing uncertainties the AWQG recommend the use of additional monitoring and assessment methods such as biological monitoring and/or direct toxicity assessment (DTA). These methods are expensive, require specialised expertise and equipment, and can be logistically difficult (if not impossible) to implement, especially when dealing with brief unpredictable episodic events and/or heterogenous ecosystems. Hence their use would usually only be considered if there was some

compelling evidence to suggest that the ecosystem is at real risk, and despite its shortcomings, water quality monitoring is still a vital tool for collecting such evidence.

One of the complications that need to be overcome when interpreting monitoring data is that concentrations of naturally-occurring contaminants often fluctuate wildly during flow events (in some cases by several orders of magnitude) and acutely harmful conditions can sometimes develop naturally even in pristine waters. In fact in the marine environment, water itself is a very significant contaminant; pure rainwater having such low ionic strength and pH that it can be acutely lethal to many obligate marine organisms. Consequently, when dealing with natural contaminants it is necessary not only to determine if existing concentrations present a potential risk to the ecosystem, but also to assess the probability that the observed effects can be attributed to unnatural causes. In this respect xenobiotics (i.e. man-made substances such as pesticides) are easier to deal with because their presence is unequivocally symptomatic of anthropogenic influences.

It must also be stressed that the TVs for toxicants relate to the bioavailable forms of the contaminants in question. Most toxicants occur in many different chemical forms (termed species), each with its own unique, and often highly distinctive chemical, physical and toxicological properties. The task of accurately determining bioavailability and toxicity can be complex and expensive. In order to avoid prohibitive costs, compliance tests are normally premised on the understanding that, if the total concentration of a potential toxicant is acceptably low then so too is the concentration of the toxic species. Hence under the AWQG protocols, assessments are carried out in a step-wise fashion starting with the most simple and inexpensive analysis possible and proceeding on to progressively more sophisticated analytical techniques only when necessary.

For example the AWQGs consider most metals and metalloids to be toxic only when they are present in freely dissolved ionic forms capable of binding to and/or passing through biological membranes. If preliminary analyses show that the total concentrations of the metal contained in an unfiltered sample are below the TV, it is valid to assume that the freely dissolved portion of the metal is at safe concentrations and there is no compulsion to examine samples more closely. However, much of the metal contained in turbid natural waters is tenaciously attached to suspended sediment particles, and is not available for immediate uptake by biota. Consequently, if total metal concentrations exceed the TV, samples are filtered to remove a large proportion of these putatively innocuous particulate metals. The filtrate is then analysed to determine “filterable” metal concentrations and if these comply with the TVs no further analysis is necessary. Under existing international conventions (e.g. APHA, USEPA) filterable metals are determined using filters with a pore size of 0.45 µm. Although the values obtained are often referred to as “dissolved” metals it is widely accepted that filtrates can still contain significant quantities of extremely fine colloidal particles that are not truly dissolved. Accordingly even if filterable metal concentrations are above the TV it may still be necessary to conduct more detailed analyses to determine how much of the filterable metal is actually in a dissolved form.

Dissolved metals can react with naturally occurring substances, such as bicarbonate, sulphate, fluoride, and humic acids to form a variety of soluble complexes, many of which are not readily bioavailable. Other parameters such as pH and calcium ions can substantially modify the toxicity of the bioavailable forms of a metal by altering the uptake capacity of biota (rather than by altering the metal itself). The nature and significance of effects such as these vary greatly between metals and metal species. For example metals such as chromium, arsenic, selenium, iron and manganese exist in more than one potentially abundant valency state, each of which has

entirely different properties. Hexavalent chromium for example is much more toxic than the trivalent form, while trivalent arsenic is substantially more toxic than pentavalent arsenic.

Although they include algorithms designed to account for the effects of water hardness (on some metals), the AWQGs provide very little quantitative information about the abovementioned effects. In practice even the hardness algorithms must be applied very cautiously as they actually encompass the joint effects of pH, alkalinity and hardness, and can only validly be used in situations where calcium bicarbonate is the principle source of water hardness and the main determinant of pH. These conditions are sometimes fulfilled in local waters but there are many situations where they are not. For example highly productive waters can develop very high pH concentrations even though they have low alkalinity, and waters subject to acid sulphate runoff can contain high concentrations of hardness but no measurable alkalinity.

The speciation of dissolved metals can be determined by employing a variety of chemical analysis and/or modelling techniques, and if necessary, bioavailability can be ascertained by conducting bioassays and/or toxicological tests. However, this would be a significant undertaking even if it was only necessary for a small number of samples, and in practice the quality of local waters fluctuates so significantly over time and space, that it would be necessary to analyse very large numbers of samples in order to accurately assess changes in metal availability. This means that monitoring costs can easily escalate to the point where water quality monitoring becomes a more expensive option than other, more constructive courses of action, such as remediation works. Accordingly, at any stage in the step-wise assessment process, decision makers can elect to accept that a potential compliance breach has occurred and instigate precautionary management action rather than carrying out more detailed investigations.

Although they are not directly applicable to stormwaters, the TVs given in the AWQG provide a useful basis for comparing the relative toxicities of different metals and assessing the relative risks associated with different metal concentrations. In this study this has been done (where possible) by dividing each metal concentration result by its respective TV to yield an index score that is notionally indicative of relative risk. Consistent with Queensland recommendations for dealing with slightly modified waters (Queensland Water Quality Guidelines 2006), the 95% protection TVs have been used for the assessment of freshwater sites. In acknowledgement of the higher conservation values of GBR waters the more stringent 99% protection TV would have been used for marine sites, but in practice the results reported for marine sites in this study were generally too low to quantify, making it impossible to perform the required calculations.

In this approach all metal results that exceed the TV yield a score greater than one, and the higher the score the greater the potential risk of ecological damage. The advantage of the index is that the scores are normalised and can be used to make direct comparisons between metals even if they have very different natural concentration ranges and/or toxicities. Scores can also be summed to provide a coarse but meaningful measure of the potential for cumulative effects. It must be stressed, however, that index scores can only be validly compared if they are derived from samples representative of similar exposure times – for example an index score that would not be considered problematic if it was sustained for only a few hours during an event, might be cause for concern if it persisted for weeks.

The dissolved metal concentration results obtained from the freshwater sampling component of this study are tabulated in Appendix F. Several metals were below the detection limit and for these it was not possible to calculate an exact index score, although it is obvious that the values were comparatively low.

The index scores obtained at freshwater sites during this study are tabulated below (Table 7). In the interests of readability non-detects and index scores below 0.6 (which are indicative of low risk situations) have been substituted with a “<” symbol. The results in this table are arranged by site and land use type. It can be seen that sites with natural and/or low usage catchments (i.e. reference sites) report some significant scores for copper and aluminium, indicating that natural background concentrations of these metals may become ecologically significant during rain events.

Table 7. Index scores based on dissolved metal concentrations and the AWQG TV's indicating relative risk at each site.

Land use	Site	Date	Silver	Aluminium	Arsenic	Copper	Manganese	Nickel	Lead	Selenium	Zinc
Natural	Campus Ck (upstream)	22-01-07 01-02-07	< <	1.5 1.0	< <	0.9 1.1	< <	< <	< <	< <	< <
Low Usage	Stuart Ck (upstream)	22-01-07 30-01-07 01-02-07	< < <	< < <	< < <	2.0 1.8 1.5	< < <	< < <	< < <	< < <	< < <
	Black R	23-01-07 01-02-07	< <	< 0.8	< <	2.1 1.3	< <	< <	< <	< <	< <
Urban	Woolcock St Drain	22-01-07 30-01-07 01-02-07	< < <	< < <	< < <	1.9 2.8 2.2	< < <	< < <	< < <	< 1.3 1.8	2.0
	Black Weir	01-02-07	<	0.7	< <	1.8 1.1	< <	< <	< <	< <	< <
	Aplins Weir	01-02-07	<	<	< <	1.1	< <	< <	< <	< <	< <
	Gordon Ck	02-01-07 21-01-07 22-01-07 31-01-07 01-02-07	< < < < <	< 20.0 < < <	< 0.6	1.1 16.4	< <	< 1.3	< <	3.0	< 53.1
	Kern Drain	21-01-07 22-01-07 23-01-07 30-01-07 01-02-07	< < < < <	< 4.2 < < 0.7	< 0.6	2.9 2.0 5.0 3.0 1.7	< < < < <	< < < < <	< < < < <	< < < < <	< < < < <
	Bohle R	22-01-07 30-01-07 01-02-07 02-02-07	< < < 1.1	< 1.4	< 1.4	0.8 1.7 1.4 1.0	< 1.7 1.4 <	< 1.4 1.4 <	< 1.4 1.4 <	< 1.4 1.4 <	< 1.4 1.4 <
	Louisa Ck	22-01-07 30-01-07 01-02-07	< < <	< 1.5 1.9	< 2.0 1.9	< 2.0 1.9	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7	1.3 0.9 1.8
	Stuart Ck (downstream)	23-01-07	<	< 1.5 1.9	< 2.5 2.5	< 2.5 2.5	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7
	Stuart Ck (Auto)	30-01-07 ???	< 10.6 ???	< 3.4	< 3.3 6.3	2.0 3.3 6.3	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7
	Captain Ck Drain	22-01-07 01-02-07	< <	< 1.5 2.1	< 1.5 2.1	< 1.5 2.1	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7	< 1.7 1.7	1.4 1.2

The above results are reproduced in Table 8, but in this case the score sheet has been adjusted by: removing reference sites and all scores that were less than the reference values; calculating cumulative risk scores, and; arranging samples in descending order of risk.

Table 8. Index scores indicating relative risk where score has exceeded reference site values.

Site	Land use	Date	Silver	Aluminium	Arsenic	Copper	Manganese	Nickel	Lead	Selenium	Zinc	Cumulative Risk Score
Gordon Ck	Urban	21-01-07		20.0	0.6	16.4		1.3			53.1	91.4
Stuart Ck (Auto)	Urban - Industrial	-	10.6			3.3						13.9
Stuart Ck (Auto)	Urban - Industrial	-	3.4			6.3						9.7
Kern Drain	Urban	23-01-07		1.0		5.0						6.0
Kern Drain	Urban	22-01-07		4.2	0.6							4.8
Woolcock St Drain	Urban	30-01-07				2.8					1.8	4.6
Woolcock St Drain	Urban	01-02-07				2.2					2.0	4.2
Kern Drain	Urban	30-01-07				3.0						3.0
Gordon Ck	Urban	02-01-07						3.0				3.0
Kern Drain	Urban	21-01-07				2.9						2.9
Stuart Ck (downstream)	Urban - Industrial	23-01-07				2.5						2.5
Louisa Ck	Urban - Industrial	01-02-07									1.8	1.8
Captain Ck Drain	Urban - Industrial	22-01-07									1.4	1.4
Louisa Ck	Urban - Industrial	22-01-07									1.3	1.3
Woolcock St Drain	Urban	22-01-07									1.3	1.3
Captain Ck Drain	Urban - Industrial	01-02-07									1.2	1.2
Bohle R	Urban - Industrial	02-02-07	1.1									1.1
Louisa Ck	Urban - Industrial	30-01-07									0.9	0.9
Kern Drain	Urban	01-02-07			0.7							0.7

5.1.6. Oil and Grease

Oil and grease residues were detected from three sub-catchments including Campus Creek, Gordon Creek and Kern Drain. Oil and grease residues were only detected once at both Campus Creek and Gordon Creek at a concentration of 1 mg/L. Oil and grease was detected on three occasions at Kern Drain with concentrations ranging from 1 to 3 mg/L (Appendix B).

5.2. Marine Sampling

From the marine sampling which occurred on the 2nd February, three separate plumes were observed as a consequence of high flows from Black, Bohle and Ross Rivers, and also Sandfly Creek. The Ross River (20km) produced the largest plume followed by Black River (6km) and Bohle River (3 km). Plumes travelled in a northerly direction adjacent to the coast. While it was apparent that the Ross River plume extended over Middle Reef, the plume did not impinge on the reefs of Magnetic Island (Fig 4).

As expected, the lowest salinities were observed closest to the mouth of the rivers and gradually increased towards the outer extent of plumes. The salinity readings, taken approximately 1 km from the mouth of the three rivers, were 7.1 ppt for Ross River (site 100), 6.1 ppt for Black River (site 196) and 15 ppt for Bohle River (site 211). At the outer edges of these plumes, salinity levels had risen to 31 ppt for Ross River, 17.8 ppt for Black River and 23.1 ppt for the Bohle River. The thickness of the freshwater plume, at the outer reaches, was only ~20-50 cm.

TSS concentrations in all three plumes typically followed a downward trend from the river's mouth to the outer edges. The mouth of the Ross (98 mg/L) and Bohle (80 mg/L) Rivers had similar TSS concentrations while the Black (32 mg/L) had a considerably lower concentration at the mouth (Table 9). TSS concentrations fell rapidly along the salinity gradient and were typically below 20 mg/L by the 10-15 ppt salinity zone (Fig 27). At the outer reaches of the plumes, TSS concentrations were 7 mg/L for the Ross River, 10 mg/L for the Bohle River and 8 mg/L for the Black River (Fig 27). An anomalous TSS concentration (45 mg/L) occurred within the Black River plume where salinity was 20 ppt; however, the salinity readings from the different instruments were highly variable in this sample (16J350-207: Table 9).

DON concentrations in the Black River plume displayed a general increase throughout the salinity gradient from 6.6 µM near the mouth to 10.8 µM at the plume edge (Fig 28). Concentrations of PN and NO_x decreased from 23.4 µM to 7.3 µM and from 4.8 µM to 3.2 µM, respectively from the mouth to the outer reaches of the freshwater plume. Ammonia displayed little variability in the Black River plume. At the mouth of the Bohle River concentrations of DON (8.6 µM), NO_x (2.9 µM), PN (6.0 µM) and ammonia (1.9 µM) were considerably higher than at the outer edge of the plume (Fig 28). The 'ambient' sample (No 197), which was taken outside of the visible plume edge from the Bohle River (Fig 4), also contained elevated concentrations of NO_x (1.6 µM) and ammonia (1.1 µM) over those reported for ambient conditions in the Townsville Region (Furnas and Brodie, 1996: NO_x = 0.05 µM and ammonia = 0.15 µM). DON and PN concentrations in the Ross River freshwater plume were variable over the salinity gradient, while NO_x and ammonia concentrations displayed a general decrease from the mouth to the outer reaches of the plume. NO_x and ammonia concentrations in all three freshwater plumes were considerably elevated over those reported in ambient conditions for the Townsville Region (Furnas and Brodie, 1996) even at the plume edges. Concentrations of DON and PN, in most cases, were either slightly higher or within the expected range of ambient coastal waters in the Townsville Region (Furnas and Brodie, 1996).

In the freshwater plumes from the Black and Bohle Rivers, concentrations of PP and FRP generally decreased from 2.0 to 0.2 µM and 1.1 µM to 0.5 µM, respectively (Fig 29a and b). DOP concentrations displayed a slight increase from the mouth to the plume edge in the Black and Bohle freshwater plumes (Fig 29a and b). The phosphorus species showed little variation in the Ross River freshwater plume across the salinity gradient (Fig 29c). The phosphorus species in the three plumes sampled in the region were all slightly elevated over ambient concentrations reported for coastal waters in the area (Furnas and Brodie, 1996).

Chlorophyll *a* concentrations ranged from 0.3 µg/L to 1.0 µg/L in the Black River plume, 0.6 µg/L to 0.9 µg/L in the Bohle River plume, and 0.6 µg/L to 3.0 µg/L in the Ross River plume (Table 9). These concentrations were higher than reported ambient chlorophyll *a* concentrations in the Townsville coastal region (Furnas and Brodie, 1996: 0.40 ± 0.09 µg/L). The chlorophyll *a* concentrations displayed no apparent trend throughout the salinity gradient for all three plumes sampled in the Townsville Thuringowa Region. In the majority of samples, chlorophyll *a* concentrations were higher than phaeophytin. Phaeophytin concentrations were typically higher in the samples taken in close proximity to the mouth of the rivers.

Three herbicide residues were detected in the flood plumes: atrazine (4 of 9 samples collected), diuron (2 of 9) and hexazinone (1 of 9). Atrazine (0.02 µg/L: two samples) and diuron (0.01 µg/L: one sample) were detected in the Ross River plume (samples 202 and 213). These samples were collected from outer reaches of the plume and no residues were detected at the Ross River mouth. Herbicide residues were found in both samples collected from the Sandfly

Creek plume (samples 210 and 225: see Fig 4). Atrazine (0.01 µg/L: both samples) and hexazinone (0.02 µg/L: one sample) were detected in this plume. No pesticide residues were detected in Halifax Bay in the plumes from the Black and Bohle Rivers.

The majority of the filterable trace metals were below detection limits and no ANZECC and ARMCANZ (2000) guideline was exceeded in any samples collected in the marine environment during the plume monitoring (Appendix B). Oil and grease residues were also below detectable limits in the marine environment.

Table 9. Salinity and chlorophyll values for the marine plume monitoring sites of Cleveland and Halifax Bays.

Sample ID	Location	Salinity (ppt)			Chlorophyll			Total Phaeo Pigments ($\mu\text{g/L}$)
		Lab Salinity*	Refractometer	YSI	TSS	Chlorophyll <i>a</i> ($\mu\text{g/L}$)	Phaeophytin ($\mu\text{g/L}$)	
16J350 -197	Ambient	25.5	21	26	7.9	0.7	< 0.2	0.7
16J350 - 196	Black River	6.1	4		31.5	0.3	0.2	0.6
16J350 - 204	Black River	19.3	14	15	15.8	0.5	0.4	0.8
16J350 - 207	Black River	0.9	17	20	44.8	1.0	< 0.2	1.0
16J350 - 219	Black River	17.8	10	13	7.9	0.5	0.3	0.8
16J350 - 205	Black River	13.8	10	13	16.4	0.2	0.2	0.4
16J350 - 195	Bohle River	18.9	15	20	27.2	0.9	< 0.2	1.0
16J350 - 200	Bohle River	14.4	12	18	80.4	0.8	1.9	2.6
16J350 - 211	Bohle River	14.6	21		65.8	0.9	0.8	1.6
16J350 - 220	Bohle River	23.1	18		10.2	0.6	0.2	0.9
16J350 - 213	Ross River	31	27	31	6.6	1.1	0.3	1.4
16J350 - 100	Ross River	7.1	2	5	98.0	3.0	7.3	10
16J350 - 113	Ross River	23.8	20	24	5.3	1.3	< 0.2	1.4
16J350 - 201	Ross River	18.3	16	16	17.8	1.1	0.3	1.4
16J350 - 202	Ross River	22.9	20	24	5.7	1.1	< 0.2	1.2
16J350 - 206	Ross River	15.9	14	14	14.2	1.1	0.2	1.3
16J350 - 214	Ross River	25.1	21	25	5.6	1.2	0.2	1.4
16J350 - 215	Ross River	25.2	20	25	8.7	0.6	1.1	1.8
16J350 - 210	Sandfly Creek	19.5	16	20	28.6	1.7	1.4	3.1
16J350 - 225	Sandfly Creek		19	22	17.0	1.8	0.9	2.6

* Salinity was than derived from an algorithm that permits practical salinity (S) to be determined from the conductivity and temperature measurements as per APHA/AWWA/WEF (2005)

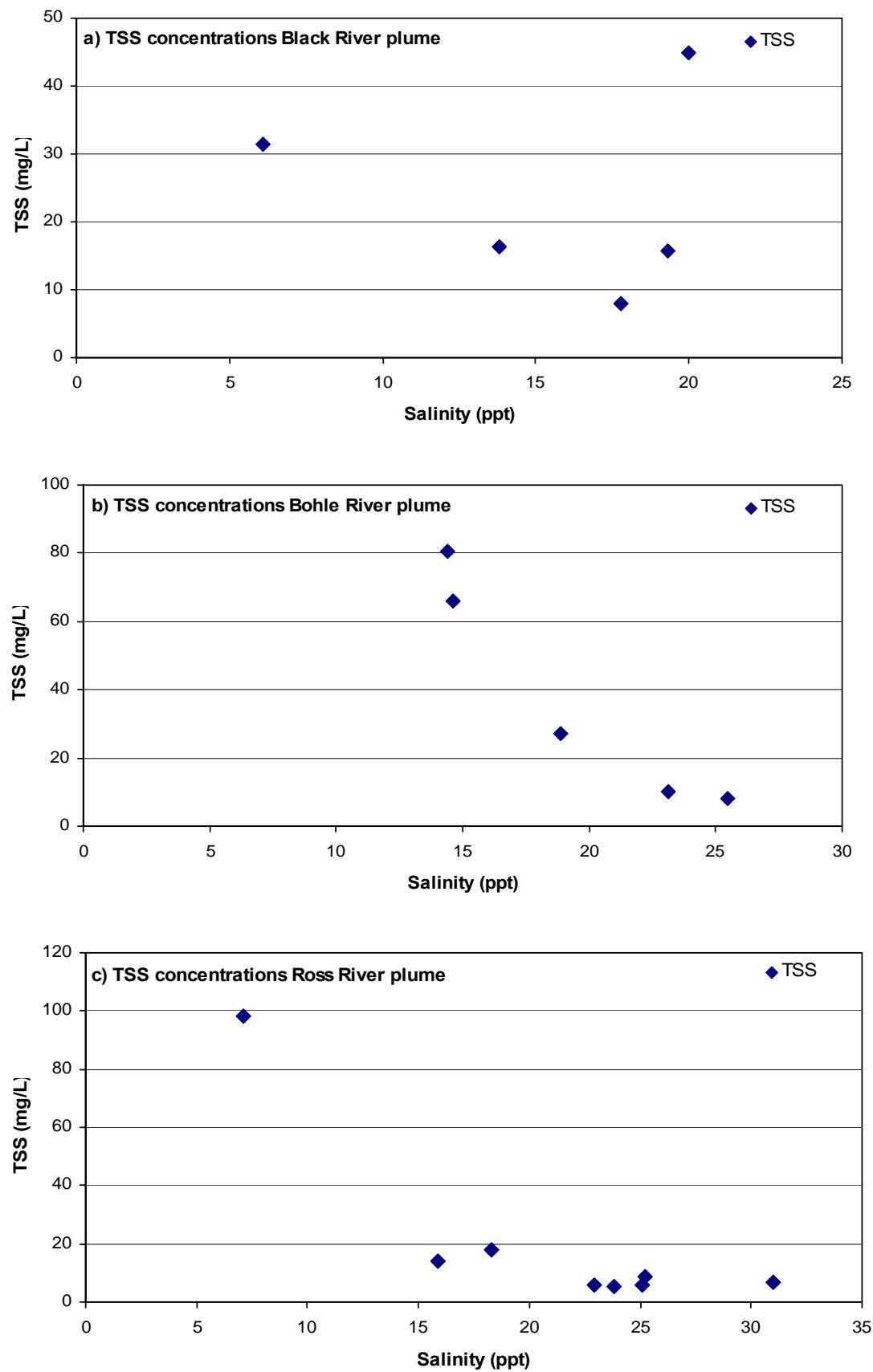


Figure 27. TSS concentrations (mg/L) along the salinity gradient in the a) Black River, b) Bohle River and c) Ross River freshwater plumes.

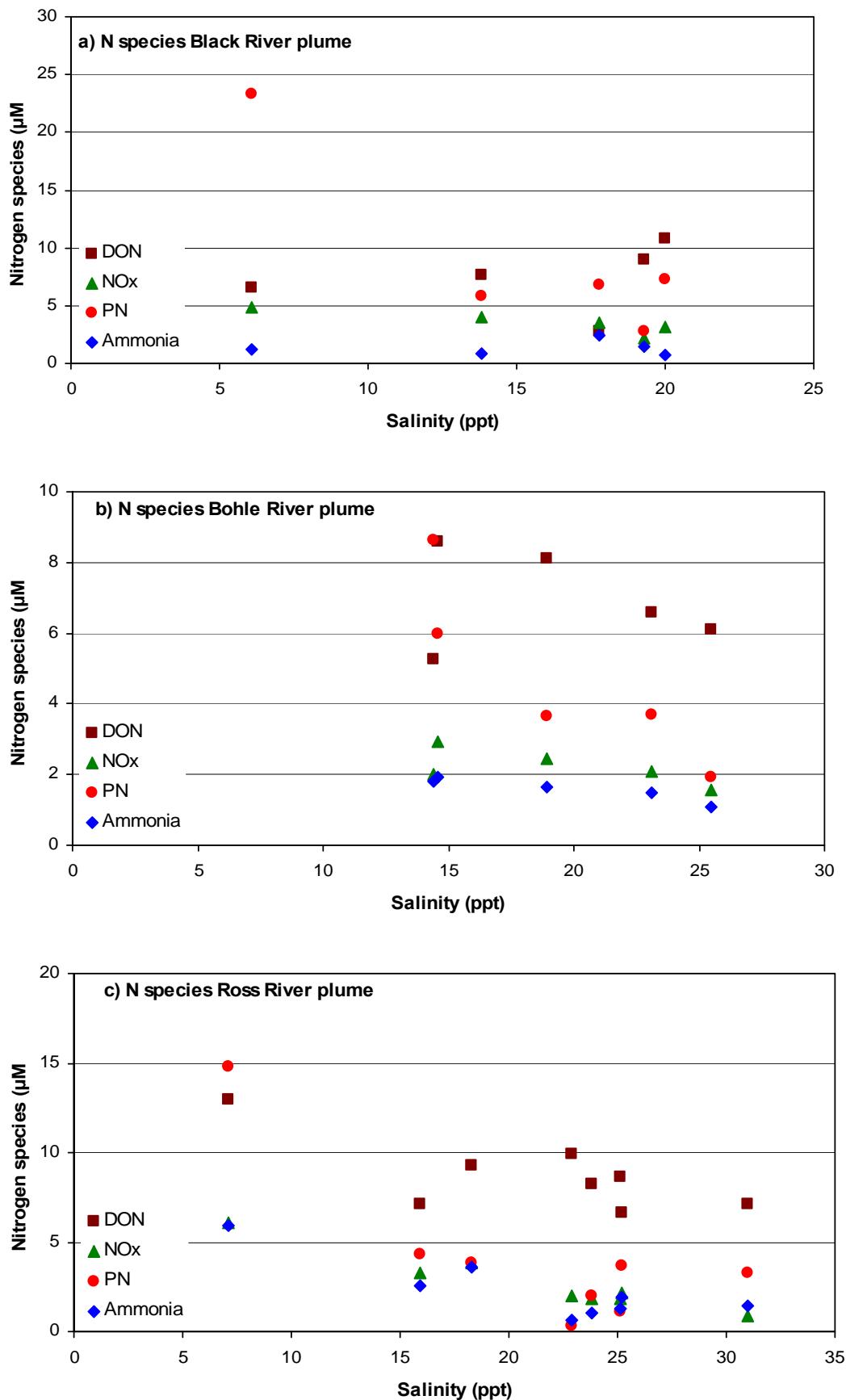


Figure 28. Nitrogen species concentrations (μM) along the salinity gradient in the a) Black River, b) Bohle River and c) Ross River freshwater plumes.

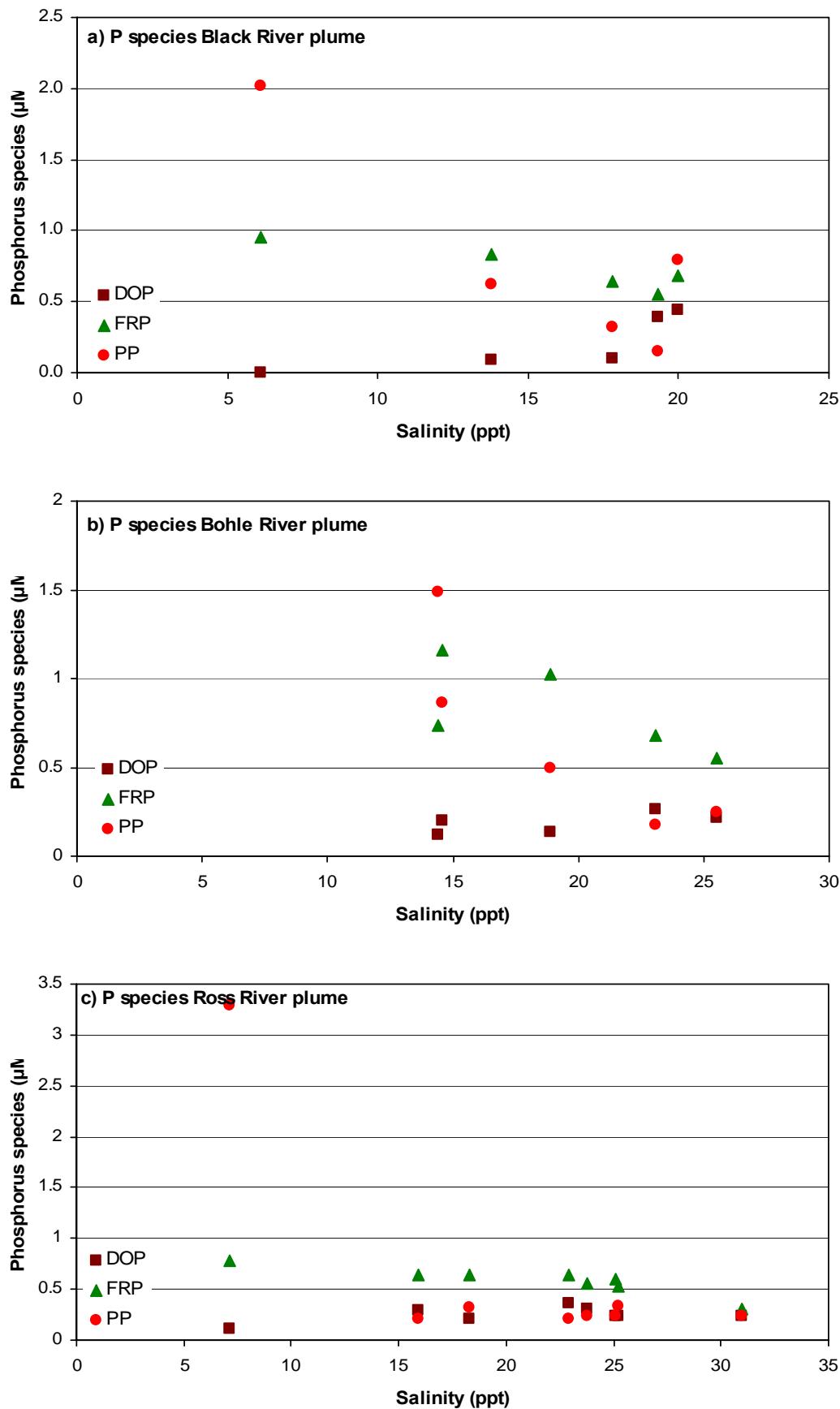


Figure 29. Phosphorus species concentrations (μM) along the salinity gradient in the a) Black River, b) Bohle River and c) Ross River freshwater plumes.

6. DISCUSSION

6.1. Conductivity

The majority of samples analysed for electrical conductivity (EC) had concentrations below 200 $\mu\text{s}/\text{cm}$, indicating a freshwater source. Samples collected from four tidally influenced sample sites (Woolcock Street Drain, Gordon Creek, Bohle River and Captain Creek Drain) sometimes displayed higher conductivities that could be correlated with the hydrographic state. For these sampling sites the samples collected prior to and during the early stages of the first flow event contained the highest EC values (period of tidal influence). Conductivity values decreased to <200 $\mu\text{s}/\text{cm}$ during periods of higher flows, which indicate these samples represent freshwater runoff from the upstream catchment area with no marine influence.

6.2. Suspended sediments

The low TSS values obtained from the natural and rural residential land use sites (medians between 3 and 20 mg/L) support their designated land use classification, and provide a good baseline to compare other land uses (Fig 10). The variability of TSS concentrations in the sites from the mixed land use category (natural, grazing or minimal use) reflects the different sizes of the catchment areas and the different land uses. The land use table (Appendix I) indicates that the Hen Camp Creek (Hwy and D/S) sites drain predominately natural (98%) land use, which explains the low TSS concentrations recorded at these sites with medians of 5 and 28 mg/L, respectively. The Stuart Creek upstream site had a higher median TSS concentration of 63 mg/L, which is linked to a higher area of grazing (65%) within this catchment. The highest median TSS concentrations within the mixed land use category sites were the Black River (199 mg/L) and Ross River (Dam: 316 mg/L) sites. The catchment areas above these sites are considerably larger than the other sites within this category, and also have a higher proportion of grazing lands (83% and 75%, respectively: Appendix I). In addition, these catchments are situated in the drier areas of the region in comparison to other sites within this study that have headwaters draining the Paluma and Mt Elliot Ranges. These drier catchments coupled with higher grazing areas have higher potential for sediment generation. These TSS concentrations are comparable with those measured from other grazed catchments of north Queensland, including the Mackay Whitsunday Region (medians of 85-210 mg/L: Rohde *et al.* 2006) and also the lower boundary of TSS medians measured in the Burdekin Region (medians of 30-2700 mg/L: Bainbridge *et al.* 2006b). However, the median TSS concentrations of the Black and Ross Rivers are considerably higher than those determined for the grazed catchments of the Tully region (2.2 to 13 mg/L); the Tully region has considerably better ground cover due to the higher rainfall in this region (Faithful *et al.* 2007). The median TSS concentration for the Black River (199 mg/L) is similar to that of the 2006 wet season (165 mg/L: Bainbridge *et al.* 2006b).

The TSS concentrations of the urban land uses were also variable between sites (Fig 10). This variability is related to the development occurring within some of the catchments. The TSS median concentrations for the developing urban sites (278 mg/L: Kern Drain; 351 mg/L: Gordon Creek) were considerably higher than the medians obtained at Woolcock Street Drain (24 mg/L), Black Weir (128 mg/L) and Aplins Weir (82 mg/L). These higher concentrations reflect the large areas of exposed soil as a consequence of excavation, which is easily transportable in intense rainfall events. Considerably higher TSS concentrations were measured from opportunistic sampling conducted at other developing urban sites within the Townsville Thuringowa Region. The highest concentrations were recorded during the peak of the first flush event, with the first intense rains of the season transporting loose soil from the cleared land to the nearby waterways. The peak concentrations exceeded 30,000 mg/L (Appendix B). These

concentrations exceed any measured TSS concentrations in current and previous event-based monitoring projects within the GBR catchments; including the Johnstone (Hunter *et al.* 1996), Tully (Faithful *et al.* 2007), Herbert (Mitchell *et al.* 1997), Burdekin (Bainbridge *et al.*, 2006a; 2006b), Mackay Whitsunday (Mitchell *et al.* 2005; Rohde *et al.* 2006) and Fitzroy (Packett, 2007) Regions. Rohde *et al.* (2006) obtained peak TSS concentrations of 4,330 mg/L from the urban developing sub-catchment Airlie Creek, within the Mackay Whitsunday Region. Even the highest peak TSS concentrations from the large Burdekin River sub-catchments rarely exceed 10,000 mg/L, where grazing has been classed as the dominant land use (Bainbridge *et al.* 2006a). The high to extreme TSS concentrations measured at the developing urban sites in the Townsville Thuringowa Region highlight the risk of increased soil erosion and potential impacts on aquatic ecosystems.

The TSS concentrations within the urban and industrial category were variable. The higher TSS concentrations obtained from the Bohle River and Stuart Creek (D/S) sites are probably the result of the land uses in these catchments, which are predominantly grazed (84% and 60%, respectively). Areas of the Bohle River catchment are currently under urban development which may also contribute to these higher TSS concentrations. This is evident by Kern Drain, a tributary to the Bohle River, which produced the 3rd highest TSS median (280 mg/L) of all monitored sites. The median and peak TSS concentrations for the Bohle River (155 mg/L and 560 mg/L, respectively) were lower than those measured in the 2006 wet season (290 and 1050 mg/L, respectively: Bainbridge *et al.* 2006b). The smaller catchment sites within the urban and industrial land use (Louisa and Captain Creeks) yielded considerably lower TSS concentrations; these sites drain established urban areas. Louisa Creek has comparable median TSS concentrations to the 2006 wet season (Bainbridge *et al.* 2006b).

Stratified sampling of upstream and downstream sites (to determine any measurable difference in water quality as a result of changes in land use) showed no discernable difference within Alligator and Bluewater Creeks. However, considerable differences were observed in the stratified sampling of Stuart Creek, with upstream median TSS concentrations of 63 mg/L compared to 200 mg/L at the downstream site (Table 4). This difference is probably due to the increase in downstream catchment area (from 700 to 7000 Ha: Appendix I) and land use which includes grazing and industrial uses.

The latest SedNet model (Kinsey-Henderson, in prep) considerably overestimates the TSS loads for the major waterways of the Townsville Thuringowa Region with the exception of the Black River (Table 5). This model applied adjustments for vegetation cover and coastal floodplains (slope), and while these results provide closer estimations to the monitoring data than those of previous models (Table 2), additional modifications may be required to improve the modelled outputs such as the acquisition of higher resolution input data for the region. However, longer time periods of monitoring data are required (~10 years) to adequately compare to the SedNet model. Overall, sediment loads produced from the Townsville Thuringowa Region (~100,000 tonnes per year) may be considered minor when compared to sediment loads of other GBR catchments, such as the Burdekin Catchment (~4,000,000 tonnes per year: Mitchell *et al.* 2007).

In general, TSS concentrations and loads were relatively low across the Townsville Thuringowa Region. However, developing urban sites provided an important point source for TSS contribution and may have detrimental implications for local receiving water ecosystems. Management strategies are necessary to control TSS runoff from developing urban sites. These data which encompass a wide range of land uses could contribute to the development of local water quality guidelines.

6.3. Nutrients

A trend between TSS concentrations and PN and PP concentrations were observed at most sites within this study (Figs 15 and 20). This trend is consistent with previous studies where PN and PP concentrations mirror those of TSS in waterways draining disturbed catchments (Rohde *et al.*, 2006; Faithful *et al.* 2007). This trend has been most commonly observed in sampling conducted in the larger (and drier) grazed catchments of the Burdekin River, where the particulate fraction of N and P often consists of 60-90% of total N and P (Bainbridge *et al.*, 2006b; Mitchell *et al.*, 2007). The two developing urban sites, Kern Drain and Gordon Creek did not conform to this underlying trend. A possible reason for the low PN and PP concentrations contained in the runoff from these developing urban sites is the low nutrient status of eroding soils, which may be derived from the nutrient-poor B horizons. These underlying horizons are now exposed as a result of excavation of topsoils for the development of urban landscapes. Median PP concentrations were slightly higher in the urban (median of 84 µg P/L), urban and industrial (median of 57 µg P/L) and mixed (median of 55 µg P/L) categories compared to the natural and rural residential land use categories, which both had a median of 20 µg P/L. These concentrations are similar to PP concentrations measured in other urban catchments within the GBR, including Mackay and Proserpine (medians of ~45 µg P/L: Rohde *et al.* 2006) and the Tully Region (median of 20 µg P/L: Faithful *et al.* 2007). PN concentrations within the urban (median of 130 µg N/L) and urban and industrial (median of 179 µg N/L) categories are also similar to those determined for Mackay and Proserpine (median of 206 µg N/L and 91 µg N/L, respectively: Rohde *et al.* 2006) and the Tully Region (median of 90 µg N/L: Faithful *et al.* 2007). Overall, PN and PP concentrations were relatively low when compared to the larger GBR catchments, such as the predominantly grazing subcatchments of the Burdekin (median ranges from 325 µg N/L to 2240 µg N/L and from 105 µg P/L to 1475 µg P/L, respectively: Mitchell *et al.* 2007). Therefore, concentrations of PN and PP transported from the Townsville Thuringowa Region are considered of relatively low concern.

Elevated concentrations of DON and DOP were observed from both the urban (median of 388 µg N/L and 11 µg P/L, respectively) and urban and industrial (median of 350 µg N/L and 15 µg P/L, respectively) land use categories (Figs 16 and 21). Natural forest catchments can leach DON in considerable quantities and it thus forms the bulk of the nitrogen species in unpolluted streams (Brodie and Mitchell 2005). The elevated concentrations of both DON and DOP within the urban and urban and industrial land uses are possibly derived from urban gardens. These concentrations are similar to those measured in other urban centres including Mackay (median of 127 µg N/L and 2 µg P/L respectively: Rohde *et al.* 2006), Proserpine (median of 405 µg N/L and 19 µg P/L respectively: Rohde *et al.* 2006) and the Tully Region (median of 165 µg N/L and 6 µg P/L respectively: Faithful *et al.* 2007). While these concentrations are slightly elevated in comparison to the natural land use category, waters draining pristine rainforest and woodlands in northern Australia in significant flow conditions have moderate concentrations of DON and DOP (typically 30-400 µg N/L and 1-30 µg P/L, respectively: Brodie and Mitchell 2005). DON and DOP concentrations are considered the more ‘natural’ forms of N and P and not as bioavailable as the inorganic species (Brodie and Mitchell 2005). These organic species are of low concern in the Townsville Thuringowa Region.

Compared to the natural (median of 50 µg N/L) land use, slightly elevated NO_x concentrations were observed across all other land use categories (median range of 94 to 140 µg N/L) (Fig 17). The source of the slightly elevated NO_x concentrations is unknown, but may be attributed to the minimal use of fertilisers across these land use categories. These concentrations are also similar to those obtained from Proserpine (median of 174 µg N/L: Rohde *et al.* 2006), however are lower than those measured in the urban areas of Mackay (median of 220 µg N/L: Rohde *et al.*

2006) and the Tully Region (median of 268 µg N/L: Faithful *et al.* 2007). NO_x concentrations in the urban land uses are considerably lower than those obtained from intensive agricultural regions (sugarcane and horticultural lands), where nitrogen fertilisers are applied to crops. Concentrations of NO_x in sugarcane catchments from the Mackay Whitsunday (median range from 818 to 1710 µg N/L: Rohde *et al.* 2006) and Tully (median of 939 µg N/L: Faithful *et al.* 2007) Regions are nearly an order of magnitude higher than those observed in the urban land uses. However, point source contributions of NO_x may be locally significant within the region, although intensive point source sampling was beyond the scope of this study.

Ammonia concentrations within the urban land use category (median of 36 µg N/L) were considerably higher than all other land uses within the region (Fig 18). These concentrations were also slightly higher than those concentrations obtained in the Mackay (median of 17 µg N/L: Rohde *et al.* 2006) and Proserpine (median of 18 µg N/L: Rohde *et al.* 2006) urban areas. The probable sources of ammonia in the region may be sewage effluent, animal excreta (e.g. dogs) and fertiliser runoff.

FRP concentrations were considerably higher in the urban (median of 131 µg P/L) and urban and industrial (median of 99 µg P/L) land uses compared to the other land use categories (median range between 12 and 35 µg P/L) (Fig 22). Elevated concentrations of FRP probably originate from numerous artificial sources including fertilizer, detergents, wastewater, industrial effluent and animal excreta (particularly dogs). These median FRP concentrations are similar to those obtained for urban land uses in Mackay (median of 185 µg P/L: Rohde *et al.* 2006), and are considerably lower than concentrations recorded from this land use within Proserpine (median of 576 µg P/L: Rohde *et al.* 2006). The concentrations of FRP are considered of high concern in the Townsville Thuringowa Region, with the identification of the dominant source(s) of FRP in the urban and industrial areas required to enable better management of this inorganic nutrient.

The latest ANNEX model (Kinsey-Henderson and Sherman, 2007) appears to have considerably overestimated PN and PP loads in the major waterways of the Townsville Thuringowa Region when the data is compared to the (flow adjusted) loads calculated using the 2007 monitoring data. The overestimation of PN and PP loads by the ANNEX model has also been recognised for the Burdekin catchment; this overestimation is thought to be related to either a ‘carry on’ effect from the overestimation of sediment loads in the SedNet model or the overestimation of nutrient contents in soils by the Australian Soil Resource Information System (ASRIS) applied in the ANNEX model (Bainbridge *et al.* 2006b; Sherman *et al.* 2007). No reasonable explanation can be provided for the underestimation of DON loads in the Black and Bohle River or for the overestimation of NO_x and FRP in all major waterways in the region. Compared to other catchments of the Great Barrier Reef (Burdekin: Bainbridge *et al.* 2006a; 2006b and Mackay Whitsunday: Rohde *et al.* 2006), the nutrient loads were comparable or lower in the Townsville Thuringowa Region. When the event mean concentration (EMC) is used to normalise for discharge, EMC concentrations of nutrient species in the region were consistent with those obtained from other small coastal (floodplain) catchments within the Burdekin Dry Tropics Region (e.g. Barratta Creek, Haughton River, Euri Creek and Don River: Bainbridge *et al.* 2006b).

6.4. Pesticides

The frequent detection of diuron within the urban and industrial land uses is consistent with results from urban sampling in other regions including Mackay Whitsunday (maximum concentration of 0.04 mg/L Rohde *et al.* 2007) and Tully (maximum concentration of 0.66 mg/L, Faithful *et al.* 2007). Diuron has a wide variety of uses including total weed control in commercial areas, roads and railways as well as selective control of grasses and broadleaf weeds in crops (Tomlin, 1994). While one sample exceeded the ANZECC and ARMCANZ (2000) low reliability guideline for diuron (0.3 µg/L), the concentration is below the proposed revised guideline of 1 µg/L (Lankester *et al.*, 2007). The detection of diuron over a range of samples in the urban and urban and industrial land uses warrants further monitoring in both ambient and event conditions. The concentrations of other herbicides detected in the Townsville Thuringowa Region were well below ANZECC and ARMCANZ (2000) guidelines. These herbicides have many potential sources including from households, commercial/industrial areas and from public lands (e.g. stormwater drains, roads, parks). The detection of bromacil predominately in agricultural lands (Hen Camp Creek) and urban and industrial lands suggests a possible commercial application. However, with the exception of diuron, herbicides are considered of low concern in this region.

While endosulfan residues were only detected in a limited number of samples, the concentrations did exceed ANZECC and ARMCANZ (2000) guidelines, and are considered a concern for water quality within the region. Endosulfan is used as an insecticide on a variety of crops, including vegetables, fruit, nuts, cereal as well as in plant nurseries, on lawn, pasture and fodder, flowers and ornamentals (NRA, 1997). The endosulfan residue in the Alligator Creek sample (0.59 µg/L) exceeded the 95% ANZECC and ARMCANZ guideline value for ecological protection (0.2 µg/L), while the Captain Creek (0.09 µg/L) sample exceeded the 99% guideline (0.03 µg/L) (ANZECC and ARMCANZ, 2000). It should be noted that the 95% level fails to protect some important Australian species from acute toxicity (e.g. fish, invertebrates: Sunderam *et al.* 1992; ANZECC and ARMCANZ, 2000) and has been linked to fish kills in NSW (Bowmer *et al.* 1995). In addition, the half-life of α -endosulfan in freshwater is around 2 days while the β -isomer is slightly more persistent, from 4-7 days (Sunderam, 1990); residues may persist up to 70 days in soils (Tomlin, 1994). Managers are advised, where possible, to apply the 99% protection level due to the potential of endosulfan residues to bioaccumulate in the environment (ANZECC and ARMCANZ, 2000). Our data indicate that endosulfan residues were below detection limits following the subsequent sample collection of both the Alligator Creek (D/S) (62 hours) and Captain Creek Drain (26 hours) sites. Therefore the overall toxicity over these relatively short exposure times is largely unknown and requires further research.

Malathion was the other insecticide residue to be detected in the Townsville Thuringowa Region at a concentration (2.9 µg/L) which exceeded the 95% ecological protection guideline (0.05 µg/L: ANZECC and ARMCANZ, 2000). Malathion was only detected in one sample at Louisa Creek during the first flush event. Malathion is a non-systemic pesticide (low bioaccumulation potential) which has a low mammalian toxicity and has been used in situations of human and animal contact, particularly for control of disease vectors (e.g. mosquitoes) (Tomlin, 1994). Malathion is highly toxic to many fish and invertebrates (eg. freshwater crustaceans and insects), although there is a wide variation from one species to another. Unfortunately subsequent sampling of the Louisa Creek site was not undertaken until 7 days after the residue was detected and therefore the exposure time could not be estimated.

Further monitoring of pesticide residues is required in ambient conditions. Some residues have the potential to accumulate over time in freshwaters (and in sediments) and concentrations may be higher in periods of no or low flow.

6.5. Trace metals

A few of the metal toxicity index scores obtained from samples collected at urban sites (see Tables 7 and 8) are high enough to suggest that metals could potentially have had acute impacts on freshwater and/or estuarine ecosystems in close proximity to the monitoring sites. In particular, the concentrations of zinc, copper and aluminium observed in Gordon Creek on the 21st January, the silver and copper levels recorded in Stuart Ck, and to a lesser extent, the copper and zinc levels in Kern and Woolcock Street drains, all deserve closer investigation.

Stormwaters typically contain high concentrations of filterable colloids and organic carbon, and these tend to reduce the bioavailability (and therefore toxicity) of metals. Nevertheless, without carrying out much more detailed analyses it is not possible to discount the possibility that some of the elevated metal concentrations would have been acutely harmful to ecosystems in close proximity to the sampling sites.

Most significantly the high concentrations occurred at a time when flows and therefore dilution and dispersion rates were unusually high. This raises questions about how high and persistent the metal concentrations would have been if flows rates had been more moderate. Until these questions are answered further monitoring of trace metals in Stuart and Gordon Creek, under both high and low flow conditions, is strongly recommended.

The high concentrations occurred in urban watercourses that drain relatively small catchments; i.e. in catchments that deliver relatively small volumes of runoff that can be rapidly diluted in downstream environments. Stuart Ck is somewhat larger than the other waterways in question here, but its catchment still only constitutes a small proportion of the Ross River basin. Consequently, the elevated metal concentrations would be expected to have been diluted to insignificant levels by the time they reached the marine environment. This contention is supported by the findings of the flood plume sampling program which yielded no elevated metal concentrations.

6.6. Oil and Grease

Hydrocarbons such as oil and grease are hydrophobic and immiscible in water, often forming surface films that only gradually emulsify. The lighter fractions are also volatile. Accordingly specialised, and somewhat expensive, water sampling and analysis techniques must be employed in order to obtain accurate concentration estimates. The adoption of detailed assessment methods of this kind was neither feasible nor justifiable in the current study. Instead the study team elected to employ standard water quality sampling methods and conduct low cost preliminary analyses to determine if there was any evidence of the need for more detailed follow-up investigations.

Oil and grease comprises a wide range of substances, predominately hydrocarbons, each of which has distinctive chemical and physical properties. The analytical methods of choice for detailed investigations would include determination of the individual hydrocarbon and petroleum hydrocarbon fractions. The method employed in this study is a low cost alternative that involves collecting all of the solvent-extractable substances contained within a water sample and weighing what remains after the solvent is evaporated. The method is termed oil and grease because the main materials collected would normally comply with that description. This includes

mainly high boiling point hydrocarbons, fats and other lipids; however, other substances such as chlorophyll and sulphur compounds are also extracted. One of the main drawbacks is that solvent is evaporated at 85°C, so low boiling point hydrocarbons are lost.

As oil is not one specific substance and compositions vary widely it is not possible to derive guideline concentrations on toxicity. However, the most toxic fractions of oil are the lighter fractions, often containing higher proportions of aromatics. These include petroleum and diesel. For example, a diesel spill in Alaska, measuring 8 mg/L was linked to a 90% decrease in invertebrate numbers and loss of four taxa (Green and Trett, 1989). This can result in indirect effects such as loss of food sources for fish and an increase in algal growth (Chapman and Simmons. 1990). Oil and grease contamination is generally short-lived; however, the build up of heavier hydrocarbons in sediments may lead to chronic pollution through bottom resuspension (Guiney *et al.* 1987).

Oil and grease analysis was included in this program mainly to determine if there was any evidence of highly anomalous concentrations. It is important to recognise that the sampling methods employed here will tend to yield underestimates, while the analytical method may underestimate the light hydrocarbon fraction and overestimate the heavy fraction. Accordingly results must be interpreted cautiously and should be considered to be qualitative at best. Interestingly, oil and grease was detected (1 mg/L) in one sample from the Campus Creek site which lacks any known anthropogenic sources of hydrocarbons. The origin for the oil and grease detected in the two developing urban sites (Kern Drain and Gordon Creek) is uncertain. Fuel residues from mechanical excavation in these catchments are a possible contributor. It is unlikely that oil and grease at these concentrations will have any adverse effects to the environment. The detection of oil and grease within the developing urban land use warrants closer investigation and suggests that it would be wise to adopt more specific hydrocarbon analyses for both sediment and water in the future. However, the results to date provide no evidence of any urgent need to devote a significant proportion of the available monitoring budget to this parameter.

6.7. Flood plumes in Cleveland and Halifax Bays

Salinity levels from the mouth to the outer reaches of the plumes in Cleveland and Halifax Bays (from the Black River, Bohle River, Ross River and Sandfly Creek) are consistent with other plumes that have been mapped in the GBR lagoon (Devlin *et al.* 2001; Rohde *et al.* 2006). TSS concentrations over the salinity gradient in all plumes are also consistent with other studies (Devlin *et al.* 2001; Devlin and Brodie, 2005; Rohde *et al.* 2006) where TSS levels fell below 20 mg/L by the 10-15 ppt salinity zone.

The concentration ranges of DON (5.3 to 12.9 µM) and DOP (<0.03 to 0.43 µM) as well as the variability of these species over the salinity gradient are consistent with studies of other freshwater plumes in the GBR lagoon (Devlin *et al.* 2001). DON and DOP concentrations are considered natural in the freshwater and marine environment (Brodie and Mitchell, 2005) and DON commonly makes up the highest proportion of TN in ambient marine waters (Furnas and Brodie, 1996). The concentrations of PN, PP and NO_x in the sampled plumes in the Townsville Thuringowa Region are similar to previous studies (Devlin *et al.* 2001; Rohde *et al.* 2006), while the range of FRP concentrations (0.29 to 1.13 µM) were considerably higher than the range reported by Devlin *et al.* (2001: 0.2 to 0.5 µM). However, the FRP concentrations are consistent with freshwater plumes in the Mackay Whitsunday Region which range from 0.10 to 1.17 µM (Rohde *et al.* 2006). The PN, PP, NO_x and FRP nutrient species displayed conservative mixing within the flood plumes as the concentrations decreased over the increasing salinity gradient.

Ammonia concentrations were variable in the freshwater plumes which is also consistent with previous studies (Devlin *et al.* 2001; Devlin and Brodie, 2005; Rohde *et al.* 2006).

The finding that chlorophyll *a* concentrations were higher than phaeophytin (average chlorophyll *a* to total chlorophyll proportion of 69%) suggests that the majority of biological productivity in the plumes were sourced from new algae produced within the plume waters. Phaeophytin concentrations were higher closer to the river mouths which indicates that this algal biomass is from a freshwater source. Most nutrient species were elevated in the freshwater plumes by several-fold compared to those of ambient conditions. While river plumes provide an essential source of new nutrients to the GBR lagoon, changes in the loads delivered by waterways can alter biological processes in the GBR (Furnas, 2003). The range of chlorophyll *a* concentrations are within the lower range obtained from other plume studies in the GBR lagoon (Devlin *et al.* 2001; Rohde *et al.* 2006). However, the freshwater plumes in Cleveland and Halifax Bays were sampled during the peak discharge of the waterways in the Townsville Thuringowa Region and coincided with overcast conditions. Satellite imagery of GBR flood plumes suggest that biological productivity is highest two to three days after peak discharge is achieved and once full sunlight becomes available and turbidity level decrease for increased photosynthesis potential (Brodie *et al.*, 2007). Therefore, chlorophyll *a* concentrations would have been higher a few days after the plumes were sampled.

The three pesticide (all herbicides) residues detected in the Ross River (and Sandfly Creek) plume were well below ANZECC and ARMCANZ (2000) guidelines and are not of current concern in Cleveland and Halifax Bays. Oil and grease residues and important filterable trace metals (Ag, Al, As, Co, Cr, Cu, Cr, Cu, Ni, Pb and Zn) were all below detection limits in the freshwater plumes and are not of concern in the marine environment. However, we note that trace metals may be important for freshwater receiving waters (e.g. coastal wetlands).

7. CONCLUSIONS

This monitoring study was designed to determine the presence/absence of ‘bulk’ materials in the waterways of the Townsville Thuringowa Region during event flow conditions, to identify the pollutants of greatest potential concern to the marine environment and relate their occurrences to land use. The study was not intended to investigate ambient water quality or the health of aquatic ecosystems within the catchment. Accordingly the range of water quality variables covered was not comprehensive and notably did not include some key ambient water quality indicators (such as dissolved oxygen, BOD and microbial contaminants for example). However, the main parameters that are of potential concern for marine receiving waters, namely total suspended solids, total and dissolved nitrogen and phosphorus species, pesticide residues and trace metals, were all included. Selected samples were also analysed for oil and grease residues, but the chosen analytical method yielded equivocal results and more sophisticated petroleum hydrocarbon analyses are recommended for future monitoring purposes.

This was a short term study that utilised only a few sites per catchment. A low resolution monitoring program of this kind does not provide a definitive basis for assessing risks, especially within complex urban subcatchments that contain a diversity of potential pollutant sources. Nevertheless, it proved possible to identify some key differences in the amounts and concentrations of contaminants that were transported from subcatchments with different dominant land uses.

The results indicate that there are five combinations of contaminant and land use type that stand out as potential issues in the context of this project:

- FRP (phosphate) in the urban and industrial land uses;
- Insecticides (endosulfan and malathion) in the rural residential and urban land use categories;
- Diuron residues in urban and industrial land uses;
- TSS concentrations in developing urban landscapes; and
- Trace metals in urban and industrial land uses.

The possible sources of the elevated FRP in the region include fertilizer, detergents, wastewater, industrial effluents and animal excreta. The dominant specific source(s) of this nutrient is important to identify and manage in the urban and industrial areas of the region. Likewise, the source(s) for the endosulfan and malathion residues, which exceeded ANZECC and ARMCANZ (2000) guidelines in some samples, need to be identified and further monitoring of these insecticides (in ambient and event flows) is recommended in the region. While diuron residues were below the proposed revised guideline for the region (1 µg/L), the frequent detection of this herbicide in waterways that drain urban and industrial areas also needs to be monitored in the future. It is unclear if these pesticides were present in the waterways prior to the significant runoff events, and future monitoring needs to incorporate both ambient and event monitoring components. If pesticides are present during ambient conditions they are likely to be found in higher concentrations.

TSS concentrations were very high at the developing urban sites in the region and may have serious implications for downstream aquatic environments. Improved sediment retention practices at these development sites need to be adopted in order to reduce this sediment runoff.

The concentrations of trace metals reported in some of the urban water samples were high enough to suggest the potential for impacts on ecosystems that lie within close proximity to the sampling sites. In particular, the concentrations of zinc, copper and aluminium observed in Gordon Creek on 21st January, the silver and copper levels recorded in Stuart Ck, and to a lesser extent, the copper and zinc levels in Kern and Woolcock Street drains, all deserve closer investigation. Specifically, further monitoring of filterable trace metals under both high and low flow conditions, is strongly recommended, especially for Stuart and Gordon Creeks. If elevated metal concentrations prove to be recurrent or persistent problem it would be considered advisable to implement biological monitoring to determine if there are detectable impacts.

During this study metal concentrations were not high enough to suggest that the marine environments further downstream would be at threat and no anomalous concentrations were detected in flood plume samples. However, further monitoring is recommended to ensure that this situation does not change over time.

Additional water quality monitoring in the region would benefit greatly by aligning with existing programs (includes ambient monitoring) including those carried out by industrial stakeholders such as QNI, Sun Metals, Port of Townsville, Copper Refinery and the Australian Meat Holdings. This alignment will allow for better identification of specific water quality parameters, which will in turn allow for better management of pollutants, including specific trace metals, oil and grease residues and FRP.

The sediment and nutrient loads for the Townsville Thuringowa Region are typically lower than those measured for other catchments of the GBR, such as in the Burdekin (Bainbridge *et al.* 2006a; 2006b) and Mackay Whitsunday (Rohde *et al.* 2006) Regions. When the event mean concentration (EMC) is applied to normalise the data for discharge, the concentrations of nutrients and sediments are comparable to several coastal catchments within the Dry Tropics Region (between the Haughton River and Don River: Bainbridge *et al.* 2006b). Higher resolution input data may be required before SedNet and ANNEX models can provide reliable predictions of sediment and nutrient loads in the region.

The freshwater plumes generated by the Black, Bohle and Ross Rivers impinged on a small number of coral reefs (e.g. middle Reef) within Cleveland and Halifax Bays. TSS concentrations decreased away from the river mouths and were typically less than 20 mg/L by the 10-15 ppt salinity zone (<4 km from river mouths). Most nutrient species also decreased along the salinity gradient. Concentrations of FRP were relatively high compared to other studies of freshwater plumes in the GBR lagoon (Devlin *et al.* 2001). Three herbicides residues (diuron, atrazine and hexazinone) were detected in the Ross River and Sandfly Creek plumes at concentrations (<0.02 µg/L) well below ANZECC and ARMCANZ (2000) ecological protection guidelines. No pesticide residues were detected in the Black and Bohle River plumes. Trace metal concentrations and oil and grease residues were below detection limits in the freshwater plumes.

8. REFERENCES

- ABS 2007. Australian Bureau of Statistics (<http://www.abs.gov.au/website>).
- ANZECC and ARMCANZ 2000. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. Australian and New Zealand Environmental and Conservation Council, Agriculture and Resource Management Council of Australia and New Zealand: Canberra.
- APHA, AWWA and WEF 2005. *Standard methods for the examination of water and wastewater*. 20th edition, eds LS Clesceri, AE Greenberg & AD Eaton, American Public Health Association, American Water Work Association, Water Environment Federation, Washington DC.
- Bainbridge, Z., Brodie, J., Lewis, S., Faithful, J., Duncan, I., Furnas, M. and Post, D. 2006a. *Event-based water quality monitoring in the Burdekin Dry Tropics Region 2004-2005 wet season*. ACTFR Report 06/01 for BDTNRM, Australian Centre for Tropical Freshwater Research, James Cook University, Townsville.
- Bainbridge, Z., Lewis, S., Brodie, J., Faithful, J., Maughan, M., Post, D., O'Reagain, P., Bartley, R., Ross, S., Schaffelke, B., McShane, T. Baynes, L. 2006b. *Monitoring of sediments and nutrients in the Burdekin Dry Tropics Region: 2005/06 wet season*. ACTFR Report No. 06/13 for the BDTNRM. Australian Centre for Tropical Freshwater Research, James Cook University, Townsville. 101pp.
- Bainbridge, Z., Faithful, J., Masters, B. and Fries, N. 2005. WSP: GBR Catchments Water Quality Monitoring. Produced by ACTFR, JCU and Queensland Department of Natural Resources and Water, Mackay for the BDTNRM and MWNRM Community Event Monitoring Programs.
- Belperio, A.P. 1983. Late Quaternary terrigenous sedimentation in the Great Barrier Reef lagoon. In: Baker, J.T. Carter, R.M. Sammarco, P.W. Stark, K.P. *Proceedings of the inaugural Great Barrier Reef Conference*, Townsville, Queensland. JCU Press, pp. 71-76.
- Bowmer, K.H., Fairweather, P.G., Napier G.M. and Scott, A.C. 1995. *Review of data on the biological impact of cotton pesticides*. CSIRO Division of Water Resources, Consultancy Report 95/13.
- Brodie, J., Lewis, S., McCulloch, M. 2007. *Connectivity and Risk: tracing of materials from the upper catchment to the reef*. Report to the Australian Government Marine and Tropical Sciences Research Facility, Townsville.
- Brodie, J., McKergow, L.A., Prosser, I.P., Furnas, M., Hughes, A.O. and Hunter, H. 2003. *Sources of sediment and nutrient exports to the Great Barrier Reef World Heritage Area*. ACTFR Report No. 03/11, Australian Centre for Tropical Freshwater Research, James Cook University, Townsville, 208 pp.
- Brodie, J. and Mitchell, A. 2005. Nutrients in Australian tropical rivers: changes with agricultural development and implications for receiving environments. *Marine and Freshwater Research*, **56**: 279-302.
- Chapman, J.C. and Simmons, B.S. 1990. The effects of sewage on alpine streams in Kosciusko National Park. *Environmental Monitoring and Assessment* **14**: 275-295.
- Devlin, M.J. and Brodie, J. 2005. Terrestrial discharge into the Great Barrier Reef Lagoon: nutrient behaviour in coastal waters. *Marine Pollution Bulletin*, **51**: 9-22.
- Devlin, M., Waterhouse, J., Taylor, J. and Brodie, J. 2001. *Flood Plumes in the Great Barrier Reef: Spatial and Temporal Patterns in Composition and Distribution*. Research Report No. 68. Great Barrier Reef Marine Park Authority, Townsville.

Faithful, J.W. and Finlayson W. 2003. *Water Quality Assessment for Sustainable Agriculture - Tully-Murray Rivers Catchment Area and Granite Creek on the Atherton Tablelands*. ACTFR Report No 03/18 for the Natural Resource Management Board (Wet Tropics) Inc., Innisfail, Project No. 2012015.

Faithful, J., Liessmann, L., Brodie, J., Ledee, E., Sydes, D. and Maughan, M. 2007. Water Quality Characteristics of Waters Draining Different Land Uses in the Tully/Murray Rivers Region ACTFR DRAFT Report No. 06/25, February 2007 Australian Centre for Tropical Freshwater Research. 27pp.

Fentie, B., Duncan, I., Cogle, A.L., Sherman, B.S., Read, A., Chen, Y. and Brodie, J. 2006. Sediment and nutrient modelling in the Burdekin NRM region. Volume 3. **In:** Cogle, A.L. Carroll, C. & Sherman, B.S. (eds.) *The use of SedNet and ANNEX models to guide GBR catchment sediment and nutrient target setting*. Department of Natural Resources Mines and Water. ISBN 1 74172 148 2.

Furnas, M. 2003. *Catchments and Corals: Terrestrial Runoff to the Great Barrier Reef*. Australian Institute of Marine Science, Townsville, Queensland.

Furnas, M. and Brodie, J. 1996. Current status of nutrient levels and other water quality parameters in the Great Barrier Reef. **In:** Hunter, H.M. Eyles, A.G. Rayment, G.E. (eds). *Downstream effects of land use*, Department of Natural Resources, Brisbane, p 9-21.

Furnas, M. and Mitchell, A. 2001. Runoff of terrestrial sediment and nutrients into the Great Barrier Reef World Heritage Area. In: *Oceanographic Processes of Coral Reefs: Physical and Biological Links in the Great Barrier Reef*. Wolanski, E. (Ed). CRC Press, Boca Raton. pp. 37 – 51.

Green, J. and Trett, M.W. 1989. *The fate and effects of oil in freshwater*. Elsevier Applied Science, London.

Guiney, P.D., Sykora, J.L. and Keleti. G. 1987. Environmental impact of an aviation kerosene spill on stream water quality in Cumbria County, Pennsylvania. *Environmental Toxicology and Chemistry*, **6**: 977-988.

Hart, B.T. 1982. *Australian water criteria for heavy metals*. Australian Water Resources Technical Paper 77, Australian Government Publishing Service, Canberra.

Health and Welfare Canada 1980. Selenium. In *Guidelines for Canadian drinking water quality 1978: Supporting documentation*. Supply and Services, Canada, Hull, 541-554.

Horn, A., Joo, M. and Poplawski, W. 1998. *Queensland Riverine Sediment Transport Rates – A Progress Report*. Department of Natural Resources, Brisbane, Queensland.

Hosomi, M. and Sudo, R. 1987. Simultaneous determination of total nitrogen and total phosphorus in freshwater samples using persulfate digestion. *International Journal of Environmental Studies*, **27**: 267-275.

Hunter, H.M., Walton, R.S. and Russell, D.J. 1996. Contemporary Water Quality in the Johnstone River Catchment. **In:** Hunter, H.M., Eyles, A.G. and Rayment, G.E. (eds.) *Proceedings of the National Conference on Downstream Effects of Land Use, 26-28 April, University of Central Queensland, Rockhampton*. Department of Natural Resources, Queensland, Australia, pp 339-345.

Kinsey-Henderson, A. In prep. Target setting scenario modelling using SedNet for the Burdekin River sub-catchments for the Burdekin WQIP. CSIRO Land and Water Client Report for BDTNRM CCI, Davies Lab, Townsville.

Kinsey-Henderson, A. and Sherman, B. 2007. SedNet loads reported in the Meat and Livestock Australia Burdekin SedNet Model for Selected Sites, Improved SedNet Modelling of Grazing Lands in the Burdekin Catchment.

Lankester, A., Dight, I., Brodie, J., Bainbridge, Z. and Lewis, S. 2007. Draft Environmental values and water quality objectives for the estuarine and coastal areas of the Lower Burdekin region. ACTFR and BDTNRM Report for the BDTNRM CCI. 35pp.

McKergow, L.A. Prosser, I.P. Hughes, A.O. Brodie, J. 2005a. Sources of sediment to the Great Barrier Reef World Heritage Area. *Marine Pollution Bulletin*, **51**: 200-211.

McKergow, L. A., Prosser, I. P., Hughes, A. O. and Brodie, J. 2005b. "Sources of sediment to the Great Barrier Reef World Heritage Area." *Marine Pollution Bulletin*, **51**(1-4): 200-211 pp.

Mitchell, A.W., Bramley, R.G.V. and Johnson, A.L.K. 1997. Export of nutrients and suspended sediment during a cyclone-mediated flood event in the Herbert River catchment, Australia. *Marine and Freshwater Research*, **48** (1): 79-88.

Mitchell, A. Lewis, S. Brodie, J. Bainbridge, Z. and Maughan, M. 2007. *Water quality issues in the Burdekin Region*. ACTFR Report No. **07/03** For the Burdekin Dry Tropics NRM Coastal Catchment Initiative.

Mitchell, C., Brodie, J. and White, I. 2005. Sediments, nutrients and pesticide residues in event flow conditions in streams of the Mackay Whitsunday Region, Australia. *Marine Pollution Bulletin*, **51**: 23-36.

NLWRA (National Land and Water Resources Audit). 2002. *Australian Catchment, River and Estuary Assessment 2002*. Volume 1, pp. 1-192. National Land and Water Resources Audit, Commonwealth of Australia, Canberra.

NRA, 1997. *Database extraction of selected pesticides: Registered uses in Australia*, National Registration Authority, July 1997, Canberra.

Packett, R. 2007. A mouthful of mud: the fate of contaminants from the Fitzroy River, Queensland, Australia and implications for reef water policy. In: *Proceedings of the 5th Australian Stream Management Conference. Australian rivers: making a difference*. Eds. Wilson, A.L., Dehaan, R.L., Watts, R.J., Page, K.J., Bowmer, K.H., and Curtis, A. Charles Sturt University, Thuringowa, New South Wales.

Prosser, I.P., Moran, C.J., Lu, H., Scott, A., Rustomji, P., Stevenson, J., Priestly, G., Roth, C.H. and Post, D. 2002. *Regional patterns of erosion and sediment transport in the Burdekin River catchment*. CSIRO Land and Water Technical Report 5/02, CSIRO, Canberra.

Prosser, I.P. Rustomji, P. Young, W.J. Moran, C.J. and Hughes, A. 2001. *Constructing river basin sediment budgets for the National Land and Water Resources Audit*. CSIRO Land and Water Technical Report 15/01, CSIRO, Canberra.

Raimondo, S., Montague, B. and Barron, M. 2007. Determinants of variability in acute to chronic toxicity ratios for aquatic invertebrates and fish. *Environmental Toxicology and Chemistry*, **6** (9): 2019-2023.

Rohde, K., Masters, B., Brodie, J., Faithful, J., Noble, R. and Carroll, C. 2006. *Fresh and Marine Water Quality in the Mackay Whitsunday Region 2004/2005*. Mackay Whitsunday Natural Resource Management Group, Mackay, Australia.

Sherman, B., Brodie, J., Cogle, L. and Carroll, C. 2007. *The appropriate use of catchment models for water quality target setting and land use management*. For: IAHS Symposium on Water Quality and Sediment Behaviour of the Future: Predictions for the 21st Century, 2007.

Sunderam, R.I.M., Cheng, D.M.H. and Thompson, G.B. 1992. Toxicity of endosulfan to native and introduced fish in Australia. *Environmental Toxicology and Chemistry*, **11**: 1469–1476.

Tomlin, C. 1994. *The pesticide manual: A world compendium*. 10th edn, British Crop Protection Council and Royal Society of Chemistry, Bath, UK.

Zweig, R.D., Morton, J.D. and Stewart M.M., 1999. *Source water quality for aquaculture: a guide for assessment*. The World bank, Washington DC.