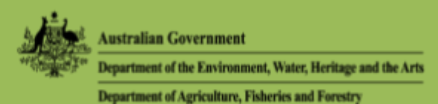


Annan and Endeavour River Freshwater and Estuarine Water Quality Report

An Assessment of Ambient Water Quality and Effects of Land Use
2002 – 2009



CY MAG
Environmental



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March 2012



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CYMAG: Formed in 1992 as the Cooktown Marine Advisory Committee, CYMAG (Cape York Marine Advisory Group) has evolved from that of a purely advisory capacity to a group that concentrates on a diverse range of environmental mapping, monitoring and assessment programmes. Based on local community concerns, CYMAG developed and implemented a community based water quality monitoring project for the Annan and the Endeavour Rivers in 2002. Monthly monitoring of these rivers has created the first extensive database of water quality monitored on a regular basis on Cape York Peninsula. This baseline data has allowed us to observe impacts that have occurred to these rivers from mining and other developments within the catchments. Data from all of our water quality monitoring projects is entered in the QLD DERM database making it available to natural resource managers and other land users. (Ian McCollum, CEO)

Acknowledgements

From 2002 to 2005 all work was conducted by CYMAG & SCYC volunteers. Logistical support, boats, vehicles, fuel, monitoring design and project management were contributed by local scientists and volunteers. Initial funding for monitoring equipment came from the Great Barrier Reef Marine Park Authority (GBRMPA). Additional funding came from Envirofund and Bundaberg Rum (2005), Natural Heritage Trust (NHT2) and Caring For Our Country (CFOC) (2006 - 2009). The Queensland Environmental Protection Agency (now DERM) provided analytical support while SCYC provided on-going field assistance. This report was funded by the CFOC Reef Rescue Program.

CYMAG Environmental would like to thank:

- Andrew Moss, Mark Davidson & Sharmane Wickings (DERM)
- SCYC, especially Jason Carroll for assistance with Fieldwork and Map Production (Figures 1, 3 and 4)
- FSS EnvWaters Laboratory; ALS, and Entox for sample analyses
- All the many local volunteers, and the Bana Yalanji Rangers

Cover photos: Aerial photos: Annan River mouth, Endeavour River mouth and Endeavour River estuary (Peter Pal). Ian McCollum & Christina Howley monitoring by boat & nutrient sample bottles (Kerry Trapnell)

Photo above right: Water Quality Multi-meter (Kerry Trapnell)

Disclaimer

While reasonable efforts have been made to ensure that the contents of this document are factually correct, the authors, reviewers and CYMAG Environmental do not accept responsibility for the accuracy of the contents or for the results of any use of, or reliance on, the contents of this report.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	7
1 INTRODUCTION	10
2 BACKGROUND INFORMATION	11
2.1 Catchment Area	11
2.2 Climate & Rainfall	12
2.3 Topography and Hydrology	13
2.4 Aquatic Ecosystems	13
2.5 Land Use	14
2.6 Potential Threats to Water Quality	14
2.7 Previous Water Quality Monitoring & Research	16
3 CYMAG/SCYC WATER QUALITY MONITORING PROGRAM	17
3.1 Aims of program	17
3.2 Sampling Design	17
3.3 Monitoring Locations & Timing	18
3.4 Ambient Water Quality Monitoring & Analysis Methods	21
3.5 Land-use Impact Assessment Methods & Analyses	22
3.6 Quality Control	25
3.6.1 Field Sampling QC Methods	25
3.6.2 Nutrients Data Quality Summary	26
3.6.3 Chlorophyll- α Data Quality Summary	26
3.6.4 Contaminant & Metals Analysis Data Quality Summary	26
4 WATER QUALITY RESULTS	27
4.1 Ambient Water Quality Parameters	27
4.2 Statistics	27
4.3 Temperature	31
4.4 Salinity & Conductivity	31
4.5 pH	33
4.6 Dissolved Oxygen	35
4.7 Turbidity	36
4.8 Nutrients	39
4.8.1 Annan River	39
4.8.2 Endeavour River	40
4.8.3 Dry Season, Wet Season and Flood Event Nutrient Levels	41
4.8.4 Sediment Nutrients	43
4.9 Chlorophyll- α	45
4.10 Metals Concentrations	46
4.10.1 Annan River	46
4.10.2 Endeavour River	49
4.10.3 Jeannie River	52
4.11 Bacteria	52
5 LAND USE IMPACT ASSESSMENT RESULTS	54
5.1 Annan River Land Use Assessment	54
5.1.1 Collingwood Bluestone Tin Mine	54
5.1.2 Vehicle Emissions and Boat Fuel	56
5.1.3 Acid Sulphate Soils	57
5.2 Endeavour River Land Use Assessments	57
5.2.1 Agricultural Land-Use	58
5.2.2 Cooktown Sewerage Treatment Plant Effluent Outfall	60
5.2.3 Hope Vale Sewerage Treatment Plant	62

5.2.4	Cooktown Rubbish Tip	63
5.2.5	Cooktown harbour and surface water run-off	63
6	SUMMARY OF RESULTS	66
6.1	Endeavour River	66
6.2	Annan River	68
6.3	Jeannie River.....	70
6.4	Conclusion	71
7	RECOMMENDATIONS.....	72
8	REFERENCES	73
	APPENDIX A – Annan & Endeavour River Sample Location Photos.....	74
	APPENDIX B – Methods And Equipment Details	77
	APPENDIX C – CYMAG QAQC Samples & Data Validation Results.....	79
	APPENDIX D – Water Quality Data Tables	93
	APPENDIX E – Passive Sampler Pah And Pesticide/ Herbicide Analyte List... 114	

FIGURES

Figure 1:	Annan & Endeavour Catchment Area & Jeannie River.....	11
Figure 2:	Mean Monthly Rainfall (mm)	12
Figure 3:	Endeavour River Water Quality Monitoring Locations.....	20
Figure 4:	Annan River Water Quality Monitoring Locations.....	20
Figure 5:	Annan & Endeavour River Temperature Box Plots.....	31
Figure 6:	Annual Salinity Cycles at Endeavour River Estuary Site ER-01	32
Figure 7:	Endeavour River Site Salinity & Conductivity Box Plots	33
Figure 8:	Annan River Freshwater Seasonal Conductivity Cycles (2005-2008)... 33	
Figure 9:	Annan & Endeavour River pH Box Plots	34
Figure 10:	Endeavour River Estuary Site ER-01 Seasonal pH Cycle	34
Figure 11:	Seasonal pH Cycle at Annan River Freshwater Sites.....	35
Figure 12:	Annan & Endeavour River Dissolved Oxygen Box Plots.....	36
Figure 13:	Turbidity Cycle at Endeavour Estuary Site ER-01	37
Figure 14:	Turbidity Cycle at Annan River Freshwater Site AR-02	37
Figure 15:	Annan & Endeavour Estuary Turbidity Box Plots: Dry Season, Wet Season and Flood Events.....	38
Figure 16:	Annan River Turbidity Box Plots.....	38
Figure 17:	Endeavour River Turbidity Box Plots.....	39
Figure 18:	Annan River Total & Dissolved Nutrients Box Plots (by Site)	40
Figure 19:	Endeavour River Nutrient Box Plots (by Site).....	41
Figure 20:	Phosphorous Box Plots: Dry Season, Wet Season and Flood Events.. 42	
Figure 21:	Nitrogen Box Plots: Dry Season, Wet Season and Flood Event	43
Figure 22:	Walker Bay Sediment Sample Locations.....	44
Figure 23:	Endeavour River Sediment Sample Locations.....	44
Figure 24:	Annan & Endeavour Chlorophyll- α Box Plots	45
Figure 25:	Seasonal Chlorophyll- α Cycles at Endeavour Estuary Site ER-04..... 46	
Figure 26:	Seasonal Chlorophyll- α Cycles at Annan Freshwater Site AR-02	46
Figure 27:	Annan River – Bluestone Mine Impact Sample Locations	54
Figure 28:	Turbidity Levels at AR-03	55
Figure 29:	Endeavour River Contaminant Sample Locations	58
Figure 30:	Linear Regression for Total Nitrogen, Total Phosphorous, Nitrates and Ammonia Concentrations over time (2005-2008).....	61
Figure 31:	Graph of ER-01 Chlorophyll- α with Linear Regression Trendline	62

TABLES

Table 1: Annan River Water Quality Monitoring Locations	18
Table 2: Endeavour River Water Quality Monitoring Locations	19
Table 3: Jeannie River Water Quality Monitoring Locations.....	19
Table 4: Potential Land Use Impact Assessments and Contaminant Analyses	23
Table 5: Number of Grab Samples Collected for Each River & Analysis Type ..	24
Table 6: Comparison of Ambient Water Quality in the Annan, Endeavour & Jeannie Rivers (2002-2009)	29
Table 7: Minimum, Maximum and Median Nutrient & Chlorophyll-a Concentrations	30
Table 8: Walker Bay (Annan River) Sediment Sample Analytical Results- Nutrients (mg/kg).....	44
Table 9: Endeavour River Estuary Sediment Sample Analytical Results – Nutrients (mg/kg).....	44
Table 10: Minimum and Maximum Total & Dissolved Metals Concentrations - Annan River Sites	48
Table 11: Minimum and Maximum Metals & Mercury Concentrations- Annan River Sediments (mg/kg).....	49
Table 12: Minimum and Maximum Total & Dissolved Metals Concentrations - Endeavour River Sites	51
Table 13: Annan & Endeavour River Bacteria Sample Results	53
Table 14: Annan River Water Sample Analytical Results- TPH & PAH.....	56
Table 15: Annan River Sediment Sample Analytical Results- TPH & PAH	57
Table 16: Herbicides detected in Endeavour River Passive Samplers	59
Table 17: Mean and Median Annual Nutrient & Chlorophyll concentrations Endeavour River Site ER-01: 2005-2008	60
Table 18: Endeavour River at Hope Vale STP: Nutrient Concentrations (mg/L)	63
Table 19: Petroleum Hydrocarbons Detections- Endeavour River Water Grab Samples (µg/L)	65
Table 20: TPH and PAH Detections in Endeavour River Sediments (mg/kg)	65
Table 21: PAHs detected in Endeavour River Passive Samplers	66

APPENDIX D: WATER QUALITY DATA TABLES:

Table 1: Comparison of Ambient Water Quality at Endeavour River Monitoring Locations (2002-2009).....	93
Table 2: Comparison of Ambient Water Quality at Annan River Monitoring Locations (2002-2009).....	94
Table 3: Minimum, Maximum And Median Nutrient Levels At Annan And Endeavour River Sites	95
Table 4: Mean, Median, Minimum and Maximum Nutrient Level; Wet Season, Dry Season and Flood Events	96
Table 5: Annan River Estuary (AR-01) Water Sample Analytical Results –Total & Dissolved Metals and Mercury	97
Table 6: Annan River Freshwater Sample Analytical Results – Total & Dissolved Metals and Mercury	98
Table 7: Annan River Sediment Analytical Results- Metals & Mercury	100
Table 8: Walker Bay Sediment Analytical Results – Metals & Mercury.....	100
Table 9: Endeavour River Water Sample Results- Metals & Mercury	101
Table 10: Endeavour River Sediment Sample Results – Metals and Mercury...	103

Table 11: Jeannie River Water Sample Results- Metals & Mercury (mg/L)	105
Table 12: Metals Concentrations Upstream and Downstream from the Bluestone Tin Mine and Tailings Dam.....	106
Table 13: Endeavour River Analytical Results – OC/OP Pesticides in Water ...	108
Table 14: Endeavour River Water Sample Analytical Results – Herbicides.....	109
Table 15: Pesticides, Herbicides and PAH Analytical Results for Endeavour River Passive Samplers.....	110
Table 16: Endeavour River Sediment Analytical Results- Phenoxyacetic Acid Herbicides & Triazines (mg/kg)	111
Table 17: Endeavour River Sediment Analytical Results- Organochlorine and Organophosphate Pesticides (mg/kg)	111
Table 18: Endeavour River Estuary Analytical Results- Hydrocarbons and Solvents in Water Grab Samples (µg/L).....	112
Table 19: Endeavour River Estuary Analytical Results- Hydrocarbons in Sediments (mg/kg).....	113
APPENDIX E- Passive Sampler PAH, Pesticide/ Herbicide Analyte List	114

Executive Summary

The Cape York Marine Advisory Group (CYMAG) and South Cape York Catchments (SCYC) monitored ambient water quality in the Annan & Endeavour Rivers between July 2002 and May 2009, and the Jeannie River between 2007 and 2009. The Annan & Endeavour Rivers are located near Cooktown in southeast Cape York Peninsula between latitude 15° 11' to the north and 15° 53' to the south, and longitude 145° 00' to 145 ° 21'. The Jeannie River is an undeveloped catchment located 50 km north of Cooktown at 14° 39' and 144° 55'.

Prior to 2002, there had been little monitoring of water quality in the Annan, Endeavour or Jeannie Rivers and no known monitoring of estuary waters. The aim of the CYMAG monitoring program was to document baseline water quality in these rivers during the wet and dry seasons and to assess for potential anthropogenic impacts, including effluent outfall in the Endeavour River from a new sewerage treatment plant (STP) and the Bluestone tin mine in the Annan River catchment.

Monitoring was conducted monthly at six Endeavour River estuary sites and five Annan River freshwater and estuary locations. Four Jeannie River estuary sites and one freshwater site were monitored quarterly. Monitoring included: temperature, conductivity, salinity, dissolved oxygen, and pH (2002 – 2009), and nutrients and chlorophyll-a (2005- 2008). Water and sediment grab samples were analysed annually for metals, pesticides, herbicides and hydrocarbons, and 30-day passive samplers for herbicides and PAHs were deployed in the Endeavour River during the 2008/2009 wet season. Additional monitoring has occurred at some sites since 2009.

Key Outcomes from this program

1. For the first time a set of water quality guidelines have been developed that are specifically attuned to the conditions in a south-eastern Cape York estuary
2. Dramatically different water quality conditions were documented in the wet and dry season, particularly during floods, and this must be considered when setting guidelines and assessing anthropogenic impacts.
3. Recognition that impacts from dry season disturbances generally do not show up until the following wet season (as was the case with the Bluestone Tin Mine on the Annan River). This has major implications for monitoring land-use impacts on rivers.
4. We believe that this study represents an example of how an independent community driven water quality monitoring program can and should be run.
5. At the time of the program's inception there were a number of community concerns regarding water quality threats in this region and the program was established as an independent community driven program to evaluate these perceived threats using best practice scientific methods. As a result of the rigour applied to the program we were able to establish that:
 - a. The perceived threat to water quality from the Cooktown STP established in 2006 has not been substantiated. Monitoring of nutrients, chlorophyll-a and bacteria showed no evidence (as of 2009) of impacts from effluent outfall.
 - b. Concerns regarding potential impacts on the Annan River from the Bluestone Tin Mine were found to be justified, with significant increases in turbidity and metals recorded. Thanks largely to community pressure, the mine was required to alter operations to reduce the impact on water quality.
6. It is argued that these two examples alone demonstrate the benefit to the community of an independent water quality monitoring program.

7. The dataset developed as part of this program will now form an invaluable baseline against which future threats to water quality in the region can be evaluated, and from which additional freshwater guidelines can be developed.
8. The available data from the relatively pristine Jeannie River estuary demonstrate the need for understanding site specific geomorphic and hydrodynamic characteristics in the interpretation of water quality data. At face value some of the data could be interpreted as indicating poor WQ, requiring remediation – when in fact it is likely that they are the natural conditions for that system.

Results Summary

Endeavour River Estuary

- Temperatures ranged from 21°C (July) to 33°C (February and March)
- Salinity ranged from 0.0 ppt (during flood events) to a maximum of 37.3 ppt.
- pH ranged from 5.31 to 8.37 (median 7.70). Low pH levels in the upper estuary may be related to disturbance of acid-sulphate soils by feral pigs.
- Dissolved oxygen ranged from 60.1% – 126.7% (median 82.9%).
- Turbidity ranged from 0 NTU to 456 NTU (median 4.7 NTU). The dry season mean was 4.3 NTU compared to 36.4 NTU in the wet season. Elevated turbidity levels were recorded in the lower estuary as a result of erosion from earthworks in the Cooktown area.
- Nutrient concentrations were generally low but median dissolved nitrogen values in the upper estuary exceeded the relevant water quality guidelines.
- Total nitrogen and phosphorous and dissolved nitrogen levels were 1.5 to 3 times higher during the wet season and up to 4 times higher during flood events. Filterable reactive phosphorous did not change significantly.
- Chlorophyll ranged from 0.01 µg/L to 3.64 µg/L. Maximum chlorophyll- α concentrations in the estuary occurred immediately after wet season floods.
- Bacteria concentrations in the lower estuary were below 100 cfu/100ml in the wet and dry seasons. Bacteria levels were highest (490 - 690 cfu/100ml) in the upper estuary, possibly associated with pigs and cattle.
- Zinc, chromium, copper and lead were slightly elevated above background in water and sediment samples in the Cooktown harbour. Mercury detected at 1.1 mg/kg in sediments at Four Mile Creek (below the Cooktown rubbish tip) exceeded the “high range” of the ANZECC 2000 sediment quality guidelines.
- Clopyralid, a broad leaf herbicide, was detected at 0.28 mg/kg in sediment from the Endeavour estuary. The herbicides diuron, atrazine and simazine were detected in 30-day passive samplers at low (ng/L) concentrations, and are not considered a threat to aquatic organisms.
- Galaxolide, a fragrance contained in shampoos and cleaning products, was detected at 3 ng/L, and could be entering the estuary via STP effluent.
- A range of PAHs, including the carcinogenic benzo(a)pyrene, and low concentrations (180 µg/L) of petroleum hydrocarbons were detected in water and sediment samples from the Cooktown harbour.

Annan River

- Temperatures in the Annan River ranged from 18.3°C to 31.3°C.
- Salinity within the estuary ranged from 0.0 ppt during wet season flood events to 35.7 ppt during the dry season.
- Conductivity at freshwater sites ranged from 0.012 mS/cm to 0.120 mS/cm (median 0.062 mS/cm).
- pH values ranged from 5.54 to 8.68 with a freshwater median of 6.61 and median estuary pH of 7.84.

- Dissolved oxygen levels ranged from 56.3% – 110.8%, with median values of 89.9% (freshwater sites) and 88.8% (estuary).
- Turbidity ranged from 1 NTU to 704 NTU. Mean turbidity values were 4.1 NTU (dry season) and 43.5 NTU (wet season). Maximum values were recorded at the Little Annan Bridge downstream from extensive erosion gullies.
- Median nutrient values for Annan estuary and freshwater sites were below the water quality guidelines.
- Total and dissolved nutrient levels showed significant seasonal differences. Mean nitrogen oxide concentrations were 10 to 20 times higher during the wet season, and 15 to 34 times higher during flood events than dry season means.
- Chlorophyll- α concentrations ranged from <0.01 $\mu\text{g/L}$ to 5.61 $\mu\text{g/L}$. Maximum chlorophyll- α levels occurred at freshwater sites at the end of the dry season.
- Elevated levels of zinc, copper and arsenic were detected in the Annan below the Bluestone mine tailings dam. Turbidity and nutrient levels (possibly attributed to nitrogen- and phosphorous-based explosives) also significantly increased downstream from the mine during the 2006 and 2007 wet seasons.
- Bacteria counts in the Annan increased during the wet season but all samples from within the river were below 100 cfu/100ml. Bacteria levels >8000 cfu/100ml were detected at Keatings Lagoon before a pig fence was constructed in 2008. Bacteria levels have decreased since 2008.

Jeannie River

Insufficient data exists to capture the full seasonal range of water quality in the Jeannie River, however the water quality recorded was similar to that of the Endeavour estuary under ambient conditions. The Jeannie is much more narrow and shallow than the Endeavour River, with more extreme conditions during the dry season. The upper estuary became hypersaline (maximum 47.3 ppt) at the end of the dry season when freshwater in-flow ceased. Dissolved oxygen levels were below 50% on two occasions and reached as low as 17% saturation in the upper estuary. Maximum ammonia concentrations recorded during the dry season were significantly higher than those recorded in the Annan or Endeavour. Chlorophyll- α concentrations in the upper and mid-estuary were also higher than those recorded in the Annan and Endeavour Rivers. Copper and zinc concentrations exceeded the ANZECC 2000 water quality guidelines. These values appear to represent the natural dynamics of this system.

Conclusions

The Endeavour and Annan Rivers are generally in good condition with very low contaminant levels. Metals, hydrocarbons, herbicides and ambient nutrient levels detected in the Annan and Endeavour Rivers are not likely to pose a threat to aquatic ecosystems at the concentrations detected in water and sediment samples. The concentration of mercury detected in one Endeavour River estuary sample has a 50% chance of affecting aquatic biota, according to the ANZECC 2000 guidelines.

Elevated turbidity levels were recorded during the wet season in both the Annan and Endeavour Rivers as a result of various developments including tin mining in the Annan catchment and earthworks in the Cooktown region. The significance of the increased erosion in terms of total sediment and nutrient loads leaving the estuaries is unknown. Erosion is also a threat in the Jeannie River catchment as evidenced by an extensive gully system that is likely to contribute significant levels of sediments to the river and marine receiving environment.

1 INTRODUCTION

Scientists and volunteers from the Cape York Marine Advisory Group (CYMAG) and South Cape York Catchments (SCYC) monitored ambient water quality in the Annan & Endeavour Rivers between July 2002 and May 2009. The aim of the program was to document ambient water quality and to assess potential anthropogenic effects upon water quality. Monitoring of water quality was initiated by CYMAG due to community concerns over perceived changes in water clarity and the potential impacts of future developments including sewerage effluent and mining.

In 2005/2006 the Cooktown sewerage system was expanded and upgraded to treat sewerage from the entire town area. Effluent from the sewerage treatment plant (STP) is released near the mouth of the Endeavour River. Also in 2005, a tin mine re-opened at Shiptons Flat in the Annan River catchment. The mine and tailings dam were located upstream from the Cooktown drinking water supply on the Annan and the potential impact on the Annan river is an on-going concern for the Bana Yalanji Traditional Owners. One of the primary goals of this project was to gather baseline water quality data prior to the STP upgrade and commencement of mining and to monitor for changes in water quality.

Water quality monitoring was conducted at six Endeavour River estuary sites and five Annan River estuary and freshwater sites. Monitoring was conducted quarterly between 2002- 2004, and monthly from 2005 – 2008. During the 2005/2006 and 2007/2008 wet seasons, water and sediment grab samples were analysed for a range of contaminants including metals, pesticides and petroleum hydrocarbons. Passive herbicide samplers were deployed in the Endeavour River for 30 days during the 2008/2009 wet season. On-going monitoring at specific sites has occurred irregularly since 2009.

In addition, quarterly water quality monitoring was conducted at the Jeannie River between December 2007 and May 2009. The Jeannie River is an undeveloped catchment approximately 50 km north of the Endeavour River and is a proposed Wild River. Mining for tin in the upper catchment has also been proposed.

This report provides an overview of the results of this monitoring program, including ambient water quality in the Annan and Endeavour Rivers over the 2002 – 2009 sampling period and the effects on water quality from various land-uses within the catchment.

2 BACKGROUND INFORMATION

2.1 Catchment Area

The Annan & Endeavour Rivers are located in southeast Cape York Peninsula between latitude 15° 11' to the north and 15° 53' to the south, and longitude 145° 00' to 145 ° 21' (**Figure 1**).

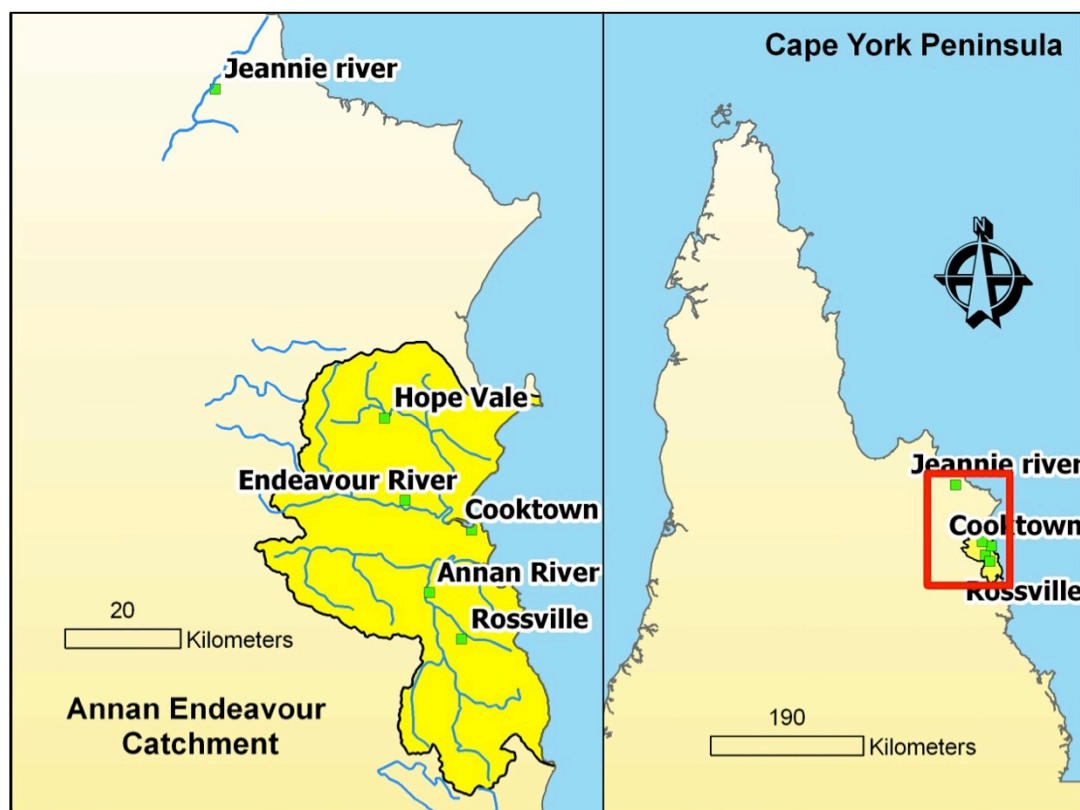


Figure 1: Annan & Endeavour Catchment Area & Jeannie River

The Annan River catchment area covers 750 km². The Annan originates in the Northern Wet Tropics World Heritage Area, flowing north from Mt. Misery, Mt Poverty, Mt Romeo, Mt McMillan and Mt Finnegan. At the confluence of Oakey Creek, the Annan heads east and becomes tidal, winding approximately 13 km to the coast at Walker Bay, 8 km south of Cooktown. Flow in the Annan is derived year-round from Wallaby Creek and the Little Annan River and seasonally from Mungumby, Trevethan and Oakey creeks.

The Endeavour River has a catchment area of 1315 km². The Endeavour is fed by three main tributaries, the North and South branches and the Right Branch (also called the North Arm) flowing past Hope Vale. The overall direction of flow is to the southeast with the Endeavour reaching the sea at Cooktown.

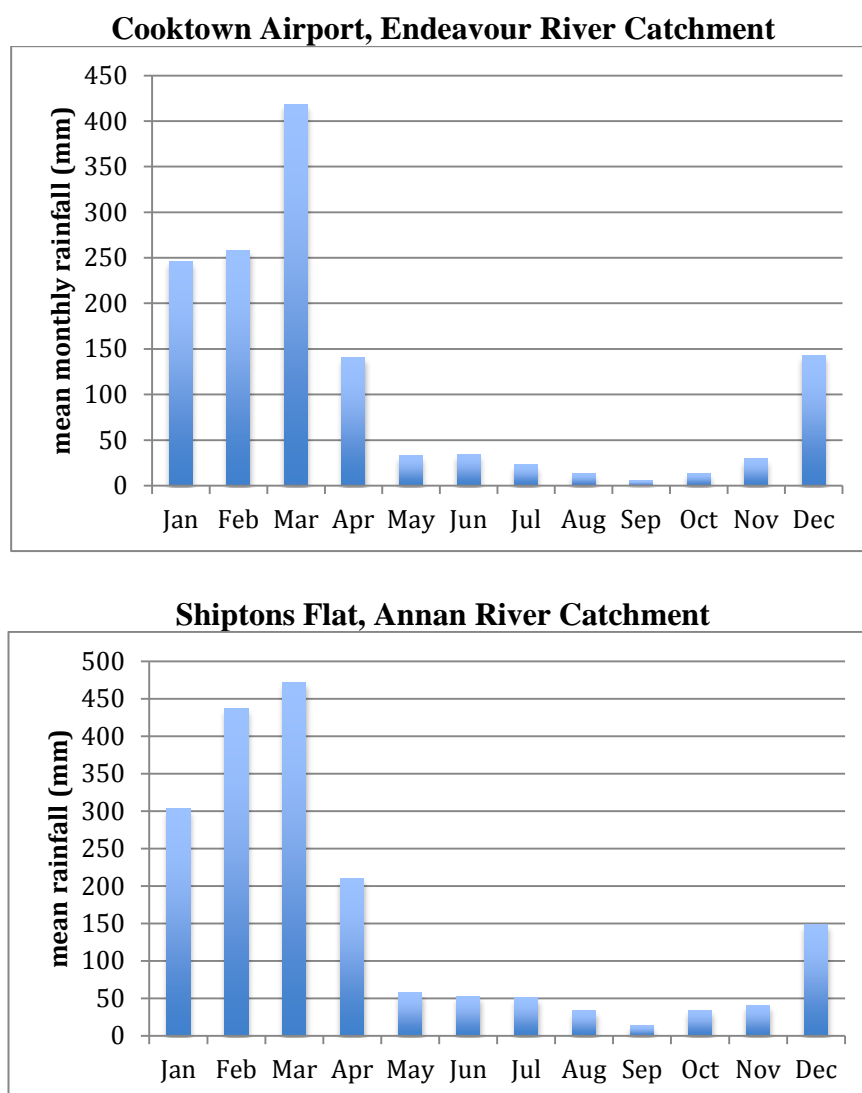
The Jeannie River Basin has a catchment area of 3755 km² (National Land and Water Resources Audit, 2000); however this area includes the Starcke and McIvor Rivers. The Jeannie is a small river with the main branch flowing for approximately 43 km to the northeast starting at an elevation of 230m. Many

tributaries flow into the Jeannie from Cape Melville to the north and the mountains to the west.

2.2 Climate & Rainfall

The Annan and Endeavour catchments experience dry winters and wet summers. The wet season is generally from December to April, with summer monsoons and occasional tropical cyclones, and the dry season from May to November with only occasional showers. Showers continue regularly until August in the Wet Tropics region of the southern Annan Catchment.

The annual rainfall for Cooktown ranges between 1600 mm to 2000 mm. Mean monthly rainfall at the Cooktown Airport ranges from 383 mm in March to 14.4 mm in September (BOM). The Wet Tropics section of the southern Annan catchment experiences higher rainfall than the northern catchment. Monthly rainfall patterns for the Annan and Endeavour catchments are presented in **Figure 2**.



**Figure 2: Mean Monthly Rainfall (mm)-
Annan and Endeavour River Catchments, 2003 – 2009 (BOM)**

Mean annual maximum temperature ranges from 32°C in December to a mean annual minimum of 17.9°C in July (Bureau of Meteorology). Temperatures reach as low as 10°C in the mountain areas to the south (Carroll et al 2007). Strong southeasterly trade winds predominate between April and October. From November to March northeasterly winds become more frequent, often associated with monsoonal troughs.

2.3 Topography and Hydrology

The Trevethan Range to the southeast and the Finlayson Range to the south dominate the topography of the upper Annan River catchment. The highest peak is Mt Finnegan with an elevation of 1146 m. Oakey Creek is separated from the upper Annan Catchment by the Barron's Range, which has a lower relief and maximum elevation of 406 m. The remainder of the Annan Catchment north of Black Mountain is relatively flat.

The Endeavour Valley topography is dominated by the sandstone escarpment of the Henderson Range to the west and by seven low relief peaks (330m -369m) from Mt Unbelievable to Tabletop Mountain to the north of the Endeavour River. The Right Branch is separated from the other branches of the Endeavour River by these seven peaks. The highest point is Henderson's Lookout (450 m) (Carroll et al 2007).

The Endeavour River North Branch is fed from perennial springs in the sandstone escarpment to the north west of Cooktown. North Branch tributaries flow south past Isabella Falls and the Endeavour Falls. The South Branch originates behind Henderson's Lookout and flows east to join the North Branch near the Endeavour Falls, approximately 30 km upstream from the mouth. The combined branches flow east past the small town of Marton until the river reaches the sea at Cooktown. The Right Branch of the Endeavour originates north of Hope Vale and flows south past Hope Vale and to the east of Mt Unbelievable and Mt Surprise to join the Endeavour River estuary 10 km upstream from its mouth. The Endeavour River tidal influence reaches up to 20 km upstream.

2.4 Aquatic Ecosystems

Maintenance of good water quality and quantity is necessary for the preservation of aquatic ecosystems in the rivers, estuaries and the Great Barrier Reef. In 2003, the Annan River and Walker Bay became a Declared Fish Habitat Area for "the protection of valuable commercial, recreational and Indigenous fisheries' resources and the management of diverse habitats in near pristine condition". The habitat values listed include mangrove forests with at least 11 species dominated by *Rhizophora* and *Ceriops*; salt couch flats; sand and mud flats; rock bars; seagrass beds; coral reefs; and rocky headlands (Sheppard and Helmke 1999).

Walker Bay at the mouth of the Annan River supports extensive and diverse seagrass meadows. The Endeavour River estuary supports a number of smaller seagrass meadows from the mouth of the river up as far as Four Mile Creek. These seagrass meadows support local commercial and recreational fisheries and provide food for marine turtles and dugongs.

Reefs such as Dawson and Cowlshaw, approximately 6.5 km and 8 km from the mouth of the Annan, and Egret and Boulder Reef, less than 20 km from the Endeavour River mouth, are subjected to wet-season run-off from the Annan & Endeavour Rivers. Changes in the amount of sediment, nutrients, or other contaminants in run-off could impact these coral reef and seagrass ecosystems.

2.5 Land Use

The Endeavour River Catchment has been subject to more development than the Annan, including residential development at Cooktown (pop. 1515), Marton (pop. 200) and Hope Vale (pop. 781). Small-scale agriculture (including passionfruit, mangos and a turf farm) and cattle grazing occurs in the Endeavour Valley along the North and South Branch. The Cooktown Rubbish Tip and Sewerage Treatment Plant are located adjacent to the Endeavour River estuary. The Cooktown harbor supports a small commercial and recreational fishing fleet and visiting boats. The harbor also has a slipway for boat maintenance and several jetties selling fuel.

The small communities of Rossville and Helenvale (combined pop. 288) are located along the Annan River and Wallaby Creek (2006 ABS Census data). These houses rely primarily on domestic septic systems and leach fields. The Rossville Rubbish Tip is located on top of a small hill south of Rossville, but stopped receiving waste in 2003. A small creek (Three Jim Creek) runs past the rubbish tip into the Annan River approximately 2 km upstream from Rossville. Extensive mining for tin, gold and silver has occurred over the past 100 years in the mountains in the southern Annan catchment. Tin mining at the Bluestone Mine occurred between January 2006 and 2008. Cattle graze over much of the Annan catchment area.

A reservoir on the Annan River downstream from the Little Annan Bridge supplies town water for Cooktown. Rossville & Helenvale residents obtain water from Wallaby Creek or the Annan River, rainwater tanks and groundwater bores. Hope Vale residents obtain water from a reservoir on the Endeavour River Right Branch.

The Jeannie River is a relatively undeveloped catchment. Cattle grazing and tin mining have occurred historically and feral cattle are a common site along the river. A new tin mine has been recently proposed for the mountains of the upper catchment. There are no major roads but several dirt tracks criss-cross the catchment. A former gravel pit located on the south side of the river has created a major erosion gully.

2.6 Potential Threats to Water Quality

Prior to the CYMAG Monitoring Program, there had been little monitoring of water quality in the Annan or Endeavour Rivers. What data did exist comprised one-off research projects or irregular monitoring at DERM stream flow gauging stations. To the best of the author's knowledge no estuary sampling had been conducted.

Water quality in these rivers was generally assumed to be near pristine, yet the local communities were concerned about changes they had observed over the years. The results from a 2005 SCYC survey of local stakeholders showed that 71% of respondents had either a high or medium level of concern regarding water quality in the Catchment area (Carroll et al 2007). Community surveys have identified a number of specific concerns, including the following:

- Sewerage, Rubbish, & Oil Spills from boats
- Oil & fuel run-off from land based pollution
- Erosion & siltation from cleared land & dirt roads
- Sewerage effluent outfalls into Endeavour river
- Run-off from Cooktown & Rossville rubbish tips
- Pollution from cattle manure entering waterways and erosion from cattle grazing
- Impacts from unmanaged camping along waterways
- Mining Impacts
- Feral Pigs in waterways
- Disturbance of Acid Sulphate Soils
- Fertilizer and other agricultural chemical run-off from farms
- Ash from fires

Specific developments that were monitored as part of this project included the Bluestone tin mine and the Cooktown sewerage treatment plant upgrade.

Collingwood Bluestone Tin Mine

The Collingwood Bluestone Tin Mine is located in the Annan River catchment at Shiptons' Flat. Earthworks at the mine began in 2005. Production commenced in January 2006 and it was Australia's main tin producer through 2007. Since 2008, the mine has ceased operations, however the tailings dam remains and continues to release water into the Annan River. CYMAG and SCYC scientists received reports and photos of waste oil spills and poor erosion control works at the mine.

Cooktown Sewerage Treatment Plant

In 2005 the Cooktown Sewerage Treatment Plant (STP) was upgraded from a small secondary treatment plant which serviced only commercial properties on the main street of Cooktown, to a tertiary treatment plant that services the entire town and has a capacity of 10,000 persons. The plant is an IDEA (Intermittent Decant Extended Aeration) Plant, which includes treatment with liquid aluminium sulphide to remove phosphates and sodium hydroxide to raise the effluent pH. UV light is used to sterilise the effluent before it is released into the estuary.

The new STP began releasing effluent into the Endeavour estuary approximately 100m upstream from ER-01 in August 2005, with a rolling increase in effluent volume as households connected to the STP in the following years. The daily volume of effluent released in July 2010 (during peak visitor season) was approximately 500 kilolitres. Effluent is released during both outgoing and incoming tides.

2.7 Previous Water Quality Monitoring & Research

In addition to the CYMAG monitoring project, monitoring of water quality and water quantity in the Annan and Endeavour Rivers has been conducted by:

- Qld Dept of Environment, Resources and Mines (DERM): stream flow and water quality opportunistically
- Cook Shire Council (CSC): Monthly water quality monitoring 1 km upstream from sewerage effluent outfall at Endeavour River (1998-2005); on-going monitoring 500m upstream and downstream from outfall

Department of Environment, Resources and Mines (previously NRMW): DERM monitors two gauging stations in the Annan-Endeavour Catchment. These are located at Beesbike in the upper Annan Catchment area (monitored since 1990), and Flaggy Creek on the Endeavour River (monitored since 1958). Water quality sampling conducted on an irregular basis at the gauging stations generally has included conductivity, pH, dissolved ions and nutrients. The NRMW water-gauging network previously included water-gauging stations on the Annan River at Mt Simon, and on the Endeavour River at Hazelmere and Jensen's Crossing.

Very limited interpretation and reporting of the NRMW water quality data has been undertaken. Grinter & Hunter (2005) analysed water quality data from the Beesbike location in 2003-2004 and reported that "the Annan River was found to have good condition ratings, consistent with ecological health determined by Wet Tropics guideline values, for electrical conductivity, total nitrogen, total phosphorous and turbidity".

Cook Shire Council: CSC monitored water quality on a monthly basis between 1998 and 2005 (prior to the STP upgrade) approximately 1 km upstream from the sewerage treatment plant outfall near the mouth of the Endeavour River.

The results were reviewed by SCYC and compared against the Queensland Water Quality Guidelines for Wet Tropics estuaries (Qld 2009). The mean total phosphorous concentration, and all ammonia sample concentrations fell outside of the ANZECC 2000 guidelines for the protection of aquatic ecosystems; however maximum ammonia concentrations also exceeded the total nitrogen concentration, indicating sample contamination.

CSC has continued to monitor water quality in the vicinity of the upgraded STP outfall; however the results have not been reviewed for this report.

Water Quality Research

Hart et al. (1988) published a report on water quality in the Annan River during a major flood event. The results of the report indicated that during flood conditions, river water quality was influenced predominantly by surface water run-off and the flushing of ions from surface soils. Heavy metals were mostly transported in particulate forms (Fe- 99%; Mn- 95%; Pb, Zn & Sn- 80%; Cu- 60%), while dissolved metal concentrations were low and changed little with flow. At low river flow, water quality was dominated by groundwater flow into the river systems.

Eyre & Davies (1996) conducted an assessment of suspended sediment and nutrient concentrations during the dry season (1994) and wet season (1995) at a number of locations in the upper Annan River Catchment area. They compared these results with data from more heavily modified north Queensland Catchments and from the more pristine Jardine River. They reported that particulate inorganic phosphorous and dissolved nitrate concentrations showed a clear relationship to the level of disturbance in the different catchments. The Annan River showed significantly higher suspended sediment levels than the Jardine, Daintree or Moresby Rivers during the wet season. (The Annan and Jardine Rivers are not similar in relief or geology, so any differences may not be related to disturbance.)

3 CYMAG/SCYC WATER QUALITY MONITORING PROGRAM

3.1 Aims of program

Monitoring of the Annan and Endeavour Rivers was designed to gather ambient water quality data from representative locations across the catchment in order to establish baseline water quality in these systems during the wet and dry seasons. This baseline data is required to assess future changes in water quality resulting from developments within the catchment. Sampling was also conducted to test for potential impacts upon water quality from current land use.

The objectives of the CYMAG monitoring program were:

- 1) To gather baseline water quality data from the Endeavour and Annan Rivers and document the natural variation in water quality through the seasons;
- 2) To compare data from the Annan-Endeavour Rivers with state and federal water quality guidelines and to develop local guidelines if required; and
- 3) To assess potential anthropogenic impacts on water quality (e.g. mining, sewerage and leachates from landfill).

3.2 Sampling Design

The monitoring project included both monthly monitoring to document baseline water quality conditions and annual sampling for contaminants. Although the sampling locations and parameters sometimes overlapped, the analytical results are described in two sections:

- Ambient Monitoring- monthly sampling at 11 sites across the Catchment
- Impact Assessment- annual or bi-annual sampling for contaminants at select sites

3.3 Monitoring Locations & Timing

Ambient water quality parameters were monitored regularly between July 2002 and January 2008. Monitoring was conducted once a month (when access was possible) between 9am and 3pm. Estuary sites were monitored on an out-going tide. Additional monitoring continued opportunistically until May 2009.

Monitoring was conducted at six primary locations within the Endeavour River estuary and five Annan River freshwater and estuary locations (**Figure 3 and 4**). Four estuary sites and 1 freshwater site were monitored at the Jeannie River. Monitoring sites were determined in part by accessibility. Locations were also selected to correspond with existing gauging stations and to assess potential impacts from sewerage outfalls, mining and town rubbish tips.

Each site was assigned an ID, starting with AR (Annan River), ER (Endeavour River) or JR (Jeannie River). The list of monitoring sites, Site ID, corresponding latitude and longitude (WGS 84) and rationale behind each location is described in **Tables 1, 2 and 3**. Photos of the Annan & Endeavour Monitoring Sites are presented in **Appendix A**.

Table 1: Annan River Water Quality Monitoring Locations

Sample Location	Site ID	Latitude/Longitude	Rationale
Mouth of the Annan	AR-00	15° 31' 38.28" S 145° 16' 10.56" E	Document conditions at mouth of river, adjacent seagrass meadows & reefs
Annan Bridge	AR-01	15° 31' 16.1" S 145° 13' 23.9" E	Run-off from road & campers
Little Annan bridge	AR-02	15° 40' 49.6" S 145° 12' 23.4" E	Upstream of the drinking water intake
Wallaby Creek below Leswall Cr.	AR-03	15° 45' 14.2" S 145° 13' 39.7" E	Potential mining impacts on water quality
Wallaby Creek at Rossville markets	AR-04 (WC-01)	15° 44' 49.5" S 145° 15' 56" E	Run-off from Rossville: septic systems, road erosion, historic tin mining
Wallaby Creek below 3Jim Cr	AR-05 (AR-3Jim)	15° 45' 03.9" 145° 16' 29.2"	Downstream from Rossville tip (below 3 Jim Creek)
Additional Sample Locations*			
Leswall Creek (Adams Gully)	AR-LES	15° 45' 16.20" 145° 13' 43.32"	Leswall Cr. (Adams) flows from Collingwood tin mine into the Annan River
Annan River below tailings Dam	AR- US TD	15° 46' 02.8" 145° 13' 25.4"	Background Annan River sample upstream from Collingwood Mine Tailings Dam
Annan River upstream from Tailings Dam	AR- DSTD	15° 45' 18.3" 145° 13' 41.1"	Sampling Annan River immediately downstream from tailings dam outfalls
Tailings Dam Drain	AR-TD Drain	15° 45' 19.7" 145° 13' 40.5"	Drain from Collingwood Mine Tailings Dam into Annan River
Tailings Dam Overflow	AR-TD Overflow	15° 46' 5.16" 145 13' 39.72"	Overflow Drain from Tailings Dam into Annan River

*Additional sampling for impacts on water quality was conducted at these sites

Table 2: Endeavour River Water Quality Monitoring Locations

Sample Location	ID	Latitude/Longitude	Rationale
Mouth of the Endeavour	ER-00	15° 27' 25.8" S 145° 15' 2.8" E	Document conditions at mouth of river, export to reefs, seagrass meadows
Coast Guard Slipway Site	ER-01	15° 27' 46.5" S 145° 14' 57.6" E	Cooktown run-off, downstream from Sewage Treatment Plant outfall
Two Mile Creek confluence	ER-02	15° 27' 56.1" S 145° 14' 6.5" E	Upstream from Sewage Treatment Plant, sillage dumping in catchment
Four Mile Creek confluence	ER-03	15° 27' 47.7" S 145° 12' 34.7" E	Potential impact from landfill, developments along Endeavour Rd
North Arm (Right Arm)	ER-04	15° 27' 27.0" S 145° 12' 11.6" E	Hopevale run-off & road erosion
Main Arm, 200m upstream from N Arm confluence	ER-05	15° 26' 44.7" S 145° 12' 3.5" E	Upstream from NARM, potential impact from acid sulphate soils, pig wallows
Additional Sample Locations*			
Endeavour River at Leprosy Creek	ER-LEP	15° 27' 29.7" S 145° 14' 12.5" E	Testing for herbicide impacts on seagrass meadows at Leprosy Cr.
Endeavour River Light	Passive Samplers	15° 27' 74.3" S 145° 14' 78.2" E	Endeavour River Light- passive sampler location
Endeavour River-Chainman's Cr	ER-CC	15° 27' 55.7" S 145° 14' 52.2" E	Endeavour River at Chinaman's Creek, upstream from STP outfall
Endeavour Main Channel	ER-2.5	15° 27' 30.3" S 145° 13' 43.1" E	Main Channel of the Endeavour River between ER-02 and ER-03

*Additional sampling for impacts on water quality was conducted at these sites

Table 3: Jeannie River Water Quality Monitoring Locations

Sample Location	ID	Latitude/Longitude	Rationale
Mouth of the Jeannie	JR-00	14°39'25.3" 144°55'18.1"	Collect baseline data from an undeveloped catchment with similar conditions to the Endeavour River
Jeannie River estuary 2 km upstream	JR-01	14°40'08.5" 144°55'16.6"	
Jeannie River estuary 6 km upstream	JR-02	14°42'25.8" 144°54'26.0"	
Jeannie River below waterfall- top of estuary	JR-03	14°43'01.1" 144°53'53.1"	
Jeannie River freshwater branch	JR-04	14°43'41.4" 144°52'26.9"	

Endeavour River monitoring was conducted by boat. Annan and Jeannie River samples were collected from the banks using a 3m extended sampling pole. All measurements were collected from approximately 10cm below the water surface.

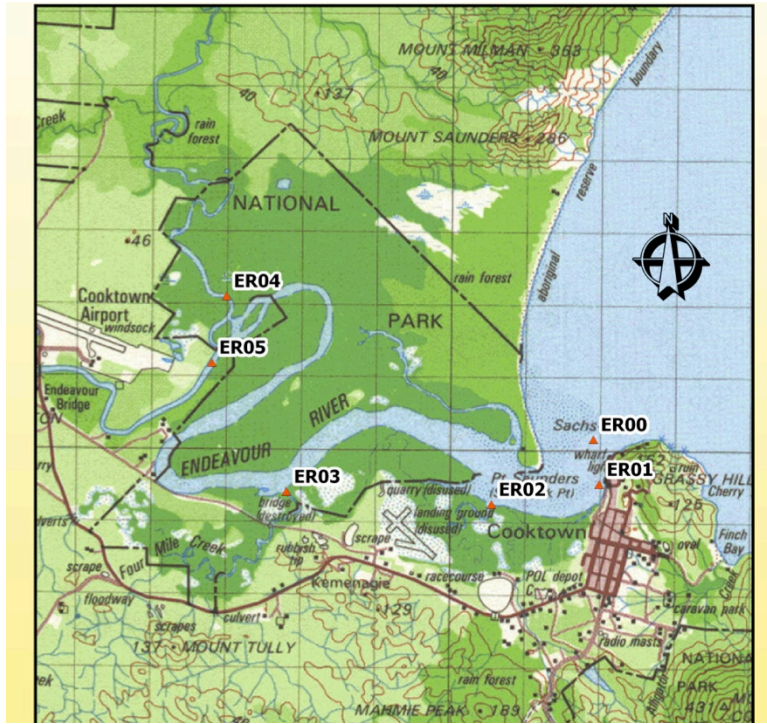


Figure 3: Endeavour River Water Quality Monitoring Locations



Figure 4: Annan River Water Quality Monitoring Locations

3.4 Ambient Water Quality Monitoring & Analysis Methods

The ambient monitoring programme included monthly monitoring of the following indicators at all primary monitoring sites:

- pH
- Electrical conductivity ($\mu\text{S}/\text{cm}$)
- Salinity (ppt)
- Water temperature ($^{\circ}\text{C}$)
- Dissolved Oxygen (mg/L & % saturation)
- Turbidity (NTU)

In November 2004 monthly monitoring was expanded to include the following laboratory analyses:

- Chlorophyll- α ($\mu\text{g}/\text{L}$), and
- Nutrients (mg/L):
 - Total phosphorous
 - Total reactive phosphorous
 - Total nitrogen
 - Ammonia
 - Nitrogen oxides

Water pH, dissolved oxygen (DO), temperature, salinity and conductivity were measured in-situ using the Orion 5 Star Portable Multi-parameter Meter. Turbidity samples were analysed in the field using the HACH 2100P Turbidity Meter. All equipment was calibrated prior to use to ensure accuracy of measurements. The range and accuracy of the monitoring equipment for each parameter is listed in Appendix B.

Nutrient and chlorophyll- α samples were collected as per the Queensland Environmental Protection Agency (EPA) Waterways Sciences Unit (now part of DERM) standard procedures using laboratory-sterilised bottles. Total nutrients were filled directly into a 250 mL polypropylene bottle. Dissolved nutrients were filtered using a syringe and 0.45-micron filter and collected in a 125 mL polypropylene bottle. Nutrient samples were placed on ice in the field and stored frozen until being shipped via freezer truck to the Queensland Health Environmental Waters Laboratory in Brisbane for analysis.

Nutrient analytical methods are listed in Appendix B, Table 1.

Chlorophyll- α sample collection involved filling two 1-L Nalgene bottles with site water which was filtered through a 47 mm diameter Whatman brand 1.2 μm glass fibre/course filter paper using a hand operated vacuum pump connected to a glass Buchner vacuum flask (Millipore side arm flask). The filters were placed in a High Density Polyethylene (HDPE) 15 ml screw top tube preserved with 0.1 g magnesium carbonate, wrapped in aluminium foil, frozen immediately and sent to

the Water Quality & Aquatic Ecosystem Health division of DERM for analysis. Chlorophyll- α and phaeophytin analysis was conducted by acetone extraction and visible spectrophotometry.

3.5 Land-use Impact Assessment Methods & Analyses

Sampling for contaminants was conducted annually or bi-annually during the first major rain event of the wet season (first flush) and subsequent events when possible. Some contaminant samples were also collected during the dry season.

During the 2005/2006 and 2007/2008 wet seasons, water and sediment grab samples were analysed for a range of contaminants including metals, pesticides and petroleum hydrocarbons. Passive samplers were deployed in the Endeavour River for 30 day and 5-day periods during the 2008/2009 wet season to measure herbicide and hydrocarbon levels in the water.

Table 4 lists land uses in the Annan & Endeavour catchments and the specific contaminant analyses conducted to assess the potential impacts on water quality.

Table 4: Potential Land Use Impact Assessments and Contaminant Analyses

Land-Use	Location	Contaminant Analyses Conducted
Cooktown Sewerage Treatment Plant effluent outfall	Endeavour River upstream from ER-01	<ul style="list-style-type: none"> • Nutrients (as per ambient monitoring project) • Bacteria
Endeavour Rubbish Tip	Endeavour River near ER-02 & ER-03	<ul style="list-style-type: none"> • Heavy metals (total and dissolved) • Hydrocarbons: <ul style="list-style-type: none"> -Total Petroleum Hydrocarbons (TPH C₆ – C₃₆), -Polycyclic aromatic Hydrocarbons (PAH) -Benzene, Toluene, Ethylene & Xylene (BTEX) • Solvents: <ul style="list-style-type: none"> -Volatile Organic Compounds (VOCs) -Semi-Volatile Organic Compounds (SVOCs)
Agricultural Land Use	Endeavour River upstream from ER-05	<ul style="list-style-type: none"> • Pesticides & Herbicides: <ul style="list-style-type: none"> -Phenoxyacetic Acid Herbicides -Organochlorine & Organophosphorus Pesticides (OC/OP) -Glyphosate (Round-up) -Diuron -Triazines (Atrazine and Simazine) • Nutrients (as per ambient monitoring project)
Bluestone Tin Mine	Annan River upstream from AR-03	<ul style="list-style-type: none"> • Heavy metals (total and dissolved) • Turbidity • Hydrocarbons
Septic Systems, Feral pigs and cattle in waterways	Annan River at Rossville & Keatings Lagoon, Endeavour River near ER-05	<ul style="list-style-type: none"> • Bacteria (ambient monitoring project) • Nutrients (ambient monitoring project)

Grab Samples

Grab samples for contaminants and metals were collected directly from the water source into the appropriate sterilised sample bottles. Sediment samples were collected using decontaminated stainless steel spoons or sediment grab sampler and placed in sterilised sample jars. All samples were placed immediately on ice and sent via JAT refrigerator truck to the NATA accredited ALS Laboratory in Brisbane.

Bacteria samples were collected in sterilised sample bottles and submitted to the NATA accredited Cairns Water Laboratory for analysis within 24 hours of collection.

Laboratory Analytical Methods for contaminants and metals are listed in Appendix B, Table 2.

The number of grab samples collected for each analysis type from the Annan & Endeavour Rivers is listed in Table 5.

Table 5: Number of Grab Samples Collected for Each River & Analysis Type

	Annan River	Endeavour River	Jeannie River
Water Analysis			
Metals	56	22	16
PAH / Phenols	9 / 2	12 / 5	0
TPH / BTEX	10 / 5	13 / 7	0
VOCs	2	2	0
Pesticides & Herbicides	0	10	0
Bacteria	9	14	2
Sediment Analysis			
Metals	13	28	0
Pesticides/Herbicides	1	21	0
PAH / phenols	4	12	0
TPH / BTEX	4	14	0

Passive Samplers

In order to detect ultra-trace concentrations of contaminants, passive samplers developed by ENTOX (Qld University) were deployed in the Endeavour River estuary during the 2008/2009 wet season. These devices passively adsorb contaminants from the water column during the period of deployment, and can detect contaminants such as herbicides at much lower concentrations (ng/mL) than grab samples.

Two types of passive samplers were deployed:

- Empore Disks (EDs): herbicide samplers (polar organic compounds)
- Polydimethylsiloxane (PDMS): pesticide, herbicide & PAH samplers (non-polar organics)

Passive samplers were deployed over a period of 30 days during the first rain events of the wet season and for 5-day periods during subsequent floods in order to detect

contaminants entering the river. Upon retrieval the samplers were placed on ice and sent via air courier to ENTOX in Brisbane, who processed the samplers for analysis by the Queensland Health Environmental Waters Laboratory. Pesticides and PAHs were analysed by GC-MS. Herbicides were analysed by LC-MS. The complete list of pesticides, herbicides and PAHs screened for are listed in **Appendix B, Table 3**.

Contaminant concentrations were calculated using an estimate of flow rates measured by flow monitors deployed with the passive samplers, the solubility of the compounds in water and the uptake rate for the chemicals detected. It is not known whether the accumulated amounts of contaminants in the passive samplers accumulated rapidly during short flushes or were slowly accumulated over the period of deployment. Due to the nature of the passive samplers and the methods of calculating daily rates over a 30-day sampling period, all concentrations reported are only considered to be indicative estimates of the presence of that contaminant.

Passive samplers were deployed in the Endeavour River lower estuary near site ER-01 (**Figure 26**).

3.6 Quality Control

The collection of reliable high quality data was a priority for the Annan-Endeavour Water Quality Monitoring project, which included detailed Quality Control (QC) procedures for field monitoring and laboratory sample collection. QC samples were used to determine the representativeness of the environmental samples, the precision of sample collection and handling procedures, the thoroughness of the field equipment decontamination procedures, and the accuracy of laboratory analysis. When breaches in quality control were identified, the associated sample results were discarded. We are confident that the analytical results provided in this report are of a high data quality.

3.6.1 Field Sampling QC Methods

The field sampling programme included the following quality assurance procedures:

- Documented equipment calibration daily to ensure meter accuracy
- Three water quality measurements taken at each site to ensure equipment stability, identify outliers and variation (averages recorded for each site)
- Nitrile gloves worn by all samplers to avoid sample contamination
- QC Sample Collection:
 - Sample Duplicates (QC-01) collected to assess laboratory precision
 - Field Method Blanks (QC-02) submitted to assess for sample contamination during transport or analysis.

- Equipment Rinsate Blanks (QC-03) submitted for analysis to assess for potential cross-contamination of samples from equipment such as sample collection bottles or syringes used for multiple samples.
- Certified Reference Material (CRM) samples (QC-04) were submitted for nutrient analysis to document laboratory accuracy and potential loss of nutrients during storage and transportation.
- Trip blanks (QC-05) were submitted along with samples analysed for volatile organics (petroleum hydrocarbons & VOCs).
- All QC samples were submitted blind to the laboratory.

The field and laboratory QA/QC methods and data validation results are detailed in Appendix C. The data validation results are summarised in the following sections.

3.6.2 Nutrients Data Quality Summary

The review of the QC analytical results indicates that all but a small fraction of the nutrient data collected between June 2006 and March 2010 is of acceptable data quality. Out of 42 batches of samples, nitrogen oxide results from one sample batch (March 2007) were discarded due to potential cross contamination identified in rinsate samples. Total nitrogen results from December 2007 and ammonia results from July 2008 were discarded due to excessive differences between duplicate samples. Relatively low levels of nutrients were detected in several field blanks and rinsate blanks but the results do not indicate that there has been any significant level of sample contamination during collection, transportation or analysis. The results from the analysis of certified reference material indicate that there is a high level of accuracy in the laboratory analytical results.

3.6.3 Chlorophyll- α Data Quality Summary

A low frequency of quality control samples were analysed for chlorophyll-a, therefore the results are largely un-validated; however, the results showed no detectable chlorophyll contamination from the field sampling, filtering and lab analysis process.

3.6.4 Contaminant & Metals Analysis Data Quality Summary

The majority of the contaminant analytical results met the appropriate Field and Laboratory QC standards (outlined in Appendix C).

Holding time breaches of over 3 days resulted in the discarding of 17 out of 143 mercury sample results; 3 out of 42 TPH and PAH sample results and four out of 24 phenoxyacetic acid herbicide results. An additional five TPH/ PAH samples and five phenoxyacetic acid herbicide water samples and three OC/OP pesticide samples have been qualified due to holding time breaches of 1 to 3 days.

Duplicate sample results indicate a high level of precision for contaminant and metals analyses with all sample results being within the acceptable criteria for duplicates (<20%RPD). Field blank and rinsate results indicate that there has been a very low incidence of contamination of herbicides, pesticides, TPH, BTEX, or PAHs in grab samples or passive samplers. Field blank samples showed no evidence of sample contamination with the exception of one glyphosate detection.

Rinsate blank samples revealed contamination from filters used for dissolved metals. This has resulted in the deletion of zinc, cadmium and other metals results from 25 dissolved metals samples.

All together approximately 368 samples were submitted for contaminant and metals analyses, with 42 quality control breaches resulting in the deletion of the associated analytical results for individual analytes. The results have been qualified for an additional 32 sample analyses due to minor breaches that are not considered to have significantly affected the data.

4 WATER QUALITY RESULTS

4.1 Ambient Water Quality Parameters

The assessment of ambient water quality includes the following parameters:

- pH
- Electrical conductivity ($\mu\text{S}/\text{cm}$)
- Salinity (ppt)
- Water temperature ($^{\circ}\text{C}$),
- Dissolved oxygen (mg/L & % saturation),
- Turbidity (NTU),
- Chlorophyll- α ($\mu\text{g}/\text{L}$), and
- Total and Dissolved Nutrients (mg/L).

4.2 Statistics

The principal statistic that has been used in this report is the median (50th percentile). The median is based on between 66 to 229 data points for each river subset.

In addition to median values, minimum and maximum values have been assessed. Maximum or minimum values (depending on the indicator) represent the worst condition measured and are usually associated with extreme high or low flow events. The likelihood of monthly sampling capturing the true maximum/minimum values that occurred during a particular year is low; however additional samples were collected during extreme events, therefore the minimum/ maximum sample results should provide a good indication of extreme conditions.

The ambient water data has been analysed based on Annan-Endeavour River subsets- the Endeavour River estuary (ER-EST), Annan River estuary (AR-EST) and Annan River freshwater sites (AR-FW)- and has been characterised based on both annual

medians and wet season and dry season variations. Variations between individual sites (within each subset) have also been assessed and significant differences are discussed.

The data is presented as representative baseline data against which future changes in water quality can be compared. The data has been compared against the relevant Queensland (Qld 2009) and Australian (ANZECC 2000) Water Quality Guidelines. Potential impacts from mining, agriculture, rubbish tips, and sewerage treatment outfalls have also been assessed.

Tables 6 & 7 show the range (minimum-maximum values) and median values across each subset of the Annan, Endeavour & Jeannie Rivers for ambient water quality parameters. The range and median water quality values for individual Endeavour and Annan River sites are presented in **Appendix D, Tables 1, 2 and 3**.

The following sections contain a detailed analysis of the ambient water quality results.

**TABLE 6: Comparison of Ambient Water Quality in the Annan, Endeavour & Jeannie Rivers (2002-2009)
Minimum, Maximum and Median Values**

Site	Statistic	pH: -log [H ⁺]	Temperature: °C	Conductivity: (mS/cm)	Salinity: ppt	Dissolved Oxygen: (mg/L)	Dissolved Oxygen: (%SAT)	Turbidity: NTU
Annan River Freshwater Sites	Min	5.59	18.3	0.012	0.0	5.52	56.34	1.0
	Max	8.03	31.1	0.120	0.1	9.29	110.80	704.0
	Median	6.61	24.0	0.062	0.0	7.40	89.93	3.4
	Count	120	125	112	115	113	113	131.0
Annan River Estuary Sites	Min	5.54	20.2	0.052	0.0	4.41	63.13	1.2
	Max	8.68	31.3	53.8	35.7	8.18	104.37	230.0
	Median	7.84	26.4	36.28	23.9	6.46	88.80	4.2
	Count	66	67	64	65	61	61	72.0
Endeavour River Estuary Sites	Min	5.31	21.0	0.068	0.0	4.08	60.07	0.0
	Max	8.37	33.3	62.5	37.3	8.82	126.70	456.0
	Median	7.70	27.0	47.3	30.6	5.82	82.83	4.7
	Count	229	240	231	239	220	218	246
Jeannie River Estuary Sites	Min	7.05	23.93	0.082	0.0	1.31	17.50	4.16
	Max	8.10	34.30	68.7	47.3	7.78	110.90	19.37
	Median	7.87	26.83	53.1	35.1	5.53	79.47	9.80
	Count	20	20	20	20	20	20	20
ANZECC	Freshwater (upland river)	6.0 – 7.5					90% - 120%	2 – 15
Qld		6.0 – 7.5					90% -100%	6
ANZECC	Estuary	7.0 – 8.5					80% – 120%	1 – 20
Qld	mid-estuary	6.5 – 8.4					80% – 105%	10

1 ANZECC Guidelines for the Protection of Aquatic Ecosystems, Tropical Australia (2000)

2 Qld Water Quality Guidelines, Wet Tropics (2009)

**Table 7: Minimum, Maximum and Median Nutrient & Chlorophyll-a Concentrations-
Annan, Endeavour & Jeannie River Subsets**

		Total Phosphorus	Filt Reac Phosphorus	Ammonia Nitrogen	Nitrogen Oxides	Total Nitrogen	Chlorophyll-α
		mg/L as P	mg/L as P	mg/L as N	mg/L as N	mg/L as N	$\mu\text{g/L}$
AR-FW n = 92 / 87	min	0.003	<0.002	<0.002	<0.002	0.04	<0.01
	max	0.060	0.006	0.024	0.940	1.20	4.04
	median	0.009	0.002	0.003	0.003	0.10	0.18
AR-EST n = 31 / 49	min	0.004	<0.002	<0.002	<0.002	0.08	0.01
	max	0.067	0.006	0.043	0.160	4.80	5.61
	median	0.010	0.001	0.007	0.004	0.13	0.78
ER-EST n = 153 / 134	min	0.002	<0.002	<0.002	<0.002	0.08	0.01
	max	0.140	0.004	0.043	0.077	1.10	3.64
	median	0.009	0.001	0.007	0.009	0.17	0.85
JR-EST n = 20 / 24	min	0.004	<0.002	<0.002	<0.002	0.11	0.27
	max	0.023	0.006	0.340	0.120	0.71	9.54
	median	0.008	0.001	0.007	0.006	0.16	1.28
ANZECC 2000 Water Quality Guidelines¹							
<i>Estuary*</i>		0.020	0.005	0.015	0.030	0.250	2.0
<i>Upland River*</i>		0.010	0.005	0.006	0.030	0.150	NA
Qld 2009 Water Quality Guidelines (Wet Tropics)²							
<i>Estuary*</i>		0.020	0.005	0.015	0.030	0.250	2.0-3.0*
<i>Upland Streams*</i>		0.010	0.005	0.006	0.030	0.150	0.6
Qld 2009 Water Quality Guidelines (Endeavour River Estuary)²							
Lower estuary		0.015	0.003	0.010	0.010	0.200	2.0
Mid estuary		0.020	0.003	0.020	0.040	0.300	3.0

1 ANZECC 2000 Tropical Australia Guidelines for the Protection of Aquatic Ecosystems (95%)

2 Qld Water Quality Guidelines (2009) Regional Guideline Values for Wet Tropics & Endeavour River

* 2.0 $\mu\text{g/L}$ for enclosed coastal estuary, 3.0 for mid-estuary

n number of samples (nutrients/ chlorophyll) (2009)

4.3 Temperature

Water temperature in the Annan River ranged from 18.3°C to 31.3°C with a median of 24.0°C in the freshwater section and 26.4°C in the estuary (**Table 10**). Minimum temperatures in the Annan River occurred in June and July while maximum temperatures occurred between October and February, depending on the year and site. Median temperatures decreased with distance upstream (**Figure 5**)

The Endeavour River temperature ranged from 21.0°C to 33.3°C with a median of 27.0°C in the estuary (**Table 6**). The minimum Endeavour River temperatures occurred in July with an average July temperature of 22.3 °C. Maximum temperatures occurred in February and March, with an average February-March temperature of 28.2°C.

Jeannie River water temperatures were similar those measured in the Annan & Endeavour estuaries (**Table 6**).

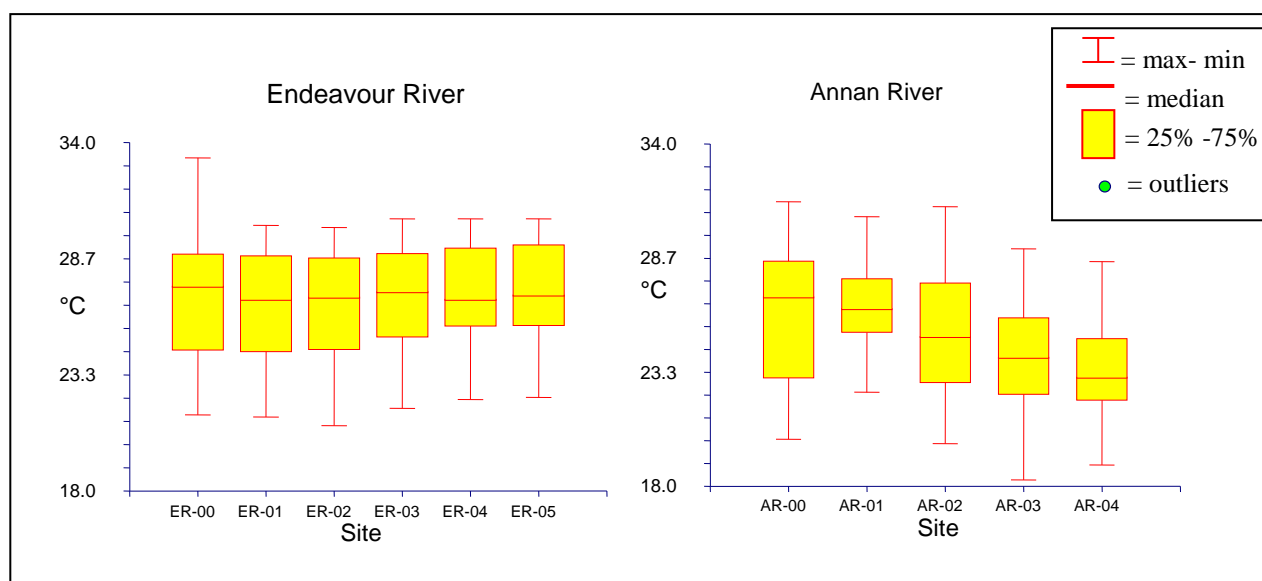


Figure 5: Annan & Endeavour River Temperature Box Plots (Median, Minimum & Maximum Values for Each Site)

4.4 Salinity & Conductivity

The climate in this region is characterised by long periods of dry weather during the winter and heavy rainfall mostly between the December to March period. This is reflected in low stream flows during the winter contrasted with short-lived flood events occurring after heavy rains. During a flood event, large quantities of freshwater enter the estuary and for a short period this dominates estuary hydrology.

Drought conditions during the first years of this monitoring program resulted in lower than usual rainfall and no significant flood events in the Endeavour River from 2002 to 2004. This is reflected in the annual salinity cycles (**Figure 6**).

Estuary

Salinity within the Annan and Endeavour estuaries ranged from 0.0 ppt during wet season flood events to a maximum of 37.3 ppt measured at ER-03 (4- Mile Creek) in August 2003 and 35.7 ppt at AR-00 (Annan River mouth) in October 2002 (**Table 6 and Appendix D, Table 1 & 2**).

Conductivity values in the Endeavour estuary ranged from 0.068 mS/cm to 62.5 mS/cm, with a median value of 47.3 mS/cm. Annan River estuary conductivity was slightly lower with a median value of 36.2 mS/cm.

The Jeannie River upper estuary became hypersaline (maximum 47.3 ppt) towards the end of the dry season when freshwater in-flow ceased. This is reflected in higher median salinity and conductivity values at the Jeannie River than the Endeavour.

Figure 6 illustrates the salinity cycle at Endeavour River estuary site ER-01 (approximately 500 m upstream from mouth) with salinity levels dropping during flood events and increasing during subsequent months.

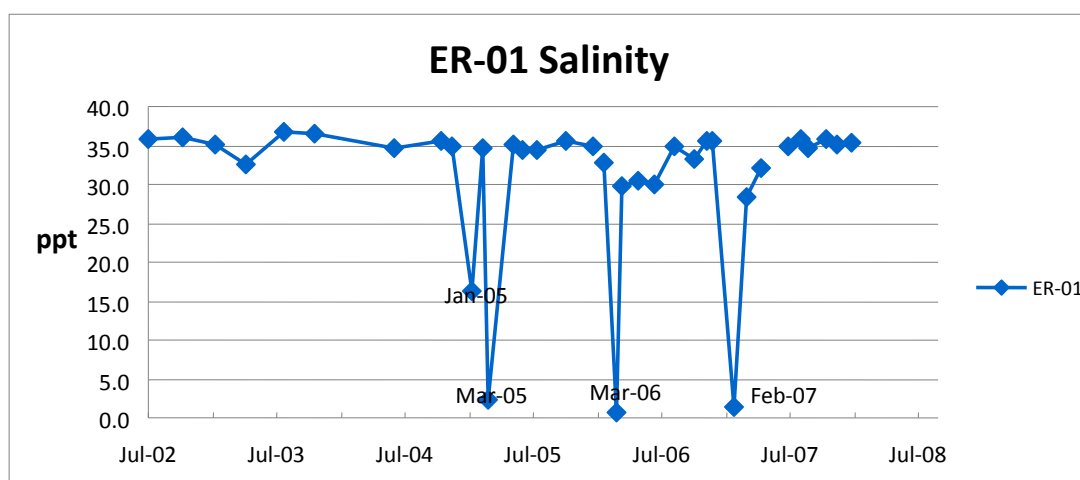


Figure 6: Annual Salinity Cycles at Endeavour River Estuary Site ER-01

Median salinity and conductivity values in the Endeavour River estuary decreased with distance upstream (**Figure 7- Box Plots**). Mid estuary Site ER-03 showed some freshwater influence with a median salinity value of 28.3 ppt. Upper estuary sites ER-04 and ER-05 were brackish, with median salinity values of 13.9 ppt and 16.6 ppt respectively.

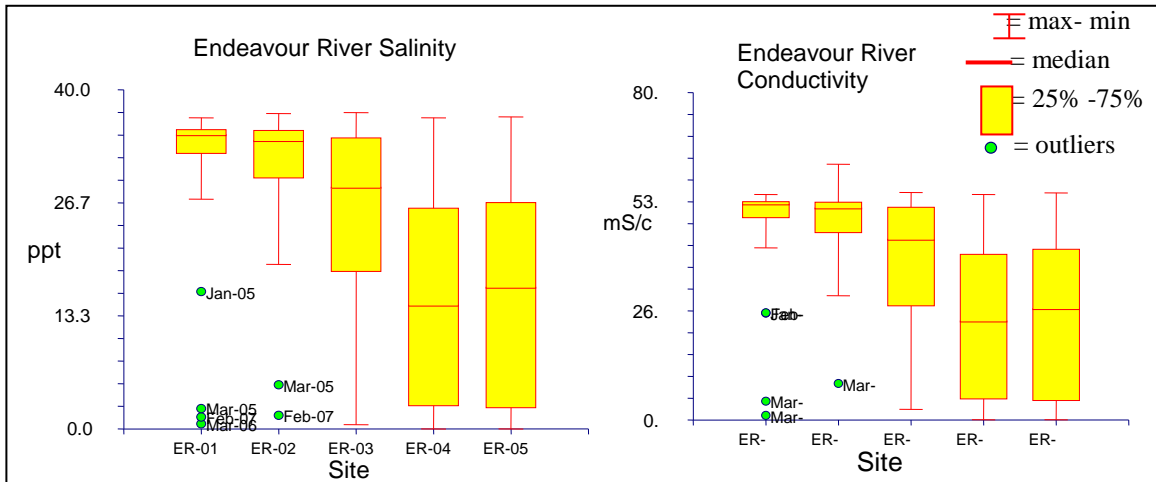


Figure 7: Endeavour River Site Salinity & Conductivity Box Plots (Median, Minimum & Maximum Values for each Site)

Freshwater

Salinity at freshwater sites in the Annan River ranged from 0.0 ppt to 0.1 ppt, with conductivity values ranging from 0.012 mS/cm to 0.120 mS/cm (median 0.062 mS/cm). Salinity and conductivity at freshwater sites generally increased during the dry season, and dropped during wet season floods (**Figure 8**).

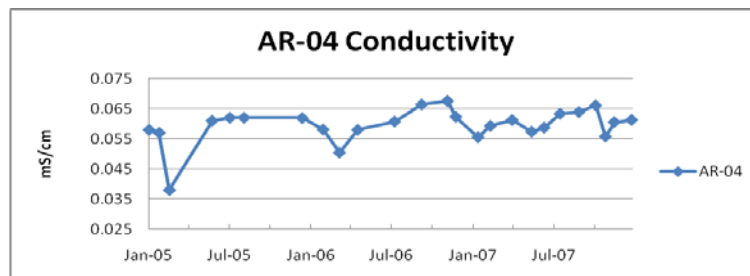
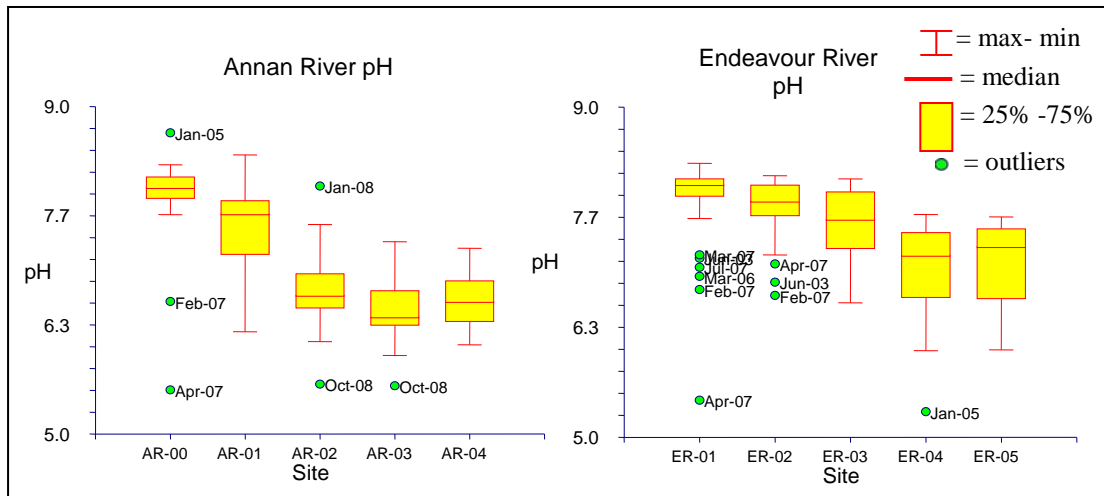


Figure 8: Annan River Freshwater Seasonal Conductivity Cycles (2005-2008)

4.5 pH

The Annan River had a median freshwater value of 6.61 and median estuary value of 7.84. The Endeavour River estuary had a median pH value of 7.70. The Jeannie River median pH value was slightly higher than the Annan or Endeavour estuaries (**Table 6**). Median pH values were within the expected Guidelines for Australian Tropical Estuaries (ANZECC 2000), however pH measurements fell below the Guidelines on several occasions during freshwater flood events in the estuaries, and low flow conditions during the dry season.

Median pH values generally decreased with distance upstream in both the Endeavour and Annan Rivers (**Figure 9**). Annan River freshwater Site AR-03 (Shiptons' Flat) had the lowest median pH value (6.43). The Endeavour River Right Arm (ER-04) had the lowest median pH Value for estuary sites (7.18). **Figure 9** shows the range and median pH values for all Annan and Endeavour River sites.



**Figure 9: Annan & Endeavour River pH Box Plots
(Median, Minimum & Maximum Values for Each Site)**

Annan & Endeavour estuary pH values decreased during freshwater flood events in the wet season (**Figure 10**). Annan River freshwater sites recorded minimum pH values during the dry season; maximum pH values occurred during both the dry season and wet season (**Figure 11**). Increases in pH can occur during the dry season when mineral rich (high conductivity) groundwater inflow increases relative to surface water run-off. Increases can also occur with increases in algae and nutrient levels. Decreases in pH during the dry season could reflect the greater proportion of inflow from acidic paperbark wetlands or drainage from acid sulphate soils.

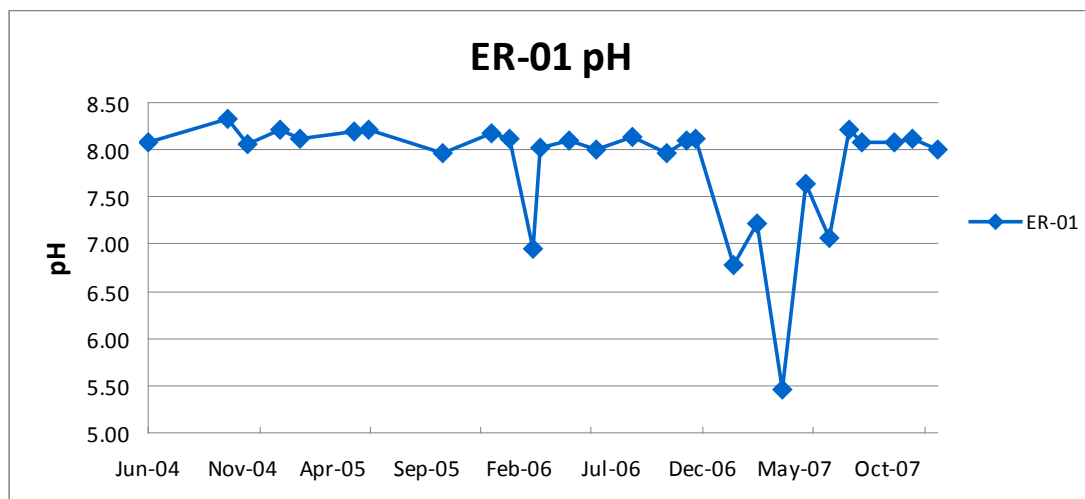


Figure 10: Endeavour River Estuary Site ER-01 Seasonal pH Cycle

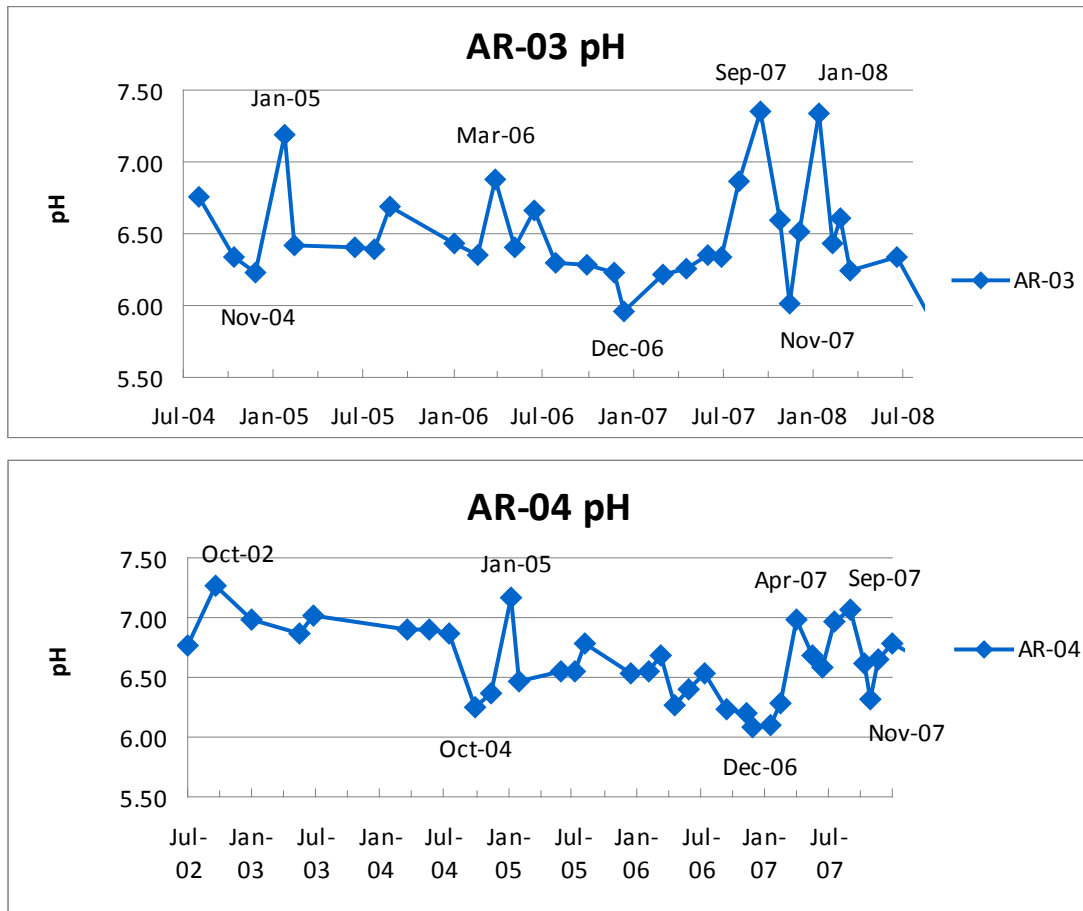


Figure 11: Seasonal pH Cycle at Annan River Freshwater Site AR-03 and AR-04

The lowest pH value (5.31) was recorded at Endeavour River Right Branch Site ER-04 after early wet season rains in January 2005. Site ER-04 also had the lowest median pH value for any estuary site (**Figure 9**). The Right Branch originates in rainforest gullies and creeks in the Hope Vale region. Acid Sulphate Soils (ASS) in this sub-catchment may have contributed to the lower pH at the North Arm compared to the adjacent Main Branch site ER-05.

4.6 Dissolved Oxygen

Oxygen levels are extremely variable and are influenced by factors such as the time of day, cloud cover, algae, organic matter and flow rates. Algal growth during the dry season low flow periods can result in high oxygen levels during the day from photosynthesis and low oxygen at night due to the consumption of oxygen during respiration, and the decomposition of algae and other organic matter. Dissolved oxygen concentrations for the Annan and Endeavour rivers reflect daytime oxygen levels (between 9am – 4pm) and flow rates ranging from low flow (dry season) to flood conditions.

Annan River dissolved oxygen levels ranged from 56.3% – 110.8%, with median values of 89.9% (freshwater sites) and 88.8% (estuary). Endeavour river estuary sites ranged from 60.1% – 126.7% with a median value of 82.9% (**Table 6**). These median

values fall within the water quality guidelines for dissolved oxygen in tropical streams and estuaries (Qld 2009, ANZECC 2000).

Oxygen levels at the Endeavour estuary site ER-00 exceeded the maximum guideline value of 120% (Qld 2009) on two occasions. Oxygen levels did not drop below the minimum guideline of 50% at any Annan or Endeavour River monitoring locations. Jeannie River oxygen levels dropped below 50% on two occasions and reached as low as 17% saturation in the upper estuary in June 2009 when freshwater inflow had ceased. Downstream Jeannie River estuary sites maintained healthy oxygen levels at this time.

Median dissolved oxygen levels in the Endeavour River generally decreased with distance upstream, and were lowest at site ER-04 (Right Branch) (**Figure 12**). Chlorophyll levels increased with distance upstream and nitrogen levels were highest at ER-04. The breakdown of organic matter from the rainforest sub-catchment may be related to the lower oxygen levels observed at this site. Increased tidal mixing and waves are likely to have resulted in higher oxygen levels at open estuary Site ER-00.

Annan River freshwater and estuary sites had similar median oxygen levels (**Figure 12**). Minimum and maximum oxygen values were recorded at Site AR-02 (Little Annan Bridge) during dry season periods of low flow and high algal growth.

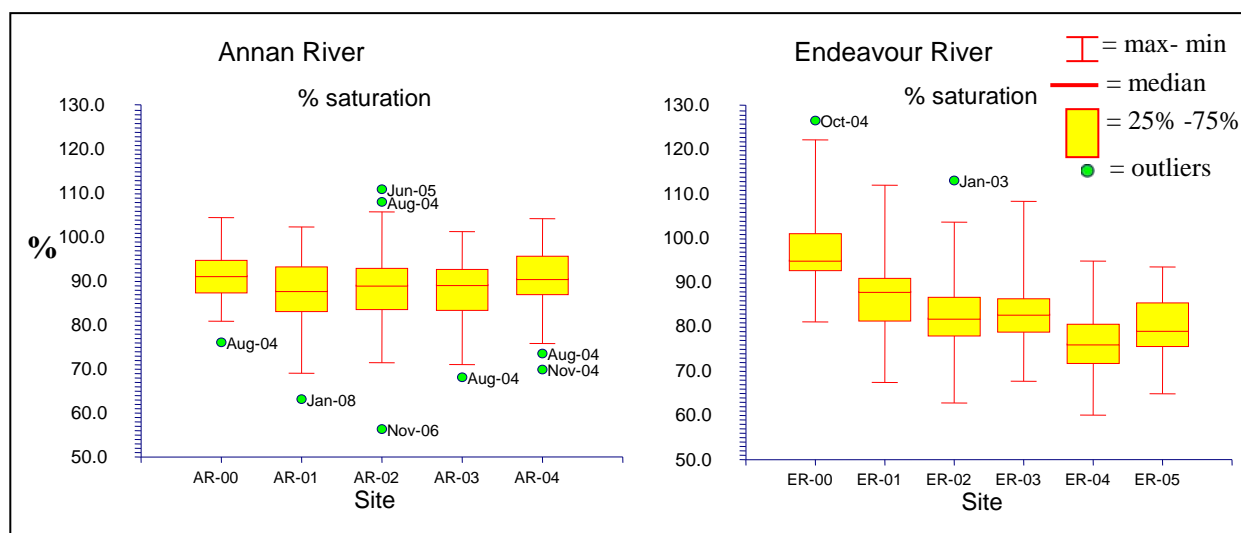


Figure 12: Annan & Endeavour River Dissolved Oxygen Box Plots (Median, Minimum & Maximum Values for each Site)

4.7 Turbidity

Turbidity is a measure of water clarity or the amount of particulate matter in the water column and can be used in some conditions to calculate total suspended sediments. The median turbidity value represents the mid-range value under base flow conditions. Maximum values in the Annan and Endeavour Rivers are associated with the introduction of sediments during or immediately after high rainfall events in the catchment. Increased erosion in catchments due to clearing, grazing, road works or other earthworks can result in increased turbidity in adjacent streams.

The Annan and Endeavour freshwater and estuary sites showed turbidity cycles common in tropical rivers with generally short-lasting peaks occurring immediately during or after high rainfall events in the catchment and low turbidity levels (<10 NTU) throughout the dry season (Figures 13 &14).

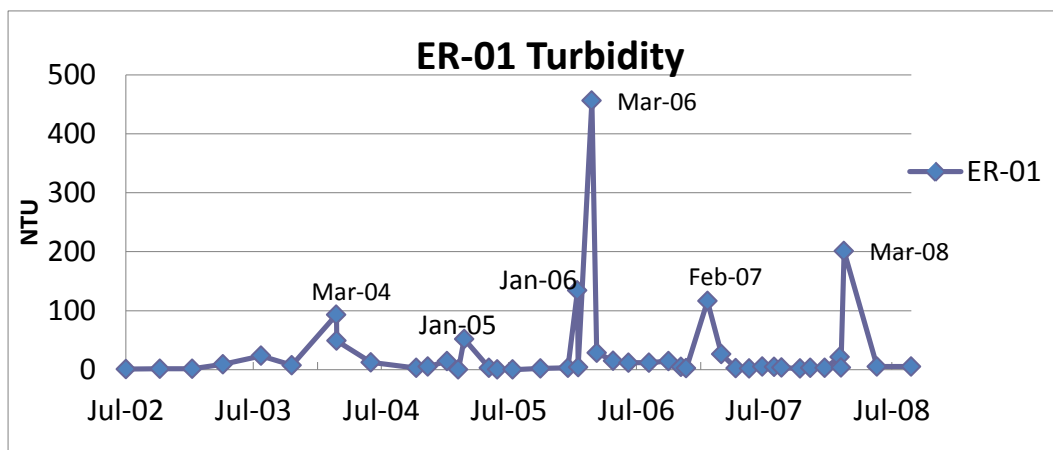


Figure 13: Turbidity Cycle at Endeavour Estuary Site ER-01

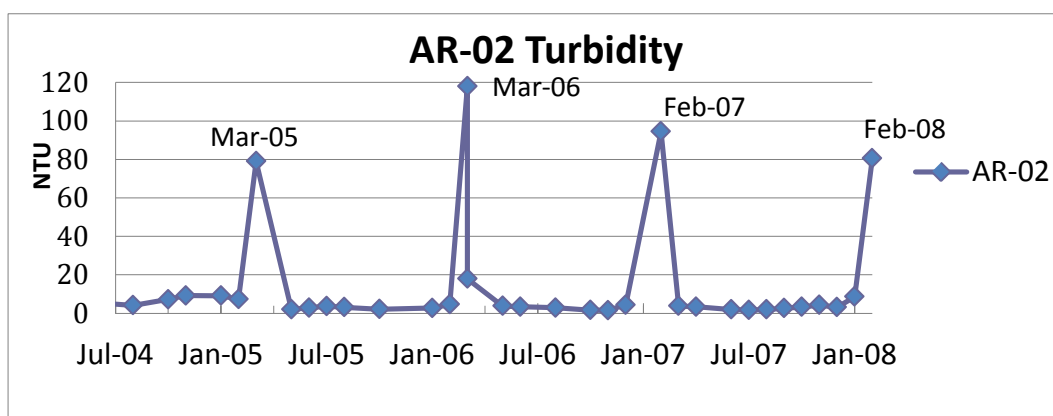


Figure 14: Turbidity Cycle at Annan River Freshwater Site AR-02

Turbidity in the Annan River ranged from 1 NTU to 704 NTU. Median turbidity values were 3.4 NTU for freshwater and 4.1 NTU for estuary sites. Turbidity in the Endeavour River ranged from 0 NTU to 456 NTU. Median turbidity values for Endeavour estuary sites ranged from 3.5 NTU to 5.8 NTU. Median turbidity values for both rivers were below the Queensland and ANZECC guidelines (Table 6).

Mean turbidity concentrations were significantly higher during the wet season, and particularly during flood events. Mean turbidity concentrations during the wet season were 49 NTU (Annan estuary) and 38 NTU (Annan freshwater sites) compared to dry season means of 4.6 and 3.5 respectively. Similarly, the Endeavour estuary had a wet season mean of 36.4 NTU and a flood event mean of 50.8 compared to a dry season mean of 4.3 NTU. Figure 15 shows dry season, wet season and flood event turbidity box plots for the Annan and Endeavour Rivers. Minimum, maximum, median and mean dry season, wet season and flood event turbidity levels are presented in Appendix D, Table 4.

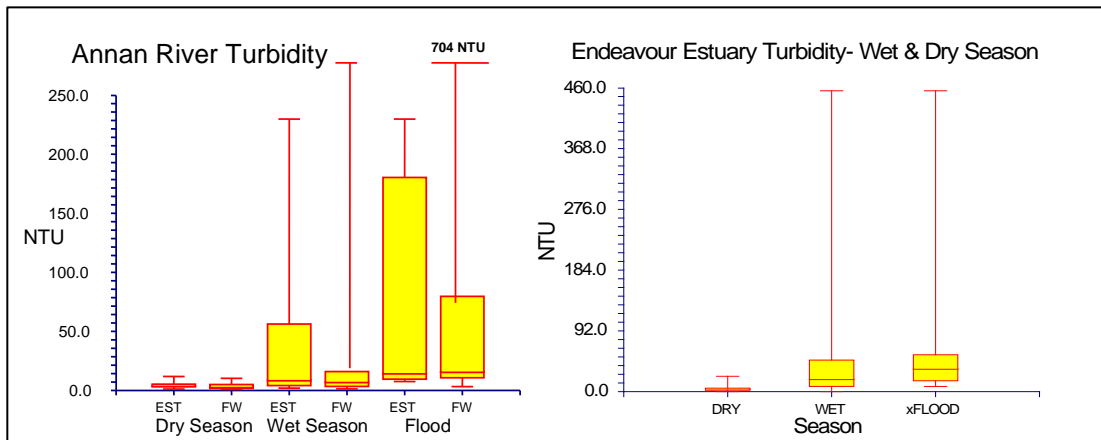


Figure 15: Annan & Endeavour Estuary Turbidity Box Plots: Dry Season, Wet Season and Flood Events

A maximum turbidity value of 704 NTU was measured opportunistically at Annan freshwater site AR-02 close to the peak of a “first flush” flood event in February 2012. Maximum turbidity values of 210 NTU and 230 NTU were recorded in the estuary during floods, although these may not represent peak flood values. Water quality at Wallaby Creek site AR-04 remained relatively clear (maximum turbidity=15 NTU), even during the wet season (**Figure 16**).

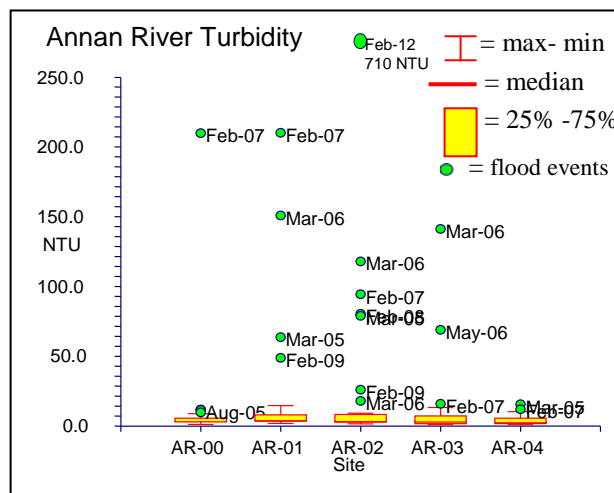


Figure 16: Annan River Turbidity Box Plots (Median, Minimum & Maximum Values per Site)

Maximum turbidity values for the Endeavour were recorded at the Endeavour mouth site ER-01 during wet season floods (**Figure 17**). Site ER-01 is adjacent to Cooktown stormwater drains and receives a large portion of town run-off. Earthworks including pipeline installation for the Cooktown STP and residential developments have increased sediment run-off into the harbour.

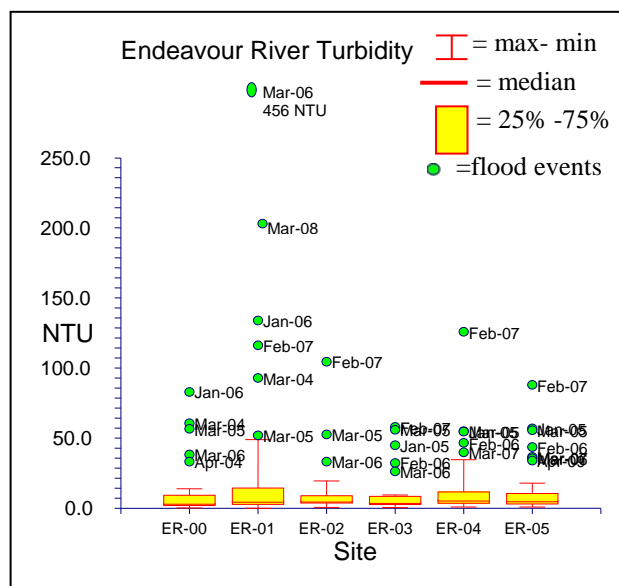


Figure 17: Endeavour River Turbidity Box Plots (Median, Minimum & Maximum Values per Site)

4.8 Nutrients

Nutrient concentrations in the Annan and Endeavour rivers were low. Median nutrient values for the freshwater and estuary subsets (**Table 7**) were below the ANZECC 2000 and Queensland (2009) Wet Tropics water quality guidelines for the Protection of Aquatic Ecosystems. However, nitrogen levels frequently exceeded the Guidelines during the wet season, when nutrient values were influenced by high loads of sediments entering the waterways.

Jeannie River median concentrations were similar to those recorded at the Annan and Endeavour. Maximum ammonia concentrations were significantly higher; these were recorded at the top of the estuary where there was little water exchange during the dry season.

The minimum, maximum and median nutrient values for individual Annan & Endeavour sites are presented in **Appendix D, Table 3**.

4.8.1 Annan River

Nutrient levels in the Annan River were generally lower at freshwater sites than the estuary. Estuary site AR-01 had the highest median total nitrogen and ammonia concentrations (**Figure 18 & Appendix D, Table 3**). There is a pit toilet and camping area immediately adjacent to site AR-01 (approximately 15m from the river) which could contribute to elevated nitrogen levels; however the concentrations are consistent with that observed in the Endeavour mid and upper estuary.

Maximum total nitrogen, ammonia and nitrogen oxide concentrations for freshwater sites were detected at Site AR-03, downstream from the Collingwood mine, in February 2007. This was the peak period of operations at the mine and large quantities of phosphorus and nitrogen based explosives were being used at the mine. Excess water from the underground mine was pumped up into the tailings pond, possibly explaining the increase in nutrient levels when the tailings pond overflowed.

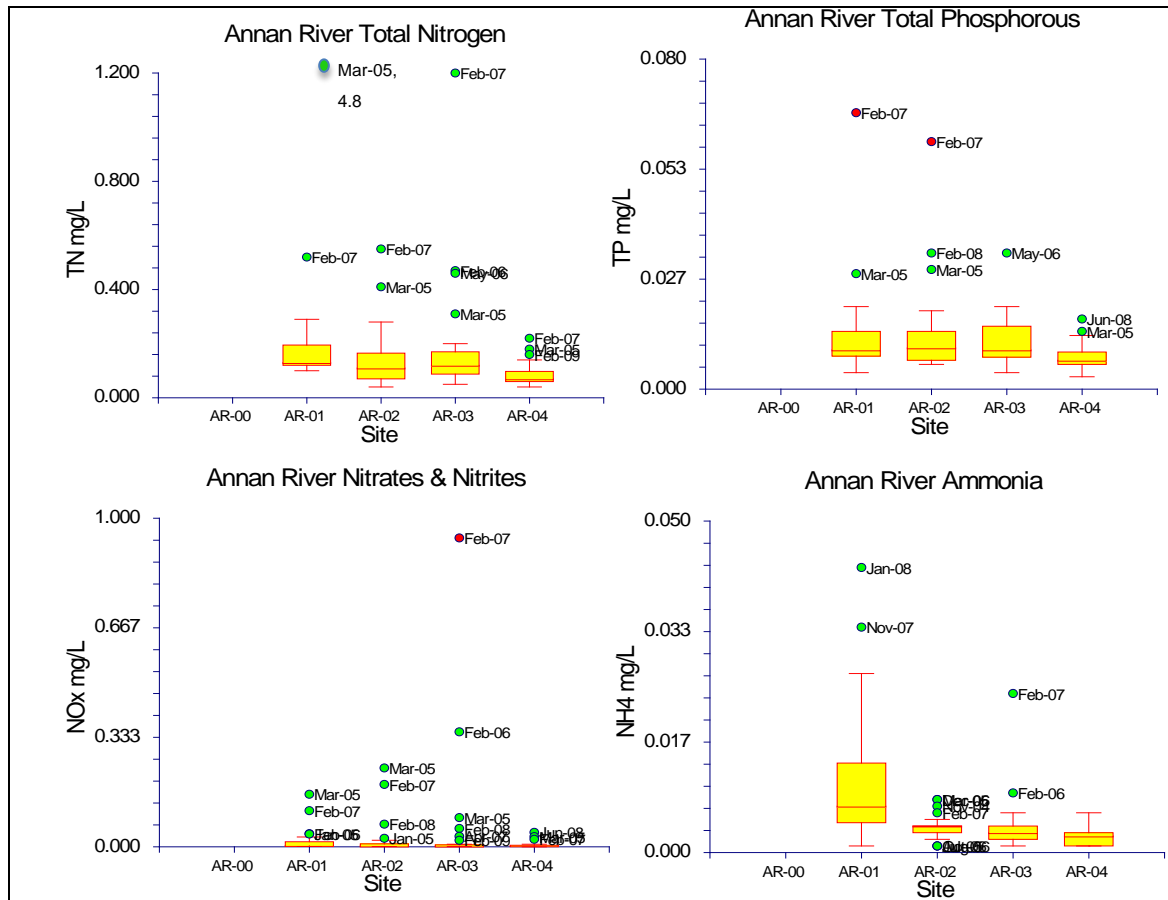


Figure 18: Annan River Total & Dissolved Nutrients Box Plots (by Site)

4.8.2 Endeavour River

The maximum total nitrogen and phosphorous values for the Endeavour River were recorded at site ER-01 during a flood event in March 2008 when turbidity levels at this site were also elevated (201 NTU) (**Figure 19**). The concentrations on this date were 2 to 3 times higher than any other Endeavour River records. Earthworks, cattle grazing and pig diggings in the catchment may all contribute to increased erosion and elevated nutrient levels associated with sediments during the wet season.

Nutrient levels, and nitrogen oxides in particular, were highest at upper Endeavour estuary sites (**Figure 19**). Median ammonia and nitrogen oxide concentrations at upper estuary sites ER-04 and ER-05 exceeded the ANZECC 2000 and Qld Wet Tropics (2009) guidelines. Based on these results, Endeavour River mid-estuary guidelines have been developed with higher guideline values for dissolved and total nitrogen than the ANZECC 2000 or Wet Tropics (Qld 2009) guidelines (**Table 7**).

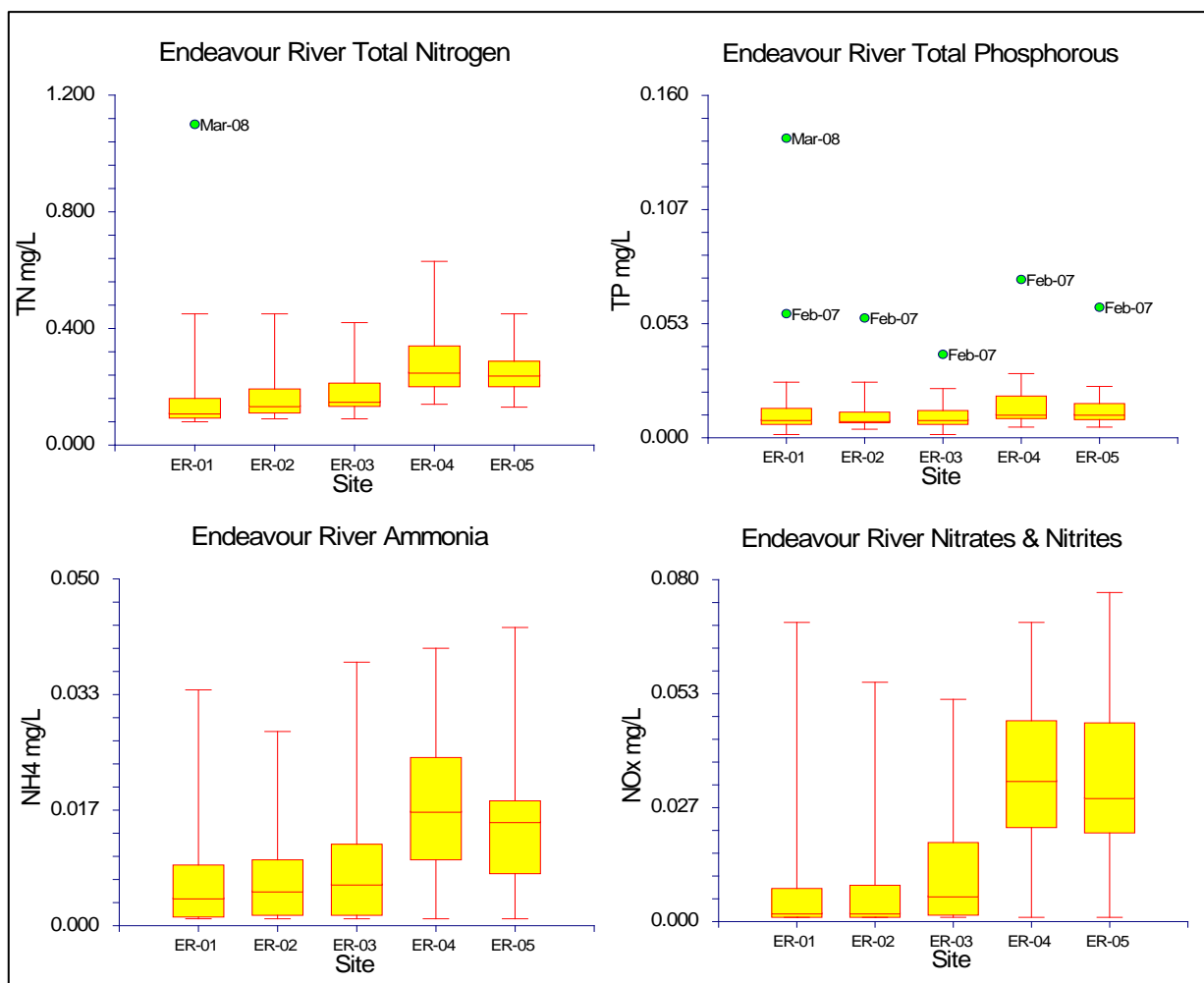
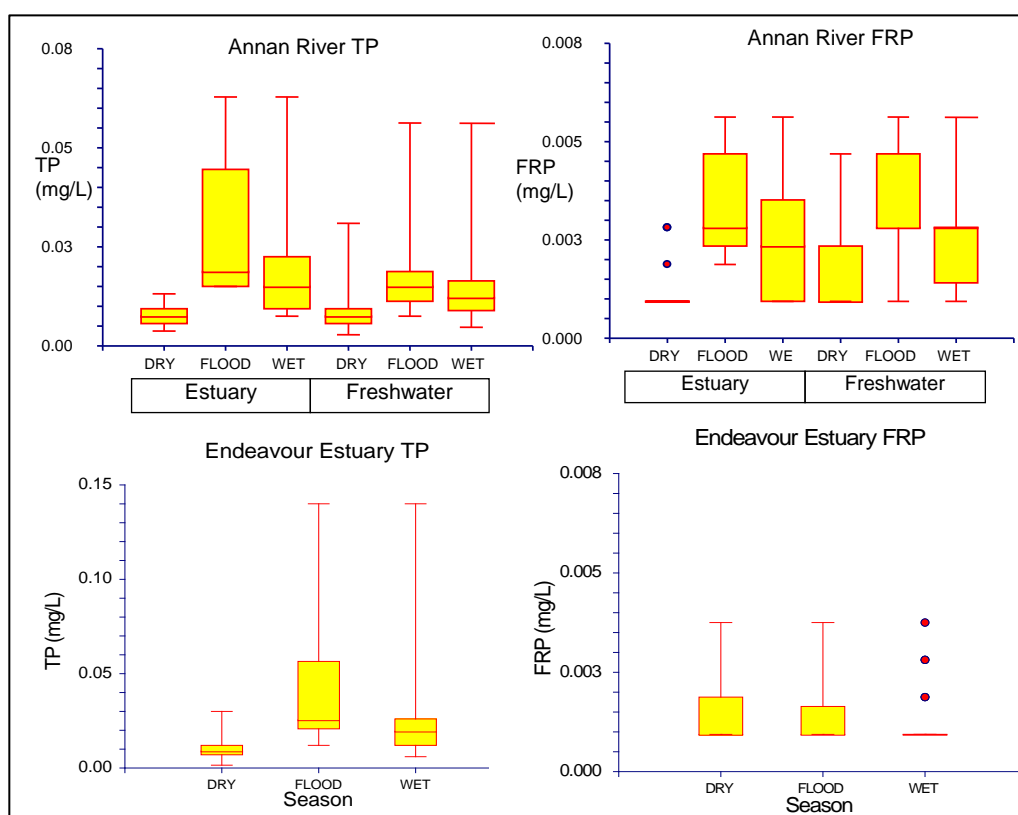


Figure 19: Endeavour River Nutrient Box Plots (by Site)

4.8.3 Dry Season, Wet Season and Flood Event Nutrient Levels

Nutrient and turbidity samples were collected opportunistically during flood events, but as the rising and falling stages were not monitored these results may not represent peak concentrations. Dry Season, Wet Season and Flood Event minimum, maximum, median and mean nutrient concentrations are presented in Appendix D, Table 4.

Both total and dissolved nutrient levels in the Annan and Endeavour Rivers were elevated during flood events compared to ambient concentrations. Mean total phosphorus concentrations were 2 to 3 times higher in the wet and up to 4 times higher during flood events than in the dry season. Dissolved phosphorous concentrations (FRP) were primarily non-detect (<0.002 mg/L) during the dry season, and increased during flood events, with the most significant increase occurring in the Annan River estuary (**Figure 20**). FRP in the Endeavour estuary remained non-detect during the wet season, and was only slightly elevated during flood events.



**Figure 20: Total and Dissolved Phosphorous Box Plots:
Dry Season, Wet Season and Flood Events**

Mean total nitrogen concentrations were between 1.5 to 5.5 times greater during the wet season, and 2 to 9 times higher during flood events than during the dry season. The difference for total nitrogen was greatest in the Annan River estuary (**Figure 21**).

Nitrogen oxides in the Annan River showed the most significant difference between dry season, wet season and flood events, with mean wet season concentrations 10 to 20 times higher than dry season concentrations, and 15 to 34 times higher during flood events. The increase in NO_x was greatest at Annan River freshwater sites (**Figure 21**). Endeavour estuary NO_x concentrations were only slightly elevated in comparison to the Annan River, with mean wet season concentrations twice the dry season concentrations, and flood event concentrations 2.5 times greater than dry season concentrations.

Mean ammonia concentrations during flood events in the estuaries were slightly elevated above dry season concentrations but were less than the mean wet season concentrations (Appendix D, Table 4), indicating that ammonia concentrations increase during the wet season but are diluted during freshwater floods.

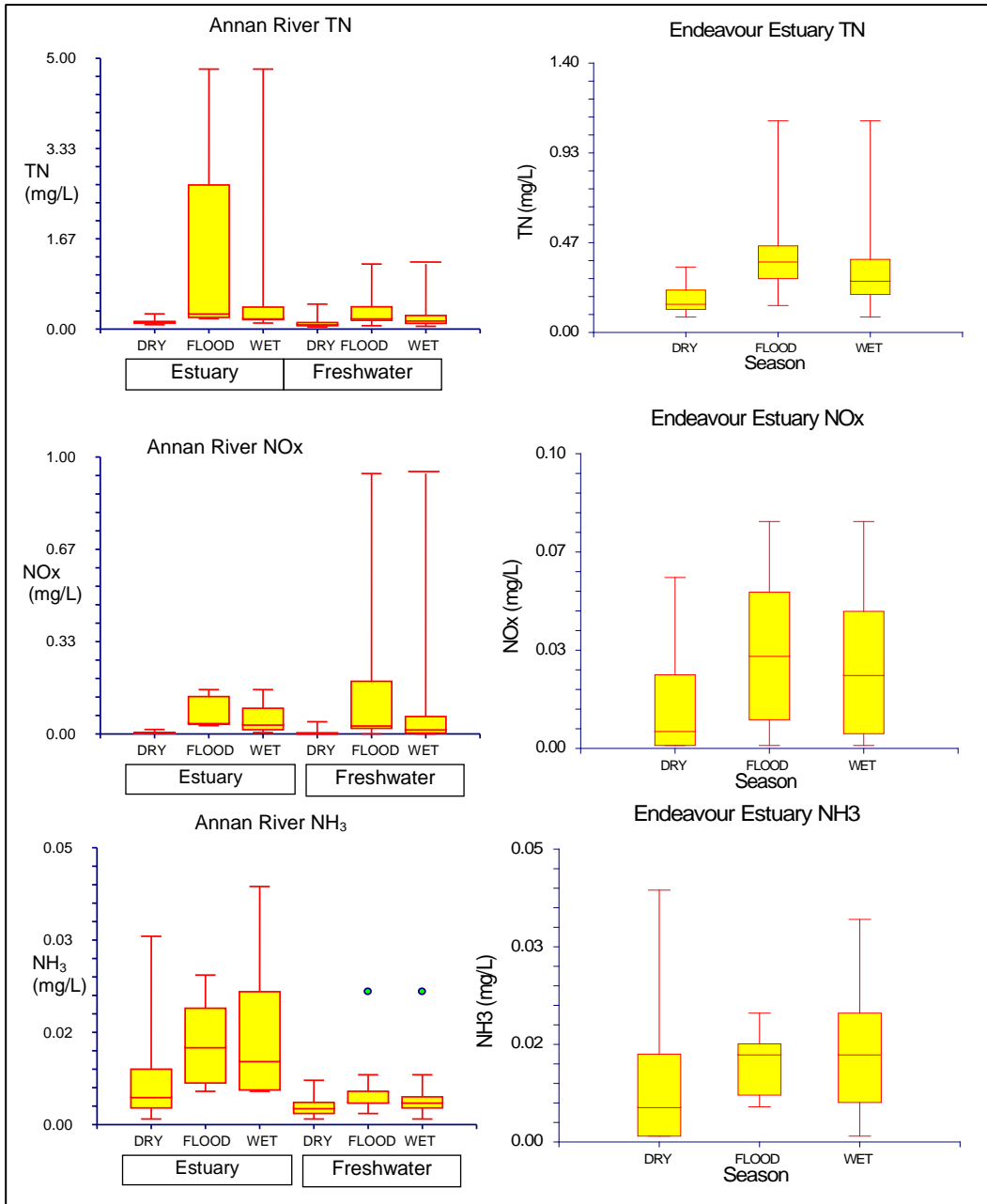


Figure 21: Annan & Endeavour Total and Dissolved Nitrogen Box Plots: Dry Season, Wet Season and Flood Event

4.8.4 Sediment Nutrients

Sediment nutrient samples were collected from Walker Bay at the Annan River mouth in November 2008. Sediment Sample locations are shown on **Figure 22**.

Total nitrogen levels in Walker Bay sediments ranged from 170 mg/kg to 1530 mg/kg and total phosphorous ranged from 79 mg/kg to 198 mg/kg (**Table 8**). Nitrogen levels were highest in the fine clay sediments located closest to the river mouth.

Table 8: Walker Bay (Annan River) Sediment Sample Analytical Results- Nutrients (mg/kg)

Date:	26/11/08						
Site:	WB-T1	WB-T3N	WB-T3S	WB-T4	WB-T5S	WB-T5mid	WB-T6
Nitrogen	320	170	230	270	640	1530	840
Phosphorus	157	161	79	154	99	198	106

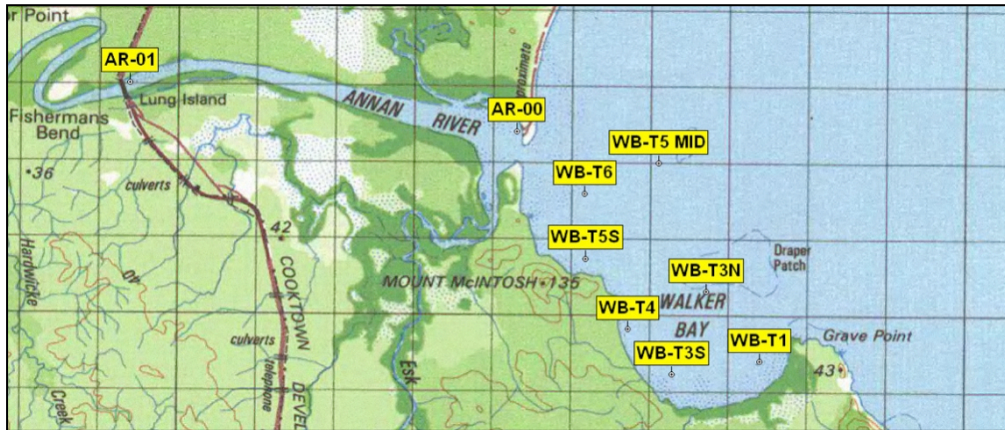


Figure 22: Walker Bay Sediment Sample Locations

Sediment nutrient samples were collected from the Endeavour River lower estuary in November 2007 and March 2010. Sediment sample locations are shown on Figure 20.

Total nitrogen levels in sediments ranged from 90 mg/kg to 1770 mg/kg (Table 9). Total phosphorous levels ranged from 33 mg/kg to 275 mg/kg. Nutrient levels were highest at site ER-2.5 and in the silty clay sediments on the north side of the Endeavour River at Leprosy Creek (ER-LEP).

Table 9: Endeavour River Estuary Sediment Sample Analytical Results – Nutrients (mg/kg)

Date:	11/12/07			16/3/10				
Site:	ER-03	ER-2.5	ER-LEP	ER-01	ER-CC	ER-02	ER-03	ER-LEP
Sediment:	Silty sand	Sandy silt	Silty clay	Sandy Silty clay	Sandy Silty clay	Sandy clay	Silty-sand	Silty clay
Total Nitrogen	820	1770	1010	360	220	90	400	1000
Total Phosphorus	105	275	192	75	68	33	144	156

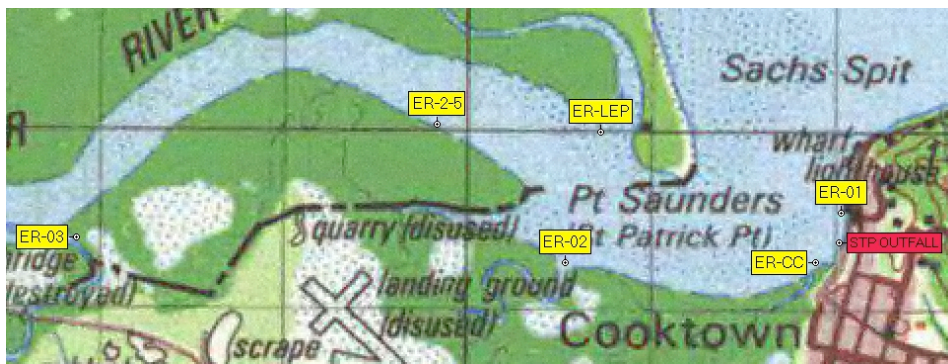


Figure 23: Endeavour River Sediment Sample Locations

4.9 Chlorophyll- α

Chlorophyll concentrations ranged from $< 0.01 \mu\text{g/L}$ to $4.04 \mu\text{g/L}$ at Annan River freshwater sites, $0.01 \mu\text{g/L}$ to $5.61 \mu\text{g/L}$ at Annan River estuary sites and $0.01 \mu\text{g/L}$ to $3.64 \mu\text{g/L}$ in the Endeavour River estuary. Concentrations as high as $9.54 \mu\text{g/L}$ were recorded in the Jeannie River upper and mid-estuary at the end of the dry season. Median Chlorophyll concentrations for all Annan, Endeavour & Jeannie sites were below the Guidelines for Estuaries and Upland Rivers (**Table 7**). Samples could not be field-filtered during highly turbid conditions, therefore chlorophyll-a concentrations were not recorded during most major flood events.

Coastal estuary sites AR-00 and ER-00 had low chlorophyll- α levels year round ($\leq 1.5 \mu\text{g/L}$). Median chlorophyll- α concentrations increased with distance upstream in the estuaries. Endeavour upper estuary sites ER-04 and ER-05 had the highest median chlorophyll-a concentrations of the Annan and Endeavour monitoring sites. Annan River freshwater sites (AR-03 and AR-04) had the lowest median values (**Figure 24**).

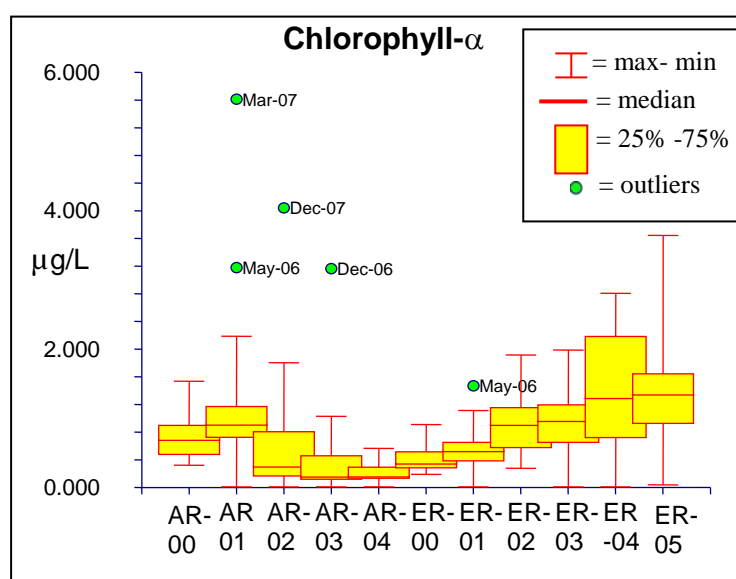


Figure 24: Annan & Endeavour Chlorophyll- α Box Plots

Maximum chlorophyll- α concentrations in Annan-Endeavour estuary sites occurred during or just after the wet season, after flood waters delivered nutrients into the estuary promoting algal growth (**Figure 25**). The maximum chlorophyll- α concentration ($5.6 \mu\text{g/L}$) was recorded at Annan River estuary site AR-01 in March 2007, one month after maximum nutrient levels at AR-01 were recorded during a flood in February 2007.

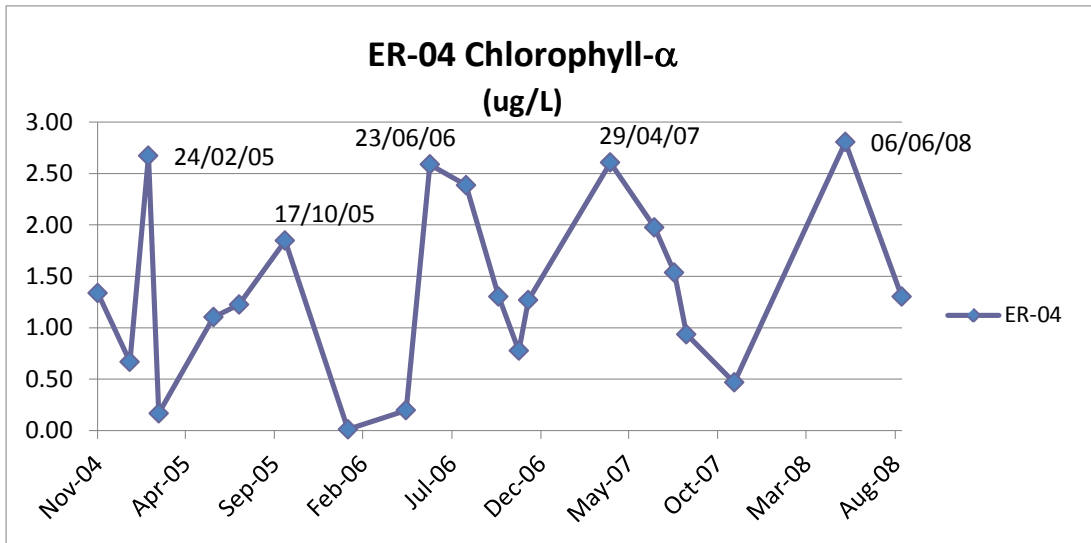


Figure 25: Seasonal Chlorophyll-α Cycles at Endeavour Estuary Site ER-04

Maximum chlorophyll-α levels at freshwater sites were recorded towards the end of the dry season, when flow rates were low and warm shallow waters promoted increased algal growth (**Figure 26**). Concentrations at freshwater sites AR-02 and AR-03 frequently exceeded the Qld Guidelines maximum concentration for freshwater (0.6 µg/L) during the dry season. Filamentous algal growth was notable at Wallaby Creek site AR-04 during the dry season, chlorophyll-α concentrations at this site did not exceed the Guidelines.

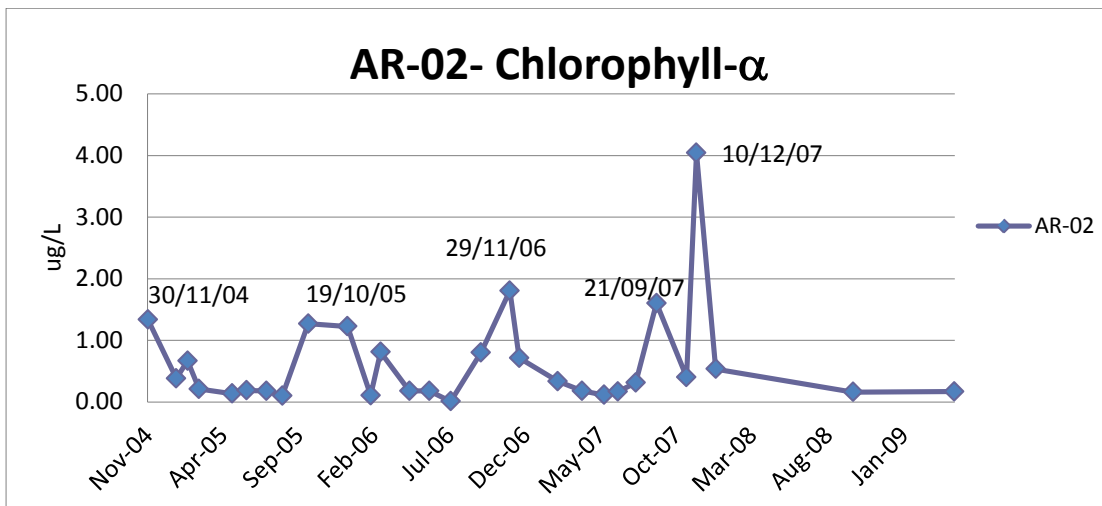


Figure 26: Seasonal Chlorophyll-α Cycles at Annan Freshwater Site AR-02

4.10 Metals Concentrations

4.10.1 Annan River

Aqueous and sediment metals samples were collected from the Annan River and Walker Bay in order to document metals concentrations across the catchment and to monitor impacts on water quality from the Bluestone tin mine. A total of 58 aqueous metals samples were collected from Annan River monitoring sites and additional sites

downstream and upstream of the mine. The range (minimum – maximum) of metals concentrations detected at monitoring sites AR-01 to AR-04 is presented in **Table 10**. A complete table of Annan River metals analytical results is presented in **Appendix D (Tables 5 and 6)**. Impacts from the Bluestone mine are discussed in Section 5.1.1.

Estuary

Metals detected in the estuary water samples (AR-01) were primarily associated with suspended sediments during wet season flood events. During base flow conditions most of the metals analysed were below the detection limits, with the exception of manganese (0.039 mg/L), arsenic (0.0012 mg/L) and cadmium (0.0002 mg/L). Iron and aluminium were not analysed but are likely to be dominant metals (**Table 10**).

During wet season flood events, total metals including cadmium, chromium, copper, lead, nickel, zinc and arsenic occurred in estuary waters in particulate form. Dissolved copper and arsenic were detected at concentrations ranging from 33% to 100% of the total concentrations (**Appendix D, Table 5**).

Total cadmium, chromium and lead, and both total and dissolved copper concentrations at AR-01 exceeded the ANZECC Water Quality Guidelines For The Protection Of Estuary Aquatic Ecosystems (95% Level of Protection) during flood events. No guidelines were exceeded during periods of base flow.

Freshwater

Metals concentrations at freshwater sites AR-02 through AR-04 were dominated by iron (0.06 mg/L – 1.78 mg/L). Aluminium was not analysed but is also likely to be a significant metal in water. Other metals present at varying concentrations were: zinc (<0.005 to 0.056 mg/L), manganese (0.002 – 0.008 mg/L), barium (<0.001 – 0.004 mg/L), and arsenic (<0.001 mg/L to 0.006 mg/L) and copper (<0.001 mg/L- 0.009 mg/L). Cadmium, chromium and lead concentrations were generally low or non-detect (<0.0001), but were elevated in one water sample collected from site AR-02 during a flood event (13/3/05). Nickel (<0.001 mg/L) and mercury (<0.0001 mg/L) were not detected above the detection limits in any freshwater samples (**Table 10**).

Dissolved concentrations of arsenic and copper accounted for between 20% to 100% of total concentrations and dissolved manganese concentrations accounted for 75% to 80% of total concentrations detected in freshwater samples (**Appendix D, Table 6**). Dissolved zinc concentrations could not be confirmed due to filter contamination.

Concentrations of cadmium, chromium, lead and zinc exceeded the Guidelines for the Protection of Aquatic Ecosystems at freshwater sites AR-02, AR-03 and AR-04 during flood events. Two freshwater metals detections exceeded the guidelines during base flow; total cadmium at AR-04 and total zinc at AR-03, both in June 2008.

Table 10: Minimum and Maximum Total & Dissolved Metals Concentrations - Annan River Sites

Site:		AR-01 (estuary)		AR-02		AR-03		AR-04		Estuary Water Quality Guidelines ¹	Freshwater Water Quality Guidelines ²
Analyte:		MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX		
Total Metals											
Arsenic	mg/L	<0.001	0.002	<0.050	0.004	<0.001	0.006	<0.001	0.002		0.013/0.024 ³
Barium	mg/L	<0.005	--	<0.001	0.004	0.002	0.003	--	0.004		--
Cadmium	mg/L	<0.0001	0.0303	<0.0001	0.02	<0.0001	0.001	<0.0001	0.0007	0.0055	0.0002
Chromium	mg/L	<0.001	0.041	<0.001	0.02	<0.001	0.0001	<0.001	<0.001	0.0274/ 0.0044 ⁴	0.001
Copper	mg/L	<0.001	0.003	<0.001	0.002	<0.001	0.009	<0.001	<0.001	0.0013	0.0014
Lead	mg/L	<0.001	0.018	<0.001	0.01	<0.001	<0.001	<0.001	<0.001	0.0044	0.0034
Manganese	mg/L	--	0.039	0.002	0.008	0.003	0.004	--	0.003		1.9
Nickel	mg/L	<0.001	0.058	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.07	0.011
Zinc	mg/L	<0.005	0.006	<0.005	0.012	<0.005	0.056	<0.005	0.010	0.015	0.008
Iron	mg/L	--	--	0.06	1.78	0.08	0.39	--	0.14		
Mercury	mg/L	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0004	0.0006
Dissolved Metals⁵											
Arsenic	mg/L	<0.050	0.001	<0.001	0.004	<0.001	0.004	<0.001	0.001		0.013/0.024
Copper	mg/L	<0.050	0.001	<0.001	0.001	<0.001	0.006	<0.001	0.001	0.0013	0.0014
Manganese	mg/L	<0.050	<0.050	<0.050	0.006	0.003	0.003	--	--		1.9
Zinc	mg/L	<0.5	del	<0.005	del	<0.005	0.052	<0.005	del	0.015	0.008

ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Marine Water (95% Level of Protection)

ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Freshwater (95% Level of Protection)

AsIII/AsV (Sample results are not speciated)

CrIII/CrVI (Sample results are not speciated)

Metals not shown were not detected above the Level of Reporting (LOR)

del Analytical results were discarded due to sample contamination from filters (dissolved Zn)

-- Not analysed

<0.005 Analyte not detected above the LOR

0.081 Results shaded green or blue exceed the ANZECC 2000 Water Quality Guidelines

Metals in Sediments

Sediment samples were collected from Annan River monitoring sites in November 2004, January 2005 and February 2007. Metals concentrations in Walker Bay sediments were sampled in November 2008. The minimum and maximum concentrations detected at freshwater, estuary and Walker Bay sites are listed in **Table 11**. The complete sediment metals analytical results are presented in **Appendix D, Tables 7 & 8**. Walker Bay sediment sample locations are shown on **Figure 22**.

Metals concentrations did not vary substantially between sites, although zinc and copper were slightly higher in sediments from AR-03.

The following metals were present in river sediments; zinc, chromium, copper, nickel, lead and arsenic. Aluminium and manganese were the dominant metals in Walker Bay sediments but were not analysed in Annan River sediment samples. Cadmium and mercury were not detected in any sediments and iron was not detected above the 50mg/L detection limit in Walker Bay. The concentrations of metals in sediments all fell below the “low effect range” of the ANZECC 2000 sediment quality guidelines, indicating that there is a low probability of effects on aquatic biota.

**Table 11: Minimum and Maximum Metals & Mercury Concentrations-
Annan River Sediments (mg/kg)**

	Estuary		Freshwater		Walker Bay	
	MIN	MAX	MIN	MAX	MIN	MAX
Aluminium	--	--	--	--	3270	9910
Arsenic	10	10	5	5	<5	10
Cadmium	<1	<1	<1	<1	<1	<1
Chromium	20	32	12	22	9	23
Copper	23	41	26	5	14	12
Iron	--	--	--	--	<50	<50
Lead	7	11	8	9	5	9
Manganese	--	--	--	--	97	228
Nickel	7	11	6	9	3	10
Zinc	16	34	23	52	9	31
Mercury	<0.1	<0.1	<0.1	0.2	<0.1	<0.1

-- Not Analysed

4.10.2 Endeavour River

Estuary Water Sample Results

Aqueous metals samples were collected from various Endeavour River locations in March 2005, February and October 2007, January and March 2008, September 2008 and March 2009. The range (minimum – maximum) of metals concentrations detected at monitoring sites ER-01 to ER-05 is presented in **Table 12**. A complete table of Endeavour River metals analytical results is presented in **Appendix D, Table 9**.

The dominant metals in unfiltered water samples from the Endeavour estuary were iron (0.38 mg/L – 5.12 mg/L) and aluminium (0.03 mg/L – 0.19 mg/L). Other elements detected included manganese (0.008 mg/L – 0.039 mg/L), barium (0.011 mg/L – 0.044 mg/L), copper (<0.0002 mg/L – 0.044 mg/L), chromium (<0.01 mg/L – 0.021 mg/L), lead (<0.001 mg/L – 0.032 mg/L), arsenic (<0.0005 mg/L – 0.024

mg/L), zinc (<0.005 mg/L – 0.081 mg/L), nickel (<0.001 mg/L – 0.002 mg/L) and cadmium (<0.0001 mg/L – 0.002 mg/L). Mercury was not detected in water samples above the detection limit (<0.0001 mg/L).

Iron, aluminium, cadmium, chromium, lead and nickel appeared to be primarily associated with suspended sediments and were not detected in filtered samples. Manganese occurred primarily in dissolved form, accounting for up to 90% of total manganese in one sample. Dissolved zinc varied accounting for 95% to 100% of total concentrations in March 2005. Dissolved copper and arsenic concentrations ranged from 25% to 100% of the total concentrations.

Iron, aluminium, chromium, copper, zinc and arsenic concentrations were highest in the lower estuary and decreased at upstream sites. Manganese, barium and nickel were highest at upper (brackish) estuary sites ER-04 and ER-05.

Zinc, copper, chromium and lead concentrations exceeded the ANZECC Guidelines for the Protection of Aquatic Ecosystems (marine) at sites ER-01, ER-02 and ER-03 on various occasions during the wet season when metals were elevated in association with suspended sediments (**Appendix D, Table 9**). Lead and chromium concentrations also exceeded the guidelines at ER-01 and ER-02 after light rains in the 2009 dry season (11/9/08).

Sediments

Sediment samples were collected from all Endeavour sites in November 2004 and from additional mid- to lower estuary sites in March and December 2007. Sediment sample locations are shown on **Figure 23**. Sediment sample results are listed in **Appendix D, Table 10**. Sediment analysis conducted in 2004 analysed metals in the fine sediment fraction only (<63µm), while subsequent analyses were conducted on the entire samples. Fine sediment samples (clay and silt dominated) were targeted at all sites.

Iron and aluminium were the dominant metals detected in Endeavour River sediments, ranging from 5180 mg/kg to 17,000 mg/kg (iron) and 1210 mg/kg to 8440 mg/kg (aluminium). Other trace metals were detected in sediments at the following maximum concentrations; manganese (124 mg/kg), zinc (121 mg/kg), vanadium (25 mg/kg), chromium (30 mg/kg), copper (39 mg/kg), arsenic (16 mg/kg), lead (86 mg/kg), nickel (16 mg/kg) and cobalt (124 mg/kg).

Barium was non-detect in most sediment with the exception of two samples collected in the vicinity of ER-01 and ER-CC. Cadmium and beryllium were not detected in any sediment samples above the detection limit (<1 mg/kg).

Mercury was non-detect at most sites (<0.1 mg/kg), but was detected in one ER-03 sediment sample at 1.1 mg/kg (**Appendix D, Table 10**). This was the highest concentration of mercury detected out of a total of 60 estuary and freshwater sediment samples collected by CYMAG across Cape York (Jardine et al, 2012). This level of mercury exceeds the “high range” of the ANZECC 2000 sediment quality guidelines, indicating that there is a >50% probability of effects on aquatic biota.

Table 12: Minimum and Maximum Total & Dissolved Metals Concentrations - Endeavour River Sites

Site:		ER-01 (estuary)		ER-02		ER-03		ER-04		ER-05		Estuary Water Quality Guidelines ¹
Analyte:		MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	MIN	MAX	
Total Metals												
Aluminium		0.16	0.16	0.13	0.19	0.05	0.05	0.07	0.07	0.05	0.05	
Arsenic	mg/L	<0.005	0.024	0.0019	0.011	0.001	0.0015	0.0005	0.004	<0.0005	0.004	
Barium	mg/L	0.012	0.012	0.011	0.016	0.030	0.030	0.044	0.044	0.042	0.042	
Cadmium	mg/L	<0.0001	<0.0010	<0.0001	<0.0010	<0.0005	<0.005	<0.0002	0.0002	<0.0002	0.0001	0.0055
Chromium ²	mg/L	<0.0002	0.021	<0.0005	0.014	<0.0005	<0.005	<0.0005	<0.001	<0.0005	0.001	0.0274/ 0.0044 ⁴
Copper	mg/L	<0.0005	0.044	<0.001	0.004	<0.001	0.001	<0.001	0.001	<0.001	0.001	0.0013
Lead	mg/L	<0.001	0.012	<0.0002	0.032	<0.0002	<0.005	<0.0002	<0.001	<0.0002	<0.001	0.0044
Manganese	mg/L	<0.0002	0.017	0.031	0.031	0.015	0.015	0.038	0.038	0.039	0.039	
Nickel	mg/L	<0.0005	<0.050	<0.0005	<0.050	<0.0005	<0.050	0.0006	0.002	0.0007	0.002	0.07
Zinc	mg/L	<0.005	0.081	<0.005	0.058	<0.005	<0.050	<0.005	<0.005	<0.005	<0.005	0.015
Iron	mg/L	1.05	5.12	<0.50	0.96	0.51	0.51	0.40	0.40	0.42	0.42	
Mercury	mg/L	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0004

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Marine Water (95% Level of Protection)

2 CrIII/CrIV

<0.050 Analyte not detected above the Level of Reporting (LOR)

0.004 Cells shaded blue exceed the Water Quality Guidelines

4.10.3 Jeannie River

A total of 16 aqueous metals samples were collected from the Jeannie River estuary (JR-00 – JR-03) and freshwater (JR-04) sites on six dates between December 2007 and May 2009, including wet and dry season samples. The results are presented in **Appendix D, Table 11**.

Iron was the dominant metal in both estuary and freshwater samples, occurring at a maximum value of 2.09 mg/L in the estuary. Aluminium (0.31 mg/L), manganese (0.202 mg/L), barium (0.16 mg/L) and zinc (0.097 mg/L) were also detected in estuary and freshwater samples. Other metals present at trace concentrations included (in order of magnitude) copper, lead, chromium, arsenic, cobalt and cadmium. Mercury and tin were not detected above the detection limits in any water samples.

Copper and zinc concentrations in the estuary exceeded the ANZECC 2000 water quality guidelines for the protection of aquatic ecosystems. Zinc exceeded the guidelines at freshwater site JR-04. The Jeannie River is an undeveloped catchment, however feral cattle, cattle pads and a large gully associated with a former gravel pit contribute to increased erosion and sedimentation in the river, which may lead to elevated metals concentrations during the wet.

4.11 Bacteria

Faecal contamination can render water unfit for drinking and at high concentrations can be harmful to aquatic species. Bacterial contamination of the Annan and Endeavour Rivers is of concern due to the number of cattle and feral pigs in the catchment, often concentrating around the water. Rossville, Helenvale, Marton and other rural septic systems are also potential sources of bacterial contamination. Cooktown and Hopevale sewerage treatment plants release effluent to the Endeavour River, however if treated correctly should not contain significant levels of bacteria.

Bacteria samples were collected opportunistically from Annan, Endeavour and Jeannie River sample locations, plus additional sites at Keatings Lagoon and Alligator Creek. The analytical results from bacteria samples collected from the Annan-Endeavour Catchment Area are listed in **Table 13**.

Bacteria levels recorded in October and November 2007 at Keatings Lagoon were among the highest levels recorded at any Cape York river or wetland by CYMAG scientists (Howley, C. unpublished data). Keatings Lagoon is a wetland in the lower Annan catchment that was heavily impacted by pigs before they were fenced out in 2008.

Bacteria counts in the Endeavour River were highest during the wet season and at upper estuary sites ER-04 and ER-05. Feral pig diggings are common at wetland sites near ER-04 and ER-05 and are likely to contribute to the high bacteria counts. Higher temperatures at this time would also contribute to the increased levels.

Alligator Creek is located at the base of Mount Cook in Cooktown and flows past residential areas and a caravan park into a small estuary at Finch Bay. The Alligator

Creek estuary at Finch Bay had high bacteria levels in March 2007 compared to the lower Endeavour estuary.

There are no Guidelines for bacteria levels for the Protection of Aquatic Ecosystems. Bacteria counts from the Annan and Jeannie Rivers were below the Guidelines for Recreational Use (swimming or bathing); however no samples were collected from the Annan during the wet season, and Jeannie River samples were only collected on one date. Bacteria levels at the Endeavour upper estuary, Alligator Creek and Keatings Lagoon exceed the Guidelines for Recreational Use.

Table 13: Annan & Endeavour River Bacteria Sample Results

Site	Date	Faecal Coliform CFU/100mL	E-coli CFU/100mL
AR-02	22/06/2007	90	--
AR-01	29/10/2007	4	5
AR-02	29/10/2007	<1	< 1
AR-03	29/10/2007	15	15
AR-04	29/10/2007	21	28
Keatings Lagoon	29/10/2007	>8000	200
Keatings Lagoon	19/11/2007	1880	--
ER-01	19/03/2007	67	--
ER-02	19/03/2007	50	--
ER-03	19/03/2007	30	--
ER-04	19/03/2007	690	--
ER-05	19/03/2007	490	--
AC-01 (Alligator Creek)	19/03/2007	500	--
ER-01	30/10/2007	1	< 1
ER-02	30/10/2007	<1	< 1
ER-03	30/10/2007	<1	< 1
ER-04	30/10/2007	<1	< 1
ER-05	30/10/2007	1	< 1
ER-CC	16/03/2010	43	44
ER-01	16/03/2010	43	39
ER-02	16/03/2010	7	4
JR-01	14/04/2008	< 10	< 10
JR-04	14/04/2008	100	130
ANZECC 2000 Guidelines for Recreational Use		150	
NHMRC 2004 Drinking Water Guidelines		0	

5 LAND USE IMPACT ASSESSMENT RESULTS

In addition to monthly ambient water quality monitoring and sample analysis, water and sediment samples were collected annually or bi-annually (depending on funding availability) from the Annan and Endeavour River to assess potential impacts from land use in the catchments. The results from these analyses are presented in the following section.

5.1 Annan River Land Use Assessment

Potential sources of water quality impacts in the Annan River include the Collingwood- Bluestone tin mine (Bluestone mine), residential septic systems, cattle grazing, pigs and the disturbance of acid sulphate soils.

5.1.1 Collingwood Bluestone Tin Mine

The Collingwood Bluestone tin mine is located in the Annan River catchment at Shiptons' Flat. Earthworks at the mine began in 2005 and production commenced in January 2006. Leswall Creek (Adams Gully) flows past the main area of operations into the Annan River at AR-03. Approximately 1 km upstream of AR-03 there is a large tailings dam that drains directly into the Annan River (**Figure 27**). The mine ceased operating in 2008 but the tailings dam remains and continues to release water into the Annan (**Appendix A**, Photos 9 & 10).

The Bana Yalanji rangers and traditional owners obtain drinking water from the Annan River approximately 1 km downstream from the mine. The Cooktown water supply weir is located approximately 13 km downstream on the Annan River.

Monitoring in the vicinity of the mine occurred at the following sites (**Figure 27**):

- AR-03: the Annan River immediately downstream from Leswall Creek (Adams Gully on map),
- AR-LES: Leswall Creek upstream from its confluence with the Annan River
- TD Drain: a small drain flowing from the northern end of the dam into the Annan throughout the wet season
- TD Overflow: the tailings dam overflows from the southern end of the dam during major overflow events such as the February 2007 overflow.
- AR-USTD: the Annan River upstream from the Tailings Dam

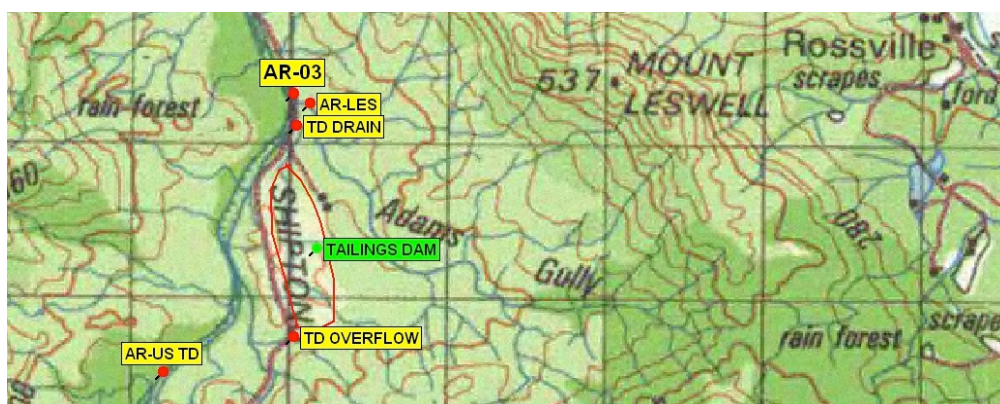


Figure 27: Annan River – Bluestone Mine Impact Sample Locations

Turbidity levels significantly increased at site AR-03 after the Collingwood Bluestone tin mine commenced operations in the adjacent catchment. Prior to 2006, turbidity at AR-03 had not been recorded above 13 NTU during the wet or dry seasons. After mining commenced at Leswall Creek, turbidity was measured at 141 NTU (March 2006) and 69 NTU (May 2006). Upstream from the confluence of Leswall Creek at AR-03, the waters remained clear (Photos below). After 2007, turbidity levels during the wet season returned to pre-mining levels (**Figure 28**).



Photo 1: Site AR-03* March 2006



Photo 2: Site AR-03* February 2007

(Photos taken facing south (upstream) at AR-03, with Leswall Creek flowing in from the east)

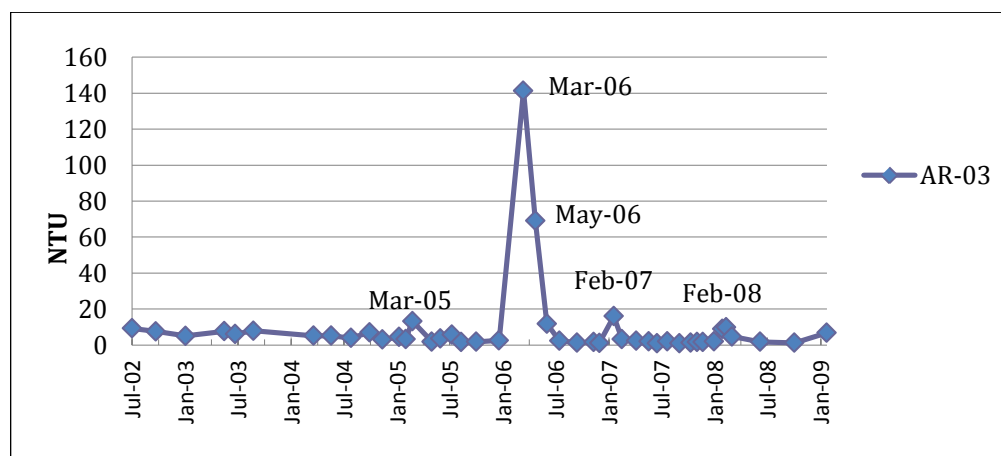


Figure 28: Turbidity Levels at AR-03

The results of metals analyses in the vicinity of the mine, and a comparison with water quality guidelines are presented in **Appendix D, Table 12**. Elevated levels of copper and arsenic were recorded at AR-03 in February 2007 when the tailings dam first overflowed into the Annan River. Total and dissolved copper concentrations exceeded the ANZECC Guidelines for the Protection of Aquatic Ecosystems. Metals concentrations 8 km downstream at AR-02 (above the Cooktown drinking water weir) remained below the Guidelines.

Samples collected after the mine ceased operating (2008 – 2010) showed that the tailings dam continued to release arsenic, copper and antimony into the Annan River at concentrations above the background levels at upstream site AR-USTD. Total and dissolved copper concentrations at AR-03 continued to exceed the ANZECC Guidelines. Copper sulfide used to settle out sediments from water in the tailings dam may contribute to the elevated copper concentrations.

Arsenic concentrations at Leswall Creek (AR-Les) and the tailings dam drain (TD-drain) exceeded the drinking water guidelines in 2008. Antimony exceeded the drinking water guidelines in the tailings dam drain in 2008 and 2010. However, arsenic and antimony concentrations detected in the Annan River at AR-03 and AR-02 (near the Cooktown and Bana Yalanji water supplies) did not exceed the Drinking Water guidelines on any occasion.

Maximum total nitrogen, ammonia and nitrogen oxide concentrations for freshwater sites were detected at Site AR-03, downstream from the Collingwood mine, in February 2007 when water from the Bluestone Mine tailings dam entered the Annan River. The nitrogen concentrations were significantly elevated above previous wet season concentrations. This was the peak period of operations at the mine and large quantities of phosphorus and nitrogen based explosives were being used at the mine, possibly explaining the increase in nutrient levels at this time.

Total petroleum hydrocarbons (TPH C29 - C36 Fraction, associated with diesel) were detected at low levels (80 µg/L) in water samples collected from Leswall Creek at AR-03 in February 2007 (Table 14). CYMAG and SCYC scientists received reports and photos of waste oil spills adjacent to Leswall Creek at the mine. The poor waste oil disposal practices may have resulted in run-off into Leswall Creek.

5.1.2 Vehicle Emissions and Boat Fuel

Total Petroleum Hydrocarbons (TPH) and Polynuclear aromatic hydrocarbons (PAHs) were analysed at Annan River sites in March 2005 and February 2007 to assess for impacts from vehicle and boat emissions and run-off from roads.

No PAHs were detected in any samples. TPH (60 – 70 µg/L) were detected in water and sediment samples from sites AR-01 and AR-02 (Table 14 and 15). Both sites are located adjacent to major road crossings and there is a boat ramp at site AR-01. The TPH detections are likely to result from vehicle emissions and/or boating activities.

TPH at these concentrations will naturally degrade and are not likely to pose a significant threat to aquatic species.

Table 14: Annan River Water Sample Analytical Results- TPH & PAH

Date:		13/03/05		06/02/07			
Site:		AR-01	AR-02	AR-01 ¹	AR-02 ¹	AR-03 ¹	AR-04 ¹
Total Petroleum Hydrocarbons							
C6 - C9 Fraction	µg/L	--	--	<20	<20	<20	<20
C10 - C14 Fraction	µg/L	<50	70	<50	<50	<50	<50
C15 - C28 Fraction	µg/L	<100	<100	<100	<100	<100	<100
C29 - C36 Fraction	µg/L	60	<50	<50	<50	80	<50
Polynuclear Aromatic Hydrocarbons							
All analytes	µg/L	<1.0	<1.0	<1.0	--	<1.0	<1.0

¹ Results exceeded the holding time by one day (minor losses may have occurred)

<1.0 Analyte not detected above the LOR

-- Not Analysed

Table 15: Annan River Sediment Sample Analytical Results- TPH & PAH

Date:		13/03/05	06/02/07		26/11/08
Site:		AR-01	AR-01	AR-02	WB - T6 mouth
Polynuclear Aromatic Hydrocarbons					
All Analytes	mg/kg	<0.5	<0.5	<0.5	<0.5 ¹
Total Petroleum Hydrocarbons					
C6 - C9 Fraction	mg/kg	2	--	--	--
C10 - C14 Fraction	mg/kg	<50	70	60	--
C15 - C28 Fraction	mg/kg	<100	190	220	--
C29 - C36 Fraction	mg/kg	<200	160	160	--

<1.0 Analyte not detected above the LOR
 1 Low recovery in surrogate sample
 -- Not analysed

5.1.3 Acid Sulphate Soils

The minimum Annan River pH value (5.54) was recorded in April 2007 at site AR-00 (**Appendix D, Table 2**). Upstream sites recorded significantly higher pH values on this date (site AR-01 4 km upstream was 6.74). Acid-sulphate soils (ASS) have been documented at a prawn farm immediately upstream of the river mouth, which was closed due to the high cost of managing ASS. Extensive areas of ASS at Keatings Lagoon, which also flows into the mouth of the Annan, were heavily disturbed by pigs prior to the instalment of a pig-proof fence around the lagoon. The pH as low as 2 has been recorded in areas of pig diggings near the Lagoon. Disturbed ASS may be responsible for the low pH measured at Site AR-00. This site was difficult to access during wet season conditions, therefore there is insufficient data to properly assess the pH during the wet season when the acid run-off impacts would be most evident.

5.2 Endeavour River Land Use Assessments

Land-use in the upper estuary of the Endeavour River includes small-scale agricultural enterprises and cattle grazing. The Right Branch of the Endeavour River (ER-04) flows past Hopevale and receives effluent from the Hopevale sewerage treatment plant. Pig diggings impact wetlands in the freshwater and upper estuary regions.

The lower Endeavour River estuary flows past Cooktown and is subject to potential impacts from town stormwater run-off, sewerage treatment plant effluent, rubbish-tip leachates and boat maintenance and fuelling activities primarily in the vicinity of ER-01 and ER-00. The Cooktown industrial area, including a gravel pit, vehicle maintenance workshops and sawmill is located in the vicinity of ER-02.

Monitoring of potential impacts from these land-uses was conducted at ER monitoring locations as well as additional sample locations shown on **Figure 29**.

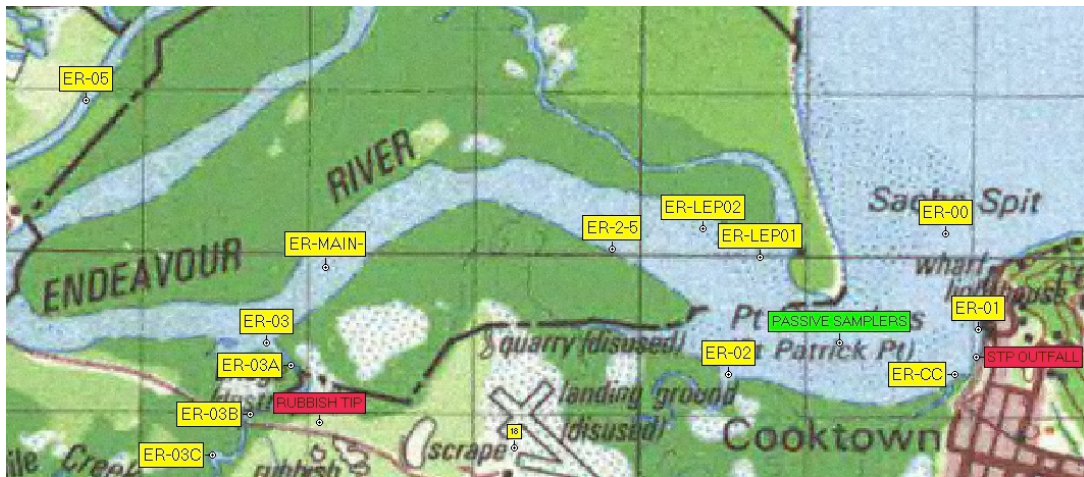


Figure 29: Endeavour River Contaminant Sample Locations

5.2.1 Agricultural Land-Use

The Endeavour Valley hosts a number of small-scale horticultural enterprises, including mango, passionfruit and turf farms. Nutrients, Pesticide and herbicide levels in the Endeavour estuary were analysed to document run-off from farms. Herbicides are also used at residential and government managed lands to control weeds.

Nutrients

Nutrient levels in the Endeavour estuary do not appear to be elevated as a result of the use of fertilisers. Median nutrient concentrations at site ER-05 (downstream from small scale farms) were similar to those at ER-04 (where there is no known horticultural land-use) (Appendix D, Table 3).

Herbicides & Pesticides

Sediment and water samples were analysed for a wide range of pesticides and herbicides, including organochlorine and organophosphate (OC/OP) pesticides, phenoxyacetic acid herbicides, glyphosate (Round-Up), triazines (atrazine & simazine) and diuron. Grab water and sediment samples were collected in February and November 2007 and 2008. Passive samplers were deployed in the Endeavour River lower estuary during the 2008 and 2009 wet seasons.

Tables 13, 14 and 15 in Appendix D list the results from pesticide and herbicide water grab samples and passive samplers. No pesticides or herbicides were detected in grab samples with the exception of glyphosate, which was also detected in the field blank sample. The herbicides diuron, atrazine and simazine were detected at low concentrations (ng/L) in 30-day and 5-day passive samplers deployed in January-February 2008 and December 2008- January 2009 (Table 16). The actual daily concentrations in the water are estimated based on the amount present in the sampler and the flow rate measured by flow monitoring devices deployed with the passive samplers.

Table 16: Herbicides detected in Endeavour River Passive Samplers 2008 & 2009 Wet Seasons – Estimated Daily Concentrations¹ (ng/L)

Sample Site:	ER-Light	ER-Light	ER-01	ER-01	ANZECC Guidelines ²
Sample Period:	23/1/08 – 21/2/08	19/2/08 – 24/2/08	22/12/08– 21/1/09	10/1/09 – 14/1/09	
Herbicides					
Diuron	6.9	1.5	1.4	1.6	ID
Simazine	1.8	<0.3	<0.3	<0.3	200
Atrazine	4.8	<0.3	<0.3	<0.3	700
Galaxolide	NA	NA	<0.05	3	ID

¹ Concentration estimated using a sampling rate of 0.08 L.day⁻¹ (30 days) or 0.59 L.day⁻¹ (5 day)

² ANZECC 2000 Guidelines for the Protection of Freshwater Aquatic Ecosystems (99% Level of Protection)- No guidelines have been established for saltwater.

ID Insufficient data exists – no guideline values have been established

Sediment samples collected from the Endeavour estuary contained few pesticides or herbicides above the detectable concentrations. The herbicide clopyralid was detected in sediments near Leprosy Creek in November 2007 at 0.28 mg/kg. Subsequent water and sediment samples collected in the vicinity of Leprosy Creek and throughout the estuary did not contain clopyralid or other herbicides (**Appendix D, Tables 16 & 17**).

Discussion on Herbicides

Atrazine, simazine and diuron were detected in estuary passive samplers at very low concentrations (1.4 ng/L to 6.9 ng/L). Clopyralid was detected in estuary sediments on one occasion at 0.28 mg/kg. Glyphosate was also detected but its presence could not be confirmed. The herbicides detected were well below the Water Quality Guidelines for the Protection of Aquatic Ecosystems (ANZECC 2000) although guidelines have not been established for most of these chemicals.

The herbicide diuron is used to control a wide variety of annual and perennial broadleaf and grassy weeds. It is soluble and very persistent in water with a half-life of 1,290 days. Diuron is reported as being moderately to highly toxic to aquatic species at concentrations as low as 1mg/L (www.pestgenie.com.au/msds/ospray/DIURON_500_25101530.pdf).

Atrazine is a pervasive environmental contaminant used in a wide range of horticultural crops and for weed control. It is classified as moderately toxic for aquatic organisms (96-h LC50 ranges from 0.5-15 mg/l; the LD50 for fish ranged from 4.3 mg/l - 7.6 mg/l) (www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC35042). It has been shown to cause demasculinization of fish at 0.5 µg/L (Haynes et al, 2011). Fish may bioaccumulate atrazine to levels 11 times the concentration in surrounding water (<http://pmep.cce.cornell.edu/profiles/extoxnet/24d-captan/atrazine-ext.html>).

Simazine is a synthetic chemical that is widely used as an herbicide to control the growth of weeds. Simazine is accumulated by fish, but is not considered to be acutely toxic with an LC50 (96 hrs) between 90 to over 100 mg/L for several fish species. It is toxic to seagrass at concentrations as low as 10 µg/L (www.pesticideinfo.org/List_AquireAll.jsp?Rec_Id=PC34340)

Clopyralid is an herbicide used to control broadleaf weeds in lawn and turf, range, pasture and rights-of-way. It is soluble in water and persistent in soils. Studies on the

aquatic toxicity of clopyralid found the LC50 for fish ranged from 440 to 630 mg/l in a number of studies (www.pesticideinfo.org/List_AquireAll.jsp?Rec_Id=PC36017).

Based on the concentrations detected, these herbicides are not considered a threat to aquatic ecosystems in the Endeavour River or to human health from the consumption of fish. However the concentrations were reported for passive samplers in the lower estuary, and pulses of higher concentrations may occur farther upstream.

5.2.2 Cooktown Sewerage Treatment Plant Effluent Outfall

The Cooktown STP began releasing effluent 100m upstream from ER-01 in August 2005. Influent volumes increased over the following 2 years as residents connected to the new service. There is insufficient pre-2005 data to compare nutrient levels before and after the new STP began discharging. However, monthly total and dissolved nitrogen and phosphorous concentrations and annual mean and median concentrations at ER-01 have been assessed for changes over time (2005- 2008) as input to the new STP increased.

Linear regression graphs (**Figure 30**) show minor (insignificant) positive trends over time for total nitrogen and phosphorous concentrations at ER-01 and negative trends for dissolved nitrogen. FRP concentrations showed no increase or decrease. There is no evidence of significant changes in nutrient levels based on the linear regression.

A comparison of annual median nutrient concentrations showed no evidence of significant changes over time as a result of sewerage effluent. The annual medians for total phosphorous and nitrogen oxide concentrations decreased slightly from 2005 to 2008; total nitrogen was slightly higher in 2008. Annual medians for ammonia and dissolved phosphorus showed no change. Peaks in total nitrogen and phosphorous concentrations detected at ER-01 during flood events resulted in significantly higher mean concentrations in 2008 compared to previous years (**Table 17**).

A comparison of median nutrient concentrations at site ER-01 with other estuary sites also provides no indication that nutrient levels at ER-01 are elevated as a result of effluent outfall. ER-01 had the lowest median nutrient concentrations of all Endeavour sites (**Appendix D, Table 14**). Any increases in total nutrient levels in the Endeavour River were associated with flood events and cannot be directly attributed to STP effluent outfalls.

Site	Year	Total Phosphorus	Filt Reac Phosphorus	Ammonia Nitrogen	Nitrogen Oxides	Total Nitrogen	Chlor-a
		mg/L	mg/L	mg/L	mg/L	mg/L	ug/L
ER-01 Annual MEDIAN	2005	0.011	<0.002	0.005	0.005	0.10	0.5239
	2006	0.012	0.002	0.005	0.005	0.13	0.5878
	2007	0.006	<0.002	0.003	<0.002	0.09	0.5344
	2008	0.008	<0.002	0.005	<0.002	0.16	0.5177
ER-01 Annual MEAN	2005	0.011	0.001	0.010	0.010	0.17	0.5522
	2006	0.013	0.002	0.005	0.005	0.13	0.6354
	2007	0.012	0.002	0.004	0.008	0.14	0.5377
	2008	0.028	0.002	0.010	0.013	0.30	0.5034

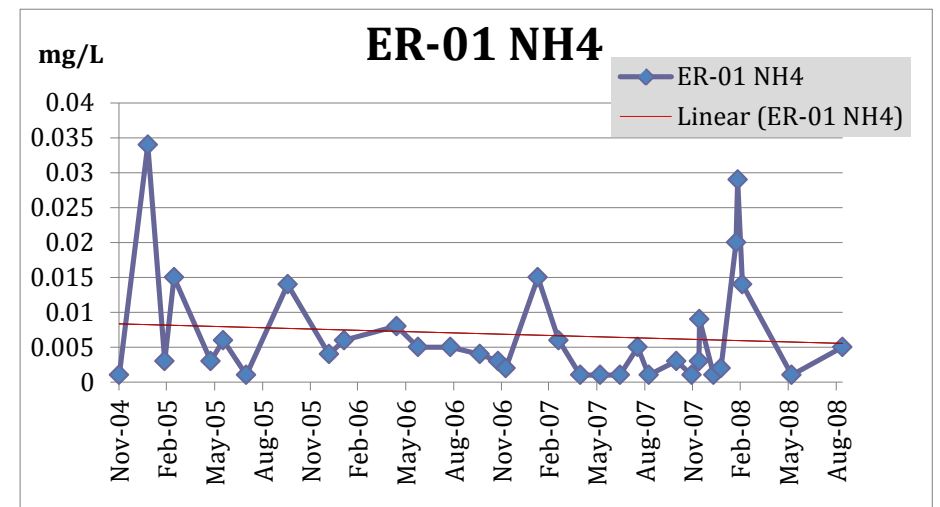
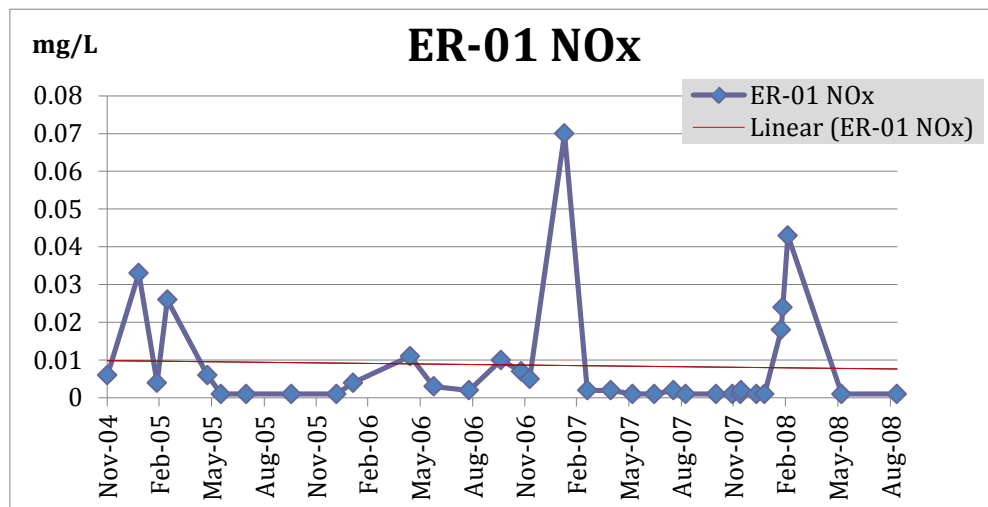
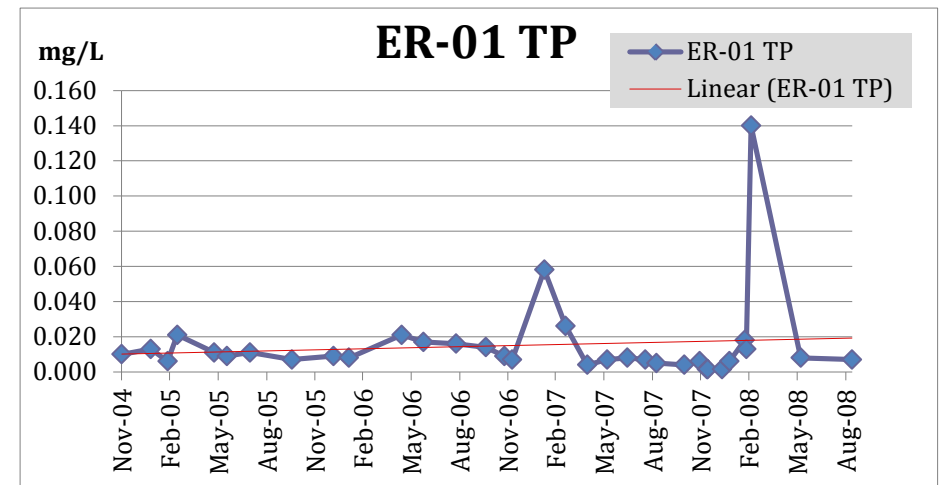
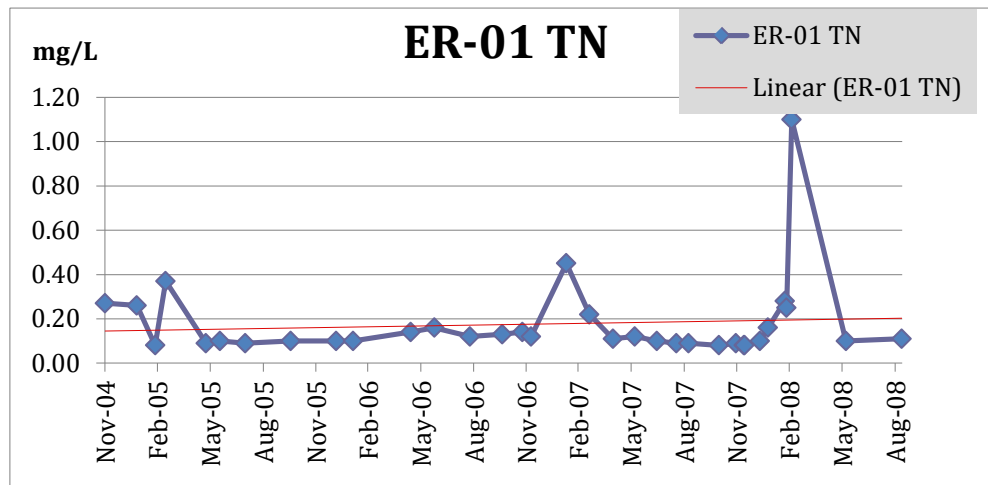


Figure 30: Linear Regression for Total Nitrogen, Total Phosphorous, Nitrates and Ammonia Concentrations over time (2005-2008)

Chlorophyll-a

An assessment of chlorophyll- α levels at ER-01 below the Cooktown STP effluent outfall did not show any evidence of an increase (or decrease) over time (2005-2008). Although the median and mean annual concentration increased in 2006 due to a chlorophyll peak after a flood (**Table 17**), the linear regression trendline showed a minor (insignificant) decrease in chlorophyll-a concentrations (**Figure 31**).

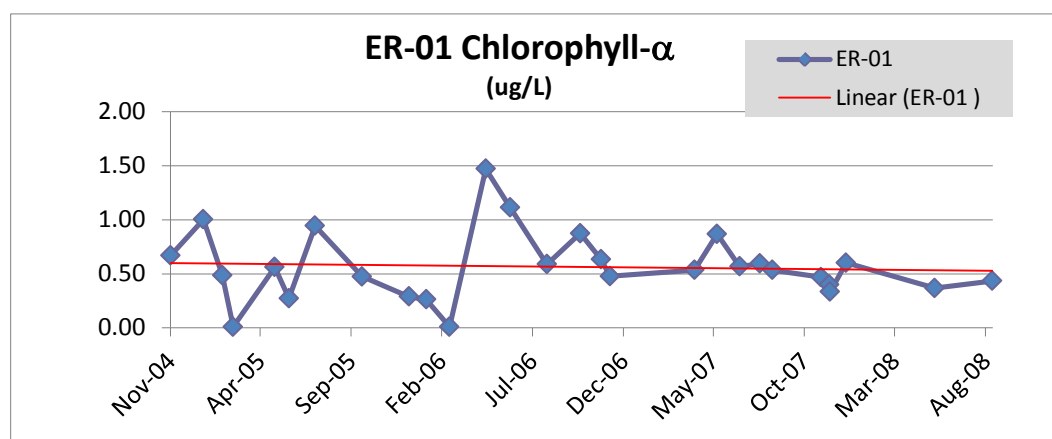


Figure 31: Graph of ER-01 Chlorophyll- α with Linear Regression Trendline

Galaxolide

Galaxolide (Hexahydrohexamethyl Cyclopentabenzopyran)- a polycyclic musk, was detected at approximately 3 ng/L in a 5-day passive sampler deployed in the estuary in January 2009 (**Table 16**). Galaxolide is a synthetic musk-like fragrance commonly found in detergents, shampoos, perfumes and fabric softener. It may be entering the estuary via sewerage treatment plant effluent containing these products. Galaxolide is considered to be very harmful to the aquatic environment, although no toxicity guidelines are available.

Bacteria

Bacteria levels were analysed both upstream and downstream from the Cooktown STP in March 2007, October 2007 and March 2010. Bacteria counts in the vicinity of the STP were slightly elevated compared to upstream site ER-02, but remained at relatively low levels (<100cfu/100mL) at all lower estuary sites (**Table 13**).

5.2.3 Hope Vale Sewerage Treatment Plant

The Hope Vale sewerage treatment plant is a secondary treatment plant that releases treated effluent into the North Arm of the Endeavour River, approximately 25 km upstream from site ER-04. Nutrient levels have not been monitored at this site, however one round of nutrient sampling was conducted downstream from the STP in May 2007. The results did not exceed the water quality guidelines for total phosphorous and nitrogen oxides (**Table 18**). Additional sampling both below and above the STP is required to determine if there have been any impacts from effluent.

Table 18: Endeavour River at Hope Vale STP: Nutrient Concentrations (mg/L)

Sample ID	Date	Total Phosphorus	Filt Reac Phosphorus	Ammonia Nitrogen	Nitrogen Oxides	Total Nitrogen
ER- Hope Vale STP	29/05/07	0.012	0.003	0.007	0.015	0.10
<i>Lowland river*</i>		<i>0.010</i>	<i>0.004</i>	<i>0.010</i>	<i>0.010</i>	<i>0.300</i>

ANZECC 2000 and Qld 2009 Guidelines for the Protection of Aquatic Ecosystems (lowland river)

5.2.4 Cooktown Rubbish Tip

The Cooktown Rubbish Tip is an un-lined pit located on top of a small hill, approximately 700 m from the Endeavour River and 380 m from Four Mile Creek, immediately upstream from site ER-03 (**Figure 29**). Household rubbish, abandoned vehicles, waste oil, and hospital waste are among the waste types previously disposed of at the tip.

A small gully at the bottom of the tip runs into saltmarsh connected to Four Mile Creek. However groundwater and surface water run-off may also enter the Endeavour River further downstream towards ER-02. In order to test for potential contamination leaching from the Cooktown Tip, a range of grab samples were collected from the Endeavour River at ER-03 and ER-02 in March 2005, February 2007 and September 2008.

Water and sediment were analysed for Polynuclear Aromatic Hydrocarbons (PAHs), Total Petroleum Hydrocarbons (TPH), Benzene, Toluene, Ethylene & Xylene (BTEX), Phenols, Halogenated Aliphatic and Aromatic compounds (solvents) and metals.

No PAHs, BTEX, phenols or solvents were detected in water samples collected from ER-03 or ER-02 (**Appendix D, Table 18**). TPH (C15-C36 fractions) were detected in sediment samples collected at Four Mile Creek (ER-03) in March 2007 at a maximum concentration of 260 mg/kg (**Appendix D, Table 19**). TPH at ER-03 could be associated with the rubbish tip or boat emissions.

Metals concentrations in water and sediment samples from ER-03 (below the Cooktown rubbish tip) were not significantly elevated above background concentrations. However, mercury was detected in ER-03 sediments at 1.1 mg/kg compared to a maximum concentration at other Endeavour river samples of 0.3 mg/kg (**Appendix D, Table 10**).

5.2.5 Cooktown harbour and surface water run-off

Endeavour river estuary water and sediment samples were analysed for metals and a wide range of hydrocarbons in order to assess potential impacts from boat maintenance, emissions and fuelling activities, run-off from Cooktown roads, petrol stations, mechanical workshops and other light industries, as well as upstream land-use activities including those discussed above.

Metals

Aqueous metals samples were collected from the Endeavour River in March 2005, February and October 2007, January and March 2008 (ER-01 only), September 2008 and March 2009 (ER-02 only). Sediment samples were collected from all primary Endeavour River sites in November 2004 and from mid- to lower estuary sites only in March and December 2007. The results from all aqueous metals analyses are listed in **Appendix D, Table 9**; minimum and maximum concentrations for each site are listed in **Table 12 (page 45)**. All sediment sample metals concentrations are listed in **Appendix D, Table 10**.

Chromium, copper, lead and zinc concentrations were elevated above background in water samples collected from sites ER-01 in the Cooktown harbour. Maximum lead concentrations in water occurred at Site ER-02. Zinc, a common contaminant from urban run-off, was detected in water samples from ER-01 and ER-02 at concentrations more than 10 times greater than other estuary sites (**Table 12**).

Lead and zinc concentrations were significantly higher in sediments from site ER-01 than at other Endeavour River locations.

The elevated metals at site ER-01 are likely to be associated with stormwater run-off from Cooktown and/or boat maintenance work at the adjacent slipway. Elevated zinc concentrations in sediments could also be associated with STP effluent based on the results of samples collected approximately 50m upstream and downstream from the STP effluent outfall in September 2008 (**Appendix D, Table 10**).

During ambient flow conditions, metals concentrations in water are not likely to pose a significant threat to aquatic ecosystems or human health. Metals concentrations only exceeded the guidelines when associated with suspended sediments in flood events, with the exception of lead and cadmium concentrations in ER-01 and ER-02 water samples after light rains in the 2009 dry season (**Appendix D, Table 9**). Metals being flushed into the Cooktown harbour from stormwater run-off or other sources will generally settle into the sediments, where they can be taken up and bioaccumulated by aquatic plants and animals, including seagrass, fish and crabs.

Total Petroleum Hydrocarbons & PAHs

Water and sediment samples from lower estuary sites ER-00, ER-01 and ER-02 were analysed for total petroleum hydrocarbons (TPH), benzene, toluene, ethylbenzene and xylene (BTEX), polynuclear aromatic hydrocarbons (PAHs), phenols and various solvents in March 2005, February and March 2007, and January and September 2008. Passive samplers capable of detecting ultra-low (ng/L) concentrations of PAHs were deployed near the mouth of the Endeavour River during the 2008 and 2009 wet seasons.

Low concentrations of total petroleum hydrocarbons (180 µg/L) were detected in water samples at sites ER-00 and ER-02 in 2005 (**Table 19**). TPHs were also detected in sediments from ER-01 at a total concentration of 290 mg/kg (**Table 20**). TPHs are associated with unleaded fuel and diesel.

**Table 19: Petroleum Hydrocarbons Detections-
Endeavour River Water Grab Samples (µg/L)**

Sample Location	ER-00	ER-02
Sample Date	14/03/05	14/03/05
<i>Total Petroleum Hydrocarbons</i>		
C10 - C14 Fraction	80	80
C15 - C28 Fraction	100	100
C29 - C36 Fraction	<50	<50

**Table 20:
TPH and PAH Detections in Endeavour River Sediments (mg/kg)**

Date:	19/03/07				
Site:	ER - 01	ER - 02	ER - 03A	ER - 03B	ER - 03C
<i>Total Petroleum Hydrocarbons</i>					
C6 - C9 Fraction	<10	<10	<10	<10	<10
C10 - C14 Fraction	50	<50	<50	<50	<50
C15 - C28 Fraction	240	<100	120	<100	<100
C29 - C36 Fraction	<100	<100	140	120	<100
<i>Polynuclear Aromatic Hydrocarbons</i>					
Naphthalene	<0.5	<0.5	<0.5	<0.5	<0.5
Acenaphthylene	0.8	<0.5	<0.5	<0.5	<0.5
Phenanthrene	8.7	<0.5	<0.5	<0.5	<0.5
Anthracene	1.6	<0.5	<0.5	<0.5	<0.5
Fluoranthene	12.3	<0.5	<0.5	<0.5	<0.5
Pyrene	9.5	<0.5	<0.5	<0.5	<0.5
Benz(a)anthracene	4.9	<0.5	<0.5	<0.5	<0.5
Chrysene	4.2	<0.5	<0.5	<0.5	<0.5
Benzo(b)fluoranthene	4.8	<0.5	<0.5	<0.5	<0.5
Benzo(k)fluoranthene	1.2	<0.5	<0.5	<0.5	<0.5
Benzo(a)pyrene	3.1	<0.5	<0.5	<0.5	<0.5
Indeno(1.2.3.cd)pyrene	1.7	<0.5	<0.5	<0.5	<0.5
Benzo(g,h,i)perylene	1.5	<0.5	<0.5	<0.5	<0.5

50 Low recovery in matrix spike, actual concentrations may be greater than shown
<1.0 Not detected above the Level of Reporting

The PAHs phenanthrene and pyrene were detected in a passive sampler deployed in January 2009 at estimated daily concentrations of 0.9 ng/L and 0.6 ng/L (**Table 21**). No PAHs, BTEX, phenols or solvents were detected in aqueous grab samples (**Appendix D, Table 18**).

A sediment sample collected from site ER-01 in March 2007 contained a range of PAHs at concentrations ranging from 0.8 mg/kg to 12.3 mg/kg (**Table 20**). Benzo(a)pyrene, one of the most toxic PAH compounds, was detected at 3.1 mg/kg. These concentrations exceeded the ANZECC 2000 recommended sediment quality guidelines, falling within the “medium effect range” which is considered to have a >50% probability of effecting aquatic biota. PAHs were not detected in any other Endeavour River sediment samples.

PAHs are widespread organic pollutants. They occur in coal, diesel, waste oil, roofing tar and asphalt, and are produced as by-products of burning fossil fuels, including diesel engines. Some PAHs are listed by the US EPA as probable human carcinogens and can bioaccumulate in aquatic organisms (www.epa.gov/iris/subst/0136.htm).

**Table 21: PAHs detected in Endeavour River Passive Samplers
Estimated Daily Concentrations (ng/L)**

Sample Site:	ER-01	ER-01
Sample Period:	22/12/08 - 21/1/09	10/1/09 – 14/1/09
Sample Duration:	30 days	5 days
PAHs ¹		
Phenanthrene	<0.1	0.9
Pyrene	<0.1	0.6

¹ No other PAHs were detected above the LOR (0.1 ng/L).
All PAH analytes are listed in Appendix B

The results of all hydrocarbon water samples and sediment sample analyses are listed in **Appendix D, Tables 18 and 19**. All passive sampler analytical results and a comparison with water quality guidelines are listed in **Appendix D, Table 15**.

6 SUMMARY OF RESULTS

6.1 Endeavour River

Temperatures in the Endeavour River estuary ranged from 21°C to 33°C. Minimum temperatures occurred in July and maximum temperatures occurred in February and March. Drought conditions during the first years of this monitoring programme resulted in lower than usual rainfall and no significant flood events in the Endeavour River from 2002 to 2004. This is reflected in the annual salinity cycles. Salinity within the estuary ranged from 0.0 ppt during freshwater events to a maximum of 37.3 ppt measured in the dry season of 2003. Conductivity values in the Endeavour estuary ranged from 0.068 mS/cm to 62.5 mS/cm, with a median value of 47.3 mS/cm.

Endeavour estuary pH values ranged from 5.31 to 8.37 with a median pH value of 7.70. The pH values decreased during freshwater flood events in the wet season and were lowest at upper estuary sites ER-04 and ER-05. Median pH values were within the expected Guidelines for Australian Tropical Estuaries (ANZECC 2000), however pH measurements at upper estuary sites fell below the ANZECC guidelines on a number of occasions during the wet. Disturbance of acid-sulphate soils by feral pigs may reduce pH levels at upper estuary sites.

Dissolved oxygen at estuary sites ranged from 60.1% – 126.7% with a median value of 82.9%. Oxygen levels at Endeavour estuary site ER-00 exceeded the maximum guideline value of 120% on 2 occasions, but this is likely to be a result of high winds and turbulent waters at the mouth of the river.

Turbidity in the Endeavour River ranged from 0 NTU to 456 NTU with a median turbidity value of 4.7 NTU, below the Queensland and ANZECC guidelines for the Protection of Aquatic Ecosystems. Maximum turbidity values were recorded at lower estuary site ER-01 during wet season floods. ER-01 turbidity values were up to four times greater than those measured in the rest of the estuary due to stormwater run-off from the Cooktown area.

Nutrient concentrations were generally low; however median values at upper estuary sites ER-04 and ER-05 exceeded the ANZECC 2000 and Qld Wet Tropics (2009)

guidelines for ammonia and nitrogen oxides. As a result Endeavour River estuary guidelines have been developed with higher guideline values for dissolved and total nitrogen.

Monthly total and dissolved nitrogen and phosphorous concentrations and annual mean and median concentrations at ER-01 (downstream from the sewerage treatment plant outfall) were assessed for changes over time (2005- 2008) as input to the new STP increased. Minor increases in total nutrients were associated with flood events: there is no indication that nutrient levels at ER-01 are elevated as a result of effluent outfall.

Chlorophyll concentrations ranged 0.01 µg/L to 3.64 µg/L in the Endeavour River estuary. Median chlorophyll concentrations for all sites were below the Guidelines for Estuaries. Endeavour upper estuary sites ER-04 and ER-05 had the highest median chlorophyll- α concentrations of the Annan and Endeavour monitoring sites. Maximum chlorophyll- α concentrations in the estuary occurred during or just after the wet season, after floodwaters delivered nutrients into the estuary promoting algal growth.

The dominant metals in unfiltered water samples from the Endeavour estuary were iron (0.38 mg/L – 5.12 mg/L) and aluminium (0.03 mg/L – 0.19 mg/L). Other trace elements detected included manganese, barium, copper, chromium, lead, arsenic, zinc, nickel and cadmium. Mercury was not detected in water samples above the detection limit (<0.0001 mg/L). Iron, aluminium, cadmium, chromium, lead and nickel appeared to be primarily or entirely in particulate form. Manganese and zinc occurred primarily in dissolved form.

Zinc, a common contaminant from urban run-off, was detected in water samples from ER-01 and ER-02 in the lower estuary at concentrations 10 times greater than at other sites. Chromium, copper and lead were also elevated above background in both wet and dry season water samples collected from these sites. Lead, zinc, and to a lesser extent copper and chromium were elevated in sediments at site ER-01 compared to other estuary sediment samples. Slightly elevated metals concentrations in the lower estuary are attributed to town stormwater run-off and/or boat maintenance work at the slipway (ER-01) and run-off from the Cooktown industrial area (ER-02).

Mercury was detected in a sediment sample from ER-03 at 1.1 mg/kg. This is significantly elevated above background concentrations (<0.0001 mg.kg – 0.3 mg.kg) and may be attributed to rubbish tip leachates.

Sediment and water grab samples from the Endeavour River were analysed for a wide range of pesticides and herbicides, including organochlorine and organophosphate (OC/OP) pesticides, phenoxyacetic acid herbicides, glyphosate (Round-Up), triazines (atrazine & simazine) and diuron. No pesticides or herbicides were detected in grab samples. Clopyralid, a broad leaf herbicide, was detected at a concentration of 0.28 mg/kg in sediment from the Endeavour estuary.

Passive samplers capable of detecting ultra-trace concentrations of herbicides were deployed in the Endeavour River lower estuary during the 2008/2009 wet season. The herbicides diuron, atrazine and simazine were detected at low concentrations (ng/L) in

30-day and 5-day passive samplers deployed in January and February 2008 and December/January 2009. At the concentrations detected, these herbicides are not considered a threat to aquatic organisms, however the concentrations may be greater upstream, closer to the source(s).

Galaxolide (Hexahydrohexamethyl Cyclopentabenzopyran)- a synthetic musk-like compound commonly found in detergents, shampoos, perfumes and fabric softener, was also detected in the estuary at very low concentrations (3 ng/L). Galaxolide may be entering the estuary via sewerage treatment plant effluent containing these products. Galaxolide is considered to be very harmful to the aquatic environment, although no toxicity guidelines are available.

Low concentrations of total petroleum hydrocarbons (180 µg/L) were detected in water samples at sites ER-00 and ER-02 in 2005. These are likely to be associated with boat fuel and/or run-off from adjacent roads. The PAHs phenanthrene and pyrene were detected at estimated daily concentrations of 0.9 ng/L and 0.6 ng/L in one passive sampler deployed at the mouth of the Endeavour River for 4 days in January 2009. A sediment sample collected from Cooktown Harbour site ER-01 in March 2007 contained a range of PAHs at concentrations ranging from 0.8 mg/kg to 12.3 mg/kg. Benzo(a)pyrene, a highly toxic PAH compound, was detected at 3.1 mg/kg.

Bacteria levels in the Endeavour River were highest in the upper estuary sites ER-04 (690 cfu/100ml) and ER-05 (490 cfu/100ml) in March 2007. Pigs and cattle in the Endeavour Valley are likely to contribute to these bacteria counts. Bacteria concentrations in the lower estuary, including near the Cooktown STP outfall, were below 100 cfu/100ml in the wet and dry seasons.

6.2 Annan River

Water temperature in the Annan River ranged from 18.3°C to 31.3°C with a median of 24.0°C in the freshwater section and 26.4°C in the estuary (**Table 13**). Minimum temperatures in the Annan River occurred in June and July while maximum temperatures occurred between October and February, depending on the year and site. Median temperatures decreased with distance upstream.

Salinity within the Annan estuary ranged from 0.0 ppt during wet season flood events to a maximum of 35.7 ppt at AR-00 (Annan River mouth) in October 2002. Conductivity in the Annan River estuary was slightly lower than the Endeavour estuary with a median value of 36.2 mS/cm. Salinity at freshwater sites in the Annan River ranged from 0.0 ppt to 0.1 ppt, with conductivity values ranging from 0.012 mS/cm to 0.120 mS/cm (median 0.062 mS/cm). Both salinity and conductivity at freshwater sites generally increased during the dry season, and dropped during wet season floods.

Annan River pH values ranged from 5.54 to 8.68 with a median freshwater value of 6.61 and median estuary value of 7.84. Median pH values were within the expected Guidelines for Australian Tropical Estuaries (ANZECC 2000), however pH measurements at both freshwater and estuary sites fell below the ANZECC guidelines on a number of occasions. The minimum Annan River pH value was recorded in April 2007 at AR-00 (5.54). Disturbed ASS may be responsible for the low pH measured at this site.

Turbidity in the Annan River ranged from 1 NTU to 210 NTU. Median turbidity values were 3.4 NTU for freshwater and 4.1 NTU for estuary sites, below the Queensland and ANZECC water quality guidelines. Mean turbidity values were 4.6 NTU (estuary) and 3.5 NTU (freshwater) during the dry season, and 48.7 and 38.3 NTU during the wet season. Maximum values were recorded in the estuary during February 2007 floods (230 NTU) and at the Little Annan Bridge downstream from extensive erosion gullies in Scrubby Creek during a flood in 2012 (704 NTU).

Annan River dissolved oxygen levels ranged from 56.3% – 110.8%, with median values of 89.9% (freshwater sites) and 88.8% (estuary). The minimum and maximum oxygen values were recorded at Site AR-02 (Little Annan Bridge) during dry season periods of low flow and high algal growth.

Nutrient concentrations in the Annan were generally low. Median values for estuary and freshwater sites were below the ANZECC 2000 and Queensland (2009) Wet Tropics water quality guidelines. Maximum total nitrogen and phosphorous values were measured at AR-03 (Shiptons Flat) in February 2007 when sediments from the Bluestone Mine tailings dam entered the Annan River.

Chlorophyll- α concentrations ranged from < 0.01 $\mu\text{g/L}$ to 4.04 $\mu\text{g/L}$ at freshwater sites and 0.01 $\mu\text{g/L}$ to 5.61 $\mu\text{g/L}$ at estuary sites. Maximum chlorophyll- α levels at freshwater sites occurred towards the end of the dry season, when flow rates were low and warm shallow waters promoted increased algal growth. Concentrations at freshwater sites AR-02 and AR-03 frequently exceeded the Qld Guidelines maximum concentration (0.6 $\mu\text{g/L}$) during the dry season. Median chlorophyll concentrations at all sites were below the Guidelines for Estuaries and Upland Rivers.

During base flow conditions most of the metals analysed for in Annan estuary samples were below the detection limits, with the exception of manganese (0.039 mg/L), arsenic (0.0012 mg/L) and cadmium (0.0002 mg/L). Total cadmium, chromium, and lead and total and dissolved copper concentrations exceeded the ANZECC water quality guidelines for the Protection of Estuary Aquatic Ecosystems (95% Level of Protection) during flood events.

Metals concentrations at Annan River freshwater sites were dominated by iron (0.06 mg/L – 1.78 mg/L). (Aluminium was not analysed but as it is a major element in sediments, it is also likely to be present in high concentrations in water.) Other trace metals present at varying concentrations were: zinc, manganese, barium and arsenic. Copper was primarily non-detect (<0.001 mg/L). Cadmium, chromium and lead concentrations were generally low or non-detect (<0.0001) during base flow periods.

Elevated concentrations of zinc, copper and arsenic were recorded at site AR-03 due to impacts from the Bluestone mine and tailings dam. The tailings dam continues to release metals into the Annan River.

Bacteria counts in the Annan increased during the wet season but all samples were below 100 cfu/100ml. The maximum bacteria levels (>8000 cfu/100ml) were detected in October 2007 at Keatings Lagoon, a wetland in the lower Annan

catchment, that had a high level of pig impacts before the lagoon was fenced in 2008. Bacteria levels have decreased since 2008.

6.3 Jeannie River

Insufficient data exists to capture the full seasonal range of water quality in the Jeannie estuary or freshwater reaches. However the water quality documented in the Jeannie River was similar to that of the Endeavour estuary under ambient conditions. The Jeannie is a much more narrow and shallow river than the Endeavour and freshwater in-flow ceased at the end of the dry season, creating more extreme water quality conditions.

The Jeannie upper estuary became hypersaline (maximum 47.3 ppt) towards the end of the dry season. This is reflected in higher median salinity and conductivity values at the Jeannie River than the Endeavour. The Jeannie River median pH value was slightly higher than the Annan or Endeavour estuaries as a result of the increased salinity. Median pH values were within the expected Guidelines for Australian Tropical Estuaries. Dissolved oxygen levels dropped below 50% on two occasions and reached as low as 17% saturation in the upper estuary in June 2009. Downstream Jeannie River estuary sites maintained healthy oxygen levels at this time.

Median nutrient concentrations were similar to those recorded at the Annan and Endeavour. Maximum ammonia concentrations were significantly higher than those recorded in the Annan or Endeavour; these were recorded at the top of the estuary where there was little water exchange during the dry season. Elevated nutrient levels corresponded to chlorophyll-a concentrations as high as 9.54 µg/L in the upper and mid-estuary at the end of the dry season compared to a maximum of 5.6 in the Annan estuary and 3.6 in the Endeavour.

Bacteria counts were below the Guidelines for Recreational Use (swimming or bathing); however samples were only collected on one date.

Iron was the dominant metal in both estuary and freshwater samples, recorded at a maximum concentration of 2.09 mg/L in the estuary. Aluminium (0.31 mg/L), manganese (0.202 mg/L), barium (0.16 mg/L) and zinc (0.097 mg/L) were also present in estuary and freshwater samples. Mercury and tin were not detected above the detection limits in any water samples.

Copper and zinc concentrations in the estuary exceeded the ANZECC 2000 water quality guidelines for the protection of aquatic ecosystems. Zinc also exceeded the guidelines at freshwater site JR-04. The Jeannie River is an undeveloped catchment, however feral cattle, cattle pads and a large gully associated with a former gravel pit contribute to increased erosion and sedimentation in the river, which may lead to elevated metals concentrations during the wet. The gully covers a large area and is a major source of sediments to the river and coastal waters.

6.4 Conclusion

The Annan and Endeavour Rivers are generally in good condition with ambient conditions falling within the water quality guidelines and very low contaminant levels.

Impacts on water quality were observed at the Annan River after mining commenced at the Bluestone tin mine, when turbidity significantly increased and there was a minor increase in metals concentrations, including arsenic and copper which exceeded the water quality guidelines. Pigs have caused high bacteria levels at wetlands such as Keatings Lagoon, and acid sulphate soils may have lowered pH levels in the estuary at the mouth of the river.

The Endeavour River lower estuary has been subject to minor impacts from boats and stormwater run-off, with elevated metals, total petroleum hydrocarbons and polycyclic aromatic hydrocarbons detected in water and sediment samples at low concentrations. The herbicides atrazine, diuron, simazine, and clopyralid were detected at low concentrations in the estuary and may be present at higher levels in the upper estuary or freshwater reaches of the river. Galaxolide, a synthetic fragrance detected in estuary waters is likely to have been released in sewerage treatment plant effluent. No other impacts from the effluent outfall were evident.

Metals, hydrocarbons, herbicides and ambient nutrient levels detected in the Annan and Endeavour Rivers are not likely to pose a threat to freshwater or marine ecosystems at the concentrations detected in water and sediment samples. Mercury was detected in one Endeavour River estuary sample from Four Mile Creek at a concentration that may affect aquatic biota; this may warrant further sampling of biota such as crabs from this popular fishing spot.

Elevated turbidity levels were recorded during the wet season in both the Annan and Endeavour Rivers as a result of various developments including tin mining on the Annan and earthworks in the Cooktown region. The increase in sediments and nutrients from erosion may pose a threat to seagrass meadows, coastal coral reefs and other aquatic habitat in the Annan & Endeavour estuaries and receiving waters. The significance of the increased erosion in any of these rivers in terms of total sediment loads leaving the estuaries is unknown at this time and deserves further investigation. Erosion is also a threat in the Jeannie River catchment as evidenced by an extensive gully system on the freshwater reaches of the river. Future mining in the Jeannie catchment, and the development of roads for mining access, could also pose a significant erosion threat.

7 RECOMMENDATIONS

ADDITIONAL MONITORING / RESEARCH

- Investigate the impact of acid-sulphate soils on AR estuary: additional wet season sampling at mouth of the Annan for pH and assessment of prawn farm and Keatings Lagoon ASS impacts
- Analyse stormwater run-off drains at ER-01 for metals and hydrocarbons
- Sampling for nutrients, bacteria and herbicides in the Endeavour River Valley to confirm if there are any impacts from cattle grazing and horticulture (further upstream from current monitoring sites)
- Monitoring nutrients and bacteria levels below and above the Hopevale STP outfall
- Assess recent CSC nutrient and bacteria data for changes resulting from STP outfall
- Investigate a major gully on the Jeannie River for link with former gravel pit and potential erosion mitigation actions
- Further research into suspended sediment loads in the Annan, Endeavour and Jeannie River, increases in suspended sediment and associated nutrients and metals from land-use in the catchments, and the potential threats to aquatic ecosystems.
- Analyse mercury concentrations in crabs in Endeavour River estuary (Four Mile Creek).

MANAGEMENT ACTION	RESPONSIBILITY	PRIORITY
Establish erosion management standards for earthworks within the Endeavour and Annan catchments	Cook Shire Council	High
Establish freshwater and estuary water quality guidelines for southeast Cape York based on the monitoring results from the Annan, Endeavour and Jeannie River results	DERM (Water Quality & Aquatic Ecosystems Dept.)	Medium
Property Owners to Register Records of Pesticide and Herbicide use	DEEDI (Dept. of Primary Industries) & Landholders	Medium

8 REFERENCES

ANZECC (2000). *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. Australian and New Zealand Environment and Conservation Council and the Agriculture and Resource Management Council of Australia and New Zealand.

Australian Bureau of Statistics (2006). Population data for the Lakeland & Laura Townships (combined).

Carroll, J., Stephan, K., Howley, C., Seabrook, W. and Wood, D. (2007). *Annan and Endeavour Strategic Plan*. South Cape York Catchments, Cooktown.

Eyre, B. and Davies, P. (1996). *A Preliminary Assessment of Suspended Sediment and Nutrient Concentrations in Three Far North Queensland Catchments*. Department of Natural Resources, QLD, Australia.

Grinter, S., and Hunter, H. (2005) *Ambient surface water quality in Queensland 2003-04*. Natural Resources and Mines, Brisbane.

Hart, B.T.; Day, G.; Sharp-Paul, A.; Beer, T. (1988). *Water Quality Variations During a Flood Event in the Annan River, North Queensland*. Aust. J. Mar. Freshwater Research. 39: 225-243.

Jardine, T.; Hallidy, I.; Howley, C; Sinnamon, V.; Bunn, S. (2012) *Large scale survey suggest limited mercury availability in tropical north Queensland, Australia*. Science of the Total Environment 416: 385-393.

Hayes, T.B. et al. (2011). *Demasculinization and Feminization of Male Gonads by Atrazine: Consistent Effects Across Vertebrate Classes*. Journal of Steroid Biochemistry & Molecular Biology 127: 64–73

Australian Government Land and Water Australia. (2000) National Land and Water Resources Audit 1999-2000.

Personal Communication, Andrew Moss (July 2010).

Queensland Government (2009). *Queensland Water Quality Guidelines & Monitoring and Sampling Manual*. Department of Environmental Resource Management.

Sheppard, R and Helmke, S.A, 1999. *A Fisheries Resource Assessment of the Annan River, North Queensland*, DPI Information Series QI99043.

**APPENDIX A –
ANNAN & ENDEAVOUR RIVER SAMPLE LOCATION PHOTOS**



Photo 1: Annan River Mouth (Peter Pal photo)



Photo 2: AR-00 facing East



Photo 3: AR-00 facing West



Photo 4: Collecting Water Samples
at AR-01 (Annan River Bridge)



Photo 5: AR-02 (Little Annan Bridge)



Photo 5: AR-03
(Annan River at Shipton's Flat)



Photo 6: AR-03 with run-off from Leswall Creek
(after mining commenced in Leswall catchment)



Photo 7: AR-04 facing upstream
(Wallaby Creek at Rossville)



Photo 8: AR-04 facing downstream



Photo 9: Tailings Dam facing north

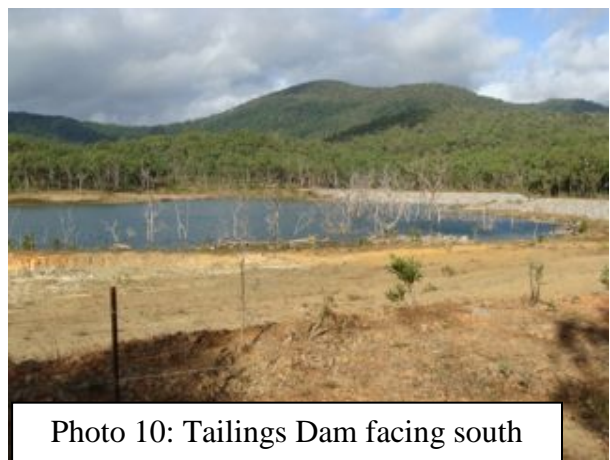


Photo 10: Tailings Dam facing south



Photo 11: ER-00 Endeavour River Mouth at entrance (photo by Kerry Trapnell)



Photo 12: ER-01 Coast Guard Slipway (photo by Kerry Trapnell)



Photo 13: Passive Samplers at Endeavour River estuary



Photo 14: ER-04: Endeavour River North Arm (P. Pal Photo)

APPENDIX B – METHODS AND EQUIPMENT DETAILS

Water Monitoring Equipment Range and Accuracy:

- Thermo Orion 5 Star Multimeter:
 - pH: range= -2 to 19.99, accuracy = +/-0.002
 - Dissolved Oxygen: range= 0 to 90.00 mg/L, 0.0 to 600 % saturation, accuracy = 0.2 mg/L (autocorrect for salinity)
 - Conductivity: range= 0 to 3000 mS/cm
 - Salinity: range= 0.01 to 80.0 ppt NaCl

- HACH 2100P Turbidity meter
 - Range: 0-1000 NTU
 - Accuracy: ± 2% of reading or ± 1 least significant digit

**Table 1: Queensland Health Environmental Waters Laboratory
Nutrient Analysis Methods:**

Total Phosphorus	Method Number	13800.R3
Ammonia Nitrogen	Method Number	13796.R3
Nitrogen Oxides	Method Number	13798.R3
Filt Reac Phosphorus	Method Number	13799.R3
Total Nitrogen	Method Number	13802.R3

Table 2: Contaminant and Metals Laboratory Analyses & Methods

Contaminant Type/ Analyte	Lab	Method
Total Metals (sediment samples)	ALS	ICP-AES EG020A-F
Total & Dissolved Metals (water samples)	ALS	ICP-MS EG020A-F
Total & Dissolved Mercury (water & sediment)	ALS	FIM-AAS AS 3550
Organochlorine Pesticides (OC)	ALS	EP131A
Organophosphorus Pesticides (OP)	ALS	EP130
Phenoxyacetic Acid Herbicides	ALS	LCMS EP202-LL
Glyphosate Herbicide “Round-up”	ALS	EP204
Volatile and Semi-Volatile Organics (VOCs) (Solvents, etc.)	ALS	EP074 D-E
PolyAromatic Hydrocarbons (PAHs) & Phenols	ALS	EP075
Total Petroleum Hydrocarbons (TPH) (C ₆ – C ₃₆ Fractions)/ Benzene, Toluene, Ethyltoluene, Xylene (BTEX)	ALS	EP080
Bacteria: Faecal coliform & e-coli	Cairns Water	TPB070

**TABLE 3: PDMS PASSIVE SAMPLERS
PESTICIDES & PAH ANALYTES LIST (GCMS Analysis)**

Acephate	Diclofop Methyl	Metolachlor	Tetrachlorvinphos
Aldrin	Dieldrin	Metribuzin	Tetradifon
Ametryn	Dimethoate	Mevinphos Z+E	Tetramethrin
Amitraz	Dimethomorph	Molinate	Thiabendazole
Atrazine	Dioxathion	Monocrotophos	Tonalid
Azinphos Ethyl	Disulfoton	Musk Ketone	Transfluthrin
Azinphos Methyl	Diuron Breakdown	Musk Xylene	Triadimefon
Benalaxyl	Endosulfan Alpha	Nicotine	Triadimenol
Bendiocarb	Endosulfan Beta	Nonachlor Cis	Triallate
Bifenthrin	Endosulfan Ether	Nonachlor Trans	Trifluralin
Bioresmethrin	Endosulfan Lactone	Omethoate	Vinclozalin
Bitertanol	Endosulfan Sulphate	Oxadiazon	
Bromacil	Endrin	Oxychlor	
Bromophos Ethyl	Endrin Aldehyde	Oxydemeton Methyl	PAHs
Cadusaphos	Ethion	Oxyfluorfen	Naphthalene
Captan	Ethoprop	Parathion Ethyl	Acenaphthylene
Carbaryl	Etrimiphos	Parathion Methyl	Acenaphthene
Carbophenothion	Famphur	Pendimethalin	Fluorene
Chlordane Cis	Fenamiphos	Permethrin	Phenanthrene
Chlordane Trans	Fenchlorphos	Phenothrin	Anthracene
Chlordene	Fenitrothion	Phorate	Fluoranthene
Chlordene Epoxide	Fenthion Ethyl	Phosmet	Pyrene
Chlorfenvinphos E+Z	Fenthion Methyl	Phosphamidon	Benz[A]Anthracene
Chlorothalonil	Fenvalerate	Phosphate Tri-N-Butyl	Chrysene
Chlorpyrifos	Fipronil	Piperonyl Butoxide	Benzo[B+K]Fluoranthene
Chlorpyrifos Me	Fluazifop Butyl	Pirimicarb	Benz[E]Pyrene
Chlorpyrifos Oxon	Fluometuron	Pirimiphos Methyl	Benz[A]Pyrene
Coumaphos	Fluvalinate	Procymidone	Perylene
Cyfluthrin	Furalaxyl	Profenophos	Indeno[123cd]Pyrene
Cyhalothrin	Galaxolide	Prometryn	Benzo[Ghi]Perylene
Cypermethrin	Haloxifop 2-Etoet	Propagite	Dibenz[Ah]Anthracene
Dcpp	Haloxifop Methyl	Propanil	
Ddd O,P	Hcb	Propazine	
Ddd P,P	Hch-A	Propiconazole	
Dde O,P	Hch-B	Propoxur	
Dde Pp	Hch-D	Prothiophos	
Ddt O,P	Heptachlor	Pyrazaphos	
Ddt P,P	Heptachlor Epoxide	Rotenone	
Deet	Hexazinone	Simazine	
Deltamethrin	Iprodione	Sulprofos	
Demeton-S-Methyl	Isophenophos	Tcep	
Desethylatrazine	Lindane	Tcpp	
Desisopropylatrazine	Malathion	Tebuconazole	
Diazinon	Metalaxyl	Tebuthiuron	
Dichloroaniline	Methamidophos	Temephos	
Dichlorvos	Methidathion	Terbuphos	
Dicofol P,P	Methoprene	Terbutylazine	
	Methoxychlor	Terbutryn	

APPENDIX C

CYMAG QAQC SAMPLES & DATA VALIDATION RESULTS

QC checks of both field sampling and laboratory sample analysis are used to assess and document data quality and to identify discrepancies in the measurement process. QC samples are used to determine the representativeness of the environmental samples, the precision of sample collection and handling procedures, the thoroughness of the field equipment decontamination procedures, and the accuracy of laboratory analysis.

1. QC SAMPLE COLLECTION & DATA VALIDATION METHODS

Field Duplicates (QC-01)

Field Duplicates, submitted to the laboratory “blind”, are used to evaluate variation in analyte concentration between samples collected from the same point and/or the laboratory precision in a given matrix. The RPD (Relative % Difference) of the duplicates is used as the accept/reject criteria. The following guide was used to assess the RPD of a pair of duplicates.

- If the results are < 10 X Level of Reporting (LOR) then no RPD limit is applied.
- If the results are 10 – 20 X LOR then the RPD should be within 50%.
- If the results are > 20 X LOR then the RPD should be within 20%.

Sample non-homogeneity can lead to RPD's greater than detailed above. It should be the aim of field personnel to endeavour to obtain a pair of samples as homogenous as possible. Duplicate samples are collected simultaneously from the sample matrix.

At least one duplicate sample will be collected for each group of 20 samples of a similar matrix type and concentration. The field replicates will be handled and analyzed in the same manner as all environmental samples. The duplicate samples will be submitted blind to the laboratory.

Frequency: 1 per 20 samples

Analytes: ALL

Field Blanks/ Method Blanks (QC-02)

Field blanks were used to indicate the presence of external contaminants that may have been introduced into the samples during collection. Field blanks will be prepared on site during the sampling event by pouring laboratory supplied organic-free or inorganic-free water, as appropriate, into sample bottles.

Frequency: One blank sample per sample batch (or 1 per 20 samples)

Analytes: ALL

Rinsate Blanks (QC-03)

Rinsate Blanks are blanks prepared in the field from reagent-grade water that is poured over or passed through the sample collection device after the device has been used for sampling, then collected in a sample container and returned to the laboratory for analysis. Rinsate blanks document the thoroughness of decontamination procedures and will be used to assess the adequacy of practices to prevent cross-contamination between sampling equipment and samples.

Rinsate samples were collected during every sample trip where sampling equipment is used to collect more than one sample. Organic-free or inorganic-free water, as appropriate, was rinsed through sampling equipment such as a dissolved nutrients syringe or extendable sampling cup into sample containers.

Frequency: One per sample trip where non-dedicated equipment is used (syringe for dissolved nutrients, sampling cup if sample bottle is not filled directly from the source)

Analytes: ALL

Certified Reference Material (QC-04)

Certified Reference Material (CRM) samples were submitted for nutrient analysis. CRM samples with documented nutrient concentrations were prepared for saltwater and freshwater by the Qld Health Laboratory. CRM analysis documents laboratory accuracy and potential loss of nutrients during storage and transportation.

Relative percent differences (RPDs) were calculated between the CRM analytical results and certified values. Less than 20% difference was considered to be within the acceptable range.

Frequency: One per 20 nutrient samples

Analytes: Total and Dissolved Nutrients

Trip Blanks (QC-05)

Trip blanks were used to document potential contamination that may be introduced into sample containers by volatile organic compounds (VOCs) through diffusion during sample transport and storage. Trip blanks were prepared by the field sampling team with reagent grade blank water at a designated clean location prior to sampling activities. Trip blanks are not opened in the field and act as a check for sample contamination originating from sample transport and site conditions.

One trip blank were prepared off-site and included with each batch of samples scheduled for analysis of VOCs regardless of environmental medium.

Frequency: One per sample batch sent to laboratory

Analytes: volatile organics and passive samplers

Laboratory Quality Control Checks

In addition to field QC samples, the analytical laboratory uses a series of QC samples specified in each standard analytical method to assess laboratory performance. The types of laboratory QC samples are method blank, laboratory control standard, duplicate, matrix spike, and matrix spike duplicate. Analyses of laboratory QC samples are performed for samples of similar matrix type and concentration and for each sample batch.

Method Blank (MB): A method blank is a sample of deionized (DI) water, sea sand, or analyte-free substance that mimics the field matrix and is prepared identically to an actual sample. Contamination in the method blank is indicative of a high bias caused by the accidental addition of target analytes through the preparation or extraction, or contributed by the instrument.

LCS or Blank Spike: This is a blank that has been spiked with the compounds of interest. Since it is prepared identically to an actual sample, an LCS failure in the recovery of a spike compound could be indicative of bias introduced in the preparation or extraction process.

Matrix Spike/Matrix Spike Duplicate (MS/MSD): An actual field sample that is spiked with the compounds of interest. Failures in the MS/MSD, especially those that are duplicated well, could be indicative of matrix effect. Matrix effect is a bias caused by interference in the recovery of an analyte due to the sample matrix.

2 ANALYTICAL DATA VALIDATION RESULTS

Analytical Data Validation has been conducted to ensure that all data adheres to quality control standards and falls within the acceptable ranges for accuracy and precision. Analytical data were validated against the following criteria:

- Data Entry Review
- Instrument calibration and performance checks;
- Field Blank analysis;
- Rinsate Blank analysis
- Field duplicates analysis;
- Certified Reference Material (CRM) Analysis (nutrient only);
- Sample Holding Times and Temperature upon receipt by the Lab; and
- Laboratory QC Samples and Reports.

Where QA/QC samples exceeded the acceptable limits, data collected on that day or within the sample batch has been discarded.

2.1 Nutrient Data Quality Results

Duplicate Analysis Results (QC-01)

A total of 42 batches of water samples has been submitted for nutrient analysis. A duplicate sample was submitted to the laboratory with 37 of these batches. All duplicate results were within the acceptable RPD range with the following exceptions:

- Total nitrogen (TN) results exceeded the RPD for duplicate samples collected 20/12/2007. TN results for this sample batch were discarded.
- Ammonia exceeded the RPD for a duplicate sample collected on 16/7/2008. Ammonia results for this batch were discarded.

Nutrient analysis was conducted on three batches of sediment samples from the Endeavour River and Walker Bay (Annan River). Three duplicate sediment samples were submitted with these batches. The RPDs were all within acceptable limits.

Field Blank Analysis Results (QC-02)

A total of 18 field blank samples were submitted for nutrient analysis with Annan-Endeavour sample batches. Field blanks were infrequently submitted prior to 2007, as a suitable source of nutrient free re-agent had not been sourced. The field blank samples contained no signs of introduced nutrient contamination with the following exceptions:

- Total Phosphorous (TP) was detected at 0.004 mg/L in the field blank sample from March 2009.
- Total Nitrogen (TN) was detected at 0.05 mg/L in field blank samples from February 2009 and March 2009 and at 0.03 mg/L in July 2008.

The total nutrient concentrations detected in blank samples were low and are not believed to have significantly compromised sample data quality. The TN and TP data collected during the above sample trips has been accepted but is qualified as having potential low-level contamination.

Dissolved nutrient levels did not exceed the detection limit in any blank samples.

Nutrient Equipment Rinsate Analysis Results (QC-03)

Nutrient rinsate samples (QC-03) were collected from sample collection bottles or syringes used for filtering multiple nutrient samples. A total of 11 rinsate samples were collected and assessed for indications of potential cross-contamination between samples. Rinsate samples contained no detectable nutrient levels with the following exceptions:

- Syringe rinsate sample QC-03 collected January 2005 contained 0.005 mg/L Total Phosphorous.
- Concentrations of 0.03 mg/L TN were detected in QC-03 syringe rinsate sample collected May 2005 and sample cup rinsate collected July 2008. Samples collected with these batches have been qualified as potentially having low level cross-contamination; however the detections barely exceeded the detection limits and are not believed to have compromised sample data quality.

- Endeavour River syringe rinsate sample QC-03 collected March 2007 contained 0.013 mg/L Nitrogen oxides (NO_x). This indicates that there may have been cross-contamination between ER sites and the NO_x results from this date have been deleted.

Certified Reference Material Results (QC-04)

Ten total nutrients and 11 dissolved nutrients CRM samples were submitted for analysis with Annan-Endeavour sample batches. The analytical results were compared against the certified values to evaluate the accuracy of laboratory analysis and potential contamination or loss of nutrients during transportation. The RPDs between CRM samples (QC-04) and the certified values were within the acceptable range (<20% difference) for all samples. This indicates a high level of accuracy.

Nutrients Data Quality Summary

The review of the QC analytical results indicates that all but a small fraction of the nutrient data collected between June 2006 and March 2010 is of acceptable data quality. Out of 42 batches of samples, nitrogen oxide results from one sample batch (March 2007) have been discarded due to potential cross contamination identified in rinsate samples. Jeannie River total nitrogen results from December 2007 and ammonia results from July 2008 were discarded because duplicate sample results exceeded 20% RPD. Results from several batches have been qualified as potentially having low level cross-contamination; however the relatively low concentrations detected in field blanks and rinsate blanks do not indicate that there has been any significant level of sample contamination during collection, transportation or analysis. The results from the analysis of certified reference material indicate that there is a high level of accuracy in the laboratory analytical results.

2.2 Chlorophyll- α Data Quality Results

Only a small number of chlorophyll- α duplicates, blank and rinsate samples were analysed due primarily to the time required to collect and filter these samples. No CRM samples were submitted for chlorophyll as suitable CRM was not available. Therefore the chlorophyll- α data presented here is largely un-validated.

Chlorophyll- α QA/QC results are as follows:

- 2 duplicate chlorophyll samples (QC-01) analysed- RPD was within acceptable limits
- 1 blank sample (QC-02) submitted. No chlorophyll detected in blank.
- 2 sample cup & filter cup rinsate samples (QC-03) submitted. No chlorophyll detected in blank rinsates.

Although there is a low frequency of QC data, the results showed no detectable chlorophyll contamination from the field sampling, filtering and lab analysis process.

2.3 Metals and Mercury Data Quality Results

Field Duplicate (QC-01) Results for Metals

Twenty batches of water and/or sediment samples were submitted for metals and mercury analyses. Seven duplicate water samples and five duplicate sediment samples were submitted for analysis with these batches (**Table 9**). The RPDs between duplicate and original samples were all within the acceptable range, indicating a high level of precision for metals analysis.

Field Blank (QC-02) Results for Metals

A total of seven field blank samples was submitted to ALS Laboratory with Annan-Endeavour grab sample batches for metals and mercury analysis. There were no detections of metals or mercury in field blank samples, indicating that metals contamination was not introduced to the samples during sample collection or analysis.

Metals Equipment Rinsate Blank (QC-03) Results

The majority of metals samples were collected directly from the river into the sample bottle, and syringes used for filtering dissolved metals samples were disposed of after each site, therefore the risk of cross-contamination was minimal for most sample batches. Five total metals and mercury rinsate samples and three dissolved metals and mercury rinsates were submitted for analysis with Annan-Endeavour metals and mercury sample batches to check for cross-contamination in the collection process.

Low levels of total metals were detected in the following rinsate samples:

- 09/02/2009: Cadmium (0.0002mg/L) and zinc (0.006mg/L) were detected in the syringe rinsate sample. Primary samples collected on this date did not contain cadmium. Dissolved zinc concentrations exceeded the total concentrations, indicating that there has been contamination from the filters used for obtaining dissolved samples. Dissolved zinc concentrations were deleted from this batch and numerous others. (See **Section 4.4.4** below.)
- 11/09/2008: Mercury was detected at the Limit of Reporting (0.0001 mg/L) in sample cup rinsate sample. Mercury detected in sample ER-03 at the same level has been discarded. No other samples in this sample batch contained mercury.
- 16/08/2008: Jeannie River collection cup rinsate sample QC-03 contained low levels of aluminium, arsenic, chromium, cobalt, copper, lead and iron. Metals concentrations detected at low levels in Jeannie River samples JR-02 and JR-03 have been discarded.

Metals Filter Contamination

A number of dissolved metals samples contained zinc at concentrations that exceeded the total zinc concentrations. This has been attributed to contamination from sample filters which also was identified in syringe and filter rinsate samples (QC-03). Dissolved zinc concentrations were deleted from a total of 25 dissolved metals samples. Some dissolved arsenic, barium, chromium, cadmium, aluminium, manganese and iron results were also deleted due to suspected filter contamination.

2.4 Contaminant Analysis Data Quality Results

Contaminant Analysis Field Duplicate (QC-01) Results

The table below shows the number of duplicate samples submitted to ALS and Cairns Water Laboratory for analysis in comparison to the total number of samples collected from the Annan and Endeavour for each contaminant type. Duplicate sample frequency was greater than 1 duplicate per 20 primary samples as per the CYMAG QA/QC protocols.

The majority of contaminant sample results (and duplicate sample results) were non-detect (concentrations were below the detection limit). The RPDs were within the acceptable range for all analyses.

Number of Primary and Duplicate Grab Samples for Metals and Contaminant Analysis

Analysis	Water samples		Sediment samples	
	Primary	Duplicate	Primary	Duplicate
Total Metals	94	8	41	5
TPH/ BTEX	23 /11	2 /1	17 / 9	1 / 0
PAHs and phenols	21	1	16	1
Phenoxyacetic acid herbicides	8	1	6	2
OC/OP pesticides	6	2	12	2
Triazines	3	1	6	1
Glyphosate	9	1	0	0
Bacteria	23	1	0	0

Field Blank (QC-02) Contaminant Results

The following field blank samples were submitted to ALS Laboratory for analysis with Annan-Endeavour contaminant grab sample batches:

- 2 blank samples for petroleum hydrocarbons (TPH/ BTEX/ PAHs);
- 1 blank sample for solvents and volatile organics (VOCs/SVOCs);
- 2 blank grab samples for herbicides and pesticides (OC/OP Pesticides, Phenoxyacetic acid pesticides and glyphosate); and
- 1 blank sample for diuron.

There were no detections of any contaminants in the field blank samples, with the following exception:

- Glyphosate (34 µg/L) was detected in blank sample QC-02 collected on 11/12/2007 with 2 other Endeavour estuary samples. A glyphosate detection in the primary ER sample was discarded due to potential contamination.

The remaining field blank samples indicate that there has been no contamination of samples during sample collection, transportation or analysis. Blank samples were not submitted with every sample batch as per CYMAG QA/QC protocol; however, the

majority of Annan-Endeavour contaminant analysis results were “non-detect” (contaminant concentrations were below the level of detection), indicating that there had been no contamination of the samples.

Rinsate Blank (QC-03) Contaminant Results

The majority of contaminant samples were collected directly from the river into the sample bottle, therefore rinsate samples checking for cross-contamination from non-dedicated equipment were not required for most contaminant grab sample batches.

One rinsate blank sample was submitted for herbicide and pesticide analysis (OC/OP Pesticides, Phenoxyacetic acid herbicides and glyphosate) with Annan-Endeavour contaminant grab sample batches. No herbicides or pesticides were detected in the rinsate blank sample, indicating that there has been no identified cross-contamination of samples resulting from sample collection cups.

Passive Sampler Blank & Duplicate Results

Blank passive samplers were transported along with the actual samplers but were not deployed in the rivers. Blank ED and PDMS samplers were non-detect for all herbicides, pesticides and PAHs, indicating that there had been no contamination of the passive samplers during transportation, deployment, retrieval or analysis.

One duplicate passive sampler was deployed with each batch of passive samplers. The duplicate samplers were lost or torn during heavy flood events so the analytical precision could not be assessed. Due to the nature of the passive samplers, all concentrations reported are considered to be indicative estimates of the presence of that analyte, therefore the accuracy or precision is not confirmed.

Laboratory QC Sample Results - Metals and Contaminants

A total of 20 batches of water samples and 11 soil sample batches were submitted to ALS Laboratory for contaminant and metals analyses. The laboratory conducted quality control tests including laboratory control spikes, blank spikes and matrix spikes to assess the accuracy and precision of their analytical methods. ALS provided a quality control report with the sample results identifying any breaches in their quality control sample results. These reports also identify any instances in which samples were not analysed within the accepted holding times, which range from one week to 6 months depending on the analysis and methods of sample preservation.

Table 1 in **Appendix C** lists all breaches in Laboratory Quality Control Sample Results or analytical Holding Times (the acceptable amount of time between sample collection and analysis). Where the quality of the data is considered to have been significantly impacted, results from the relevant batches were discarded and have not been included in this report. Where minor breaches occurred that are not believed to significantly affect the data, the data in question has been qualified as breaching QC limits, and the results are reported with qualifications.

Holding Times

Holding times for various analytes were breached for nine batches of samples, due primarily to difficulties in transporting samples from remote Cape York sites to Brisbane laboratories. The most frequent holding time breach was for mercury analysis, which is analysed with metals but has a shorter holding time than the other metals being analysed. Where holding times for mercury were exceeded by more than three days the results have been deleted and not included in this report. Mercury results for a total of 17 samples (all non-detect) have been deleted. However, based on the remaining water samples collected it is evident that mercury does not occur above 0.0001 mg/L (the detection limit) in the Annan-Endeavour water samples.

Some petroleum hydrocarbon and pesticide analyses require analysis within one week of the date of sampling. It was not always possible to properly transport refrigerated samples to distant laboratories within this time, and several breaches in the holding times for these analyses occurred. The results for PAH and TPH analysis have been deleted from 3 samples due to holding times being exceeded by 5 days, and have been qualified for 5 samples which exceeded the holding times by 1 to 3 days. The results for phenoxyacetic acid herbicide analysis have been qualified for 9 samples due to holding times being exceeded by between 1 to 5 days.

Laboratory Control Spike (LCS), Matrix Spike (MS) and Surrogate samples exceeded the lower or upper data quality objectives in the following samples:

- Pesticides/ herbicides: low surrogate recovery rates potentially affected four water samples and seven soil samples. The results for these samples have been qualified; however the pesticides and herbicides were non-detect in the samples and not likely to be present based on the results of previous samples.
- PAHs: high recovery rates potentially affected three soil samples- however PAH concentrations were non-detect therefore do not appear to have been affected by high surrogate recoveries.
- TPH/BTEX: low recovery rates potentially affected one soil sample and ten water samples. Results have been qualified- the actual soil or water concentrations may be greater than those detected.
- Metals: Arsenic results from 10 soil samples and 3 water samples are qualified due to low surrogate recoveries. The low recoveries were attributed to matrix interference and are not considered likely to have significantly impacted the results. However the arsenic results from these batches have been qualified- the actual concentrations may be higher than those detected.

Most of the laboratory spike or surrogate recovery breaches were outside of the acceptable limits by only 1 - 3 percentage points, and are not likely to have significantly affected the actual sample results.

Contaminant & Metals Analysis Data Quality Summary

A total of 20 batches of water samples and 11 soil sample batches were submitted for contaminant and metals analysis. Of these, the majority of the contaminant analytical results met the appropriate Field and Laboratory QC standards and are accepted for the purposes of this report. Mercury results were discarded from 17 out of 143 metals samples due to holding times being exceeded by five or more days. Three out of 42

TPH and PAH sample results and four out of 24 phenoxyacetic acid herbicide results were discarded due to holding times being exceeded by 4 - 5 days. An additional five TPH/ PAH samples and five phenoxyacetic acid herbicide water samples and three OC/OP pesticide samples have been qualified due to holding time breaches of 1 to 3 days.

Contaminant and metals duplicate samples indicate a high level of precision for these analyses with all sample results being within the acceptable criteria for duplicates (<20%RPD). Field blank and rinsate results indicate that there has been a very low incidence of contamination of herbicides, pesticides, TPH, BTEX, or PAHs in grab samples or passive samplers. Field blank samples showed no evidence of sample contamination with the exception of one glyphosate detection, which resulted in the discarding of the glyphosate detection in one Endeavour River sample.

Rinsate blank samples showed low level metals contamination on three instances, resulting in the deletion or qualification of associated results. One of the rinsate samples revealed contamination from filters used for dissolved metals. Samples contained levels of zinc and cadmium that were contaminating dissolved metals samples. This has resulted in the deletion of zinc, cadmium and other metals results from 25 dissolved metals samples.

All together approximately 368 samples were submitted for contaminant and metals analyses, with 42 quality control breaches resulting in the deletion of the associated analytical results for individual analytes. The results have been qualified for an additional 32 sample analyses due to minor breaches that are not considered to have significantly affected the data.

Table 1: Laboratory QC - Contaminant Data Quality Results

Batch	Sample Date	River	Matrix	Samples Affected	Analyte	Breach	Comments/ Action
EB0701550	18-12-06	AR	Water	AR-01, AR-02 AR-03	Total Mercury	HT (30 days)	Delete Sample Results
EB0701550	4-2-07	ER	Water	ER-Wharf	TPH, Pesticides, PAH, phenols	HT (3 days)	Results accepted with qualifications, minor losses may have occurred
EB0701550	6-2-07	AR	Water	AR-01, AR-02 AR-03, AR-04	TPH, PAH, phenols	HT (1 day)	Results accepted with qualifications.
EB0701550	4-2-07	ER	Water	ER-Wharf	Phenoxyacetic acid herbicides	HT (4 days)	Losses may have occurred, Results accepted with qualifications.
EB0701550	7-2-07	ER	Water	ER- 05	Phenoxyacetic acid herbicides	HT (1 day)	Results accepted with qualifications.
EB0701550	4-2-07 – 7-2-07	ER	Water	Water	OC Pesticides	Low Recovery on LCS and MS	Results accepted.
EB0701550	7-2-07	ER	Soil		OP Pesticides	High Recovery on LCS and MS	Results non-detect
EB0701550	4-2-07 – 9-2-07	ER/AR	Soil		PAHs	Low recovery on MS	Recovery rate 0.1% below Data Quality Objectives
EB0701550	7-2-07	ER/AR	Water		VOC, TPH, BTEX	Spike recovery exceeds data quality objective	Both below & above
EB0703353	19-3-07	ER	Soil	ER-01, ER-02, ER-03a, ER-03b, ER-03c	TPH C6-C9	LCS recovery > data quality objectives MS recovery < data quality objectives	Results accepted with qualifications, actual concentrations may be greater than shown
EB0703353	19-3-07	ER	Soil –	ER-01, ER-02, ER-03a, ER-03b, ER-03c	Arsenic	LCS recovery < data quality objectives	Results accepted with qualifications, actual concentrations may be greater than shown
EB0703353	19-3-07	ER	Soil –	ER-01, ER-02, ER-03a, ER-03b, ER-03c	TPH/ BTEX	HT exceeded by 3 days	Results accepted with qualifications, actual concentrations may be greater than shown

Batch	Sample Date	River	Matrix	Samples Affected	Analyte	Breach	Comments/ Action
EB0706135	28-5-07	AR	Water	AR-02, AR-03, AR-Les	TPH & PAHs	HT breach (5 days)	Potentially some loss of contaminants, Results deleted.
EB0714928	11/12/07	ER	Soil	ER-03, ER-03b, ER-2.5, ER-Leprosy	OP Pesticides/ Atrazine	Surrogate recovery > data quality objective	Atrazine non-detect, not affected by high recovery rates
EB0714928	11/12/07	ER	Water	ER-03,	OP Pesticides/ Atrazine	Surrogate recovery > data quality objective	Atrazine non-detect, not affected by high recovery rates
EB0714928	11/12/07	ER	Water	ER-03	Atrazine	Holding time (2 days)	Results accepted with qualifications, Potentially minor loss of contaminants
EB0714928	11/12/07	ER	Water	ER-03, ER-Leprosy	Phenoxyacetic acid Herbicides, Glyphosate, diuron	Holding time (2 days)	Results accepted with qualifications, Potentially minor loss of contaminants
EB0801036	23/01/08	ER	Water	ER-01	TPH	Low recovery on LCS	
EB0801036	23/01/08	ER	Water	ER-01	TPH	Surrogate recovery > data quality objective	No detection in samples, not affected by high recovery rate
EB0801036	23/01/08	ER	Water	ER-01	Phenoxyacetic acid Herbicides,	Holding time (2 days)	Results accepted with qualifications, Potentially minor loss of contaminants
EB0808704	25/6/08	AR	Water	AR-03, AR-04, AR-TD	Total Arsenic	Low recovery for Lab QC samples	Arsenic results may be higher than detected
EB0812747	11/09/08	ER	Water	ER-MAIN-4MC, ER-02, ER-03	OC/OP Pesticides	Holding time exceeded 1 day	Results accepted with qualifications.
EB0812747	11/09/08 & 14/9/08	ER	Water	ER-MAIN-4MC, ER-02, ER-03, ER-Leprosy	Phenoxyacetic acid Herbicides	Holding time exceeded 3 - 5 days	Results accepted with qualifications, Potentially minor loss of contaminants
EB0812747	11/09/08	ER	Water	ER-MAIN-4MC,	Diuron	Holding time exceeded 1 day	Non-detect results accepted, minor breach
EB0812747	11/09/08	ER	Soil	ER-01, ER-02, ER-03	Polynuclear Aromatic Hydrocarbons	LCS Recovery > data quality objectives	No detection in samples, not affected by high recovery rate

Batch	Sample Date	River	Matrix	Samples Affected	Analyte	Breach	Comments/ Action
EB0812747	11/09/08	ER	Soil	ER-01, ER-02, ER-03, ER-MAIN-4MC, ER-Lep01, ER-Lep02	TPH, OC/OP Pesticides	MS Recovery < data quality objectives	Potentially some loss of contaminants, however non-detect results accepted with qualifications
EB0812747	11/09/08	ER	Soil	ER-01, ER-02, ER-03, ER-MAIN-4MC, ER-Lep01, ER-Lep02	OP Pesticides	Surrogate recovery < data quality objective	Potentially some loss of contaminants, however non-detect results accepted
ES0817807	26/11/08	AR (Walker Bay)	Soil	WB-T1, WB-T3N, WB-T3S, WB-T4, WB-T5s, WB-T5 mid, WB-T6 mouth	Cadmium	LCS Recover > DQO	No detection in samples, not affected by high recovery rate
ES0817807	26/11/08	AR (Walker Bay)	Soil	WB-T6	BTEX	Recovery < DQO	Potentially some loss of contaminants, however non-detect results accepted
EB0902931	09/02/2009	AR	Water		Total Mercury	Low recovery for Lab QC samples	Mercury not-detected in most samples. Results accepted with qualifications
EB0902931	09/02/2009	AR	Water		Lead	LCS recovery > data quality objective	Lead not-detected in sample, not affected by high recovery rate. Results accepted.
EB0908148	22/03/2009	JR	Water	JR-03, JR-04	Total and Dissolved Mercury	Holding time breach (30+days)	Results deleted (non-detect)
EB0915801	5/6/09	JR	Water	JR-00, JR-01, JR-02, JR-03	Total and Dissolved Mercury	Holding time breach (30+days)	Results deleted (non-detect)
EB0915801	13/05/09	AR	Water	AR-01, AR-02, AR-03, AR-04	Total and Dissolved Mercury	Holding time breach (30+days)	Results deleted (non-detect)
EB1003574	28/01/2010	AR	Water	USTD-01,	Total and	Holding Time (by 8	Results deleted (non-detect)

Batch	Sample Date	River	Matrix	Samples Affected	Analyte	Breach	Comments/ Action
				DSTD-02, WC-01, AR-03	Dissolved Mercury	days)	
EB1006853	27/03/2010	AR	Water	USTD-01, DSTD-02, WC-01, AR-03	Dissolved Mercury	Holding Time (by 3 days)	Total mercury was analysed within holding times- all non-detect. .Dissolved non-detect results accepted.
EB1004956	16/03/2010	ER	Soil	ER-02, ER-03, ER-01, ER-CC, ER-Leprosy	Arsenic	MS Recovery < data quality objectives	Arsenic results qualified- actual concentrations may be higher than reported.

**APPENDIX D:
WATER QUALITY DATA TABLES**

**TABLE 1: Comparison of Ambient Water Quality at Endeavour River Monitoring Locations (2002-2009)
Minimum, Maximum and Median Values**

Site	Statistic	pH: -log [H ⁺]	Temperature: °C	Conductivity: (mS/cm)	Salinity: ppt	Dissolved Oxygen: (mg/L)	Dissolved Oxygen: (%SAT)	Turbidity: NTU
ER-00	min	7.02	21.50	1.500	2.70	5.03	81.10	0.17
	max	8.30	33.30	55.800	36.60	8.73	126.53	83.00
	median	8.14	27.40	52.400	34.70	6.51	95.00	3.5
	count	29	30	26	29	25	25	30
ER-01	min	5.45	21.4	1.140	0.6	4.93	69.00	0.0
	max	8.32	30.2	55.100	36.7	7.85	111.93	456.0
	median	8.07	26.9	52.633	34.7	5.91	88.00	5.0
	count	38	40	38	39	38	37	46
ER-02	min	6.72	21.0	8.930	1.6	4.30	62.80	0.6
	max	8.15	30.1	62.500	37.2	7.09	113.00	104.6
	median	7.85	27.0	51.283	33.9	5.59	81.77	4.8
	count	37	39	38	39	38	37	39
ER-03	min	6.63	21.8	2.610	0.5	4.24	67.70	0.5
	max	8.13	30.5	55.600	37.3	7.14	108.30	58.1
	median	7.60	27.2	43.867	28.3	5.82	82.62	4.3
	count	37	39	39	39	36	36	39
ER-04	min	5.31	22.2	0.082	0.0	4.08	60.07	0.9
	max	7.65	30.5	55.100	36.7	6.83	94.83	126.0
	median	7.18	26.8	23.050	13.9	5.64	76.12	5.8
	count	36	38	38	38	36	36	38
ER-05	min	6.06	22.3	0.068	0.0	4.63	64.87	0.9
	max	7.67	30.5	55.500	36.8	7.04	93.50	88.1
	median	7.31	27.0	27.043	16.6	5.69	79.17	5.3
	count	35	37	37	37	33	33	37

**TABLE 2: Comparison of Ambient Water Quality at Annan River Monitoring Locations (2002-2009)
Minimum, Maximum and Median Values**

Site	Statistic	pH: -log [H ⁺]	Temperature: °C	Conductivity: (mS/cm)	Salinity: ppt	Dissolved Oxygen: (mg/L)	Dissolved Oxygen: (%SAT)	Turbidity: NTU
AR-00	Min	5.54	20.2	0.102	0.5	4.69	76.03	1.2
	Max	8.68	31.3	53.8	35.7	8.00	104.37	210.0
	Median	8.01	26.9	51.1	33.7	6.25	91.17	3.7
	Count	27	28	27	27	26	26	29
AR-01	Min	6.25	22.4	0.052	0.0	4.41	63.13	2.0
	Max	8.57	30.6	50.7	34.4	8.18	102.27	230.0
	Median	7.85	26.7	36.2	24.1	6.46	88.80	4.2
	Count	39	39	36	38	35	35	43
AR-02	Min	5.61	20.0	0.039	0.0	5.52	56.34	1.6
	Max	8.03	31.1	0.087	0.0	8.90	110.80	704.0
	Median	6.71	25.0	0.065	0.0	7.27	89.03	4.0
	Count	40	42	38	39	36	36	44
AR-03	Min	5.59	18.3	0.012	0.0	5.63	68.10	1.0
	Max	7.35	29.1	0.120	0.1	9.05	101.20	141.3
	Median	6.43	24.0	0.062	0.0	7.41	89.15	3.9
	Count	41	43	38	39	40	40	45
AR-04	Min	6.09	19.0	0.038	0.0	5.73	69.87	1.0
	Max	7.27	28.5	0.068	0.0	9.29	104.14	15.6
	Median	6.65	23.1	0.061	0.0	7.47	90.50	3.0
	Count	39	40	36	37	37	37	42

Table 3: Minimum, Maximum And Median Nutrient Levels At Annan And Endeavour River Sites							
SITE	Statistics	Total Phosphorus	Filt Reac Phosphorus	Ammonia Nitrogen	Nitrogen Oxides	Total Nitrogen	
		mg/L as P	mg/L as P	mg/L as N	mg/L as N	mg/L as N	
AR-01 n = 29	Min	0.004	< 0.002	< 0.002	< 0.002	0.10	
	Max	0.067	0.006	0.043	0.160	4.80	
	Median	0.010	0.001	0.007	0.004	0.14	
AR-02 n = 30	Min	0.006	< 0.002	< 0.002	< 0.002	0.04	
	Max	0.060	0.005	0.008	0.240	0.55	
	Median	0.010	0.002	0.004	0.003	0.11	
AR-03 n = 34	Min	0.004	< 0.002	< 0.002	< 0.002	0.05	
	Max	0.033	0.006	0.024	0.940	1.20	
	Median	0.010	0.002	0.003	0.002	0.12	
AR-04 n = 28	Min	0.003	< 0.002	< 0.002	< 0.002	0.04	
	Max	0.017	0.003	0.006	0.044	0.22	
	Median	0.007	0.001	0.003	0.003	0.07	
ER-01 n = 36	Min	0.002	< 0.002	< 0.002	< 0.002	0.08	
	Max	0.140	0.004	0.034	0.070	1.10	
	Median	0.009	0.001	0.004	0.002	0.11	
ER-02 n = 30	Min	0.004	< 0.002	< 0.002	< 0.002	0.09	
	Max	0.056	0.003	0.028	0.056	0.45	
	Median	0.008	0.001	0.005	0.002	0.14	
ER-03 n = 29	Min	0.002	0.001	0.001	0.001	0.09	
	Max	0.039	0.003	0.038	0.052	0.42	
	Median	0.009	0.001	0.006	0.006	0.15	
ER-04 n = 29	Min	0.005	< 0.002	< 0.002	< 0.002	0.14	
	Max	0.074	0.003	0.040	0.070	0.63	
	Median	0.011	0.001	0.017	0.033	0.25	
ER-05 n = 27	Min	0.005	< 0.002	< 0.002	< 0.002	0.13	
	Max	0.061	0.004	0.043	0.077	0.45	
	Median	0.011	0.001	0.016	0.029	0.24	
Water Quality Guidelines							
ANZECC 2000	<i>Estuary</i>		<i>0.020</i>	<i>0.005</i>	<i>0.015</i>	<i>0.030</i>	<i>0.250</i>
	<i>Lowland river</i>		<i>0.010</i>	<i>0.004</i>	<i>0.010</i>	<i>0.010</i>	<i>0.300</i>
	<i>Upland River</i>		<i>0.010</i>	<i>0.005</i>	<i>0.006</i>	<i>0.030</i>	<i>0.150</i>
Qld (2009)	<i>Endeavour 80 %ile</i>	<i>LE</i>	<i>0.015</i>	<i>0.003</i>	<i>0.010</i>	<i>0.010</i>	<i>0.200</i>
		<i>ME</i>	<i>0.020</i>	<i>0.003</i>	<i>0.020</i>	<i>0.040</i>	<i>0.300</i>

0.016 Green highlights = Median concentrations Exceed ANZECC (2000) Guidelines

LE Lower estuary

ME Mid estuary

**Table 4: Mean Dry Season, Wet Season & Flood Event*
Nutrient Concentrations- Annan & Endeavour River Subsets**

		Total P	FRP	NH ₃	NOx	Total N	Turbidity
		mg/L	mg/L	mg/L	mg/L	mg/L	NTU
AR-FW DRY n = 65 / 89	min	0.003	0.001	0.001	0.001	0.04	1.0
	max	0.033	0.005	0.008	0.044	0.46	10.3
	mean	0.009	0.002	0.003	0.004	0.103	3.52
AR-FW WET n = 25 / 44	min	0.005	0.001	0.001	0.001	0.05	1.3
	max	0.060	0.006	0.024	0.940	1.20	704.0
	mean	0.016	0.003	0.005	0.084	0.230	38.33
AR-FW Flood Event n = 5 / 18	min	0.016	0.002	0.006	0.027	0.19	3.3
	max	0.067	0.006	0.027	0.160	4.80	704.0
	mean	0.029	0.004	0.014	0.075	1.208	79.5
AR-EST DRY n = 22/ 61	min	0.004	0.001	0.001	0.001	0.08	1.2
	max	0.014	0.003	0.034	0.016	0.28	11.9
	mean	0.008	0.001	0.008	0.005	0.136	4.6
AR-EST WET n = 8/ 21	min	0.008	0.001	0.006	0.005	0.11	2.0
	max	0.067	0.006	0.043	0.160	4.80	230.0
	mean	0.021	0.003	0.016	0.052	0.746	48.7
AR-EST Flood Event n = 15 / 13	min	0.008	0.001	0.002	0.004	0.06	7.6
	max	0.060	0.006	0.024	0.940	1.20	230.0
	mean	0.020	0.003	0.006	0.137	0.314	76.3
ER-EST DRY n = 107 / 161	min	0.002	0.001	0.001	0.001	0.08	0.0
	max	0.030	0.004	0.043	0.058	0.34	23.3
	mean	0.010	0.001	0.010	0.014	0.172	4.3
ER-EST WET n = 38 / 89	min	0.006	0.001	0.001	0.001	0.08	0.0
	max	0.140	0.004	0.038	0.077	1.10	456.0
	mean	0.025	0.001	0.016	0.028	0.307	36.45
ER-EST Flood Event n = 18 / 60	min	0.012	0.001	0.006	0.001	0.14	7.9
	max	0.140	0.004	0.022	0.077	1.10	456.0
	mean	0.038	0.002	0.014	0.033	0.398	50.79

* Dry season (approx. May – Dec), wet season (approx. Jan-April, varied per year), and flood events. Wet season data includes flood event data.

n number of samples (nutrients / turbidity)

Table 5: Annan River Estuary (AR-01) Water Sample Analytical Results – Total & Dissolved Metals and Mercury

Site:		AR-01 (Big Annan Bridge / estuary)						Water Quality Guidelines*
Sample Date:	13/3/05	18/12/06	06/02/07	29/10/07	13/5/09	9/2/09		
Turbidity (NTU):	63.7	2.5	210.0	2.33	4.6	48.93		
Total Metals								
Arsenic	mg/L	<0.050	<0.050	0.002	0.0012	<0.050	<0.001	
Barium	mg/L	--	--	--	--	<0.005	--	
Cadmium	mg/L	0.0303	<0.0050	0.0002	0.0002	<0.005	<0.0001	0.0055
Chromium	mg/L	0.041	<0.005	<0.001	<0.005	<0.005	0.001	0.0274/ 0.0044 ²
Copper	mg/L	<0.050	<0.050	0.003	<0.001	<0.050	0.002	0.0013
Lead	mg/L	0.018	<0.005	0.002	<0.0002	<0.005	<0.001	0.0044
Manganese	mg/L	--	--	--	--	0.039	--	
Nickel	mg/L	0.058	<0.050	<0.001	<0.0005	<0.050	<0.001	0.07
Zinc	mg/L	<0.050	<0.050	0.006	<0.005	<0.050	0.005	0.015
Iron	mg/L	--	--	--	--	<0.50	--	
Mercury	mg/L	<0.0001	<0.0001	del	<0.0001	<0.0001	<0.0001	0.0004
Dissolved Metals³								
Arsenic	mg/L	<0.050	--	0.001	--	<2.50	<0.001	
Cadmium	mg/L	<0.005	--	<0.0001	--	<0.025	<0.0001	0.0055
Chromium	mg/L	<0.050	--	<0.001	--	<0.025	<0.001	0.0274/ 0.0044
Copper	mg/L	<0.050	--	0.001	--	<2.50	0.002	0.0013
Lead	mg/L	<0.005	--	<0.001	--	<0.025	<0.001	0.0044
Manganese	mg/L	--	--	--	--	<0.05	--	
Nickel	mg/L	<0.050	--	<0.001	--	<2.50	<0.001	0.07
Zinc	mg/L	<0.050	--	del	--	<0.500	del	0.015
Iron	mg/L	--	--	--	--	<2.50	--	
Mercury	mg/L	<0.0001	--	<0.0001	--	<0.0001	<0.0001	0.0004

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Marine Water (95% Level of Protection)

2 CrIII/CrVI (Sample results are not speciated)

3 Dissolved metals were not analysed for all batches, metals not shown were not detected above the Level of Reporting (LOR)

del Analytical results were discarded due to holding time breaches (Hg) or rinsate sample contamination (dissolved Zn)

-- Not analysed

<0.005 Analyte not detected above the LOR

0.081 Results shaded green exceed the ANZECC 2000 Water Quality Guideline

Table 6: Annan River Freshwater Sample Analytical Results – Total & Dissolved Metals and Mercury

Site:	AR-02 (Little Annan Bridge)								AR-04 (Wallaby Creek, Rossville)						Water Quality Guidelines ¹	
Sample Date:	13/3/05	18/12/06	06/02/07	26/5/07	29/10/07	29/02/08	09/02/09	13/5/09	13/3/05	06/2/07	29/10/07	25/6/08	09/2/09	13/5/09		
Turbidity (NTU):	79.0	4.4	94.5		1.33	80.5	6.75	1.8	15.6	12.0	2.00	2.0	3.35	1.8		
<i>Total Metals</i>																
Arsenic	mg/L	<0.050	0.002	0.002	<0.001	0.004	0.001	<0.001	<0.001	<0.050	0.002	0.002	0.001²	0.001	<0.001	0.013/0.024 ³
Barium	mg/L	--	--	--	0.004	--	--	--	<0.001	--	--	--	--	--	0.004	
Cadmium	mg/L	0.02	<0.0001	<0.0001	<0.0001	<0.0001	0.001	<0.0001	<0.0001	<0.0050	<0.0001	0.0001	0.0007	<0.0001	<0.0001	0.0002
Chromium	mg/L	0.02	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.050	<0.001	<0.001	<0.001	<0.001	<0.001	0.001
Copper	mg/L	<0.050	<0.001	0.002	<0.001	<0.001	<0.001	0.002	<0.001	<0.050	<0.001	<0.001	<0.001	<0.001	<0.001	0.0014
Lead	mg/L	0.01	<0.001	0.002	<0.001	<0.001	0.001	<0.001	<0.001	<0.005	<0.001	<0.001	<0.001	<0.001	<0.001	0.0034
Manganese	mg/L	--	--	--	0.008	--	--	--	0.002	--	--	--	--	--	0.003	1.9
Nickel	mg/L	<0.050	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.050	<0.001	<0.001	--	<0.001	<0.001	0.011
Zinc	mg/L	<0.050	<0.005	<0.005	0.006	<0.005	<0.005	0.012	<0.005	<0.050	<0.005	<0.005	<0.005	0.010	<0.005	0.008
Iron	mg/L	--	--	--	--	--	1.78	--	0.06	--	--	--	--	--	0.14	
Mercury	mg/L	<0.0001	<0.0001	DEL	<0.0001	<0.0001		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001		0.0001	<0.0001	0.0006
<i>Dissolved Metals⁴</i>																
Arsenic	mg/L	<0.050	--	0.002	<0.001	0.004	--	0.001	DEL	<0.050	<0.001	--	--	0.001	DEL	0.013/0.024 ²
Copper	mg/L	<0.050	--	<0.001	<0.001	<0.001	--	0.001	<0.001	<0.050	<0.001	--	--	0.001	<0.001	0.0014
Lead	mg/L	<0.005	--	<0.001	<0.001	<0.001	--	<0.001	<0.001	<0.005	<0.001	--	--	<0.001	0.002	0.0034
Manganese	mg/L	<0.050	--	--	0.006	--	--	--	DEL	--	--	--	--	--	DEL	1.9

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Freshwater (95% Level of Protection)

2 Low recovery rate for arsenic in laboratory spike sample (actual concentrations may be greater than shown)

3 AsIII/AsV (Sample results are not speciated)

4 Dissolved metals were not analysed for all batches, metals not shown were not detected above the Level of Reporting (Hg, Cd, Cr, Ni) or were discarded due to contamination from filters (Zn, Ba, Fe)

del Analytical results were discarded due to holding time breaches (Hg) or potential sample contamination from filters (As, Mn)

-- Not analysed

<0.005 Analyte not detected above the LOR

0.081 Results shaded green exceed the ANZECC 2000 Water Quality Guidelines

Table 6 (continued): Annan River Freshwater Water Sample Analytical Results – Total & Dissolved Metals & Mercury

Site:		AR-03											Water Quality Guidelines ¹	
Sample Date:	13/3/05	18/12/06	06/2/07	26/5/07	29/10/07	18/1/08	15/02/08	29/2/08	20/3/08	25/6/08	09/2/09	13/5/09		
Turbidity (NTU):	13.3	1.1	16.0	--	1.33	2.00	8.97	9.73	4.7	1.7	6.75	3.9		
Total Metals														
Antimony					<0.001				<0.001	<0.001	<0.001			
Arsenic	mg/L	<0.050	0.002	0.006	<0.001	0.002	0.002	0.002	0.002	0.002	0.001	0.002	0.001	0.013/0.024 ²
Barium					0.002								0.003	
Cadmium	mg/L	<0.0050	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0001			0.001	<0.0001	<0.0001	0.0002
Chromium	mg/L	<0.050	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.0001	<0.001	<0.001	0.001
Copper	mg/L	<0.050	<0.001	0.009	<0.001	<0.001	0.001	0.004	<0.001	0.001	<0.001	0.002	<0.001	0.0014
Lead	mg/L	<0.005	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.0034
Manganese					0.004								0.003	1.9
Nickel	mg/L	<0.050	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001				<0.001	<0.001	0.011
Zinc	mg/L	0.052	<0.005	<0.005	<0.005	<0.005	0.005	<0.005	<0.005	<0.005	0.056	<0.005	<0.005	0.008
Iron									0.39	0.08			0.14	
Mercury	mg/L	<0.0001	<0.0001	DEL	<0.0001	<0.0001	<0.0001	<0.0001				<0.0001	<0.0001	0.0006
Dissolved Metals³														
Arsenic	mg/L	<0.050		0.004	<0.001	0.002	0.001	0.002		<0.001		0.001	DEL	0.013/0.024 ³
Copper	mg/L	<0.050		0.006	<0.001	<0.001	<0.001	0.003		0.001		0.002	<0.001	0.0014
Manganese					0.003								DEL	1.9
Zinc	mg/L	0.052		<0.005	<0.005	Del	<0.005	<0.005		<0.005		DEL	DEL	

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Freshwater (95% Level of Protection)

2 AsIII/AsV (Sample results are not speciated)

3 Dissolved metals were not analysed for all batches, metals not shown were not detected above the LOR (Hg, Cd, Cr, Ni, Pb) or were discarded due to filter contamination (Ba, Fe)

del Analytical results were discarded due to holding time breaches (Hg) or potential sample contamination from filters (As, Mn, Zn)

-- Not analysed

<0.005 Analyte not detected above the LOR

0.081 Results shaded green exceed the ANZECC 2000 Water Quality Guidelines

Table 7: Annan River Sediment Analytical Results- Metals & Mercury (mg/kg)

Sample Site:	AR-01	AR-03	AR-04	AR-00	AR-01	AR-02
Date:	30/11/04	30/11/04	30/11/04	29/1/05	06/02/07	06/02/07
Analysed Fraction:	<63 um	<63 um	<63 um	<63 um	All	All
Arsenic	--	--	--	--	10	5
Cadmium	<1	<1	<1	<1	<1	<1
Chromium	20	22	18	32	20	12
Copper	23	41	26	5	14	12
Lead	8	8	9	7	11	9
Nickel	9	9	6	7	11	9
Zinc	34	52	38	16	31	23
Mercury	<0.1	<0.1	<0.1	<0.1	<0.1	0.2

-- Not Analysed

Table 8: Walker Bay Sediment Analytical Results – Metals & Mercury (mg/kg)

Date:	26/11/08						
Sample Site:	WB-T1	WB - T3N	WB - T3S	WB - T4	WB - TS	WB - T5 mid	WB - T6 mouth
Aluminium	4380	4860	3270	5180	6650	9910	7400
Arsenic	9	9	<5	8	8	10	8
Cadmium	<1	<1	<1	<1	<1	<1	<1
Chromium	11	11	9	12	16	23	19
Copper	<5	<5	<5	<5	8	14	9
Iron	<50	<50	<50	<50	<50	<50	<50
Lead	5	6	<5	6	6	9	7
Manganese	132	228	101	194	97	100	202
Nickel	4	4	3	5	8	10	8
Selenium	<5	<5	<5	<5	<5	<5	<5
Zinc	12	13	9	14	22	31	25
Mercury	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

Table 9: Endeavour River Water Sample Results- Metals & Mercury

Date:		14/3/05					07/2/07			30/10/2007					Water Quality Guidelines ¹
Site:		ER-01	ER-02	ER-03	ER-04	ER-05	ER-01	ER-02	ER-03	ER01	ER02	ER03	ER04	ER05	
Turbidity:		52.0	52.7	56.0	55.7	55.0	116.3	104.6	58.1	2.0	2.0	2.0	3.0	3.0	
Total Metals															
Arsenic	mg/L	<0.050	<0.050	<0.050	<0.050	<0.050	0.002	0.002	0.001	0.0016	0.0019	0.0015	0.0005	<0.0005	
Cadmium	mg/L	<0.0050	<0.0050	<0.0050	<0.0050	<0.0050	<0.0001	<0.0001	<0.0001	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	0.0055
Chromium	mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.001	<0.001	<0.001	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.0274/0.0044 ²
Copper	mg/L	<0.050	<0.050	<0.050	<0.050	<0.050	0.001	0.004	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.0013
Lead	mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	0.001	0.001	<0.001	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	0.0044
Nickel	mg/L	<0.050	<0.050	<0.050	<0.050	<0.050	<0.001	<0.001	<0.001	<0.0005	<0.0005	<0.0005	0.0006	0.0007	0.07
Zinc	mg/L	0.081	0.058	0.060	<0.050	<0.050	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.015
Mercury	mg/L	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0004
Dissolved Metals															
Arsenic	mg/L	<0.050	<0.050	<0.050	---	---	0.001	0.001	<0.001	---	---	---	---	---	
Cadmium	mg/L	<0.0050	<0.0050	<0.0050	---	---	<0.0001	<0.0001	<0.0001	---	---	---	---	---	0.0055
Chromium	mg/L	<0.050	<0.050	<0.050	---	---	<0.001	<0.001	<0.001	---	---	---	---	---	0.0274/0.0044
Copper	mg/L	<0.050	<0.050	<0.050	---	---	0.001	0.001	<0.001	---	---	---	---	---	0.0013
Lead	mg/L	<0.005	<0.005	<0.005	---	---	<0.001	<0.001	<0.001	---	---	---	---	---	0.0044
Nickel	mg/L	<0.050	<0.050	<0.050	---	---	<0.001	<0.001	<0.001	---	---	---	---	---	0.07
Zinc	mg/L	0.080	0.055	0.060	---	---	<0.005	<0.005	<0.005	---	---	---	---	---	0.015
Mercury	mg/L	<0.0001	<0.0001	<0.0001	---	---	<0.0001	<0.0001	<0.0001	---	---	---	---	---	0.0004

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Marine Water (95% Level of Protection)

2 CrIII/CrIV

<0.050 Analyte not detected above the Level of Reporting (LOR)

0.004 Cells shaded green exceed the Water Quality Guidelines

Table 9 (continued): Endeavour River Water Sample Results- Metals & Mercury

Date:		23/01/08	04/03/08	11/09/08						20/04/09	Water Quality Guidelines ¹
Site:		ER-01	ER-01	ER-01	ER-02	ER-03	ER-04	ER-05	ER-MAIN-	ER-02	
Turbidity:		--	201.7	5.1	3.9	3.6	4.3	4.5	4.0	4.8	
Total Metals											
Aluminium	mg/L	--	--	0.16	0.19	0.05	0.07	0.05	0.03	0.13	
Arsenic	mg/L	<0.005	0.002	0.024	0.011	<0.050	0.004	0.004	0.002	<0.050	
Barium	mg/L	--	--	0.012	0.016	0.030	0.044	0.042	0.035	0.011	
Cadmium	mg/L	<0.0005	--	<0.0010	<0.0010	<0.0005	0.0002	0.0001	<0.0001	<0.005	0.0055
Chromium	mg/L	0.007	0.005	0.021	0.014	<0.005	<0.001	0.001	<0.001	<0.005	0.0274/0.0044 ³
Copper	mg/L	0.044	0.003	<0.010	<0.010	<0.050	0.001	0.001	0.001	<0.050	0.0013
Lead	mg/L	0.012	0.003	<0.010	0.032	<0.005	<0.001	<0.001	0.001	<0.005	0.0044
Manganese	mg/L	--	--	0.017	0.031	0.015	0.038	0.039	0.008	0.036	
Nickel	mg/L	<0.005	--	<0.010	<0.010	<0.050	0.002	0.002	0.002	<0.05	0.07
Zinc	mg/L	0.042	0.009	0.010	<0.010	<0.050	<0.005	<0.005	<0.005	<0.050	0.015
Iron	mg/L	--	5.12	1.05	0.96	0.51	0.40	0.42	0.38	<0.50	
Mercury	mg/L	<0.0001	--	del	del	del	del	del	del	<0.0001	0.0004
Dissolved Metals⁴											
Chromium	mg/L	0.002	<0.001	--	--	--	--	--	--	del	0.0274/ 0.0044 ³
Manganese	mg/L	--	--	--	--	--	--	--	--	0.032	
Iron	mg/L	--	0.15	--	--	--	--	--	--	--	

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Marine Water (95% Level of Protection)

2 Endeavour Main Channel east of 4 Mile Creek (See Figure 18)

3 CrIII/CrIV (Sample results are not speciated)

4 Dissolved metals were not analysed for all batches, metals not shown were not detected above the Level of Reporting (LOR)

del Analytical results were discarded due to holding time breaches (Hg) or rinsate sample contamination (dissolved Cr)

-- Not analysed

<0.005 Analyte not detected above the LOR

0.081 Cells shaded green exceed the ANZECC 2000 Water Quality Guidelines

Table 10: Endeavour River Sediment Sample Results – Metals and Mercury

Date:		29/11/04					19/03/2007					11/12/07		
Site:		ER-01	ER-02	ER-03	ER-04	ER-05	ER-01	ER-02	ER-03a	ER-03b	ER-03c	ER-03	ER-2.5	ER-LEP
Analyzed Sediment Fraction:		-63um	-63um	-63um	-63um	-63um	All	All	All	All	All	All	All	All
Total Metals														
Arsenic	mg/kg	--	--	--	--	--	9*	8*	13*	16*	8*	10	13	7
Cadmium	mg/kg	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chromium	mg/kg	23	16	30	27	30	15	6	24	26	11	13	22	12
Copper	mg/kg	39	28	33	24	33	12	<5	12	11	6	6	9	<5
Lead	mg/kg	86	9	13	12	11	56	<5	10	9	<5	5	9	<5
Nickel	mg/kg	9	7	14	12	16	6	3	10	10	6	6	9	5
Zinc	mg/kg	121	42	62	47	59	56	8	30	24	15	19	29	16
Mercury	mg/kg	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.1	0.3	<0.1

* Arsenic recovery in laboratory spike samples was below the data quality objectives, actual concentrations may be higher than those recorded

-- Not Analysed

Table 10 (continued): Endeavour River Sediment Sample Results – Metals and Mercury

Date:		11/9/08						14/09/2008		16/3/10					
Site:	ER-04	ER-03	ER-02	ER-01	ER-MAIN	ER-STP downstream	ER--STP upstream	ER-LEP1	ER-LEP2	ER-02	ER-03	ER-01	ER-CC	ER-LEP	
Sediment Fraction:	All	All	All	All	All	All	All	All	All	All	All	All	All	All	
Total Metals															
Aluminium	mg/kg	4350	1720	1400	8250	3250	6710	8440	2690	3850	2680	1210	5700	4350	6100
Arsenic	mg/kg	6	<5	11	11	<5	13	11	<5	7	5*	<5	5	6	10
Cadmium	mg/kg	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chromium	mg/kg	12	5	5	20	9	17	19	7	11	5	2	14	8	13
Copper	mg/kg	5	<5	<5	9	<5	7	8	<5	<5	<5	<5	22	<5	5
Lead	mg/kg	6	<5	<5	8	<5	8	9	<5	<5	<5	<5	8	<5	6
Nickel	mg/kg	6	2	2	9	4	8	9	3	5	2	<2	5	4	6
Zinc	mg/kg	18	6	7	26	12	26	27	8	14	7	<5	22	13	17
Vanadium	mg/kg	17	7	8	25	13	23	25	9	14	--	--	--	--	--
Barium	mg/kg	<10	<10	<10	10	<10	<10	10	<10	<10	--	--	--	--	--
Beryllium	mg/kg	<1	<1	<1	<1	<1	<1	<1	<1	<1	--	--	--	--	--
Cobalt	mg/kg	3	<2	<2	4	3	4	4	<2	2	--	--	--	--	--
Iron	mg/kg	17000	5180	6180	16300	9930	14800	16500	5580	10200	--	--	--	--	--
Manganese	mg/kg	56	25	16	124	20	87	113	40	48	--	--	--	--	--
Mercury	mg/kg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

* Arsenic recovery in laboratory spike samples was below the data quality objectives, actual concentrations could be higher than shown

<1 Analyte not detected above the Level of Reporting (LOR)

-- Not Analysed

Table 11: Jeannie River Water Sample Results- Metals & Mercury (mg/L)

	20/01/2008		18-12-07		14/04/2008		16/08/2008			22/03/2009		5/06/09					Estuary Guidelines ¹	Freshwater Guidelines ²
	JR-01	JR-02	JR-03	JR-00	JR-01	JR-04	JR-00	JR-02	JR-04	JR03	JR04	JR-00	JR-01	JR-02	JR-03	JR-04		
Turbidity	---	---	10.1	5.1	10.3	17.6	1300	1330	7	18.0	18.2	6.23	9.65	11.93	11.83	3.11		
Total Metals																		
Aluminium	---	---	---	---	0.31	0.02	0.14	0.19	del	0.22	0.02	---	---	---	---	---		
Arsenic	0.006	<0.005	<0.050	<0.050	<0.001	<0.001	<0.050	<0.050	del	0.001	<0.001	<0.050	<0.050	<0.050	<0.050	0.001		0.013/0.024 ³
Barium	---	---	---	---	0.024	0.160	0.008	0.106	0.121	0.016	0.084	0.006	0.013	0.103	0.154	0.030		
Cadmium	<0.0005	<0.0005	<0.0050	<0.0050	<0.0001	<0.0001	<0.0005	<0.0005	0.0011	<0.0001	<0.0001	<0.0050	<0.0050	<0.0050	<0.0050	<0.0001	0.0055	0.0002
Chromium	0.008	0.013	0.009	0.008	0.002	0.001	<0.005	del	del	<0.001	<0.001	0.01	0.01	0.01	0.01	<0.001	0.0274/ 0.0044 ⁴	0.001
Cobalt	---	---	---	---	<0.001	<0.001	0.011	del	del	<0.001	<0.001	<0.005	<0.005	<0.005	<0.005	<0.001		
Copper	0.020	0.014	<0.050	<0.050	0.005	<0.001	0.057	<0.050	del	0.001	0.001	<0.050	<0.050	<0.050	<0.050	<0.001	0.0013	0.0014
Lead	0.011	0.018	0.018	0.007	<0.001	<0.001	<0.005	<0.005	<0.001	<0.001	<0.001	0.008	<0.005	<0.005	<0.005	<0.001	0.0044	0.0034
Manganese	---	---	---	---	0.037	0.007	0.038	0.110	0.021	0.013	0.005	0.016	0.012	0.103	0.202	0.036		1.9
Nickel	<0.005	<0.005	<0.050	<0.050	<0.001	<0.001	<0.050	<0.050	0.001	<0.001	<0.001	<0.050	<0.050	<0.050	<0.050	<0.001	0.07	0.011
Tin	---	---	---	---	---	---	<0.005	<0.005	<0.001	---	---	---	---	---	---	---		
Zinc	0.059	0.097	0.078	0.068	<0.005	0.011	<0.050	<0.050	0.058	0.006	0.032	<0.050	<0.050	<0.050	<0.050	<0.005	0.015	0.008
Iron	---	---	---	---	0.60	0.33	1.63	2.09	del	1.20	0.29	0.84	<0.50	1.07	1.41	0.94		
Mercury	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	del	del	del	del	del	del	del	0.0004	0.0006

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Marine Water (95% Level of Protection)

2 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Freshwater (95% Level of Protection)

3 AsIII/AsV (Sample results are not speciated)

4 CrIII/CrVI (Sample results are not speciated)

5 Dissolved metals were not analysed for all batches, metals not shown (Ba, Cd, Cobalt, Hg, Sn, Pb, were not detected above the Level of Reporting (LOR)

del Analytical results discarded due to sample contamination from filters (dissolved metals), the detection of metals in rinsate samples (16/8/08) and exceeding holding times (Hg)

-- Not analysed

<0.005 Analyte not detected above the LOR

0.081 Results shaded green

Table 12: Metals Concentrations Upstream and Downstream from the Bluestone Tin Mine and Tailings Dam

ANALYTES	Water Quality Guidelines*		2007 Tailings Dam Overflow 06/02/07		2008 Wet Season 18/01/08			2008 Wet Season 15/02/08				2008 Wet Season, Tailings Dam Release 20/03/08			
	Freshwater Ecosystems ¹	Drinking Water ²	AR-02	AR-03	AR-03	AR-LES	AR-USTD	AR-03	AR-LES	TD DRAIN	AR-US-TD	AR-03	AR-LES	TD-Overflow	TD-Drain
Turbidity (NTU)			94.5	16	2	19	1	9.0	22	--	3.8	4.8	9	--	--
Total Metals															
Antimony		0.003	--	--	--	--	--	--	--	--	--	<0.001	<0.001	<0.001	0.007
Arsenic	0.024/ 0.013 ³	0.007	0.002	0.006	0.002	0.014	0.002	0.002	0.007	0.008	0.002	0.002	0.004	0.002	0.006
Cadmium	0.0002	0.002	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0001	0.0001	0.0004	<0.0001	--	--	--	--
Chromium	0.001 ⁴		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	<0.001	<0.001	<0.001	<0.001
Copper	0.0014	2	0.002	0.009	0.001	0.032	<0.001	0.004	0.02	0.018	<0.001	0.001	0.004	0.006	0.026
Lead	0.0034	0.01	0.002	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Nickel	0.011		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.002	<0.001	--	--	--	--
Tin			--	--	--	--	--	--	--	--	--	<0.001	<0.001	<0.001	<0.001
Zinc	0.008		<0.005	<0.005	0.005	<0.005	<0.005	<0.005	<0.005	0.005	<0.005	<0.005	0.141	0.007	<0.005
Mercury	0.0006		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	--	--	--	--
Dissolved Metals⁵															
Antimony			--	--	--	--	--	--	--	--	--	<0.001	<0.001	0.001	0.006
Arsenic	0.024/ 0.013	0.007	0.002	0.004	0.001	0.011	<0.001	0.002	0.004	--	<0.001	<0.001	<0.001	0.002	0.003
Cadmium	0.0002	0.002	<0.0001	<0.0001	<0.0001	0.0001	<0.0001	0.0001	0.0001	--	0.0001	--	--	--	--
Chromium	0.001		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Copper	0.0014	2	<0.001	0.006	<0.001	0.021	<0.001	0.003	0.012	--	<0.001	0.001	0.001	0.004	0.002
Lead	0.0034	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	--	<0.001	<0.001	<0.001	<0.001	<0.001
Nickel	0.011		<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	--	<0.001	--	--	--	--
Zinc	0.008		<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	--	<0.005	<0.005	del	del	del

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Freshwater (95% Level of Protection)

2 NHMRC ? Drinking Water Guidelines

3 AsIII/AsV (Sample results are not speciated)

4 CrIII/CrVI (Sample results are not speciated)

5 Dissolved metals were not analysed for all batches, metals not shown were not detected above the Level of Reporting (LOR)

del Analytical results were discarded due to potential sample contamination from filters (dissolved Zn)

-- Not analysed

<0.005 Analyte not detected above the LOR

0.081 Results shaded green exceed the ANZECC 2000 Water Quality Guidelines. Results shaded blue exceed the NHMRC Drinking Water guidelines

Table 12 (continued): Metals Concentrations Upstream and Downstream from the Bluestone Tin Mine and Tailings Dam

ANALYTES	Water Quality Guidelines		2009 Wet Season			2010 Wet Season			2010 Wet Season		
	Freshwater Ecosystems ¹	Drinking Water ²	09/02/09			28/01/10			27/03/10		
			AR-02	AR-03	AR-US TD	AR-03	AR- TD Drain	AR-USTD	AR-03	TD Drain	AR-USTD
Turbidity (NTU)			26	7	5.6	3.9	17	4.2	15.7	24.8	9.02
Total Metals (mg/L)											
Antimony		0.003	--	--	--	--	--	--	<0.001	0.010	<0.001
Arsenic	0.024/ 0.013 ³	0.01	<0.001	0.002	0.001	0.001	0.004	0.002	0.002	0.002	<0.001
Cadmium	0.0002	0.002	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Chromium	0.001 ⁴	0.05	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001
Copper	0.0014	2	0.002	0.002	<0.001	<0.001	0.004	<0.001	0.005	0.005	<0.001
Lead	0.0034	0.01	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Nickel	0.011	0.02	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Zinc	0.008	3	0.012	<0.005	0.006	<0.005	<0.005	<0.005	<0.005	0.021	<0.005
Dissolved Metals⁵ (mg/L)											
Antimony		0.01	--	--	--	--	--	--	<0.001	0.010	<0.001
Arsenic	0.024/ 0.013	0.002	0.001	0.001	<0.001	0.002	0.003	0.001	<0.001	0.002	<0.001
Cadmium	0.0002	0.05	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Chromium	0.001	2	<0.001	<0.001	<0.001	<0.001	del	del	<0.001	<0.001	<0.001
Copper	0.0014	0.01	0.001	0.002	<0.001	0.001	0.003	<0.001	0.001	0.002	<0.001
Lead	0.0034	0.02	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Nickel	0.011	3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Zinc	0.008	0.01	del	del	del	del	del	del	<0.005	0.014	<0.005

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Freshwater (95% Level of Protection)

2 NHMRC 2011 Drinking Water Guidelines

3 AsIII/AsV (Sample results are not speciated)

4 CrIII/CrVI (Sample results are not speciated)

5 Dissolved metals were not analysed for all batches, metals not shown were not detected above the Level of Reporting (LOR)

del Analytical results were discarded due to potential sample contamination from filters (dissolved Zn)

-- Not analysed

<0.005 Analyte not detected above the LOR

0.081 Results shaded green exceed the ANZECC 2000 Water Quality Guidelines. Results shaded blue exceed the NHMRC Drinking Water guidelines

Table 13: Endeavour River Analytical Results – OC/OP Pesticides in Water

Date:	07/2/07	07/2/07	11/9/08	11/9/08	11/9/08	14/9/08
Sample ID:	ER-01	ER-05	ER-03	ER-02	ER-MAIN4MC	ER-LEP
Organophosphorus Pesticides						
Azinphos Methyl	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Bromophos-ethyl	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Carbophenothion	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Chlorfenvinphos (Z)	µg/L	<0.5	<0.5	<0.050	<0.050	<0.050
Chlorpyrifos	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Chlorpyrifos-methyl	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Demeton-S-methyl	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Diazinon	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Dichlorvos	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Dimethoate	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Ethion	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Fenamiphos	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Fenthion	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Malathion	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Monocrotophos	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Parathion	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Parathion-methyl	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Pirimphos-ethyl	µg/L	<0.5	<0.5	<0.10	<0.10	<0.10
Prothiofos	µg/L	<2	<2	<0.10	<0.10	<0.10
Organochlorine Pesticides						
4.4'-DDD	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
4.4'-DDE	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
4.4'-DDT	µg/L	<2	<2	<0.010	<0.010	<0.010
Aldrin	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
alpha-BHC	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
alpha-Endosulfan	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
beta-BHC	µg/L	<2	<2	<0.010	<0.010	<0.010
beta-Endosulfan	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
DDT (total)	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
delta-BHC	µg/L	<2	<2	<0.010	<0.010	<0.010
Dieldrin	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Endosulfan	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Endosulfan sulfate	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Endrin	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Endrin aldehyde	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Endrin ketone	µg/L	<0.5	<0.5	<0.005	<0.005	<0.005
gamma-BHC	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Heptachlor	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Heptachlor epoxide	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Hexachlorobenzene	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Methoxychlor	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010
Total Chlordane	µg/L	<0.5	<0.5	<0.010	<0.010	<0.010

<0.010 Results shown in red are qualified. Holding times have been exceeded by 1 day
 <0.5 Not detected above the LOR

Table 14: Endeavour River Water Sample Analytical Results – Herbicides

Date:		07/2/07	07/2/07	12/11/07	12/11/07	23/1/08	11/9/08	11/9/08	11/9/08	14/9/08
Sample ID:		ER-01	ER-05	ER-03	ER-LEP	ER-01	ER-03	ER-02	ER-01	ER-LEP
Phenoxyacetic Acid Herbicides										
4-Chlorophenoxy acetic acid	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
2.4-DB	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
Dicamba	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
Mecoprop	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
MCPA	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
2.4-DP	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
2.4-D	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
Triclopyr	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
2.4.5-TP (Silvex)	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
2.4.5-T	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
MCPB	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.01
Picloram	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.05
Clopyralid	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.05
Fluroxypyr	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.05
2.6-D	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.1
2.4.6-T	µg/L	<10	<10	<10	<10	<10	--	--	--	<0.1
Glyphosate and AMPA										
Glyphosate	µg/L	<10	<10	24*	34*	<10	<10	<10	<10	<10
Triazines										
Atrazine	µg/L	--	--	<0.6	--	--	--	--	<1.0	<0.7
Simazine	µg/L	--	--	--	--	--	--	--	<1.0	<0.7
Phenylurea Herbicides										
Diuron	µg/L	--	--	<5.0	<5.0	--	--	--	<5.0	<5.0

* Results not accepted due to detection of glyphosate in blank sample at 34 µg/L

<10 Results shown in red are qualified. Sample holding time (1 week) exceeded by 1 – 3 days, potentially resulting in loss of contaminants.

<10 Not detected above the Level of Reporting (LOR)

-- Not Analysed

**Table 15: Pesticides, Herbicides and PAH analytical results for Endeavour River Passive Samplers
2008 & 2009 Wet Seasons – Estimated Daily Concentrations¹ (ng/L)**

Sample Site:	ER-Light	ER-Light	Field Blank	ER-01	ER-01	Field Blank	ANZECC 2000 Guidelines ²
Sample Period:	23/1/08 – 21/2/08	19/2/08 – 24/2/08	23/1/08 – 24/2/08	22/12/08 – 21/1/09	10/1/09 – 14/1/09	22/12/08 – 21/1/09	
Sample Duration:	30 days	5 days		30days	5 Days		
ED Passive Samplers							
Herbicides							
Diuron	6.9	1.5	<0.3	1.4	1.6	<0.3	ID
Simazine	1.8	<0.3	<0.3	<0.3	<0.3	<0.3	200
Atrazine	4.8	<0.3	<0.3	<0.3	<0.3	<0.3	700
Desethyl Atrz.	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	ID
Hexazinone	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	ID
Tebuthiuron	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	20
Metolachlor	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	ID
PDMS Passive Samplers*							
Pesticides/Herbicides							
Diuron breakdown product	NA	NA	NA	<45	<45	<45	ID
Galaxolide	NA	NA	NA	<0.05	3	<0.05	ID
Pendimethalin ___ H2209	NA	NA	NA	<0.54	<3.2	<0.54	ID
Polynuclear Aromatic Hydrocarbons							
Phenanthrene 178	NA	NA	NA	<0.1	0.9	<0.1	ID
spb6 PYRENE 202	NA	NA	NA	<0.1	0.6	<0.1	ID
All other PAH analytes	NA	NA	NA	<0.1	<0.1	<0.1	

1 Concentration estimated using passive samplers with an assumed sampling rate of 0.08 L.day⁻¹ (30 days) or 0.59 L.day⁻¹ (5 day)

2 ANZECC 2000 Guidelines for the Protection of Freshwater Aquatic Ecosystems (99% Level of Protection)- No guidelines have been established for saltwater.

ID Insufficient data exists – no guideline values have been established

<0.3 Values marked with a '<' sign were not detected and are based on the blanket LOR value for a 5 or 30 days deployment period.

* The complete list of PDMS analytes is listed in Appendix B, Table 3.

NA Not analysed

Table 16: Endeavour River Sediment Analytical Results- Phenoxyacetic Acid Herbicides & Triazines (mg/kg)

Sample Date:	11/12/07	11/12/07	11/12/07	23/1/08	23/1/08	23/1/08	11/9/08	11/9/08	11/9/08	14/9/08
Sample ID:	ER-03	ER-2.5	ER-LEP	ER-LEP(3) ¹	ER-01	ER-CC	ER-03	ER-02	ER-01	ER-LEP(2) ²
Phenoxyacetic Acid Herbicides										
4-Chlorophenoxy acetic acid	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
2,4-DB	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Dicamba	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mecoprop	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
MCPA	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
2,4-DP	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
2,4-D	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Triclopyr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
2,4,5-TP (Silvex)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
2,4,5-T	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
MCPB	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Picloram	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Clopyralid	<0.02	<0.02	0.28	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Fluroxypyr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Triazines										
Atrazine	<0.05	<0.05	<0.05	--	--	--	<0.05	<0.05	<0.05	<0.05
Simazine	--	--	--	--	--	--	<0.05	<0.05	<0.05	<0.05

1 3 separate samples were collected at various locations in the vicinity of Leprosy Creek

2 2 separate samples were collected in the vicinity of Leprosy Creek

<10 Not detected above the Level of Reporting (LOR)

Table 17: Endeavour River Sediment Analytical Results- Organochlorine and Organophosphate Pesticides (mg/kg)

Sample Date:	3/13/2005	3/13/2005	3/13/2005	3/13/2005	3/13/2005	11/09/2008	11/09/2008	11/09/2008	11/09/2008	14/09/2008
Sample ID:	ER-01	ER-02	ER-03	ER-04	ER-05	ER-03	ER-02	ER-01	ER-MAIN-4MC	ER-LEP1 ER-LEP2
Organochlorine Pesticides										
22 analytes	<0.05	<0.05	<0.05	<0.05	<0.05	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Organophosphorus Pesticides										
19 analytes	<0.05	<0.05	<0.05	<0.05	<0.05	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005

<0.0005 Results in red are qualified due to low matrix spike & surrogate recovery rates.

Table 18: Endeavour River Estuary Analytical Results- Hydrocarbons and Solvents in Water Grab Samples (µg/L)

Sample Date	14/03/05					07/02/07		23/01/08	11/09/08		Water Quality Guidelines ¹
Sample Location	ER-00	ER-02	ER-03	ER-04	ER-05	ER-01	ER-03	ER-01	ER-02	ER-03	
Total Petroleum Hydrocarbons											
C10 - C14 Fraction	80	80	<50	<50	<50	<50	<50	<50	--	--	
C15 - C28 Fraction	100	100	<100	<100	<100	<100	<100	<100	--	--	
C29 - C36 Fraction	<50	<50	<50	<50	<50	<50	<50	<50	--	--	
BTEX											
Benzene	--	--	--	--	--	<1 ²	<1	<1	<1	--	700
Toluene	--	--	--	--	--	<2	<2	<2	<2	--	
Ethylbenzene	--	--	--	--	--	<2	<2	<2	<2	--	
Xylenes	--	--	--	--	--	<2	<2	<2	<2	--	
Polynuclear Aromatic Hydrocarbons											
Naphthalene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	70
Acenaphthylene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Acenaphthene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Fluorene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Phenanthrene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Anthracene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Fluoranthene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Pyrene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Benz(a)anthracene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Chrysene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Benzo(b)fluoranthene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Benzo(k)fluoranthene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Benzo(a)pyrene	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Indeno(1.2.3.cd)pyrene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Dibenz(a,h)anthracene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Benzo(g,h,i)perylene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	
Phenols	<1.0	<1.0	<1.0	<1.0	<1.0	--	--	--	--	--	
Halogenated Aliphatic Compounds	--	--	--	--	--	<5	<5	--	--	--	
Halogenated Aromatic Compounds	--	--	--	--	--	<5	<5	--	--	--	

1 ANZECC 2000 Guidelines for the Protection of Aquatic Ecosystems, Trigger Values for Marine Water (95% Level of Protection)

2 Matrix spike recoveries were outside the data quality objectives

Table 19: Endeavour River Estuary Analytical Results- Hydrocarbons in Sediments (mg/kg)

Date:	13/03/05					19/03/07					11/09/08		
Site:	ER-01	ER-02	ER-03	ER-04	ER-05	ER - 01	ER - 02	ER - 03A	ER - 03B	ER - 03C	ER-01	ER-02	ER-03
Total Petroleum Hydrocarbons													
C6 - C9 Fraction	<2	<2	<2	<2	<2	<10	<10	<10	<10	<10	<10	<10	<10
C10 - C14 Fraction	<50	<50	<50	<50	<50	50	<50	<50	<50	<50	--	--	--
C15 - C28 Fraction	<100	<100	<100	<100	<100	240	<100	120	<100	<100	--	--	--
C29 - C36 Fraction	<100	<100	<100	<100	<100	<100	<100	140	120	<100	--	--	--
BTEX													
Benzene	--	--	--	--	--	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Toluene	--	--	--	--	--	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Ethylbenzene	--	--	--	--	--	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
meta- & para-Xylene	--	--	--	--	--	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
ortho-Xylene	--	--	--	--	--	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Polynuclear Aromatic Hydrocarbons													
Naphthalene	--	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Acenaphthylene	--	<0.5	<0.5	<0.5	<0.5	0.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Acenaphthene	--	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Fluorene	--	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Phenanthrene	--	<0.5	<0.5	<0.5	<0.5	8.7	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Anthracene	--	<0.5	<0.5	<0.5	<0.5	1.6	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Fluoranthene	--	<0.5	<0.5	<0.5	<0.5	12.3	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Pyrene	--	<0.5	<0.5	<0.5	<0.5	9.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Benz(a)anthracene	--	<0.5	<0.5	<0.5	<0.5	4.9	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Chrysene	--	<0.5	<0.5	<0.5	<0.5	4.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Benzo(b)fluoranthene	--	<0.5	<0.5	<0.5	<0.5	4.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Benzo(k)fluoranthene	--	<0.5	<0.5	<0.5	<0.5	1.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Benzo(a)pyrene	--	<0.5	<0.5	<0.5	<0.5	3.1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Indeno(1.2.3.cd)pyrene	--	<0.5	<0.5	<0.5	<0.5	1.7	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Dibenz(a,h)anthracene	--	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Benzo(g,h,i)perylene	--	<0.5	<0.5	<0.5	<0.5	1.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

50 Low recovery in matrix spike, actual concentrations may be greater than shown

-- Not Analysed

<1.0 Not detected above the Level of Reporting

**APPENDIX E-
PASSIVE SAMPLER PAH AND PESTICIDE/ HERBICIDE ANALYTE LIST**

PESTICIDES & PAH ANALYTES LIST - GCMS - PDMS SAMPLERS			
Acephate	Dieldrin	Metribuzin	Tetradifon
Aldrin	Dimethoate	Mevinphos Z+E	Tetramethrin
Ametryn	Dimethomorph	Molinate	Thiabendazole
Amitraz	Dioxathion	Monocrotophos	Tonalid
Atrazine	Disulfoton	Musk Ketone	Transfluthrin
Azinphos Ethyl	Diuron Breakdown Product	Musk Xylene	Triadimefon
Azinphos Methyl	Endosulfan Alpha	Nicotine	Triadimenol
Benalaxyl	Endosulfan Beta	Nonachlor Cis	Triallate
Bendiocarb	Endosulfan Ether	Nonachlor Trans	Trifluralin
Bifenthrin	Endosulfan Lactone	Omethoate	Vinclozalin
Bioresmethrin	Endosulfan Sulphate	Oxadiazon	
Bitertanol	Endrin	Oxychlor	
Bromacil	Endrin Aldehyde	Oxydemeton Methyl	PAHs
Bromophos Ethyl	Ethion	Oxyfluorfen	Naphthalene
Cadusaphos	Ethoprop	Parathion Ethyl	Acenaphthylene
Captan	Etrimiphos	Parathion Methyl	Acenaphthene
Carbaryl	Famphur	Pendimethalin	Fluorene
Carbophenothion	Fenamiphos	Permethrin	Phenanthrene
Chlordane Cis	Fenchlorphos	Phenothrin	Anthracene
Chlordane Trans	Fenitrothion	Phorate	Fluoranthene
Chlordene	Fenthion Ethyl	Phosmet	Pyrene
Chlordene Epoxide	Fenthion Methyl	Phosphamidon	Benz[A]Anthracene
Chlorfenvinphos E+Z	Fenvalerate	Phosphate Tri-N-Butyl	Benzo[B+K]Fluoranthene
Chlorothalonil	Fipronil	Piperonyl Butoxide	Chrysene
Chlorpyrifos	Fluazifop Butyl	Pirimicarb	Benz[E]Pyrene
Chlorpyrifos Me	Fluometuron	Pirimiphos Methyl	Benz[A]Pyrene
Chlorpyrifos Oxon	Fluvalinate	Procymidone	Perylene
Coumaphos	Furalaxyl	Profenophos	Indeno[123cd]Pyrene
Cyfluthrin	Galaxolide	Prometryn	Benzo[Ghi]Perylene
Cyhalothrin	Haloxyfop 2-Etoet	Propagite	Dibenz[Ah]Anthracene
Cypermethrin	Haloxyfop Methyl	Propanil	
Dcpp	Hcb	Propazine	
Ddd O,P	Hch-A	Propiconazole	
Ddd P,P	Hch-B	Propoxur	
Dde O,P	Hch-D	Prothiophos	
Dde Pp	Heptachlor	Pyrazaphos	
Ddt O,P	Heptachlor Epoxide	Rotenone	
Ddt P,P	Hexazinone	Simazine	
Deet	Iprodione	Sulprofos	
Deltamethrin	Isophenophos	Tcep	
Demeton-S-Methyl	Lindane	Tcpp	
Desethylatrazine	Malathion	Tebuconazole	
Desisopropylatrazine	Metalaxyl	Tebuthiuron	
Diazinon	Methamidophos	Temephos	
Dichloroaniline	Methidathion	Terbuphos	
Dichlorvos	Methoprene	Terbutylazine	
Diclofop Methyl	Methoxychlor	Terbutryn	
Dicofol P,P	Metolachlor	Tetrachlorvinphos	

