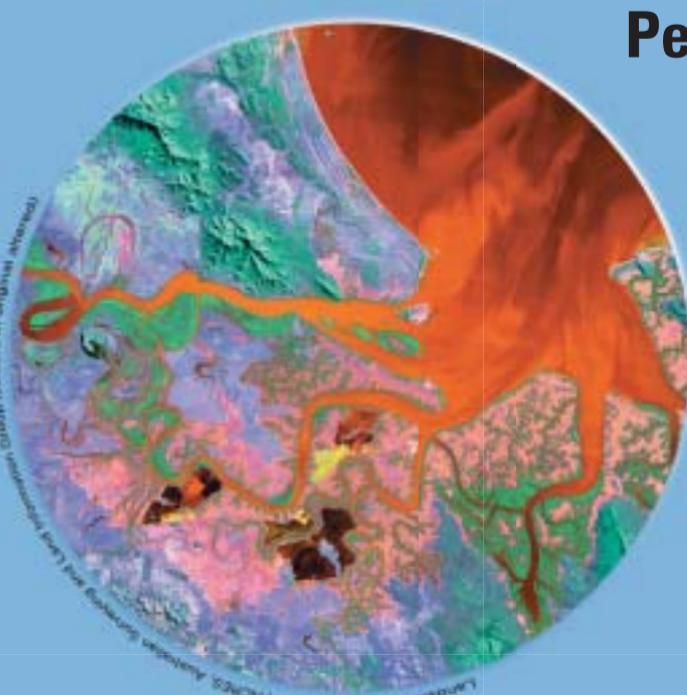




Cooperative Research Centre for Coastal Zone, Estuary & Waterway Management

Technical Report 37



**Pesticide, polycyclic aromatic
hydrocarbon and metal
contamination in the
Fitzroy Estuary, Queensland,
Australia**

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June 2006

The logo for the Cooperative Research Centre for Coastal Zone, Estuary & Waterway Management, featuring a stylized green and yellow wave and the text "CRC for Coastal Zone Estuary & Waterway Management".

**CRC for Coastal Zone
Estuary & Waterway Management**

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Pesticide, polycyclic aromatic hydrocarbon and metal contamination in the Fitzroy Estuary, Queensland, Australia

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Archived estuarine/marine benthic sediments (collected in 1998) and sediment core 3410 (collected in 2000) from Keppel Bay included in this study were sampled from the R/V *Lady Basten* with the assistance of Dr Gregg Brunskill and co-workers (Australian Institute of Marine Science). Archived Fitzroy River and Fitzroy Channel estuarine sediments obtained in 2000–2002 were also used.

Metal analyses (excepting mercury) were performed by Geoscience Australia, coordinated by Dr Lynda Radke. Stable lead isotope ratios measurements were performed at the Environmental Analytical Chemistry Unit, Charles Darwin University, Darwin.

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List of terms and acronyms

Al: Aluminium

ANZECC: Australian and New Zealand Environment and Conservation Council.

ARMCANZ: Agriculture and Resource Management Council of Australia and New Zealand.

As: Arsenic.

Ca: Calcium.

Cd: Cadmium.

Cu: Copper.

Cr: Chromium.

CRC: Cooperative Research Centre.

Detection limit: Method detection limit is the concentration of a substance that, when processed through the complete analytical method, produces a signal that has a 99% probability of being different from the blank.

Fe: Iron.

Guideline: Numerical concentration limit or narrative statement recommended to support and maintain a designated water use.

Guideline trigger levels: The concentrations (or loads) for each water quality parameter, below which there exists a low risk that adverse biological (or ecological) effects will occur. They are the levels that trigger some action, either continued monitoring in the case of low risk situations or further ecosystem-specific investigations in the case of high-risk situations.

Hg: Mercury.

ISQG: Interim sediment quality guideline.

Limit of Detection (LOD): same as detection limit.

Mn: Manganese.

Ni: Nickel.

PAHs: Polycyclic aromatic hydrocarbons.

Pb: Lead.

PbIR: Lead isotope ratio.

Quality assurance (QA): The implementation of checks on the success of quality control (e.g. replicate samples, analysis of samples of known concentration).

Quality control (QC): The implementation of procedures to maximise the integrity of monitoring data (e.g. cleaning procedures, contamination avoidance, sample preservation methods).

S: Sulfur.

Sediment: Unconsolidated mineral and organic particulate material that has settled to the bottom of aquatic environments.

TOC: Total organic carbon.

Trigger value: A Guideline value that if exceeded triggers further investigations.

Zn: Zinc.

Non-technical summary

The Coastal CRC initiated a monitoring program in 2001 to quantify the concentration and loads of pesticides delivered to the Fitzroy Estuary (FE) from the Fitzroy River catchment. This monitoring has been extended during 2003–06 to include analysis for polycyclic aromatic hydrocarbons (PAHs) and metals in fine sediments and core samples from the FE and Keppel Bay. This work adds to the very limited studies on PAH and metal contaminants particularly in benthic sediments from the Fitzroy Estuary.

Results for pesticides in fresh and estuarine waters confirmed previous data showing significant concentrations of several herbicides (particularly Atrazine, Tebuthiuron, Diuron) and lower concentrations of several others entering the estuary in flood flows from the basin. For atrazine, few concentrations detected exceeded the trigger value for protection of 99% of freshwater species while for tebuthiuron all detections exceeded this value. The environmental fate and possible impact of these herbicides on coastal and marine flora is unclear. Future monitoring should include further evaluation of these residues and their impacts and hopefully show decreasing loads of herbicides entering the estuary in the future as improved land management practices are implemented in the basin.

In contrast to the higher levels and wider range of PAH compounds found in the more industrialised area of Port Curtis, PAH concentrations in sediments from the Fitzroy Estuary were low and were predominantly from natural sources. Monitoring for PAHs in the Fitzroy estuary should be considered at least on a five-year scale.

For metals, levels of Ni, Cr, and Sb in sediments exceeded trigger values in several instances. Regression models for the ten metals regulated by ANZECC (2000) showed that Sb, Ag, Ni and Hg were enhanced in several samples, with Sb and Ag indicating some historical accumulation. While geological sources for Ni and Cr in the central Queensland region are likely, the sources and potential impact on the ecosystem of the other elements warrant investigation and inclusion in a monitoring program.

General introduction

The Fitzroy Basin in central Queensland (Figure 1), the largest catchment draining to the east coast of Australia, straddles the Tropic of Capricorn and is characterised by a humid coastal and semi-arid inland sub-tropical climate. Rainfall in the region is dominant in summer (December–February) but highly variable with annual mean rainfall ranging from 500 mm in the west to more than 800 mm along the coast. The Fitzroy Estuary, which was essentially bisected by the construction of the Fitzroy Barrage at Rockhampton in the early 1970s, now has a tidal 'length' of about 60 km and a 'volume' of about 500 000 million litres (ML). Calvert *et al.*, 2000 have reported that land use in the Fitzroy region is dominated by agricultural activities with grazing ~82% and cropping ~7%. Other uses include state forests and national parks, which account for ~9%. Mining and extractive industry use less than 1% of the land area, although land use for mining has been rapidly increasing. Water infrastructure includes one large dam with smaller weirs on most streams.

Rockhampton (population ~65 000) is the largest urban centre and is situated at the head of the Fitzroy Estuary with the remaining people in the region (~120 000) being distributed among smaller rural towns and agricultural properties throughout the basin.

The Fitzroy River flows into Keppel Bay on the Capricorn coast and while the southern sections of the main Great Barrier Reef (GBR) are far offshore, the Capricorn coast includes many beaches, inshore reefs and islands within the World Heritage Area including the Capricorn–Bunker Group. The extensive Fitzroy estuary and adjacent areas of the Capricorn coast form the basis of the central Queensland commercial and recreational fishing industries.

When considering possible contaminants that may arise from anthropogenic activities and possibly move into the estuary in freshwater flows a number of types and sources should be included, such as:

- Considerable quantities of fertilisers (nitrogen and phosphorus) and pesticides are applied for agricultural production in the Fitzroy Basin. Runoff, from often limited but intensive summer rainfall in the catchments, can carry a portion of these materials offsite into rivers and into the estuary transported on suspended solids or in solution.
- Extensive mining of coal occurs in the basin with exports of the order of 100 million tonnes per annum. Disturbance of these coal seams and historical burning of vegetation throughout the basin give rise to the possibility of metals from disturbed mineral ores and organic compounds

such as polycyclic aromatic hydrocarbons (PAHs)) being produced and transported in flows to the estuary.

- Over 100 years of mining at Mount Morgan up to the late 1900s has produced not only considerable wealth from gold, silver and copper but also a mine pit with highly acidic water and heavy metal pollution of the Dee River, which runs through the Mount Morgan township into the Don River then Dawson River, and on to the lower Fitzroy River at Rockhampton. The effects of acid mine drainage are evident for up to 30 km downstream of the minesite, with accumulation in floodplain soils about 70 km downstream of the minesite (Taylor, 2004). A lime-dosing pilot plant is about to commence operation at the tailings pit to reduce the pit water's acidity (pH = 2-3) prior to discharge into the Dee River. Some polluted streambed material from the Dee River has been removed.

There is presently a strong interest in the delivery of contaminants from terrestrial sources to the Great Barrier Reef (GBR) lagoon from floods. In 2001, the Great Barrier Reef ministerial council called for information on the impacts of the declining quality of water entering the Great Barrier Reef lagoon and for actions to reduce the threat.

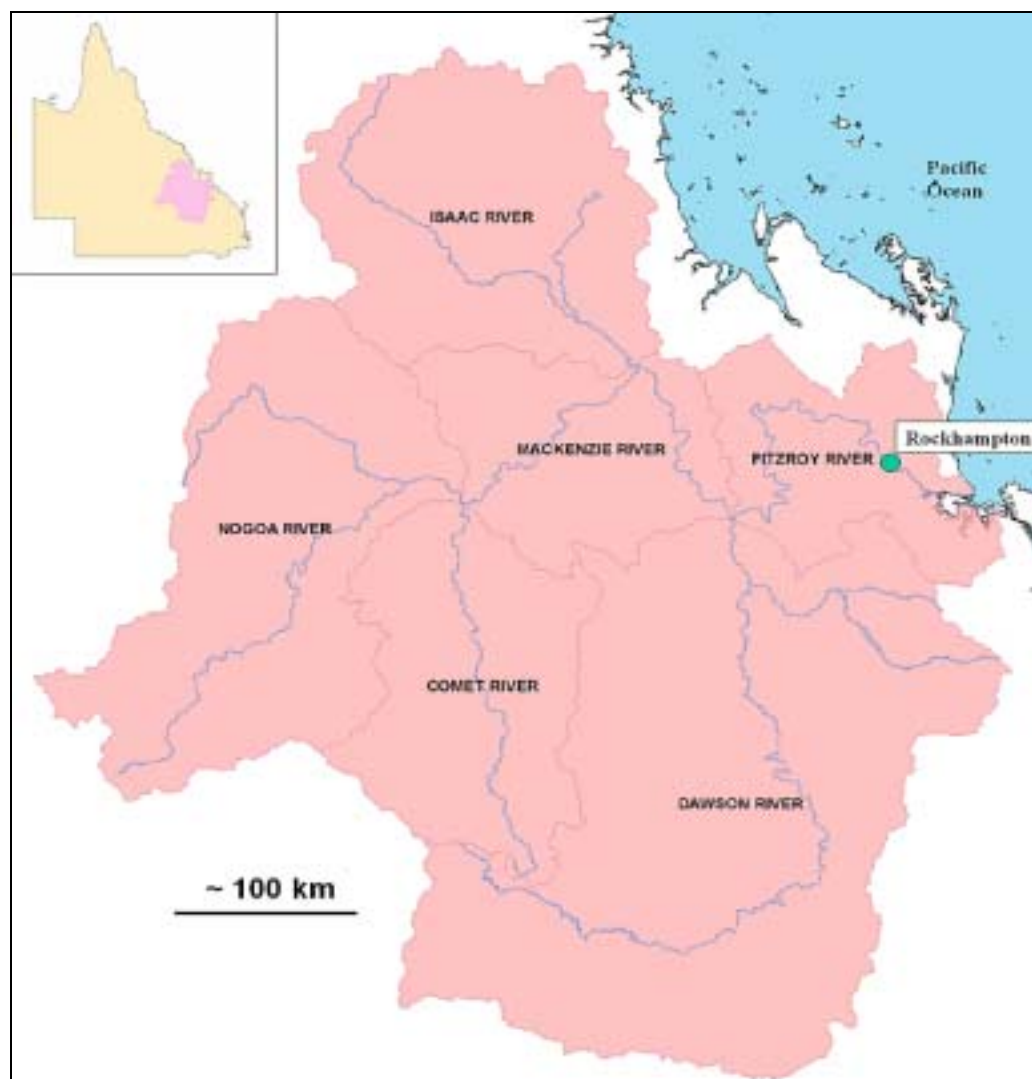


Figure 1: The Fitzroy River catchment and major sub-basins

Recently the Fitzroy River basin has been identified as a priority catchment in this process, particularly in respect to sediment and nutrient export to the Great Barrier Reef lagoon. In response, the Coastal CRC initiated a monitoring program in 2001 (as a part of a larger research effort) to monitor the concentrations of pesticides delivered to the Fitzroy Estuary from the Fitzroy River catchment. Initially the Coastal CRC Fitzroy Agricultural Contaminants Project focussed only on pesticides (particularly herbicides such as the triazines and urea based chemicals), as these were considered to be the most significant contaminants from the Fitzroy catchment to the estuary. However, some stakeholders (at the Stakeholders Workshop held by the Coastal CRC in Rockhampton on 8 Nov 2004) strongly argued that there was a need to investigate the presence of metal pollution (and other coal-mining derived

contamination, e.g. PAHs) in the estuary. Thus, metals and PAHs were included in the contaminants to be monitored in the Fitzroy Estuary.

Organic and metallic contaminants are strongly attracted to the sediment matrix through chemical interactions with organic matter and iron and aluminium oxides, which generally accumulate on the sediment surface. Fine sediments (<1 mm) have stronger affinity and hence higher concentration of PAHs, and most heavy metals (e.g. mercury, cadmium, nickel) are found in benthic sediments rather than in the water column.

The large surface area of fine sediments make them efficient sinks of contaminants; they are thus potential sources of these contaminants when the seabed is disturbed (e.g. during dredging) and/or when environmental conditions become altered (e.g. air oxidation, release of acid sulfides) causing their remobilisation into the water column and generating potential ecotoxicity. In the past, there have been very limited studies on PAH and metal contaminants particularly in benthic sediments from the Fitzroy estuary. It would be timely to investigate the presence of these contaminants especially with the current boom in mining (for metals such as nickel and coal) and industrial operations within central Queensland.

Pesticide usage and detections in the Fitzroy Basin, central Queensland

The term 'pesticide' is used here to include a range of agricultural products for controlling floral and faunal pests. Commonly this will include insecticides, herbicides, fungicides etc.

It appears that there has been no formal audit yet of pesticide usage in the Fitzroy catchment and in Queensland in general (Connell *et al.*, 1999). This usage will be closely related to the types of land use throughout the region and there are a number of studies identifying the presence of pesticide residues in the freshwater, estuarine and marine environments.

Cropping in the region (involving less than 10% of the Fitzroy Basin) includes both dryland cropping, where pesticide input is mostly restricted to herbicides, and smaller areas of irrigated cropping where more intensive usage of both insecticides and herbicides would be common. Appreciable quantities of herbicides are also expected to be used for weed control along roadways and rail lines. In urban areas both insecticide and herbicide usage is likely to be considerable along road verges, on sports and playing fields, and to a lesser extent on the typical urban house block.

Without a formal audit of pesticide usage in the basin this inferred pattern of use is the context in which results for pesticide residues in our waterways should be interpreted. Some further difficulties with regard to monitoring pesticides are, that

for some of the newer chemicals analytical methods are not yet available and/or the limits of analytical detection are not sensitive enough. This was also the case for some 'older' herbicides.

In the grazing areas (which utilise over 80% of the Fitzroy Basin), a major challenge for graziers is to control regrowth of cleared native vegetation and the spread of woody weeds. Tebuthiuron, a urea-type herbicide which is classified as slightly toxic (Kamrin, 1997), is widely used for these purposes and data for the freshwater sections of the upper Fitzroy River, and in this study for the estuarine reaches, shows that this chemical is applied in most parts of the catchment.

A number of herbicides are commonly used in the dryland cropping regions. Atrazine, a selective triazine herbicide which is classified as slightly toxic as well as a 'restricted use pesticide' due to its potential for groundwater contamination (Kamrin, 1997), was found to be ubiquitous in freshwaters of the basin (Noble *et al.*, 2000) and this study has recorded considerable concentrations and loads of this chemical in the Fitzroy Estuary.

More intensive use of herbicides and insecticides occurs in the irrigated cropping areas of the basin mostly along the Dawson and Nogoa Rivers, while substantial areas of dryland cropping occur in the Nogoa (Theresa Creek area), Comet, and Dawson sub-catchments. Summer is the peak time for application and detections occurred mostly during this season or shortly after, though some residues could persist into the winter season. Most of the insecticides used in the irrigated areas have a comparatively short half-life in the environment (Kamrin, 1997) so residues of these chemicals in adjacent streams would normally only be found if sampling were to occur shortly after application and runoff from rainfall. In previous studies (Noble, 2000), residues of a number of herbicides were commonly found in areas downstream from the irrigated cropping areas in summer.

Data for pesticide residues in samples from urban runoff are much more limited in the Fitzroy Basin. Pesticides residues had been commonly detected in water samples from many sites in the Fitzroy catchment during monitoring in the 1990s (Noble *et al.*, 1997; Noble, 2000). As well, low concentrations of some herbicides (e.g. Diuron) were recently detected in subtidal sediment samples near the mouth of the Fitzroy River (Haynes *et al.*, 2000).

During the summers (December-February) of 2002 and 2003, a timed-series of floodwater samples flowing through the Fitzroy River Barrage at Rockhampton and into the Fitzroy Estuary were collected and analysed for a number of common pesticides (Packett *et al.*, 2005). The most frequently detected pesticides at a concentration of concern in the water samples were the

herbicides Atrazine, Diuron and Tebuthiuron. Considerable concentrations of these herbicides were recorded entering the estuary. Other chemicals detected less frequently and at lower concentrations were Simazine, Hexazinone, Prometryn, Fluometuron and the degradation products of Atrazine (Desethyl atrazine and Deisopropyl atrazine).

Because of environmental concerns raised by these results for pesticide residues in floodwaters during 2002 and 2003 this investigation was continued in the Coastal CRC's Fitzroy program for the 2003/2004 and 2004/2005 wet seasons.

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) contain only carbon and hydrogen with a chemical structure containing at least two fused benzene (six carbon) rings; they may also contain other rings of carbon numbering other than six. They are mostly non-water soluble (except naphthalene) and, being hydrophobic, often attach to particulate matter such as dust. They may enter the aquatic environment from natural sources (e.g. fossil fuels, oil shales, natural forest fires, volcanoes) and from various anthropogenic sources such as oil spills from tankers, refineries and offshore drilling sites, runoff and storm waters, atmospheric deposition, and combustion processes including coal-fired electricity power plants, petrol and diesel combustion engines, incineration, burning of wood and coal, smoking of tobacco, etc. (Connell, 1997).

PAHs are persistent organic pollutants. They are increasingly of concern because of their known and potential toxicity. They have a health hazard rating of 1.3 and an environmental hazard rating of 1.5, where a score of 3 represents a very high hazard in both categories (NPI, 2004). A review of the compounds' Materials Safety Data Sheet (Chemwatch, 2005) revealed that different PAHs have varying toxicological properties and may be mutagenic, teratogenic or carcinogenic. There is still very limited information on their ecotoxicity, but toxicities of low-molecular weight PAHs to aquatic organisms have been reported and uptake by many aquatic organisms such as mussels, crabs, fish etc have been demonstrated (Kennish, 1997; Connell, 1997).

There are no published data to date on the presence of PAHs in the Fitzroy Estuary. This study addresses this lack of information.

Metals

There are many agricultural and mining activities occurring within the Fitzroy catchment, which can contribute to metal pollution. Some fertilisers may inadvertently include metal contaminants such as cadmium in phosphate salts. In the past some cattle dips used arsenic compounds as pesticides for cattle ticks.

Several past and present mining activities (copper, gold and coal) disturbed the earth's surface, leading to exposure of minerals such as pyrite, which produce acid and sulphate upon air oxidation, contributing to acid mine drainage (AMD). The classic example is the de-commissioned Mount Morgan Mine (Mount Morgan, central Queensland), which continues to generate AMD into the Dee River up to at least 25 km downstream from the minesite. There are also some current explorations for nickel in the region. The concern for the presence of metal pollutants in the Fitzroy Estuary was strongly expressed at the Stakeholders Workshop in Rockhampton on 8 Nov 2004, as there has been rather limited assessment of metal pollution in the study area.

Methods

Water sampling

Water samples were collected during the wet seasons (December to March) of 2003/4 and 2004/5 across the flood hydrograph at the pontoon of the Fitzroy Motor Boat Club downstream of the Fitzroy River Barrage in Rockhampton (see section 3.1.1 for location). A number of samples were also collected at the Fitzroy River mouth during the 2004 floods. In addition, three stormwater samples were collected from urban runoff in south Rockhampton in early January 2005.

All collection, handling and transport of samples were performed in accordance with the procedures given in the Water Quality Sampling Manual (Queensland Environmental Protection Agency, 1999).

Sediment sampling

The list of samples is indicated in Appendix 1. Sediment grabs were obtained using one of several types of grab sampler: Eckman grab, modified Van Veen and modified Smith-McIntyre.

Sixteen sediment grab samples were obtained in August 2004 (survey 268, c/- Lynda Radke, Geoscience Australia). The sampling locations are given in Table A1.1, Appendix 1 (samples analysed are indicated with a ✓). Due to project budget constraints, only nine samples (which were closest to the mouth of the river) were analysed for PAHs to obtain some idea of levels of organic contaminants in the surface sediments. The sediments varied between sandy-mud to muddy-sand in texture.

Additional surface benthic sediments were obtained in August and December 2005 from the main channel of the Fitzroy River downstream of the Barrage, as well as from a few sites upstream of the Barrage (see Table A1.2, Appendix 1).

A 2.6 m sediment core (277VC20A) from Keppel Bay was obtained using a vibracorer in September 2004 (c/- Geoscience Australia); location: -23.50329°, 150.95235°. The core was sliced into 3–5 cm thick sections, in order to have adequate mass (minimum 75 g wet sediment) for the analyses of low-level PAH contaminants, which may be approaching the analytical limits of detection. The sediments were found to be mostly muddy in texture, with a few slices of sandier texture. Fifteen (of the 78 total) slices were analysed for PAHs, while 23 other slices were analysed for metals (see Section 3).

Due to limited time and budget to undertake further sampling, some archived (V. Vicente-Beckett, CQU) Keppel Bay sediments (obtained in 1998), main Fitzroy Channel sediments (obtained in 2002), and a sediment core (3410) taken at the mouth of Raglan Creek in the Fitzroy Estuary (obtained by hydraulic coring from the RV *Lady Basten*, c/- Australian Institute of Marine Science) were included in this study (see Table A1.3, Appendix 1) in order to obtain a more extensive picture of sediment metal contents in the Fitzroy Estuary.

Analytical methods

The water and sediment samples were analysed for a range of herbicides and pesticides at the National Association of Testing Authorities (NATA)-certified laboratories of the Queensland Health and Pathology Scientific Services (QHPSS) in Brisbane, Australia. In-house methods were adapted from recommended methods of US Environmental Protection Agency and Official Methods of the Association of Official Analytical Chemists (AOAC) International.

Water analyses from urban runoff

The samples were analysed for a number of parameters expected in urban runoff including nutrients, a range of pesticides, total petroleum hydrocarbons (TPHs) and polycyclic aromatic hydrocarbons (PAHs). Analytical limits of detection (LOD) were 0.01 µg/l for pesticides, 10 µg/l for TPHs and 3 µg/l for PAHs.

No water samples were analysed for metals due to cost limitations, since water analyses require very sensitive analytical methods (sub-microgram per litre), clean laboratory (i.e. minimum filtered air) and prompt analyses (within 24–48 hours) for reliability.

Analyses of pesticides and PAHs in sediments

About 50 g of wet sediment was mixed with hydromatrix (diatomaceous earth) to form a free flowing powder, which was, then extracted using Dionex ASE100 or ASE300 (Accelerated Solvent Extraction). The extraction solvent mixture was dichloromethane-acetone 50-50. The sample was heated to 125°C with a static cycle of 5 minutes. Following extraction the solvent extract was cleaned up using gel permeation chromatography (Waters Envirogel). The extract was then concentrated and analysed by gas chromatography-mass spectrometry (GC-MS) for PAHs. Following GC-MS the extracts were split with one half undergoing liquid chromatography-mass spectrometry/mass spectrometry (LC-MS/MS) and the other half cleaned up using a Florisil column prior to analysis by GC with an electron capture detector.

Each batch of samples included a solvent blank and a sample spiked with a mixture of PAHs. All samples and quality assurance (QA) samples were spiked with a mixture of compounds, which acted as a surrogate. The recovery of the surrogates was calculated and the results compared with in-house long-term recovery for this method of analysis.

Seventeen different PAHs were analysed by NATA-certified laboratories of QHPSS. Limit of detection (LOD) for each PAH analysed was 2 µg/kg sediment dry weight.

Organic carbon in sediments

Sediments were prepared according to the Standards Australia method AS4479. Sub-2 mm sediments were ground to fine powder in a TEMA swing mill. An accurately weighed portion of the sample was pre-treated with acid to remove inorganic carbon. The total organic carbon was determined by a thermal process where the sample was rapidly heated by an induction coil (Leco C200 carbon analyser). The sample underwent induction furnace combustion with iron and copper accelerator in a stream of oxygen. Carbon in the sample was converted to carbon dioxide by a platinum-on-silica catalyst and the amount of carbon dioxide was then measured by a thermal conductivity detector for direct digital display of carbon content. A reagent blank and secondary reference material was run with each batch of samples analysed.

Analyses were performed by NATA-certified analytical laboratories of QHPSS.

Analysis of metals in sediments

Frozen sediment samples were thawed at room temperature shortly before analysis. Sediments were wet-sieved using nylon mesh.

Particle size distribution (<60 µm, <125 µm, <1 mm) was determined gravimetrically using oven-dried (at 40–50°C) fractions following wet-sieving.

Dried sediments (particles ≤1 mm or <60 µm in size) were analysed for ANZECC (2000)-regulated metals (except mercury) in the laboratories of Geoscience Australia (Canberra, Australia) using inductively-coupled plasma-mass spectrometry (ICP-MS) for Ag, As, Cd, Pb and Sb and x-ray fluorescence spectrometry (XRF) for Cr, Cu, Ni and Zn. Certified reference materials were included for QA purposes analyses and the recoveries obtained are summarised in Table A5.1, Appendix 5.

Mercury was analysed (using cold-vapour atomic absorption spectroscopy) by NATA-accredited laboratory, Genalysis Laboratory Services (Gosnells, Western Australia). Sediments for Hg analyses were heated at 121°C for 2 hours as part of quarantine requirements for interstate materials. However, analysis of the

certified reference material (BEST-1; see Appendix 5) included in the batch of samples showed 98.7% recovery for Hg, indicating that the heating process did not lead to any significant loss of Hg from the sediments.

Analysis of stable lead isotope ratios in sediments

For the analysis of stable lead isotope ratios (PbIRs), sediments <60µm size were digested in 1 ml concentrated nitric acid plus 4 ml concentrated perchloric acid in an open tube block digester at 200°C for 6 hours. PbIRs were analysed as $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ calibrated to National Institute of Standards and Technology (NIST; Maryland, USA) standard reference material 981 (common lead); the digests were also used to determine pseudo-total analyses of lead and other metals using ICP-MS. Experimental procedures used were similar to those given in Munksgaard *et al.* (2003). Analyses were performed at the Environmental Analytical Chemistry Unit, Charles Darwin University (Darwin, Australia). Table A5.2, Appendix 5 provides QA data for the analytical techniques.

Results and discussion

Pesticides

Herbicides detected in 2003/2004 and 2004/2005 floods

Floodwater samples were collected below the Barrage at Rockhampton for pesticides analysis of the major flows during the 2003/2004 and 2004/2005 wet seasons (Figure 2).

The peak discharge of floods during the 2003/2004 and 2004/2005 wet seasons was minor in comparison to major floods for the Fitzroy Basin, which have a return period of around a decade or longer on average. For example, the 1991 flood exceeded 10 000 m³/second compared to the peak discharge of around 900 m³/second for the 2005 event. Figure 2 gives the discharge in cubic meters per second recorded at the lowest gauge in the catchment (The Gap GS 130005A) for the period of this study time corrected (travel time) for the Barrage at Rockhampton.

The 2004 flow originated from widespread rainfall in the western catchments around the 8th and 9th of January. The most intense rains fell in the Nogoia and Comet river sub-catchments with totals of around 250 mm. The Dawson and Mackenzie sub-catchments contributed minor volumes compared to the western areas. For the event monitored at Rockhampton a total flow volume of around 885 gegalitres (1 gegalitre = 1000 megalitres) reached the end of the valley.

In comparison, the 2005 event delivered around 365 gegalitres and originated from localised rain of around 255 mm on the 24th and 25th of January in the extreme north eastern parts of the Isaac/Connors sub-catchment; less extensive rains fell over the Mackenzie and Fitzroy sub-catchments and contributed minor volumes to the total flow that passed Rockhampton.

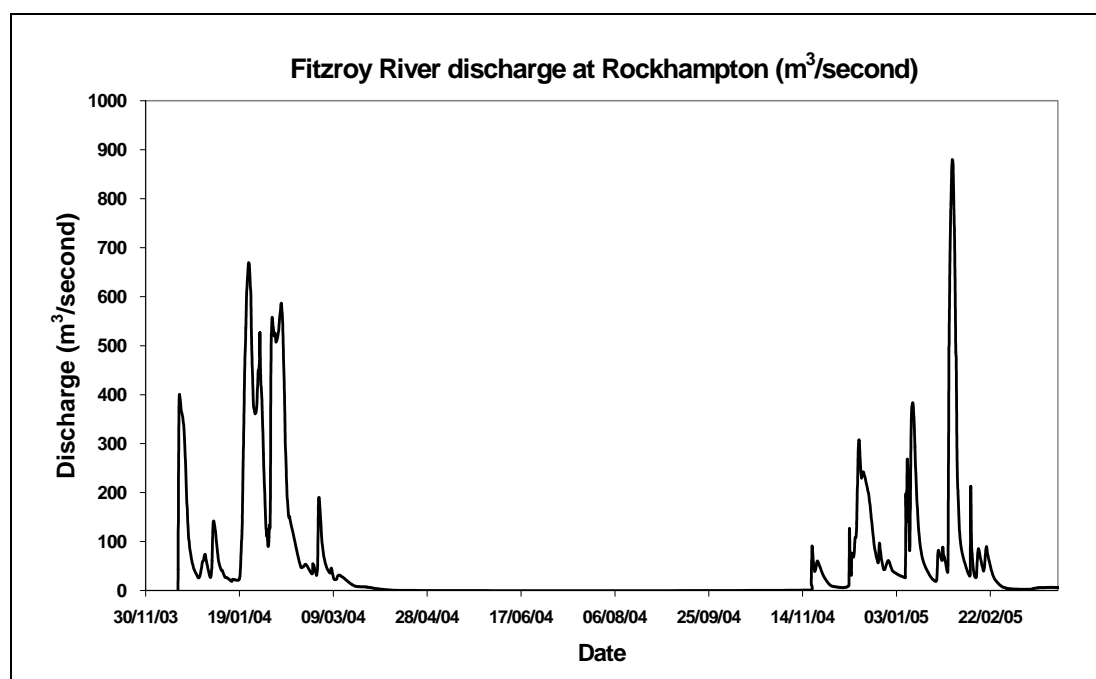


Figure 2: Discharge at Rockhampton for the 2004 and 2005 wet seasons

In addition, there were minor flows from the catchment leading up to and during the monitoring of the 2004 and 2005 floods, causing minor fluctuations in pesticide concentrations (see Appendix 2).

Detailed results for the all samples collected in 2003/2004 and 2004/2005 wet seasons are given in Appendix 2. Residues of Atrazine and Tebuthiuron were detected in all 35 samples, while residues of Diuron, Hexazinone, Fluometuron and Prometryn were less common. Atrazine, Diuron and Tebuthiuron concentrations are summarised in Table 1.

When comparing the results for the two wet season flows it is apparent that the 2004 event produced higher maximum and mean concentrations for Atrazine and Diuron in particular and slightly lower maximum and mean concentrations for Tebuthiuron than the 2005 event. This may be attributed to the western catchments (2004 event) having substantial areas of dryland cropping (and minor irrigated cropping areas) while the north eastern Connors sub-catchment (2005 event) has extensive cattle grazing as the major land use, with negligible areas of cropping.

Antecedent conditions were similar for both areas with extended dry periods leading up to the wet season in both cases. These results are similar to events monitored during 2001/2002 and 2002/2003 wet seasons at Rockhampton (Packett *et al.*, 2005). Inland monitoring of floods and minor flows during the

1990s indicates similar patterns of pesticides contamination in surface water linked to land use (Noble, 2000).

Table 1: Summary of pesticide concentrations for 2004 and 2005 floods at Rockhampton

Pesticide sampling at Rockhampton	2003/2004 wet season			2004/2005 wet season		
	Atrazine	Diuron	Tebuthiuron	Atrazine	Diuron	Tebuthiuron
Number of samples	17	17	17	18	18	18
Number of samples below limits of reporting	0	4	0	0	13	0
Maximum concentration (µg/l)	0.95	0.43	0.69	0.32	0.03	0.83
Mean concentration (µg/l)	0.39	0.07	0.21	0.14	0.02	0.28
ANZECC (2000) trigger values (µg/l) for freshwater (99% species protection)	0.7	ID	0.02	0.7	ID	0.02

ID = insufficient data to determine a guideline value

Maximum concentrations exceeded the ANZECC (2000) guideline trigger values for Atrazine and Tebuthiuron on a number of occasions. While there is no 99% species protection trigger value for Diuron due to insufficient data to set a guideline value, the 95% species protection value of 0.02 µg/l value was exceeded for a number of samples (see Appendix 2).

While Atrazine and Diuron have been commonly detected in flood flows historically (Noble *et al.* 1997; Noble, 2000; Jones *et al.*, 2000; Haynes *et al.*, 2000) the detection of Tebuthiuron is relatively recent in comparison. There is apparently widespread use of this chemical to control woody weeds and to chemically clear native trees, resulting in the detection of the chemical in surface waters. At present there is little available information on the impact of Tebuthiuron on non-target species. Less intensive sampling of the 2004 event at the Fitzroy River mouth indicated that low concentrations of Atrazine, Diuron and Tebuthiuron were entering Keppel Bay and therefore the Great Barrier Reef lagoon.

Recent studies into the effects of pesticides on corals and seagrasses have highlighted the potential for some agrochemicals to impact on marine organisms at relatively low concentrations (Jones *et al.*, 2003; Haynes *et al.*, 2000). There is presently a strong interest in the transport and export of suspended sediments, nutrients and pesticides from GBR catchments to estuarine and coastal waters (Brodie *et al.*, 2003; Prosser *et al.*, 2001a, b).

Urban stormwater samples from south Rockhampton

The results of analyses of three stormwater samples collected from drains flowing into the estuary at south Rockhampton on 7 January 2005 are shown in Table 2. The inadvertent prolonged storage of these samples at the laboratory before analysis should be noted, as well as the very limited size of this dataset.

Low concentrations of Atrazine and Hexazinone were detected in two of three stormwater samples collected from drains flowing into the Fitzroy River at Rockhampton in January 2005.

Table 2: Urban stormwater samples from south Rockhampton, 7 January 2005

Sample	Nutrients					PAHs µg/l	TPH µg/l	Herbicides µg/l
	TP mg/l as P	FRP mg/l as P	TN mg/l as N	NOx mg/l as N	NH3 mg/l as N			
SWD1	0.25	0.16	0.89	0.36	0.015	<3	<10	Atrazine: 0.1 Hexazinone: 0.4
SWD2	0.24	0.16	0.89	0.37	0.024	<3	C15–C28: 17 others: <10	Atrazine: 0.1 Hexazinone: 0.4
SWNB	0.22	0.16	1.80	1.0	0.006	<3	<10	Not detected

While residues of organochlorine and organophosphorus pesticides were not detected, the herbicides Atrazine and Hexazinone were detected in two of the samples. The concentration of Atrazine was comparable with concentrations recorded for the concurrent catchment floodwaters, while levels of Hexazinone in the urban runoff were an order of magnitude higher than levels in the catchment floodwaters. Under most conditions of summer floods, the total flow into the estuary from urban runoff around Rockhampton would be expected to be much less than flows moving past the Barrage into the estuary from upper catchment sources. Notwithstanding this, further and more comprehensive sampling of urban runoff at Rockhampton (and perhaps other large regional towns such as Emerald) should be carried out to estimate loads of pesticides entering surface waters of the Fitzroy Basin and estuary from these sources.

One sample showed a low level of total petroleum hydrocarbons (TPHs) (17 µg/l of C15–C28), which did exceed the low ANZECC (2000) trigger value (7 µg/L) for TPHs for protection of aquatic life. As well, polycyclic aromatic hydrocarbons (PAHs) were below the analytical limit of detection of 3 µg/L.

Concentrations of nutrients (Nitrogen and Phosphorus species) in the urban runoff samples all exceeded (for several parameters by more than an order of magnitude) the default trigger values for slightly disturbed estuarine ecosystems in tropical Australia (ANZECC, 2000). However, the volume of this urban

stormwater runoff flowing into the estuary at Rockhampton will mostly be insignificant compared with the input from the three Sewage Treatment Plants (~20 ML/day) and summer flows from the upper catchment. Thus, nutrient loads from the urban runoff should not be an issue except perhaps at times of intense local rainfall.

Herbicides in benthic sediments

Herbicides (Atrazines, Tebuthiuron, Diuron, etc.) were not detectable in benthic sediments (LOD 2 µg/kg). Herbicides tend to partition more readily into the water column than onto sediments, as suggested by their relatively high water solubilities (25°C): Atrazine = 28, Diuron = 42 and Tebuthiuron = 2500 mg/l (Karim, 1997). In contrast, PAHs adsorb readily onto sediments due to their much lower aqueous solubility: e.g. Fluoranthene = 0.26 mg/l, Pyrene = 0.13 mg/l (Connell, 1997). The presence of significant concentration of PAHs in benthic sediments was demonstrated in benthic sediments (grabs) and sediment core samples from the Fitzroy Estuary (see section below) and in a similar study of sediments of Port Curtis (Vicente-Beckett *et al.*, 2006).

Polycyclic aromatic hydrocarbons (PAHs) in sediments

Keppel Bay benthic sediments

The acronyms used to represent the PAHs and some relevant information are given in Table A3.1, Appendix 3. The sites for all surface sediment samples as well as the two cores (discussed in the next section) for PAH analyses are mapped in Figure 3. Concentrations of PAHs in all sediment grab samples are compiled in Table A3.2, Appendix 3.

Only nine (out of 16) sediment grabs taken from Keppel Bay in August 2004 (see Table A1.1, Appendix 1) were analysed due to budget constraints. Of the nine samples analysed for the suite of pesticides and PAHs, only three samples gave positive results for PAHs (see Table 3), which were very low compared to the ANZECC (2000) trigger value (or low interim sediment quality guideline, ISQG-low). All other contaminants (pesticides/herbicides) were less than LOD (2 µg/kg).

Table 3: PAHs* in Keppel Bay surface sediments, August 2004

PAH	Sample ID			ANZECC ISQG-low
	124	130	134	
Fluoranthene	5.7	5.7	5.0	600
Pyrene	<2	5.7	<2	685

* Concentrations in µg/kg dry weight, normalised to 1% total organic carbon.

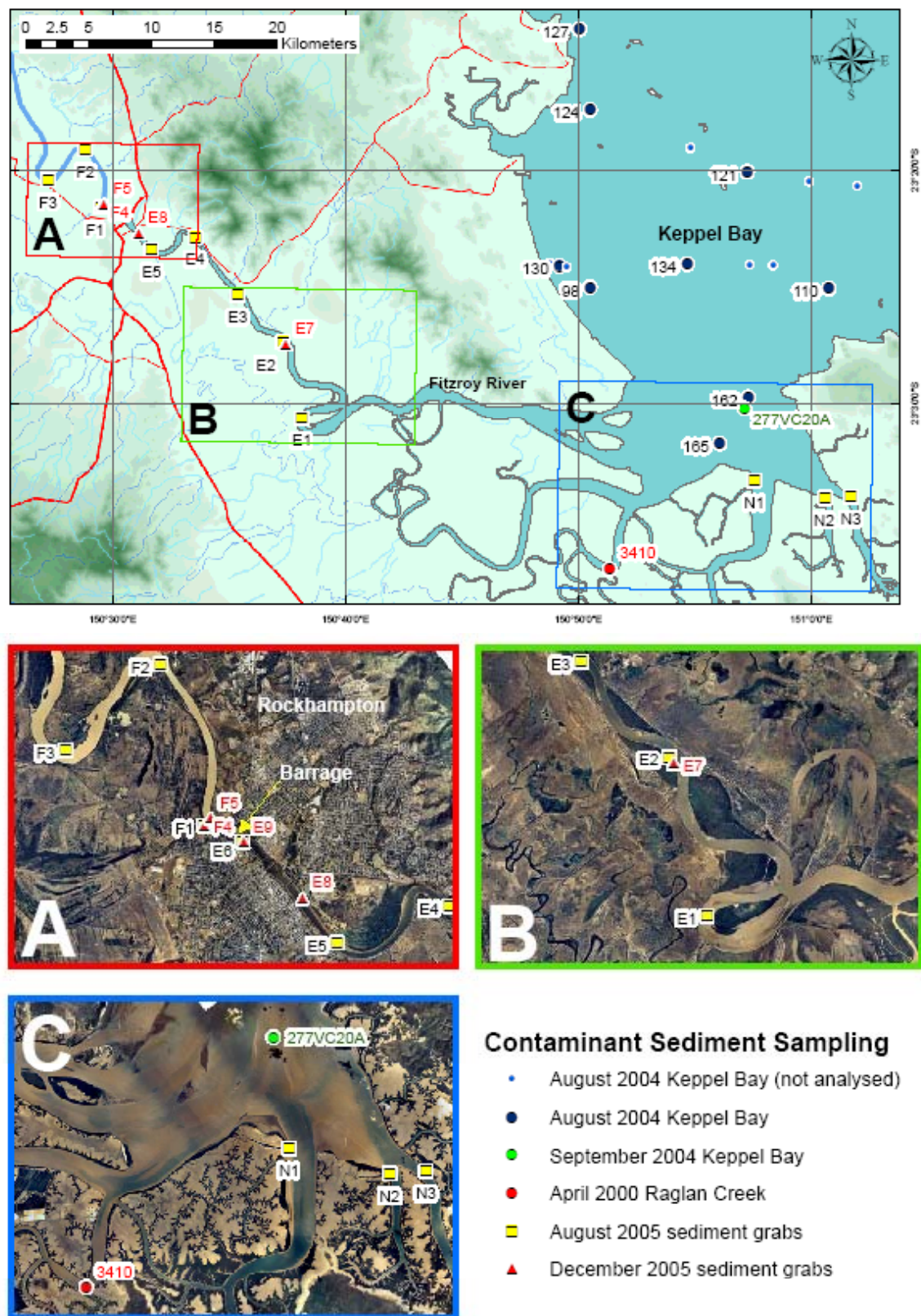


Figure 3: Location of benthic sediments and core samples in Fitzroy Estuary

Fitzroy River benthic sediments

Samples were collected in August and December 2005 (see Table A1.3, Appendix 1) from upstream Fitzroy River and downstream of the Barrage in Rockhampton up to The Narrows.

The PAHs detected in the Fitzroy channel grab samples are presented in Figure 4. Some sediments immediately upstream and downstream of the Barrage showed much higher total PAHs compared to the other samples, with the five highest total PAH concentrations being found in samples (in decreasing total PAH concentration) F1 > E9 > E6 > F4 > E2. Samples F1 and F4 were obtained in the vicinity of the discharge point of the Lions Creek wastewater treatment plant. These samples also had the lowest perylene content. In contrast, samples F3 (most upstream Fitzroy River sample) and N1 (at The Narrows) had the highest perylene content (88 and 82%, respectively). None of the detected PAHs exceeded the ANZECC (2000) trigger value. It is noted that there are no guidelines set for some high molecular weight (MW) PAHs, such as perylene (or its derivatives). Perylene appears to be of natural origin, as discussed in the section, Sources of PAHs (page 24).

Sediment cores

The PAHs detected in slices of the 2.6 m sediment core (277VC20A) from Keppel Bay are given in Table A3.3, Appendix 3 and the results are plotted in Figure 5. All observed PAH levels were below ANZECC (2000) trigger values. Perylene was the dominant PAH in all slices, consisting at least 74% (at 61 cm depth) and up to 98% of the total PAHs at the two deepest slices analysed. There was no clear trend in PAH levels versus depth of slice, except that the lower portions of the core contained more perylene, a trend which has also been observed in other sediment cores elsewhere (Jiang *et al.*, 2000).

A parallel core sampled at the same site on the same day was dated and found to consist of very old sediments (see Appendix 4), about 1000 years for the upper slices and over 4000 years from depths of 0.5–2.6 m. It appears that the site may have undergone some deep scouring (e.g. dredging), exposing very old sediment layers.

This led to the investigation of an archived (V. Vicente-Beckett, CQU) sediment core (core 3410) from Raglan Creek near the mouth of the Fitzroy River, which had been stored frozen since it was sampled in April 2000. The analyses are depicted in Figure 6; actual data are given in Table A3.4, Appendix 3. The low-MW PAHs were not detectable in the three upper slices of the core. As found in the case of the Keppel Bay core, perylene was the dominant PAH, ranging between 80-100% of the total PAHs detected.

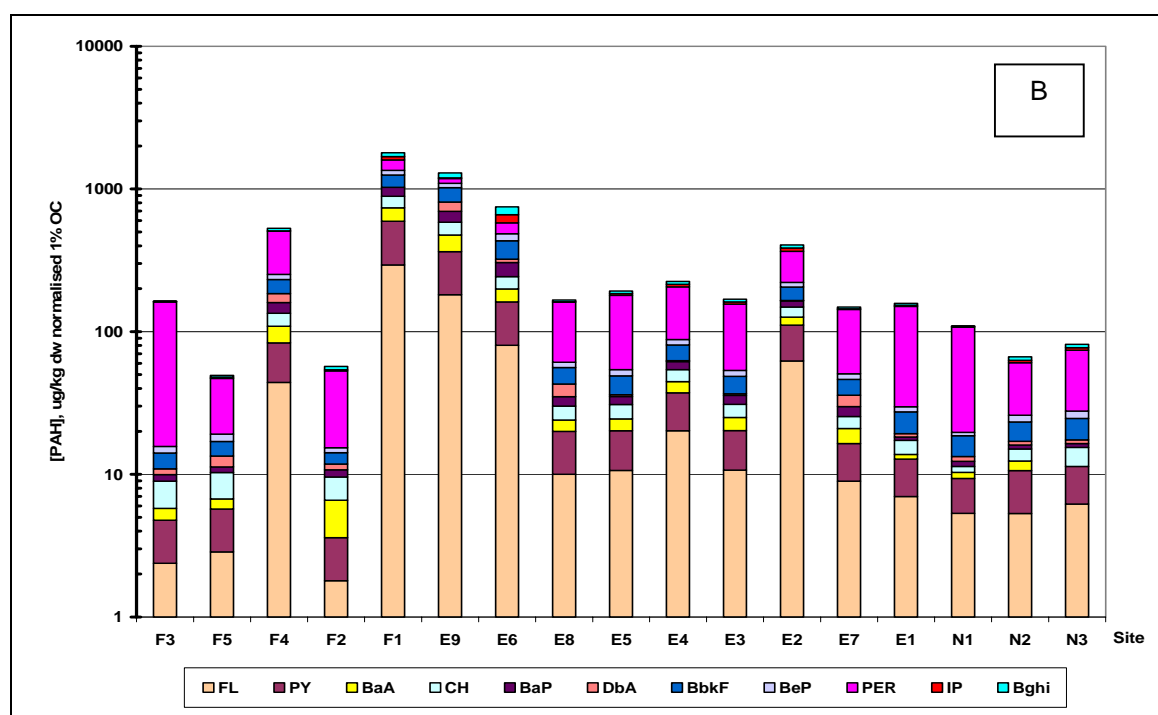
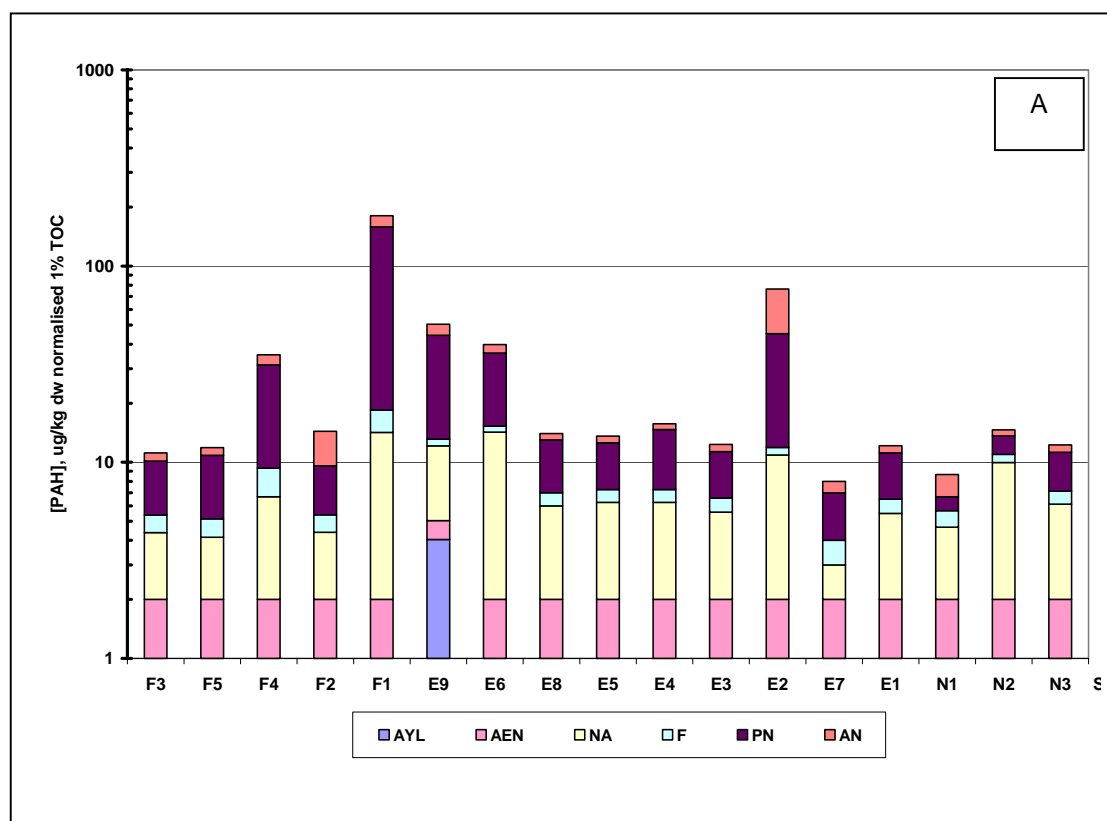


Figure 4: Low-MW (A) and high-MW (B) PAHs detected in Fitzroy channel sediment grabs. (AEN = Acenaphthene, AYL = Acenaphthylene, AN = Anthracene, BaA = Benz[a]Anthracene, BaP = Benz[a]Pyrene, Bbkf = Benzo[b+k]Fluoranthene, BeP = Benz[e]Pyrene, Bghi = Benzo[ghi]Perylene, CH = Chrysene, DbA = Dibenzo[ah]Anthracene, F = Fluorene, FL = Fluoranthene, IP = Indeno[123cd]Pyrene, NA = Naphthalene, PN = Phenanthrene, PER = Perylene, PY = Pyrene)

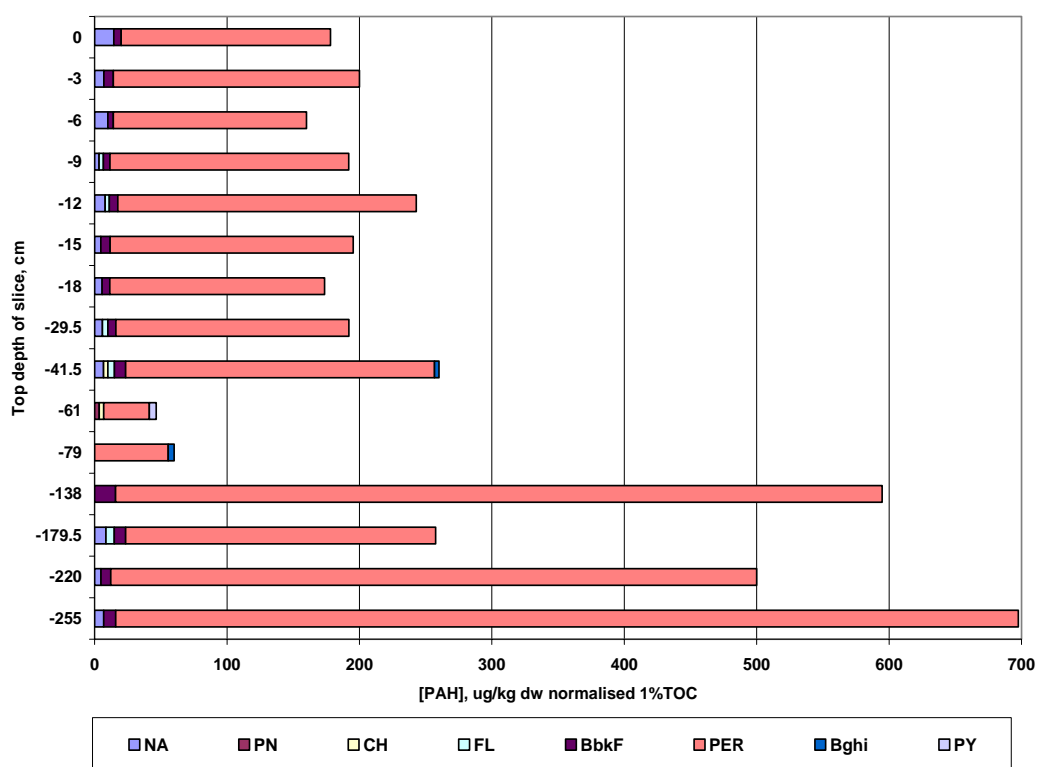


Figure 5: PAHs in Keppel Bay sediment core (277VC20A). (BbkF = Benzo[b+k]Fluoranthene, Bghi = Benzo[ghi]Perylene, CH = Chrysene, FL = Fluoranthene, NA = Naphthalene, PN = Phenanthrene, PER = Perylene, PY = Pyrene)

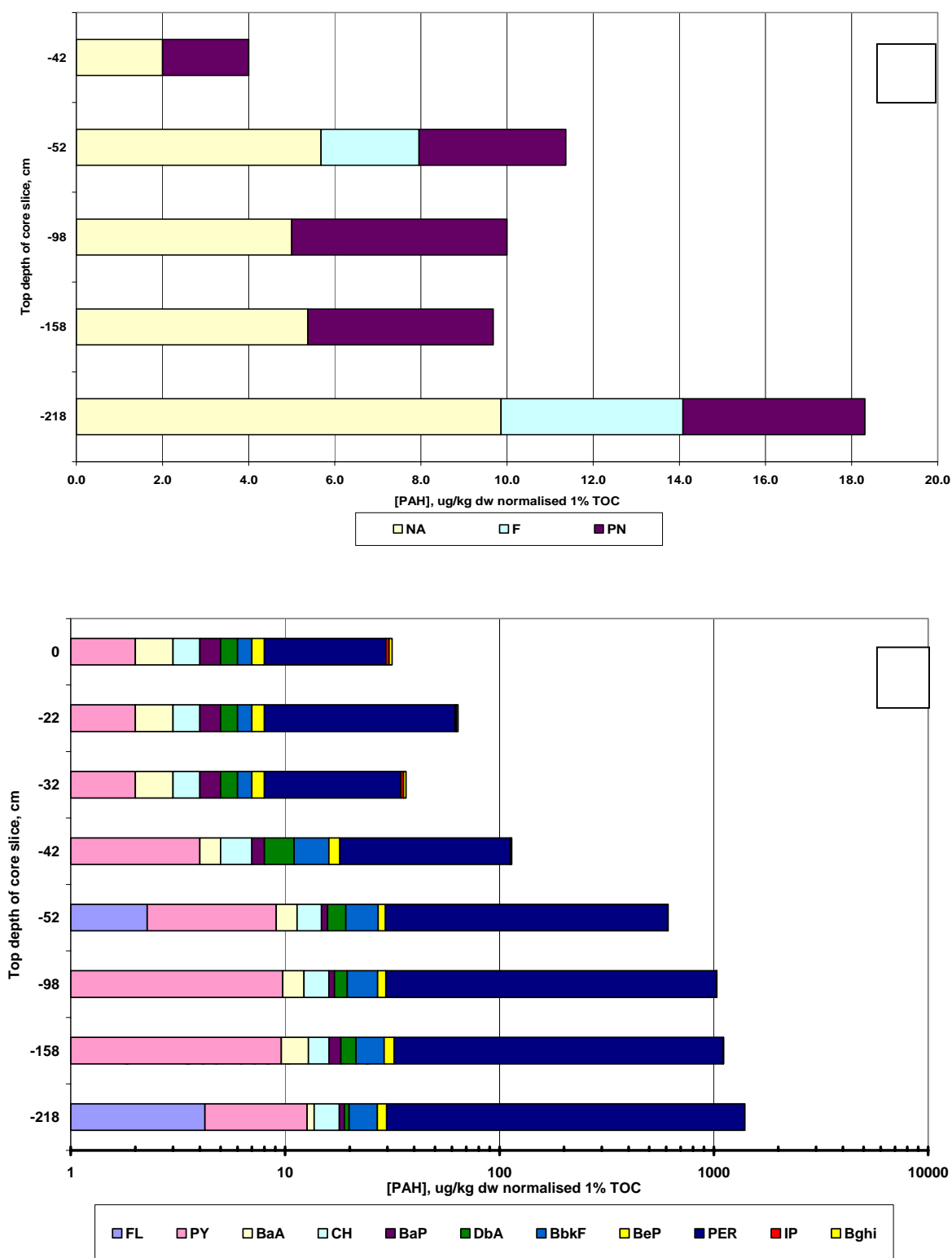


Figure 6: Low-MW (A) and high-MW (B) PAHs in Raglan Creek sediment core 3410. (BbkF = Benzo[b+k]Fluoranthene, BaA = Benz[a]Anthracene, BaP = Benz[a]Pyrene, BeP = Benz[e]Pyrene, Bghi = Benzo[ghi]Perylene, CH = Chrysene, DbA = Dibenzo[ah]Anthracene, F = Fluorene, FL = Fluoranthene, IP = Indeno[123cd]Pyrene, NA = Naphthalene, PN = Phenanthrene, PER = Perylene, PY = Pyrene)

Sources of PAHs

PAH isomer pair ratios have been used as diagnostic traces to infer sources of PAHs in water and sediments (Yunker *et al.*, 2002; Ross and Oros, 2004). For example, for PAHs of MW = 178 (i.e. anthracene and phenanthrene; see Table A3.1, Appendix 3), a ratio less than 0.10 of the concentration of anthracene (AN) to the sum of the concentrations of anthracene and phenanthrene (AN + PN) is taken as an indication of PAHs coming from *petrogenic* sources (e.g. fossil fuels), while a ratio greater than 0.10 indicates a dominance of *pyrolytic* sources (PAHs resulting from incomplete but high-temperature combustion of biomass and fossil fuels) (Yunker *et al.*, 2002). Ratios of concentrations of several other PAH isomers have also been used for this purpose (Readman *et al.*, 2002; Gallon *et al.*, 2005), as shown in Table A3.5, Appendix 3. A third source category is *diagenetic*, i.e. originating from constituent plant or animal matter in sediments, which after burial during sedimentation are transformed into hydrocarbons due to increased temperature and pressure (Silliman *et al.*, 2001). Perylene is believed to be produced only in trace amounts during combustion and is considered largely of diagenetic origin, although the formation process is still not well understood (Jiang *et al.*, 2000; Silliman *et al.*, 2001). A ratio greater than 0.10 of the concentration of perylene (a five-ring PAH) to the sum of the concentrations of all penta-aromatic isomers indicates a probable diagenetic input, whereas those in which this ratio is less than 0.10 indicates a probable pyrolytic origin of the compound (Readman *et al.*, 2002).

Table 4 summarises the sources of the suite of PAHs detected in sediment samples as inferred from several PAH isomer ratios. The actual values are found in Table A3.2, Appendix 3; ratios of unity were obtained when the concentration of other isomer(s) involved in the ratio was at the limit of detection. Table 4 shows that the PAHs in grab samples were largely from pyrolytic and diagenetic sources. PAHs from grab samples taken near the Rockhampton Barrage (F1, F4, E6 and E9) originated from pyrolytic, petrogenic and diagenetic sources. Perylene was found in all samples, with its concentration ratio to the sum of penta-aromatic PAH isomers being consistently high (approaching 1.00) in all slices of the two sediment cores analysed. This provides evidence that the other PAHs have entered the water bodies only in more recent times.

Table 4: Indicative sources of PAHs (see Table A3.5 for PAH isomer ratios)

Site and Sample ID	Sources*
Fitzroy Channel	
F3	Dia
F5	Dia
F4	Pyr, Pet, Dia
F2	Pyr, Dia
F1	Pyr, Pet, Dia
E9	Pyr, Pet, Dia
E6	Pyr, Pet, Dia
E8	Pyr, Dia
E5	Pyr, Dia
E4	Pyr, Dia
E3	Pyr, Dia
E2	Pyr, Dia
E7	Pyr, Dia
E1	Pyr, Dia
N1	Pyr, Dia
N2	Pyr, Dia
N3	Pyr, Dia
Raglan Creek – Core 3410	
0 cm	Dia
22 cm	Dia
32 cm	Dia
42 cm	Pyr, Dia
52 cm	Pyr, Dia
98 cm	Pyr, Dia
158 cm	Pyr, Dia
218 cm	Pyr, Dia
Keppel Bay – Core 277VC20A	
15 Slices (0–260 cm)	Dia

* Types of sources:

Pyr = Pyrolytic sources (incomplete high-T combustion of biomass, fossil fuels)

Pet = Petrogenic sources (fossil fuels, shale oils)

Dia = Diagenetic sources (plant or animal precursors)

Metals

Metal analyses of benthic sediments and sediment cores

Table 5 provides an overview of the average sediment (grabs and core slices combined) metal concentrations (and other sediment parameters) of the Fitzroy Estuary, together with the ANZECC (2000) ISQG values. It is seen from the table that Ni had the largest number of exceedances of the guidelines (both high and low values), followed by Cr and Sb. The highest mean Ni levels were found in sediment grabs from the Fitzroy channel, followed by those from upstream of the Barrage, and the slices of core 3410 (located in Raglan Creek near the mouth of the Fitzroy). The highest mean Cr levels were found in sediment grabs upstream of the Barrage, followed by those from the Fitzroy channel and the 3410 core slices. The highest mean Sb concentrations were found in the slices of the Keppel Bay core 277VC20, followed by the Fitzroy channel grabs and the 3410 core slices. The Keppel Bay nearcoast grabs (sample number 1903-2007) gave the lowest mean concentrations for all ANZECC-regulated metals, except As, Hg and Sb.

Figure 7 shows the metal profiles of the core slices for the two cores included in this study. There appears to be no clear evidence of metal accumulation at the upper layers of the core, except for As and Sb in core 3410. It is also seen that Sb had highly variable content in the slices of the Keppel Bay core.

Table 6 provides a comparison of the mean concentrations observed for Port Curtis (Vicente-Beckett *et al.*, 2006), the recent upper continental crust estimates for Queensland (Kamber *et al.*, 2005) and the range of concentrations for Fitzroy sediment data (Semple and Williams, 1998). The mean levels for Cr, Ni and Sb in the Fitzroy estuary were higher than those found in Port Curtis, while levels for the other metals were reasonably similar for the two study areas.

An estimate of the background levels was obtained from the data of the present study using a simple approach adopted from several methods reported in the literature (e.g. Roussiez *et al.*, 2005; Doherty *et al.*, 2000a; Liu *et al.*, 2003). All data outside of the upper 95% confidence level of the mean for each metal of the original dataset were removed, and a new mean calculated; the process was repeated until all remaining data were within the 95% confidence level of the mean of the remaining dataset, which was assumed to be estimates of the background levels. It is noted that the estimated background Ni concentration in the Fitzroy Estuary is higher than the ANZECC low-ISQG for Ni. This is not surprising since there are known Ni geological sources in the central Queensland region (Kirkegaard *et al.*, 1970), which are currently being commercially explored. The estimated background levels for all other metals were consistent

or slightly lower than the values reported for the recent estimate of the upper continental crust for Queensland (Kamber *et al.*, 2005). The exercise has provided estimates of background levels for Ag, As, Cd, Hg and Sb, for which the Kamber *et al.* (2005) study has no reported values.

Table 5a: Mean benthic and core sediment metal concentration in Fitzroy Estuary

	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn
N	73	73	73	73	73	65	73	73	73	73
Mean	12.50	10.90	53.20	88.60	25.50	14.00	46.00	14.60	1.14	66.60
std dev	16.00	3.20	1.80	91.10	11.80	10.30	28.70	4.50	1.23	28.20
Min	<10.00	2.60	<0.10	7.00	4.00	<10.00	1.00	5.20	0.21	5.00
Max	81.90	21.90	57.20	792.00	49.40	43.10	130.00	29.00	5.36	116.80
ANZECC ISQG-low	1 000	20	1 500	80	65	150	21	50	2	200
ANZECC ISQG-high	3 700	70	10 000	370	270	1 000	52	220	25	410
n > ANZECC ISQG-low	0	1	0	34	0	0	42	0	13	0
n > ANZECC ISQG-high	0	0	0	0	0	0	20	0	0	0

Metal concentrations in mg/kg dry weight, except for Ag, Cd and Hg which are given in µg/kg dry weight

N = total number of samples; n = number of samples exceeding ANZECC guideline

Table 5b: Mean benthic and core sediment element concentrations and other parameters in the Fitzroy Estuary

	Fe	Al	Ca	S	Mn	% Mud (<60 µm)	% Organic Matter
N	73	73	73	73	73	44	53
Mean	40 983.00	73 014.00	18 637.00	2 344.00	651.00	69.00	2.40
std dev	16 823.00	24 969.00	15 634.00	1 483.00	350.00	23.00	1.29
Min	6 608.00	15 610.00	3 548.00	107.00	178.00	1.35	0.41
Max	82 986.00	109 684.00	92 101.00	5 189.00	2 217.00	99.50	5.51

Element concentrations in mg/kg dry weight

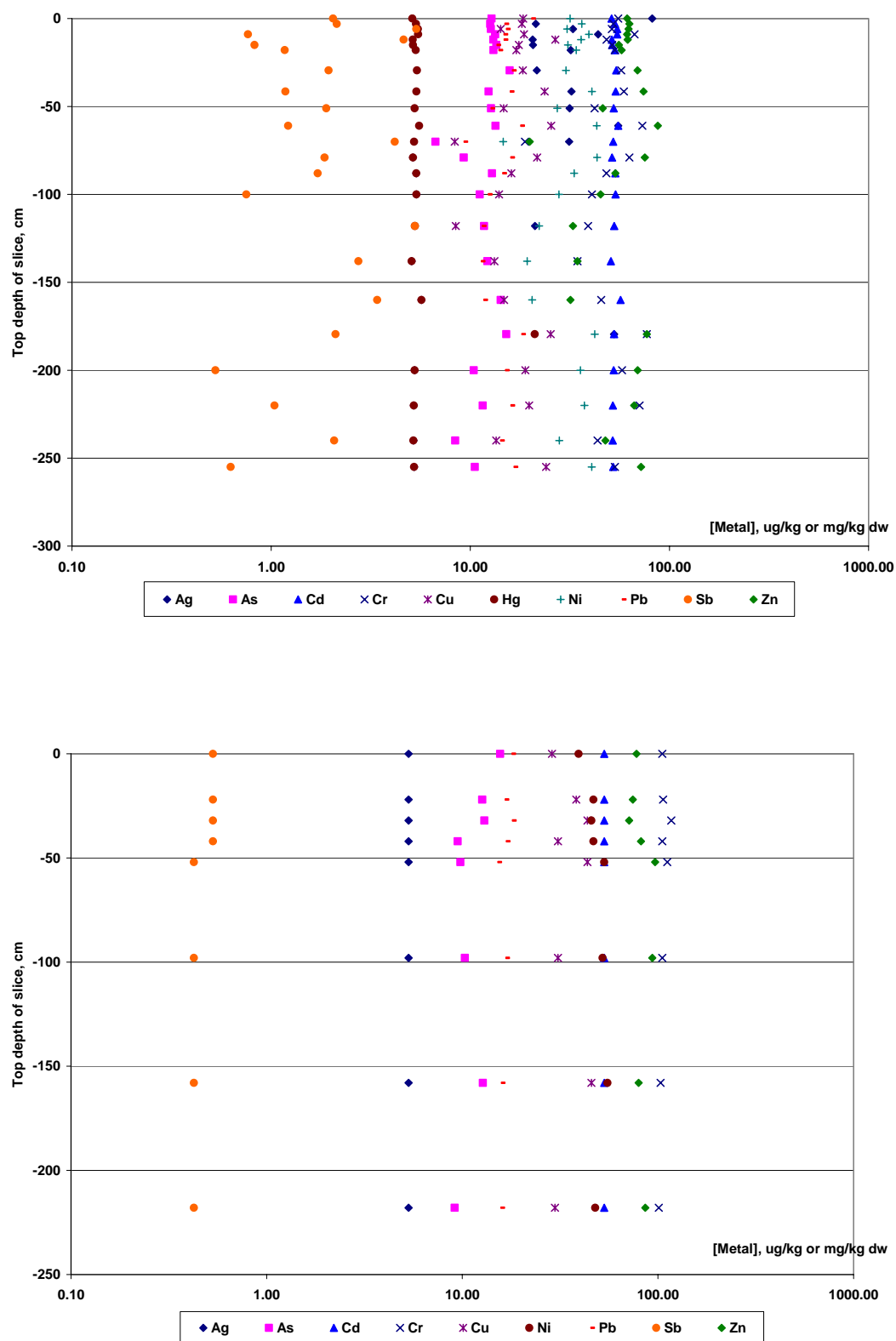


Figure 7: Metal concentration versus depth of core slice: Keppel Bay – 277VC20 core (top); Raglan Creek – core 3410 (bottom).

Table 6: Comparison of metal concentrations in sediments from the Fitzroy estuary and Port Curtis (mg/kg dry weight)

	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn
Mean values of original dataset for Fitzroy Estuary sediment grabs and core slices; <1 mm fraction; this study (see Appendix 6)	0.0125	10.90	0.0532	88.6	25.50	0.0140	46.00	14.60	1.140	66.60
Estimated background levels of Fitzroy Estuary derived from original dataset of this study	0.0056	6.87	0.0520	66.1	17.10	0.0065	31.80	11.60	0.560	47.90
Fitzroy River min–max of 1970–1992 data; <63 µm fraction (Semple and Williams, 1998)	nd	nd	<1–10.0000	25– 604.0	10–65.00	<0.1000	10–480.00	<10–320.00	nd	11–370.00
Port Curtis intertidal and estuarine sediments; <1 mm fraction; N = 182–245 (Vicente-Beckett <i>et al.</i> , 2006)	0.0520	15.90	0.0520	57.2	22.70	0.0213	20.40	12.40	0.546	58.90
MUQ – upper continental crust (Kamber <i>et al.</i> , 2005); <150 µm fraction	nd	nd	nd	64.5	32.36	nd	31.57	20.44	nd	73.47
ANZECC ISQG-low	1.0000	20.00	1.5000	80.0	65.00	0.1500	21.00	50.00	2.000	200.00

nd = no data

Predicting the natural gradient of metal concentration in sediments

The spatial variability exhibited by the metal data reflects the influence of the several sediment variables such Fe and/or Al contents, organic matter (OM) content, particle size, etc. In practice, attempts to reduce variability in sediment data involves analysing only the fine sediment fractions (e.g. <63 µm); the finer fraction also provides a better estimate of the total metal concentration, which is diluted when the bulk sediment is analysed. However, size normalisation cannot fully deal with the complex interactions of these variables within the sediment. Modelling the natural gradient (i.e. variation between sites) of metal concentration in sediments has been a useful strategy in seeking to minimise the effects of multiple sources of variance (Roussiez *et al.*, 2005; Liu *et al.*, 2003). A statistical approach would also help estimate the extent of metal enhancement in individual sediment samples (Doherty *et al.*, 2000a, b).

A multivariate analysis of the sediment data set was undertaken to attempt to model the natural gradient of metal concentration in sediments. The statistical software SPSS v.13 and Microsoft Excel were used to determine multiple linear regression models and predict metal contents in sediments.

The metal analyses for all surface sediments and core slices analysed are summarised in Appendix 6. The dataset consists of six groups and includes 42 sediment grabs and 31 core slices, or a total of 73 samples from: 1) upstream of the Barrage – 10 sediment grabs; 2) Fitzroy channel (downstream of the Barrage) – 16 sediment grabs; 3) Narrows – 3 sediment grabs; 4) Keppel Bay 277VC20 core – 23 slices; Raglan Creek 3410 core – 8 slices; and Keppel Bay transect – 13 sediment grabs. One-way ANOVA showed significant ($p < 0.05$) differences in concentrations of metals in some benthic sediments and core slices from the groups. Scheffe's test showed that the dataset consisted of 1 (for Ag and Cd), 2 (for As, Hg, Ni, Pb and Zn), 3 (for Cu and Sb) and 4 (for Cr) homogeneous subsets. In order to perform multiple regression analysis it was necessary to reduce the dataset to one population by removing outliers. The criterion used to define an outlier was the standardised value of the measurement, which exceeded ± 2.5 . The outliers were then replaced by the mean values for the remaining (adjusted) dataset, which was used for the multiple regression analysis (Hair *et al.*, 1998). Mercury, Ag and Cd occurred at the limits of detection for some samples; in this case, values used in the adjusted data set used half the respective detection limits. Any data gaps were filled in with the mean of the adjusted dataset (Hair *et al.*, 1998).

Table 7 summarises the Pearson correlations for the various metal concentrations and other sediment parameters. Manganese was included since it has been suggested to be an important variable relating to the biogeochemistry

of metals in sediments (Reimann and de Caritat, 2005). These correlations are helpful in deciding the sediment variables to consider in multivariate analysis. Iron, Al, OM and Ca show moderate to strong correlations (minimum value of 0.6, shown in bold font in Table 7) with several metals. Factor analysis was also conducted to gain further insight into the sources of variances in the metal concentrations. The log-transformed dataset was used in order to minimise the skewness or differences in magnitude of the variables. Table 8 shows that three principal components (PC) account for about 75% of all variances from the various metals or sediment parameters, with PC1, PC2 and PC3 accounting for 52%, 15% and 8% of the variances, respectively. Log-transformed variables were employed for this analyses; using standardised variables gave similar results. PC1 indicates strong contributions (values of at least 0.6 in Table 8) from six of the 10 ANZECC-regulated metals, plus Fe, Al, Mn and % organic matter (OM); similarly PC2 involves strong loadings from Hg, Cr, Ca and % mud (MUD); while PC3 involves S, Sb, As and Pb. The negative value of Ca (which may serve as a surrogate for CaCO_3) suggests a negative influence possibly arising from the dilution of the silicate sediment matrix.

Table 7: Pearson correlations between metal concentrations and other sediment parameters (N=73)

	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn	Fe	Al	Ca	S	Mn	Mud	OUM
Ag	0.146	0.731**	0.351**	0.401**	0.106	0.320**	0.365**	0.300**	0.556**	0.475**	0.532**	-0.074	0.194	0.481**	-0.018	0.459**
As		-0.023	-0.166	-0.129	-0.071	-0.036	0.332**	0.233*	-0.082	-0.063	0.041	0.145	0.598**	-0.188	-0.062	0.087
Cd			0.618**	0.622**	0.286**	0.427**	0.354**	0.107	0.733**	0.658**	0.688**	-0.302**	0.021	0.534**	0.097	0.605**
Cr				0.882**	0.481**	0.741**	0.391**	-0.214	0.829**	0.815**	0.788**	-0.737	-0.193	0.489**	0.245*	0.618**
Cu					0.502**	0.757**	0.519**	-0.151	0.878**	0.863**	0.870**	0.666**	-0.129	0.548**	0.401**	0.575**
Hg						0.530**	0.467**	-0.026	0.475**	0.487**	0.459**	-0.413	-0.083	0.230	0.187	0.495**
Ni							0.624**	0.124	0.754**	0.739**	0.769**	-0.723	0.044	0.504**	0.346**	0.684**
Pb								0.344**	0.646**	0.658**	0.759**	-0.378	0.505**	0.361**	0.236*	0.601**
Sb									0.046	0.055	0.093	0.179	0.480**	0.195	-0.204	0.251*
Zn										0.926**	0.969**	-0.628	0.061	0.584**	0.361**	0.675**
Fe											0.922**	-0.645	0.069	0.3546**	0.345**	0.679**
Al												-0.599	0.205	0.549**	0.371**	0.695**
Ca													0.106	-0.406	-0.361	-0.480
S														-0.108	-0.086	0.188
Mn															0.266	0.332**
Mud																0.058

N = Number of samples

** correlation significant at 0.01 level (2-tailed)

* correlation significant at 0.05 level (2-tailed)

Table 8: Factor analysis showing loadings for metals and sediment parameters.

	Component		
	PC 1	PC 2	PC 3
Cd	0.863		
Ag	0.856		
Zn	0.769	0.550	
Al	0.743	0.548	
Mn	0.724		
Fe	0.719	0.614	
OM	0.704	0.455	
Ni	0.680	0.518	
Cr	0.673	0.663	
Ca		-0.808	
Cu	0.664	0.690	
Hg		0.611	
Mud		0.603	
S			0.933
Sb			0.701
As			0.691
Pb	0.488	0.428	0.677
% variance	52.030	15.090	7.990

Extraction method: Principal component analysis

Rotation method: Varimax with Kaiser normalisation

Rotation converged in 7 iterations

Table 9 summarises the prediction equations obtained after performing multiple linear regression on the adjusted data set using Fe, Al, Ca, Mn, S, % organic matter (OM) and % mud fraction (particle size <60 µm) (MUD) as independent variables, which were gleaned from Tables 7 and 8 as variables, which strongly correlate with or affect metal concentrations. Log-transformed data were used for the multiple regression analysis to reduce skewness in the dataset. A stepwise forward addition of independent variables was used in the prediction estimation procedure, and the final prediction model was used. It is seen from Table 9 that the resulting regression model involved a different set of predictors (i.e. independent variables) for each metal.

The regression equations given in Table 9 were used to predict metal concentrations, using the observed values for the predictors, and the predicted concentrations are plotted against the observed concentrations in Figure 8. Also included in Figure 8 for comparison are the adjusted dataset (i.e. where outliers were removed and replaced by the mean of the remaining dataset), the upper 95% confidence interval (UCI), and the ANZECC (2000) trigger values (except for Ag and Cd, where the guideline values are off-scale). The correlation coefficients (R^2) are also given in Table 9, as well as the standard error of the estimate (SEE), which describes the variation in the predicted value that is analogous to the standard deviation of the mean (Hair *et al.*, 1998). It is seen that very good correlations occurred between predicted and observed concentrations for Cr, Cu, Pb and Zn, and only weak-to-moderate correlations for Ag, Cd and Sb. A larger dataset would be needed to improve the models, especially for As and Hg (plots not shown) which showed poor correlations. Figure 8 shows several outliers for Ag (although the levels were below the trigger value of 1 mg/kg) and for Sb, where 13 samples (cf. Table 5a) exceeded the trigger value of 2 mg/kg. The reasons for these high levels of Ag and Sb compared to the rest of the data are unknown and require further study. It is noted that similar behaviour in the case of Ag was exhibited by several sediment samples from Port Curtis, particularly around the mangrove and industrial sites (Vicente-Beckett *et al.*, 2006) suggesting possible anthropogenic sources.

Table 9: Regression models for predicting sediment metal concentration

Metal	Prediction Equation	Adjusted R ²	SEE	N
Ag	$\log [\text{Ag}] = 0.316 + 0.051 \log [\text{Al}] + 0.019 \log [\text{Ca}] + 0.033 \log [\text{Mn}]$	0.449	0.0131	73
As	$\log [\text{As}] = 0.644 + 0.12 \log [\text{S}]$	0.270	0.0915	73
Cd	$\log [\text{Cd}] = 1.477 + 0.035 \log [\text{Al}] - 0.009 \log [\text{S}] + 0.012 \log [\text{Ca}] + 0.029 \log [\text{OM}] + 0.018 \log [\text{Mn}]$	0.556	0.0098	73
Cr	$\log [\text{Cr}] = -0.926 + 0.329 \log [\text{Fe}] - 0.141 \log [\text{S}] + 0.545 \log [\text{OM}] - 0.169 \log [\text{Ca}] + 0.463 \log [\text{Al}]$	0.897	0.0925	73
Cu	$\log [\text{Cu}] = -2.92 + 0.357 \log [\text{Fe}] - 0.100 \log [\text{S}] + 0.703 \log [\text{Al}] - 0.104 \log [\text{Ca}]$	0.891	0.0799	73
Hg	$\log [\text{Hg}] = 2.64 + 0.423 \log [\text{Fe}] - 0.283 \log [\text{Ca}]$	0.269	0.2556	63
Ni	$\log [\text{Ni}] = -2.585 + 1.011 \log [\text{Al}] + 1.035 \log [\text{OM}] - 0.276 \log [\text{Ca}]$	0.790	0.2167	73
Pb	$\log [\text{Pb}] = -1.773 + 0.515 \log [\text{Al}] + 0.132 \log [\text{S}]$	0.836	0.0605	73
Sb	$\log [\text{Sb}] = -2.148 + 0.177 \log [\text{S}] + 0.324 \log [\text{Mn}] + 0.103 \log [\text{Ca}]$	0.535	0.0956	73
Zn	$\log [\text{Zn}] = -4.401 + 0.859 \log [\text{Al}] + 0.466 \log [\text{Fe}] - 0.032 \log [\text{S}]$	0.964	0.0515	73

N = number of samples

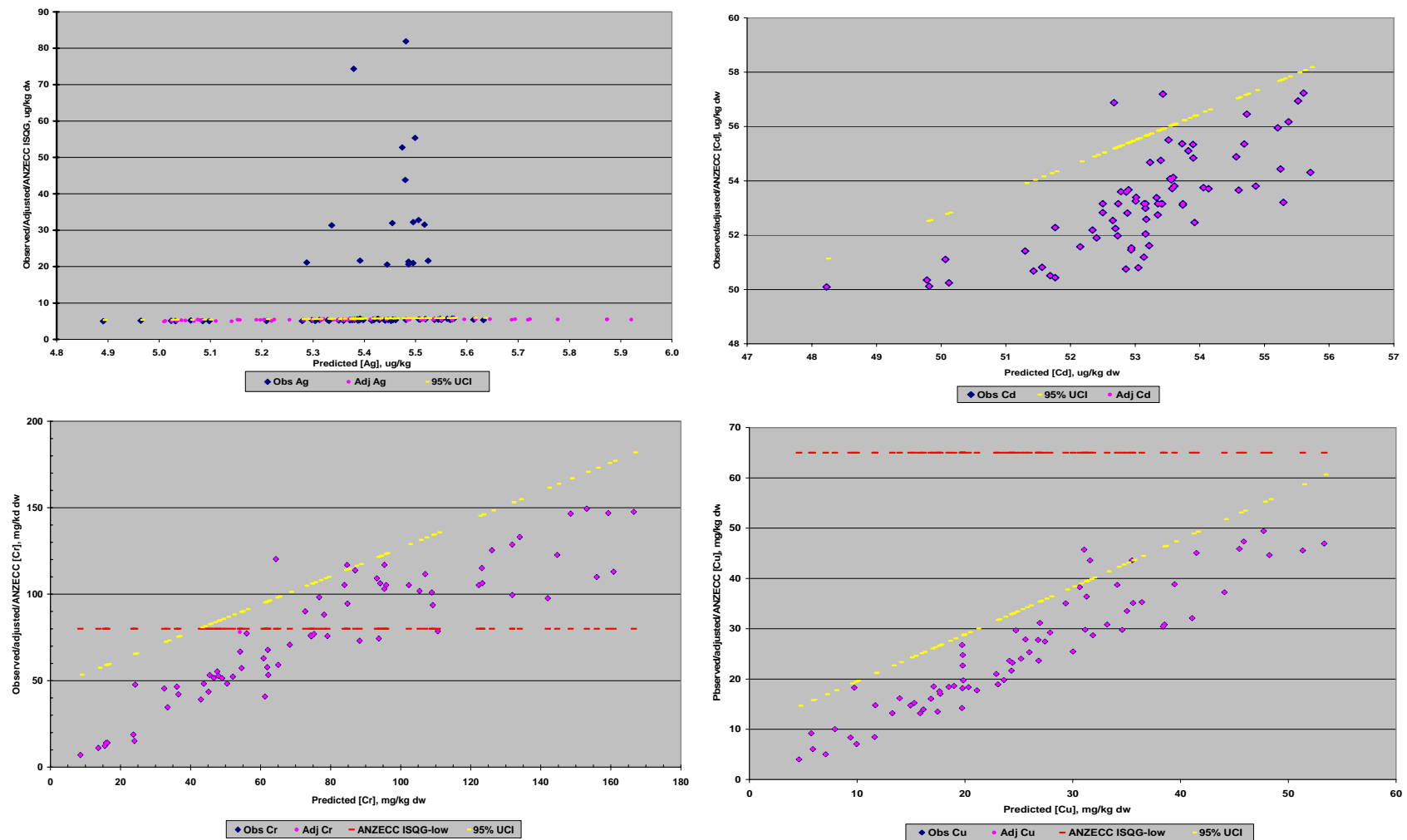


Figure 8: Predicted versus observed or adjusted metal concentration; also indicated are the upper 95% confidence interval and the ANZECC ISQG-low values (except for Ag and Cd, which are off-scale)

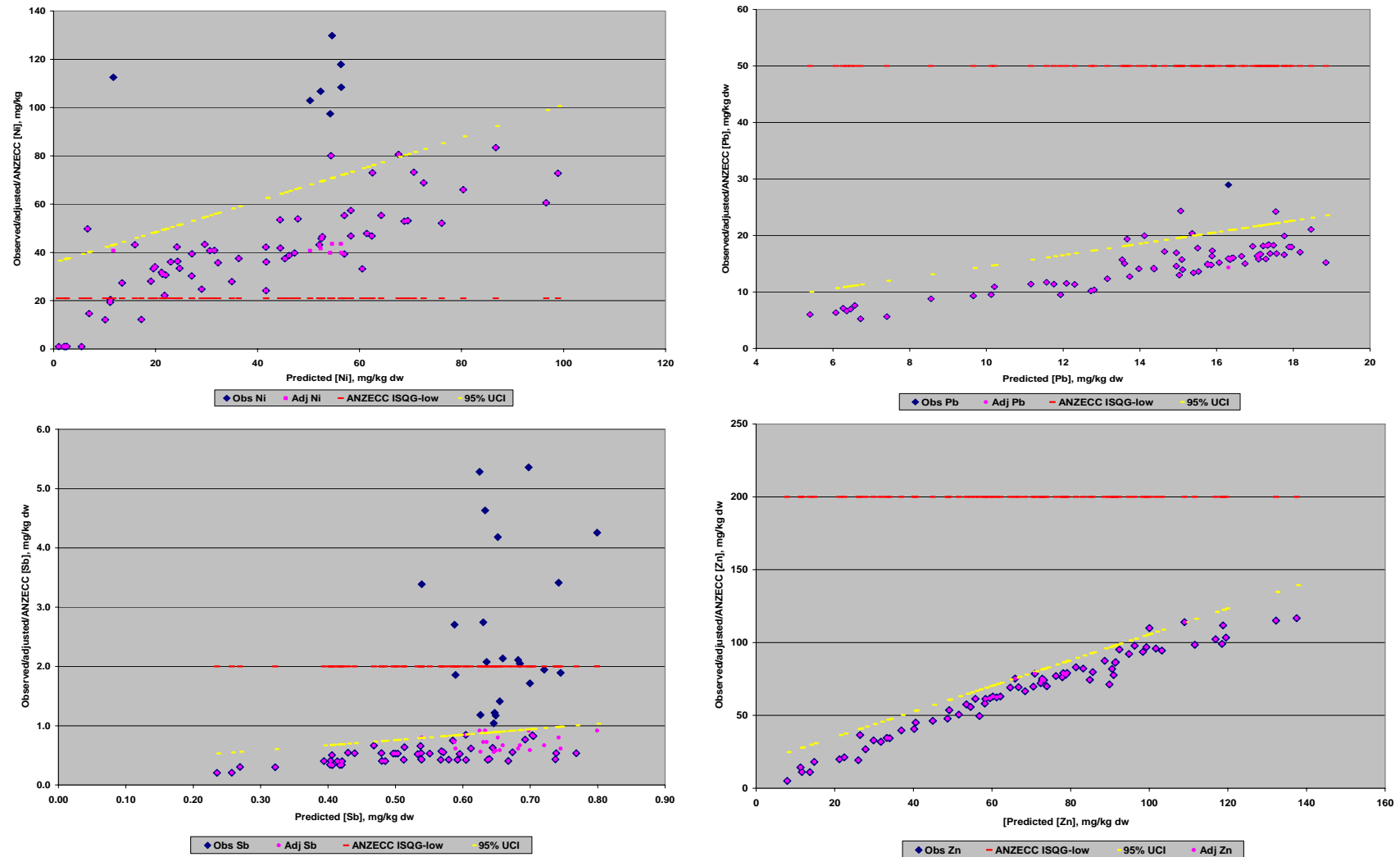


Figure 8 (continued)

It is also seen from Figure 8 that Cr and Ni levels for many samples were very close to the trigger values (80 and 21 mg/kg, respectively), with several samples at levels exceeding the respective guidelines (cf. Table 5a). The observed behaviour could be attributed to the presence of geological sources of these metals within the central Queensland region (Kirkegaard *et al.*, 1970), which were in the past or are currently explored commercially.

Degree of metal enhancement in sediments

It is obvious from Figure 8 that some sediments appear to be enhanced or enriched in some metals when compared to either background or the upper 95% confidence interval of the predicted concentrations. Attempts have been made to quantify this enhancement or enrichment. The term enrichment factor (EF) has been introduced to describe the degree of metal contamination in sediments. It has been defined (see for example, Reimann and de Caritat, 2005) as:

$$EF = (\text{element}/X)_{\text{sediment}} / (\text{element}/X)_{\text{crust}}$$

where X is the normalising element (e.g. Al, Fe, etc.). This study has demonstrated existing interactions between metals and other components of the sediments (see Tables 7–9). The regression models identified different predictors that affected the natural variation of metal concentrations in sediments; hence using only one element as a normalising factor would appear unjustified.

Doherty *et al.*, 2000a considered the gradient in metal concentrations in Cleveland Bay to be derived from anthropogenic sources. They described enhancement as the increase in metal concentration over the upper 95% prediction interval of the regression model, which was generated by a dataset of metal concentrations in sediments taken from a control (uncontaminated) site within the study region.

Although many sediments gave metal contents which did not exceed the ANZECC (2000) trigger values, it is important to remember that regions vary and background levels may be much lower than these trigger values (cf. Table 6). Quantifying metal enhancement would assist in identifying any incipient or potential ‘hot spots’ in the study area. Enhancement was calculated by taking the ratio of the observed metal concentration ([metal]) to the upper 95% confidence interval (UCI) of the prediction model (cf. Table 10):

$$E = [\text{metal}] / \text{UCI}$$

Table 10 summarises the enhancement (E) values obtained. An E value of at least 1.5 has been taken arbitrarily to indicate the onset of a potential ‘hot spot’, which requires future monitoring. The highest incidences (i.e. % samples with E

>1.5) were exhibited (in decreasing order) by Sb > Ag > Ni > Hg. Figure 9 maps the enhancement values for Ag and Ni. Based on the locations of the sites with enhanced levels, it appears that there may be some point sources of Ag and Sb (not shown, but very similar in behaviour to Ag) from the upstream Fitzroy River, causing accumulation of these metals in the sediments. High E values for Sb and Ag were also obtained for the upper 73–180 cm of the Keppel Bay core, suggesting some historical accumulation of these two metals. In contrast, sediments enhanced in Ni and Hg (not shown) were somewhat more widely distributed in upstream Fitzroy River and the estuary, suggesting some diffuse anthropogenic sources.

Table 10: Enhancement (E) of metals in sediments

	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn
Mean E	3.04	0.95	0.95	1.10	0.90	1.17	1.25	0.99	2.66	0.91
sd	4.06	0.26	0.20	1.44	0.27	1.42	1.95	0.31	4.52	0.24
Median E	0.99	0.93	0.99	0.94	0.91	0.70	0.92	0.93	1.08	0.99
Max E	19.20	1.73	1.07	12.60	1.48	9.23	13.70	2.74	30.10	1.15
N (E >1.5)	14	1	0	2	0	6	10	2	22	0
% n	19.2	1.4	0.0	2.7	0.0	9.2	13.7	2.7	30.1	0.0
N	73	73	73	73	73	63	73	73	73	73

n = number of samples; N = total number of samples

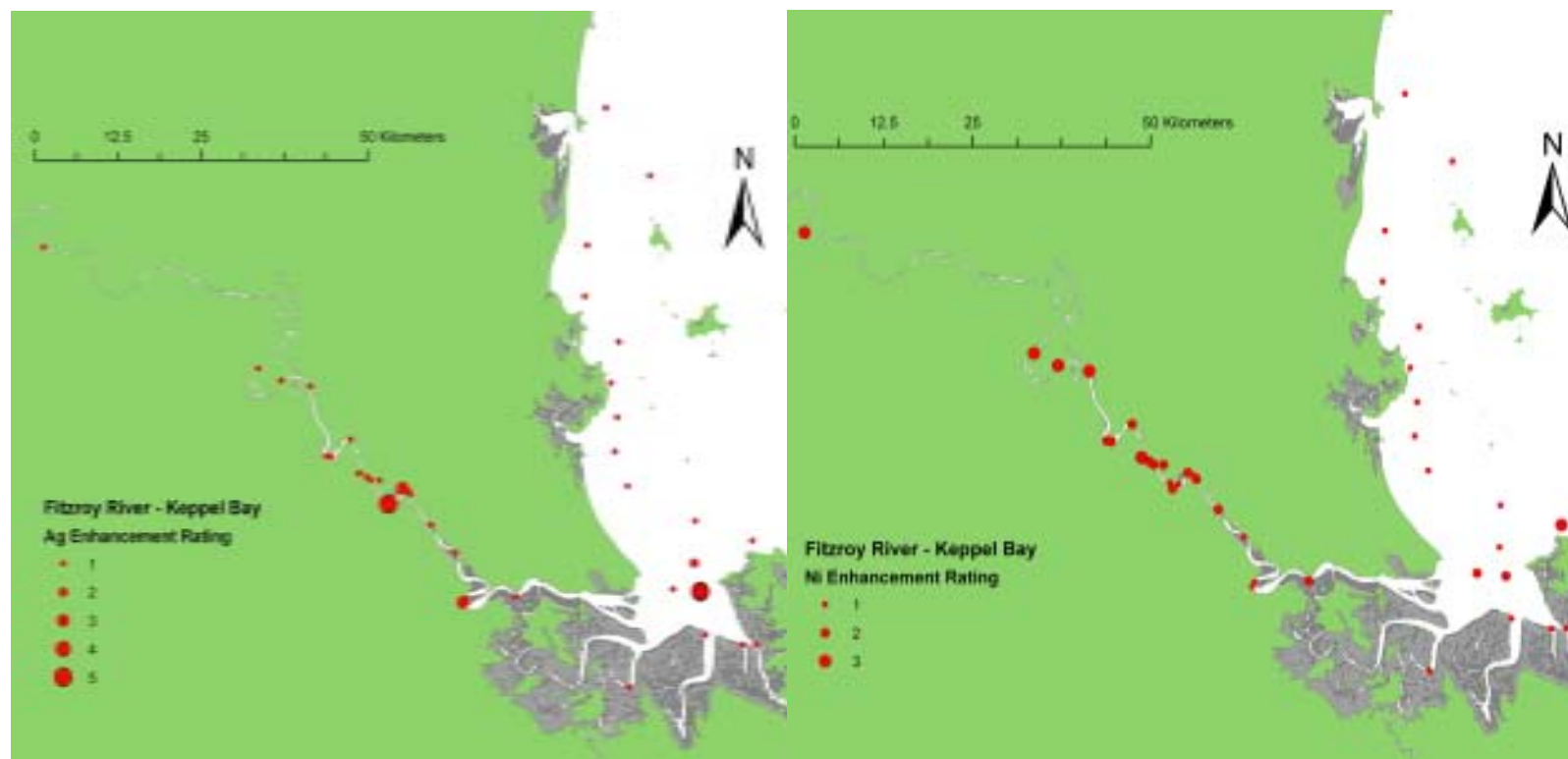


Figure 9: Enhancement maps for Ag and Ni. Rating and E values: 1 = 0–1; 2 = 1–2; 3 = 2–5; 4 = 5–10; 5 = 10–15.

Stable lead isotope ratios (PbIR) in sediments

There are a variety of lead ores used in various industrial applications nationally and worldwide, which has led to the introduction of lead in the environment with distinct relative isotopes abundance. The relative ratios of the four stable lead isotopes ^{206}Pb (from radioactive decay of ^{238}U), ^{207}Pb (from ^{235}U decay), ^{208}Pb (from ^{232}Th decay) and ^{204}Pb (no known radioactive parent) depends upon the age and U/Pb and Th/Pb ratios of the ore from which the lead was derived. Very old ores such as those from Broken Hill (Australia) contain small amounts of radiogenic Pb isotopes; younger ores derived from high U/Pb sources such as mined in Missouri (USA) have much higher proportions of ^{206}Pb , ^{207}Pb and ^{208}Pb relative to ^{204}Pb (Chillrud *et al.*, 2003). Munoz *et al.* (2004) used the stable lead isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$) to trace Pb sources to coastal sediments from various possible sources including industrial effluents, leaded petrol and riverine and marine suspended particulate material. Gallon *et al.* (2005) have tracked the sources and chronology of atmospheric lead deposition using stable PbIRs.

PbIRs of sediments from the Keppel Bay core 277VC20 are plotted in Figure 10. The ratios hardly correlated to the Pb concentration, as gleaned from Figure 10. The y-intercepts of these plots may be taken as the background values: $^{208}\text{Pb}/^{206}\text{Pb} = 2.0834$ and $^{207}\text{Pb}/^{206}\text{Pb} = 0.8301$. The mean Pb content in the 23 core slices analysed was 15.0 ± 1.0 mg/kg dry weight; the mean PbIRs were $^{208}\text{Pb}/^{206}\text{Pb} = 2.0755 \pm 0.0113$ and $^{207}\text{Pb}/^{206}\text{Pb} = 0.8330 \pm 0.0032$. The mean $^{208}\text{Pb}/^{206}\text{Pb}$ ratio is comparable to the value of 2.0635 measured for near-pristine estuarine and marine tropical coastal areas of northern Australia bordering Timor and Arafura Seas and the Gulf of Carpentaria (Munksgaard and Parry, 2002). Reported PbIRs for Murray River (Australia) suspended sediments converted in terms of measured ratios reported in this study were $^{208}\text{Pb}/^{206}\text{Pb} = 2.0757$ and $^{207}\text{Pb}/^{206}\text{Pb} = 0.8451$ (Millot *et al.*, 2004).

The modelled present-day average PbIR values of the earth's crust was reported by Stacey and Kramers (1975) as $^{208}\text{Pb}/^{206}\text{Pb} = 2.06058$ and $^{207}\text{Pb}/^{206}\text{Pb} = 0.83572$ (converted values from other stable Pb isotope ratios reported). This point was included in Figure 11, as well as the Pb isotope ratios for Mount Isa (Australia) Pb deposits and those for oceanic sediments (Atlantic and Pacific) (Stacey and Kramers, 1975). The measured ratios from samples from the upper Fitzroy Catchment, i.e. 3 samples of contaminated soils (a former cattle dip in Stanwell, Central Queensland) and a wastewater sludge sample from the Lions Creek wastewater treatment plant (Pb concentration range for these samples was 30-153 mg/kg, indicating Pb contamination), are also included in the figure, with the sludge sample showing the highest PbIRs.

The plot shows a linear trend ($r^2 = 0.9281$) starting from average modern or present-day Pb and ending at the least radiogenic Mount Isa Pb (Munksgaard *et al.*, 2003), with the core sediments being closer to the PbIRs for present-day Pb. Higher PbIRs indicate more anthropogenic Pb inputs, probably via atmospheric lead (e.g. leaded petrol emissions) and industrial sources (e.g. coal-fired operations), such as found for the contaminated Fitzroy soils and sludge samples. Duzgoren-Aydin *et al.* (2004) reported (in converted ratios) $^{208}\text{Pb}/^{206}\text{Pb} = 2.2190$ for alkyl Pb sources from Australian ores; the range of this ratio for Australia and New Zealand atmospheric lead in 1997 was 2.1565–2.1847 (Bollhofer and Rosman, 2000). The lower observed mean ratio ($^{208}\text{Pb}/^{206}\text{Pb} = 2.0755$) in the sediment core slices appears to reflect the decrease in these PbIRs, which started in the 1970s when leaded petrol was phased out. Such decrease in these ratios has been clearly demonstrated elsewhere, e.g. from a fairly isolated Canadian lake (Gallon *et al.*, 2005). The lower observed mean ratio ($^{208}\text{Pb}/^{206}\text{Pb} = 2.0755$) in the VC20 sediment core slices compared to reported values for Australian samples is consistent with the fact that the VC20 was a very old sediment core and would not have any industrial lead inputs.

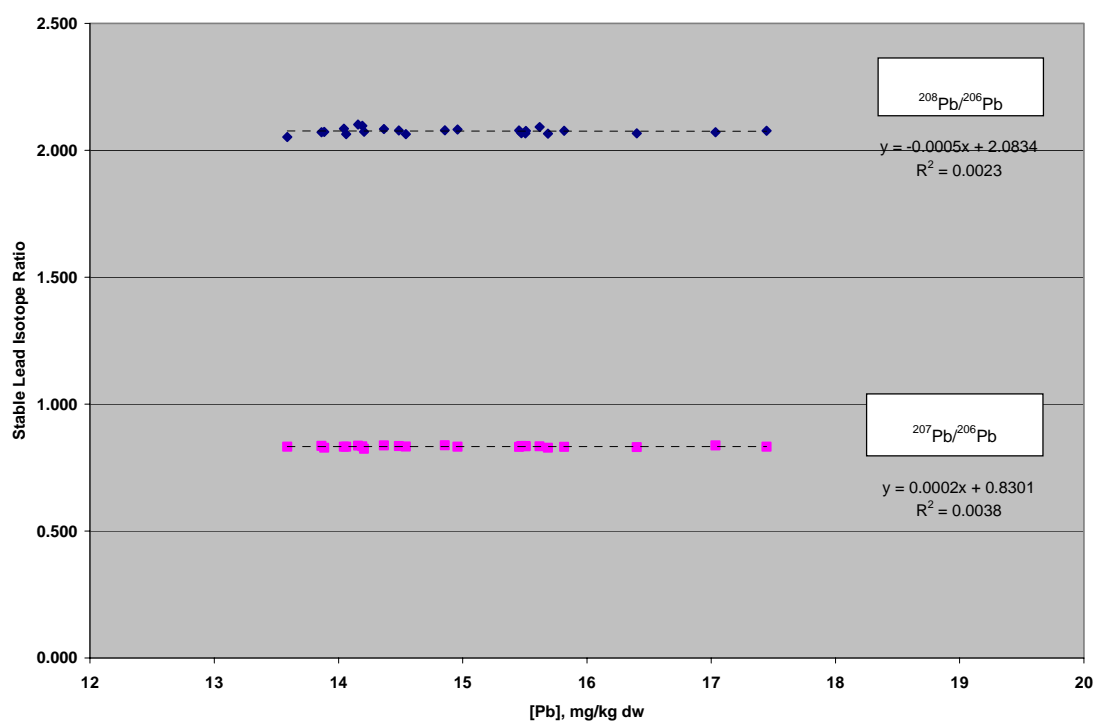


Figure 10: Stable lead isotope ratios versus Pb concentration in 23 slices of Keppel Bay core 277VC20

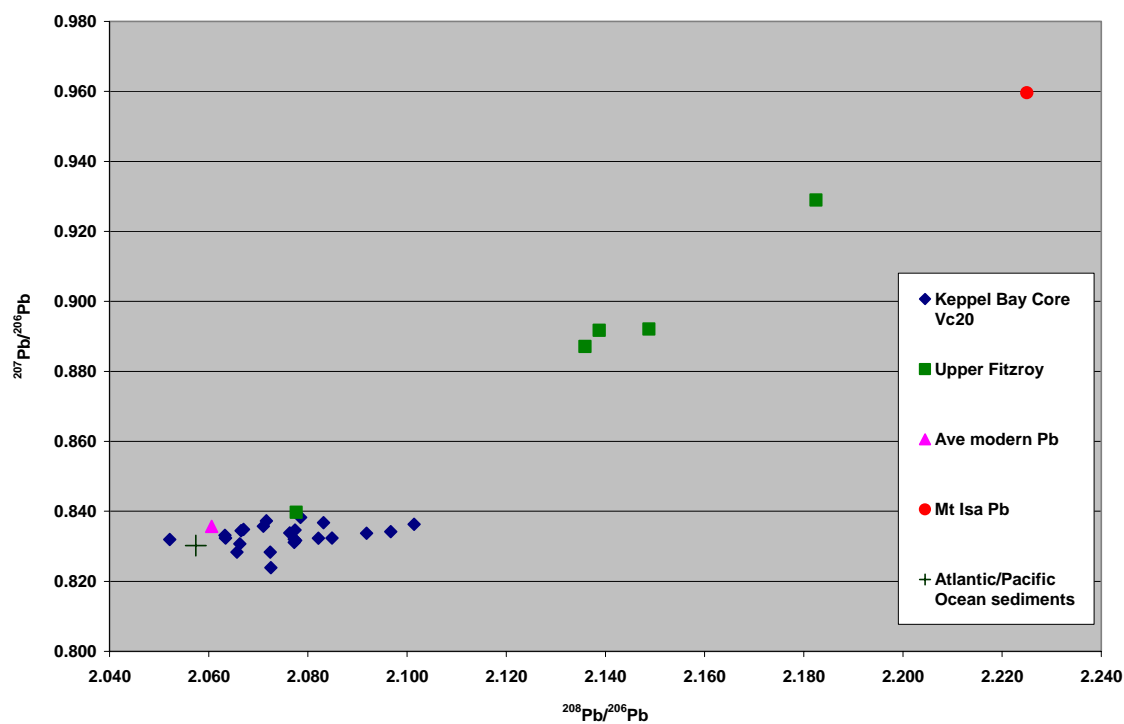


Figure 11: PbIRs for Fitzroy estuary sediments and other samples for comparison

Conclusions and recommendations for further study

It is likely that there are considerable inputs of a range of possible contaminants from anthropogenic activities in the Fitzroy basin to the estuary and Keppel Bay but these are largely undocumented. Potential impacts of these contaminants on the coastal ecosystem are also still poorly understood. This study focussed on determining pesticides concentrations in flows of freshwater entering the Fitzroy Estuary and on PAH and metal concentrations in benthic and core sediment samples from the Fitzroy Estuary and Keppel Bay.

Results for pesticides confirmed previous observations of significant concentrations of several herbicides (Atrazine, Tebuthiuron, Diuron) and lower concentrations of several other herbicides entering the estuary in summer flows from the basin (Packett *et al.*, 2005). The environmental fate and possible impact of these herbicide loads on coastal and marine flora have still to be clearly demonstrated. Future monitoring of these residues would be essential if trends in pesticide contamination from the catchment are to be assessed over time.

While other contaminants such as suspended sediments and nutrients can be monitored in floodwaters it is sometimes difficult to determine the degree to which anthropogenic inputs have added to natural sources. In comparison, and from a land management point of view (e.g. water quality target setting), pesticides are entirely man-made contaminants and therefore a reduction in the use of these chemicals should be reflected in lower pesticide residue detected in surface waters over time. It is therefore critical that long-term floodwater monitoring continue in the Fitzroy catchment so that trends in agrochemical use and contamination of surface waters and marine systems can be assessed.

The benthic sediments (grabs) and sediment cores showed generally low levels of PAHs. This is consistent with the fact that the Fitzroy catchment is not highly industrialised or urbanised. PAHs found in the Fitzroy cores consisted predominantly of perylene, which appears to be largely of natural (diagenetic) origin. In contrast, many more types of PAHs and higher concentrations were detected in benthic sediments of the more industrialised part of central Queensland, Port Curtis, including some PAHs (e.g. benzo[b+k]fluoranthene and benz[a]pyrene), which are potentially toxic to biota and carcinogenic to humans (Vicente-Becket *et al.*, 2006). This apparent contrast in the PAH 'profile / fingerprint' between the Fitzroy mouth and Port Curtis warrants further investigation and monitoring in view of the potential harmful impacts of PAHs. Monitoring for PAHs in the Fitzroy may be considered on at least a five-year scale.

Based on the limited number of samples, metal contamination in the Fitzroy Estuary appears to be low. Several sediment samples exhibited exceedances of ANZECC (2000) trigger values for Ni, Cr and Sb. Natural levels of Ni and Cr were found to be close to the ANZECC (2000) trigger values, probably due to the presence of geological sources in the central Queensland region. This needs to be considered when assessing Cr or Ni contamination of sediments in the region. Antimony and Ag were found to be particularly enhanced in the Keppel Bay sediment core, suggesting some historical accumulation of these metals. The sources of these metals and their potential impacts on the ecosystem warrant investigation and inclusion in a monitoring program. Nickel and Hg were enhanced in some sediments that were more widely distributed in the estuary suggesting possible diffuse anthropogenic sources.

Stable lead isotope ratios measured in 23 slices of the 2.6 m Keppel Bay core for sediment were consistent with those observed for relatively pristine far northern Queensland sediments, suggesting no significant radiogenic lead sources and low Pb pollution.

The recent rapid expansion of commercial mining activities in the central Queensland region could result in increased PAH and metal contamination. The data obtained in this study represent timely measurements, which could serve as baseline data for the region. Continuing monitoring of these contaminants in the Fitzroy Estuary is therefore essential.

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Appendix 1

Location of sediment samples

Table A1.1: Keppel Bay sediment grabs (August 2004)

Sample ID	Date	Start Lat	Start Long	Analysed
98	Aug 2004	-23.416925	150.8418333	✓
110	Aug 2004	-23.41789167	151.0126667	✓
119	Aug 2004	-23.34435	151.0331167	
120	Aug 2004	-23.34135	150.9986333	
121	Aug 2004	-23.33446667	150.9544833	✓
122	Aug 2004	-23.31745	150.9137167	
124	Aug 2004	-23.29035	150.8419167	✓
127	Aug 2004	-23.232875	150.83435	✓
129	Aug 2004	-23.39953333	150.8130167	
130	Aug 2004	-23.40183333	150.8198333	✓
131	Aug 2004	-23.40258333	150.8251167	
134	Aug 2004	-23.40021667	150.9114333	✓
141	Aug 2004	-23.40063333	150.9560833	
151	Aug 2004	-23.40131667	150.9728333	
162	Aug 2004	-23.49538333	150.9550667	✓
165	Aug 2004	-23.52891667	150.9346333	✓

Table A1.2: Fitzroy channel

Sample ID	Date	Start Lat	Start Long
E1	18 Aug 2005	-23.51092	150.63550
E2	18 Aug 2005	-23.45588	150.62216
E3	18 Aug 2005	-23.42233	150.58961
E4	18 Aug 2005	-23.38109	150.55916
E5	18 Aug 2005	-23.38995	150.52800
E6	18 Aug 2005	-23.36393	150.50242
F1	18 Aug 2005	-23.35972	150.49192
F2	18 Aug 2005	-23.31848	150.48056
F3	18 Aug 2005	-23.33990	150.45400
N1	18 Aug 2005	-23.55539	150.95950
N2	18 Aug 2005	-23.56778	151.01010
N3	18 Aug 2005	-23.56699	151.02858
E7	1 Dec 2005	-23.45815	150.62389
E8	1 Dec 2005	-23.37863	150.51869
E9	1 Dec 2005	-23.36426	150.5027
F4	1 Dec 2005	-23.35967	150.49193
F5	1 Dec 2005	-23.35799	150.4937

Table A1.3: Sediment cores

Sample ID	Date	Start Lat	Start Long
277VC20A (2.6 m) – Keppel Bay	1 Sep 2004	-23.50329	150.95235
3410 (2.22 m; archive) – Raglan Creek	13 Apr 2000	-23.618833	150.85583

Table A1.4 Archived sediment grab samples

Sample ID	Date	Start Lat	Start Long
EPA1	21 Mar 2002	-23.5095	150.7036667
EPA7	21 Mar 2002	-23.51635	150.632416667
EPA19	21 Mar 2002	-23.42208333	150.589116667
EPA23	21 Mar 2002	-23.385333	150.56153333
EPA25	21 Mar 2002	-23.3776333	150.55076667
EPA30	21 Mar 2002	-23.39115	150.53905
EPA31	21 Mar 2002	-23.39706667	150.53158333
EPA34	23 Mar 2002	-23.39016667	150.5289667
EPA36	23 Mar 2002	-23.36788333	150.5199
EPA42	23 Mar 2002	-23.36775	150.5076333
FR-EB1-0	6 Apr 1999	-23.085116667	150.06728333
FR2	16 Apr 1999	-23.359166667	150.49263889
FR6	16 Apr 1999	-23.338527778	150.44858333
FR9	16 Apr 1999	-23.253861111	150.42641667
FR10	16 Apr 1999	-23.247055556	150.38722222
FR11	16 Apr 1999	-23.247055556	150.38722222
FR12	16 Apr 1999	-23.232138889	150.35663889
1903	10 Aug 98	-23.200000000	150.84266667
1914	10 Aug 98	-23.144833333	150.79700000
1917	10 Aug 98	-23.082833333	150.80000000
1925	11 Aug 98	-22.916000000	150.82500000
1930	11 Aug 98	-22.998333333	150.88500000
1947	12 Aug 98	-23.250000000	150.83166667
1958	13 Aug 98	-23.291666667	150.84050000
1982	13 Aug 98	-23.333166667	150.83733333
1983	13 Aug 98	-23.375000000	150.85433333
1995	14 Aug 98	-23.500000000	150.91575000
1997	14 Aug 98	-23.468333333	150.94433333
2000	14 Aug 98	-23.441166667	151.02250000
2007	14 Aug 98	-23.41731667	150.94556667

Appendix 2

Pesticide concentrations (µg/L) for 2004 and 2005 minor floods at Rockhampton

Date	Atrazine	Des ethyl Atrazine	Des isopropyl Atrazine	Diuron	Tebuthiuron	Hexazinone	Flumeturon	Prometryn
20/01/2004	0.03	0.01	BL	BL	0.69	0.01	BL	BL
22/01/2004	0.03	0.01	BL	BL	0.30	BL	BL	BL
24/01/004	0.18	0.02	0.01	0.06	0.22	0.01	0.01	BL
26/01/2004	0.60	0.08	0.03	0.09	0.26	BL	BL	BL
27/01/2004	0.95	0.09	0.05	0.43	0.31	BL	BL	BL
28/01/2004	0.83	0.07	0.02	0.08	0.30	BL	0.01	0.01
29/01/2004	0.53	0.04	0.01	0.04	0.20	BL	0.01	BL
30/01/20004	0.37	0.03	0.02	0.08	0.17	BL	BL	BL
31/0/2004	0.33	0.03	0.01	0.02	0.16	BL	0.01	BL
01/02/2004	0.29	0.03	0.01	0.03	0.13	BL	0.01	BL
02/02/2004	0.21	0.02	0.01	0.03	0.12	BL	BL	BL
07/02/2004	0.38	0.02	0.01	0.06	0.11	0.01	0.01	0.03
09/02/2004	0.88	0.05	0.02	BL	0.14	BL	BL	BL
11/02/2004	0.22	0.02	BL	BL	0.08	0.01	BL	BL
14/02/2004	0.16	0.02	BL	0.02	0.08	BL	BL	BL
16/02/2004	0.31	0.03	0.02	0.01	0.09	BL	BL	BL
18/02/2004	0.36	0.03	0.01	0.01	0.13	0.01	BL	BL
15/12/2004	0.30	0.03	BL	BL	0.13	0.02	0.28	0.01
17/12/2004	0.31	0.04	BL	BL	0.07	0.04	0.26	0.02
20/12/2004	0.13	0.02	BL	BL	0.83	0.02	0.05	BL
22/12/2004	0.06	BL	BL	BL	0.46	0.01	0.01	BL
24/12/2004	0.06	BL	BL	BL	0.20	0.01	0.01	BL
31/12/2004	0.07	BL	BL	BL	0.20	0.02	0.02	BL
11/01/2005	0.13	0.02	BL	BL	0.29	0.02	BL	BL
13/01/2005	0.11	BL	BL	0.03	0.19	0.02	BL	0.02
18/01/2005	0.09	BL	BL	0.01	0.15	BL	BL	BL
25/01/2005	0.19	0.01	BL	0.03	0.24	BL	BL	BL
30/01/2005	0.32	0.03	BL	0.02	0.72	BL	BL	0.01
01/02/2005	0.29	0.04	BL	BL	0.18	0.03	BL	BL
01/02/2005	0.23	0.04	BL	BL	0.25	BL	BL	BL
02/02/2005	0.10	BL	BL	0.01	0.31	BL	BL	BL
02/02/2005	0.07	BL	BL	BL	0.20	BL	BL	BL
03/02/2005	0.03	BL	BL	BL	0.17	BL	BL	BL
03/02/2005	0.04	BL	BL	BL	0.18	BL	BL	BL
04/02/2005	0.03	BL	BL	BL	0.14	BL	BL	BL

BL = below limit of reporting

Appendix 3

Polycyclic aromatic hydrocarbons

Table A3.1: List of PAHs and some properties (source: Kennish, 1997)

PAH	Acronym	MW	Number of rings	Relative carcinogenicity index (a)	Toxicity to aquatic organisms (b)
Napthalene	NA	128	2	?	Y
Acenaphthylene	AYL	152	3	?	?
Acenaphthene	AEN	154	3	?	?
Fluorene	F	166	3	?	Y
Anthracene	AN	178	3	?	?
Phenanthrene	PH	178	3	?	Y
Fluoranthene	FL	202	4	?	Y
Pyrene	PY	202	4	?	?
Benz[a]Anthracene	BaA	228	4	1	?
Chrysene	CH	228	4	?	Y
Benz[a]Pyrene	BaP	252	5	3	Y
Benz[e]Pyrene	BeP	252	5	?	?
Benzo[b+k]Fluoranthene	BbkF	252	5	2	?
Perylene	PER	252	5	?	?
Benzo[ghi]Perylene	Bghi	276	6	?	?
Indeno[123cd]Pyrene	IP	276	6	1	?
Dibenz[ah]Anthracene	DbA	278	5	1	Y

a. Index: 4 = high; 3 = moderate; 2 = low-moderate; 1 = low; ? = unknown

b. Y = yes; ? = unknown

Table A3.2: PAHs ($\mu\text{g/kg}$ dry weight, normalised to 1% TOC) in Keppel Bay and Fitzroy channel sediment grabs

Sample ID	Acenaphthylene	Acenaphthene	Naphthalene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz[a]-Anthracene
	AYL	AEN	NA	F	PN	AN	FL	PY	BaA
124	<2	<2	<2	<2	<2	<2	5.7	<2	<2
130	<2	<2	<2	<2	<2	<2	5.7	5.7	<2
134	<2	<2	<2	<2	<2	<2	5.0	<2	<2
F3	<2	<2	2.38	<2	4.76	<2	2.38	2.38	<2
F5	<2	<2	2.14	<2	5.71	<2	2.86	2.86	<2
F4	<2	<2	4.67	2.67	22.0	4.00	44.0	39.3	26.0
F2	<2	<2	2.40	<2	4.19	4.79	1.80	1.80	2.99
F1	1.22	4.27	12.20	4.27	140	22.6	293	301	145
E9	4.04	<2	7.07	<2	31.3	6.06	182	182	111
E6	2.83	<2	12.26	<2	20.8	3.77	80.2	81.1	37.7
E8	<2	<2	4	<2	6.00	<2	10.0	10.0	4.00
E5	<2	<2	4.26	<2	5.32	<2	10.6	9.57	4.26
E4	<2	<2	4.26	<2	7.45	<2	20.2	17.0	7.45
E3	<2	<2	3.57	<2	4.76	1.0	10.7	9.52	4.76
E2	<2	<2	8.89	<2	33.3	31.1	62.2	48.89	15.6
E7	<2	<2	<2	<2	2.99	<2	8.96	7.46	4.48
E1	<2	<2	3.49	<2	4.65	<2	6.98	5.81	<2
N1	<2	<2	2.67	<2	<2	2	5.33	4.00	<2
N2	<2	<2	7.96	<2	2.65	<2	5.31	5.31	1.77
N3	<2	<2	4.12	<2	4.12	<2	6.19	5.15	2.06
ANZECC ISQG-low, low-MW PAH	44	16	160	19	240	85			
ANZECC ISQG-low, high-MW PAH							600	665	261

Table A3.2 (continued)

Sample ID	Chrysene	Benz[a]-Pyrene	Dibenz[ah]-Anthracene	Benzo[b+k]-Fluoranthene	Benz[e]-Pyrene	Perylene	Indeno[123cd]-Pyrene	Benzo[ghi]-Perylene	Total PAHs
	CH	BaP	DbA	BbkF	BeP	PER	IP	Bghi	
124	<2	<2	<2	<2	<2	<2	<2	<2	5.7
130	<2	<2	<2	<2	<2	<2	<2	<2	5.7
134	<2	<2	<2	<2	<2	<2	<2	<2	5.0
F3	3.17	<2	<2	3.17	1.59	146	<2	<2	15
F5	3.57	<2	2.14	3.57	2.14	27.9	<2	1.43	19.3
F4	25.3	25.3	24.7	47.3	20	253	3.33	21.3	218
F2	2.99	1.20	<2	2.4	1.2	37.7	<2	2.99	22.2
F1	151	135	<2	227	95.7	248	92.1	107	1204
E9	111	111	111	212	75.8	85.9	16.2	96	857
E6	44.3	61.3	17.9	111	50.9	94.3	82.1	88.7	359
E8	6.00	5.00	8.00	13	5	100	<2	5	53.0
E5	6.38	4.26	<2	12.8	5.32	126	5.32	7.45	45.0
E4	9.57	7.45	<2	18.1	7.45	118	8.51	10.6	73.0
E3	5.95	4.76	<2	11.9	4.76	102	5.95	7.14	45.0
E2	22.2	15.6	<2	40	15.6	144	20	20	238
E7	4.48	4.48	5.97	10.4	4.48	92.5	<2	4.48	39.0
E1	3.49	<2	<2	8.14	2.33	121	2.33	4.65	24.0
N1	<2	<2	<2	5.33	<2	88	<2	<2	14.0
N2	2.65	<2	<2	6.19	2.65	34.5	2.65	3.54	25.7
N3	3.09	<2	<2	7.22	3.09	46.4	3.09	4.12	24.7
ANZECC ISQG-low guidelines									
High MW PAHs	384	430	63				No guidelines		1700
Low MW PAHs only									552
Total PAHs									4000

Table A3.3: PAHs ($\mu\text{g/kg}$ dry weight, normalised to 1% TOC) in Keppel Bay sediment core Vc20

Depth of slice (cm)	Naphthalene NA	Phenanthrene PN	Chrysene CH	Fluoranthene FL	Pyrene PY	Benzo[b+k]- Fluoranthene BbkF	Perylene PER	Benzo[ghi] -Perylene Bghi	Total PAHs	
0–3	15	<2	<2	<2	<2	5	158	<2	178	
3–6	7	<2	<2	<2	<2	7	186	<2	200	
6–9	10	<2	<2	<2	<2	4	146	<2	160	
9–12	3	<2	<2	3	<2	5	180	<2	192	
12–15	8	<2	<2	3	<2	6	225	<2	243	
15–18	5	<2	<2	<2	<2	7	184	<2	195	
18–21	6	<2	<2	<2	<2	6	162	<2	174	
29.5–32.5	6	<2	<2	4	<2	6	176	<2	192	
41.5–44.5	7	<2	3	5	<2	8	233	3	260	
61–64	<2	3	3	<2	5	<2	34	<2	47	
79–82	<2	<2	<2	<2	<2	<2	56	4	60	
138–141	<2	<2	<2	<2	<2	16	579	<2	595	
179.5–182.5	9	<2	<2	6	<2	9	234	<2	257	
220–224	5	<2	<2	<2	<2	7	488	<2	500	
255–260	7	<2	<2	<2	<2	9	682	<2	698	
ANZECC ISQG-low Guidelines										
Low MW	160	240	384	600	665	no guidelines			552	
High MW	no guidelines								1700	
Total PAHs										4000

Table A3.4: PAHs ($\mu\text{g/kg}$ dry weight, normalised to 1% TOC) in Raglan Creek – Core 3410

Sample ID	Top depth of slice, cm	Acenaphthylene	Acenaphthene	Naphthalene	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Benz[a]-Anthracene
		AYL	AEN	NA	F	PN	AN	FL	PY	BaA
3410A	0	<2	<2	<2	<2	<2	<2	<2	<2	<2
3410B	-22	<2	<2	<2	<2	<2	<2	<2	<2	<2
3410C	-32	<2	<2	<2	<2	<2	<2	<2	<2	<2
3410D	-42	<2	<2	2.0	<2	2.0	<2	4.0	3.0	<2
3410E	-52	<2	<2	5.7	2.3	3.4	<2	6.8	6.8	2.3
3410F	-98	<2	<2	5.0	<2	5.0	<2	8.8	8.8	2.5
3410G	-158	<2	<2	5.4	<2	4.3	<2	9.7	8.6	3.2
3410H	-218	<2	<2	9.9	4.2	4.2	<2	9.9	8.5	<2
ANZECC ISQG-low, low MW		44	16	160	19	240	85			
ANZECC ISQG-low, high MW								600	665	261

Sample ID	Top depth of slice, cm	Chrysene	Benz[a]-Pyrene	Dibenz[ah]-Anthracene	Benzo[b+k]-Fluoranthene	Benz[e]-Pyrene	Perylene	Indeno[123cd]-pyrene	Benzo[ghi]-Perylene	Total PAHs
3410A	0	<2	<2	<2	<2	<2	21.5	<2	<2	21.5
3410B	-22	<2	<2	<2	<2	<2	54.1	<2	<2	54.1
3410C	-32	<2	<2	<2	<2	<2	26.7	<2	<2	26.7
3410D	-42	2	<2	3	5	2	94.0	<2	<2	117
3410E	-52	3.4	<2	3.4	8.0	2.3	580	<2	2.3	626
3410F	-98	3.8	<2	2.5	7.5	2.5	1000	<2	2.5	1049
3410G	-158	3.2	2.2	3.2	7.5	3.2	1075	<2	2.2	1128
3410H	-218	4.2	<2	<2	7.0	2.8	1366	<2	<2	1417
ANZECC ISQG-low, high MW		384	430	63						
ANZECC ISQG-low, total PAHs										4000

Table A3.5: PAH isomer ratios and origins of PAHs

PAH Isomer Ratios*								
Site	AN/(AN+PN)	FL/(FL+PY)	BaA/(BaA+CH)	IP/(IP+Bghi)	PN/AN	FL/PY	BaA/CH	PER/(sum 5-rings)
Fitzroy Channel								
F3		0.50				1.00		0.970
F5		0.50				1.00		0.780
F4	0.15	0.53	0.51	0.14	0.18	1.12	1.03	0.680
F2	0.53	0.50	0.50		1.14	1.00	1.00	0.890
F1	0.14	0.49	0.49	0.46	0.16	0.98	0.96	0.350
E9	0.16	0.50	0.50	0.14	0.19	1.00	1.00	0.140
E6	0.15	0.50	0.46	0.48	0.18	0.99	0.85	0.280
E8		0.50	0.40			1.00	0.67	0.760
E5		0.53	0.40	0.42		1.11	0.67	0.850
E4		0.54	0.44	0.44		1.19	0.78	0.780
E3	0.17	0.53	0.44	0.45	0.21	1.13	0.80	0.830
E2	0.48	0.56	0.41	0.50	0.93	1.27	0.70	0.670
E7		0.55	0.50			1.20	1.00	0.780
E1		0.55		0.33		1.20		0.920
N1	1.00	0.57				1.33		0.940
N2		0.50	0.40	0.43		1.00	0.67	0.800
N3		0.55	0.40	0.43		1.20	0.67	0.820
Raglan Creek – Core 3410								
0 cm								1.000
22 cm								1.000
32 cm								1.000
42 cm		0.57				1.33		0.904
52 cm		0.50	0.40			1.00	0.67	0.977
98 cm		0.50	0.40			1.00	0.67	0.988
158 cm		0.53	0.50			1.13	1.00	0.985
218 cm		0.54				1.17		0.993
Keppel Bay – Core 277VC20A								
15 Slices (0–260)								0.963–1.000
Types of sources and empirical PAH isomer ratios (Yunker <i>et al.</i>, 2004)								
Pyrolytic sources (high-T combustion of fossil fuels and biomass)								
	>0.10	>0.5	>0.35	>0.5	<10	>1	>0.9	<0.1
Petrogenic sources (eg fossil fuels, petroleum, shale oil etc)								
	<0.10	<0.5	<0.2	<0.2	>15	<1	≤ 0.4	
Diagenetic sources (formed from plant or animal precursors)								
								>0.1

* AN = Anthracene, BaA = Benz[a]Anthracene, Bghi = Benzo[ghi]Perylene, CH = Chrysene, FL = Fluoranthene, IP = Indeno[123cd]Pyrene, NA = Naphthalene, PN = Phenanthrene, PY = Pyrene. Five-ring PAHs include: PER = Perylene, BaP = Benz[a]Pyrene, BeP = Benz[e]Pyrene, BbKf = Benzo[b+k]Fluoranthene and DbA = Dibenzo[ah]Anthracene.

Appendix 4

Age of Keppel Bay sediment core

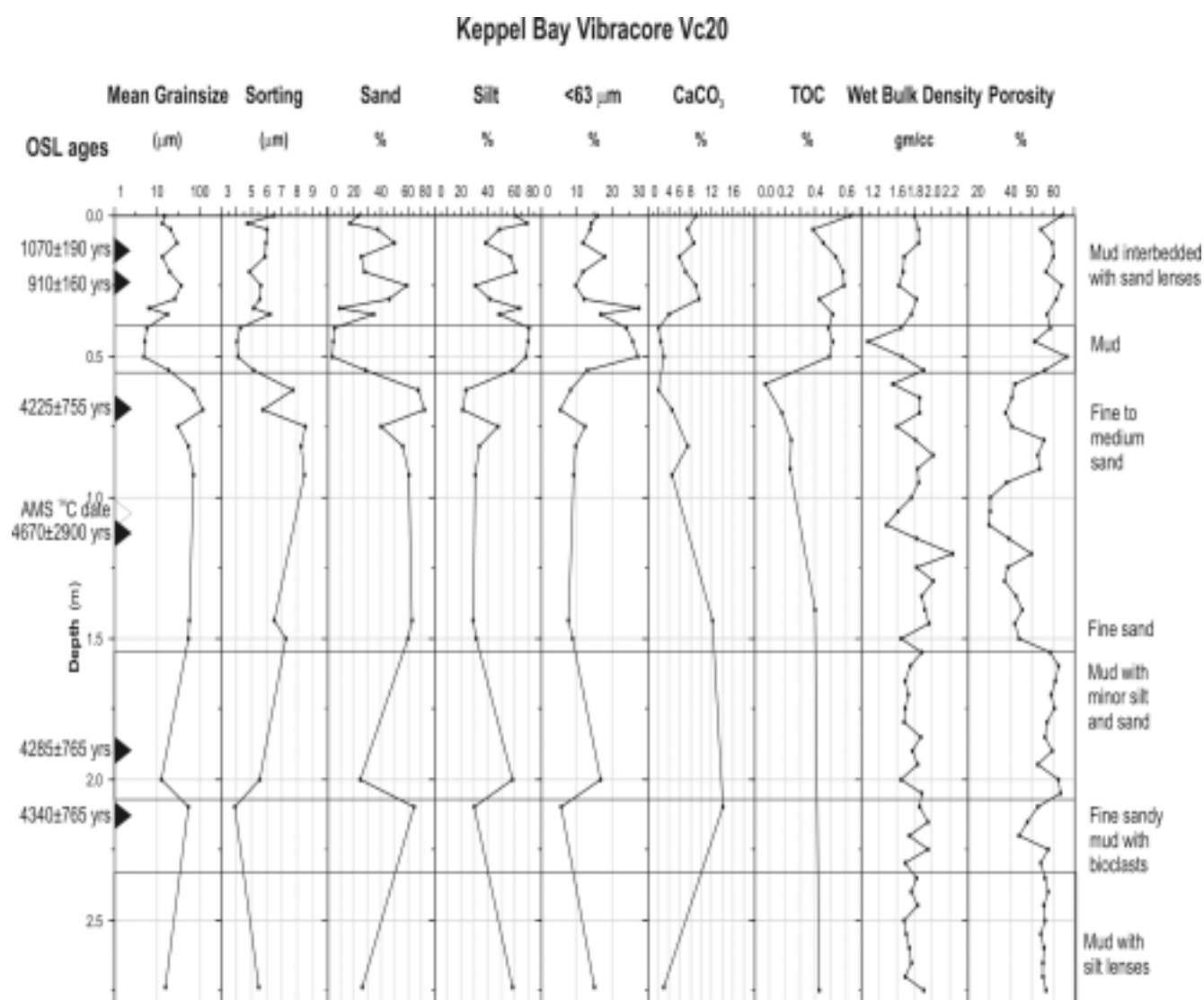


Figure A4.1: Dating and Physico-chemical Analysis of Keppel Bay Sediment Core VC20
(Source: Dr Helen Bostock, Geoscience Australia, 2005)

Appendix 5

Quality assurance controls for metal analyses

Table A5.1: Analyses of certified reference material – sediments (mg kg^{-1} dry weight) and analytical techniques used

Lab SampleID	Reference Materials*	Ag ICP-MS	As ICP-MS	Cd ICP-MS	Cr XRF	Cu XRF	Hg CV-AAS	Ni XRF	Pb ICP-MS	Sb ICP-MS	Zn XRF
1631178	PACS-2 (trial 1)	0.04	23.3	0.71	71	190	na	36	121.9	16.2	246
(Geoscience Australia)	certified value	1.22	26.2	2.11	90.7	310	3.04	39.5	183	11.3	364
	% recovery	3.28	88.9	33.6	78.3	61.3		91.1	66.6	143.4	67.6
1682705	PACS-2 (trial 2)	<0.01	24.2	1.52	75	281	na	33	184.3	11.1	382
(Geoscience Australia)	certified value	1.22	26.2	2.11	90.7	310	3.04	39.5	183	11.3	364
	% recovery	~0.4	92.4	72.0	82.7	90.6		83.5	100.7	98.2	104.9
1682706	BCSS-1	<0.01	9.9	<0.1	109	20	nc	53	24.1	0.6	112
(Geoscience Australia)	certified value	nc	11.1	0.25	123	18.5		55.3	22.7	0.59	119
	% recovery		89.2	20.0	88.6	108.1		95.8	106.2	101.7	94.1
(Genalysis)	BEST-1						0.090				
	certified value						0.092				
	% recovery						97.83				

na =not analysed

nc = no certified value

*PACS-2, BCSS-1 and BEST-1 are marine sediment certified reference materials (CRM) for trace metals and other constituents obtained from National the Research Council Canada (Ottawa, Canada). These CRMs roughly cover the concentration ranges for the metals in the ANZECC interim sediment quality guidelines (low and high).

Table A5.2: ICP-MS analyses for lead and stable lead isotope ratios

Quality Control	Pb, mg/kg dry weight	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$
MESS-3 ave (n=3)	21.8	2.0247	0.8075
stdev.	1.3	0.0009	0.0038
RSD%	5.8	0.0456	0.4669
Certified value	21.1	nc	nc
% recovery	103.3		
NMI Biosoil av. (n=2)	33.9	2.1434	0.8857
stdev.	1.4	0.0055	0.0033
RSD%	4.1	0.2553	0.3779
Certified value*	31.4	nc	nc
% recovery	107.9		
IAEA Soil-7 av. (n=2)	59.5	2.0647	0.8387
stdev	2.2	0.0040	0.0004
RSD%	3.6	0.1929	0.0507
Certified value	60.0	nc	nc
% recovery	99.2		
NIST 2710 av. (n=2)	5830	na	na
stdev	139		
RSD%	2.4		
Certified value	5530		
% recovery	105.4		
Detection limit	0.1		
Digest blank ave (n=3)	<DL		

nc = not certified; na = not analysed

<DL: less than detection limit

Appendix 6

Metals analyses and other sediment parameters (all mg/kg dry weight except for Ag, Cd, Hg, µg/kg dry weight)

Sample ID	Group	Depth, cm	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn
FR-EB1-0	1	0–5	5.1	7.0	50.7	791.6	13.2	5.1	112.5	7.6	0.3	36.5
FR2	1	0–10	5.7	9.2	57.2	147.7	46.9	5.7	117.9	10.2	0.3	116.7
FR6	1	0–10	5.1	2.6	51.4	120.3	18.5	5.1	43.2	5.2	0.2	26.7
FR9	1	0–10	5.7	8.4	56.9	146.9	45.6	11.4	129.8	10.4	0.3	115.00
FR10	1	0–10	5.6	7.3	56.0	146.6	45.9	5.6	102.9	9.5	0.3	98.5
FR11	1	0–10	5.2	2.9	52.2	113.8	17.7	5.2	33.4	5.6	0.2	39.7
FR12	1	0–10	5.6	8.1	56.2	149.4	49.4	22.5	106.7	11.3	0.3	103.4
F1	1	0–10	5.4	8.3	53.7	133.1	45.1	32.2	73.0	20.0	0.5	94.4
F2	1	0–10	5.4	10.0	54.4	110.0	44.6	21.8	80.6	19.4	0.5	99.1
F3	1	0–10	5.4	10.4	53.8	122.7	47.3	21.5	73.2	24.3	0.5	102.2
EPA1	2	0–10	5.3	13.1	52.8	98.2	23.2	21.1	53.9	16.8	0.8	69.7
EPA7	2	0–10	21.6	14.7	54.1	99.5	33.5	21.6	60.6	24.2	2.7	86.5
EPA19	2	0–10	5.2	7.9	51.5	77.3	22.7	10.3	42.3	15.0	0.6	50.5
EPA23	2	0–10	5.5	6.8	54.9	97.7	35.1	22.0	83.4	13.4	0.7	92.2
EPA25	2	0–10	21.0	9.9	52.5	88.1	21.0	21.0	53.5	15.7	0.8	63.0
EPA30	2	0–10	5.3	14.6	53.2	106.4	29.8	31.9	66.0	17.8	4.3	83.0
EPA31	2	0–10	74.4	7.5	53.1	78.6	35.1	21.2	57.4	15.7	0.6	78.6
EPA34	2	0–10	5.4	9.6	54.3	113.0	30.4	21.7	72.8	17.2	1.4	97.8
EPA36	2	0–10	5.6	6.2	56.5	128.7	37.3	11.3	108.4	13.0	3.4	111.8
EPA42	2	0–10	5.5	6.0	55.4	115.1	32.1	22.1	97.4	16.9	0.6	114.0
E1	2	0–10	5.5	13.0	55.1	93.7	35.3	22.0	52.9	21.0	0.4	95.9
E2	2	0–10	5.4	11.4	54.1	116.9	29.2	32.5	46.5	19.9	0.4	77.9
E3	2	0–10	5.4	11.2	53.7	105.3	23.6	21.5	38.7	16.3	0.5	74.2
E4	2	0–10	5.4	10.7	53.7	94.5	31.2	21.5	39.7	17.3	0.5	75.2
E5	2	0–10	5.5	12.6	55.3	101.8	38.7	33.2	55.3	18.3	0.6	95.2
E6	2	0–10	5.6	10.0	55.5	125.4	38.9	33.3	68.8	29.0	0.7	109.9
N1	3	0–10	5.3	14.7	53.0	90.1	29.7	21.2	36.0	18.2	0.4	69.9
N2	3	0–10	5.4	13.7	53.6	76.1	27.9	21.4	41.8	17.0	0.4	76.1
N3	3	0–10	5.3	14.0	53.4	75.8	27.8	21.4	37.4	18.4	0.4	79.0

Sample ID	Group	Depth, cm	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn
K1	4	0–3	81.9	12.8	51.2	55.3	18.4	5.1	31.7	20.4	2.0	61.4
K2	4	3–6	21.4	12.6	53.4	52.3	18.1	5.3	36.3	14.9	2.1	63.0
K3	4	6–9	32.8	12.7	54.7	51.4	14.2	5.5	30.6	15.2	5.4	62.3
K4	4	9–12	43.8	13.4	54.7	66.8	18.6	5.5	39.4	14.8	0.8	61.3
K5	4	12–15	20.6	13.1	51.5	48.4	26.8	5.1	36.0	14.8	4.6	61.7
K6	4	15–18	20.6	13.5	51.6	51.6	17.5	5.2	31.0	13.6	0.8	55.7
K7	4	18–21	32.0	13.1	53.3	53.3	17.0	5.3	34.1	14.0	1.2	57.5
K11	4	29.5–32.5	21.6	15.8	54.0	57.3	18.4	5.4	30.3	16.3	1.9	69.2
K15B	4	41.5–44.5	32.2	12.4	53.7	59.1	23.6	5.4	40.8	15.9	1.2	74.1
KB40	4	51–55	31.5	12.7	52.6	42.1	14.7	5.3	27.3	12.7	1.9	46.3
KB30	4	61–64	55.4	13.4	55.4	73.1	25.5	5.5	43.2	17.9	1.2	87.5
KB21	4	70–73	31.4	6.7	52.3	18.8	8.4	5.2	14.6	9.3	4.2	19.9
KB12	4	79–82	5.2	9.3	51.6	62.9	21.7	5.2	43.3	16.0	1.9	75.3
KB3	4	88–91	5.4	12.9	53.6	48.2	16.1	5.4	33.2	14.6	1.7	53.6
K18	4	100–103	5.4	11.2	53.7	40.8	14.0	5.4	27.9	12.3	0.8	45.1
K24	4	118–121	21.1	11.7	52.8	39.1	8.5	5.3	22.2	11.5	5.3	32.8
K30	4	138–141	5.1	12.2	50.8	34.6	13.2	5.1	19.3	11.4	2.7	34.6
K37	4	160–163	5.7	14.2	56.9	45.5	14.8	5.7	20.5	11.7	3.4	31.9
K43	4	179.5–182.5	52.7	15.2	52.7	77.0	25.3	21.1	45.2	18.1	2.1	77.0
KB204	4	200–204	5.3	10.4	52.5	57.8	18.9	5.3	35.7	15.0	0.5	69.4
KB224	4	220–224	5.2	11.6	52.0	70.8	19.8	5.2	37.5	16.0	1.0	66.6
KB243	4	240–243	5.2	8.4	51.9	43.6	13.5	5.2	28.0	14.2	2.1	47.7
KB260	4	255–260	5.2	10.6	52.2	53.3	24.0	5.2	40.8	16.6	0.6	72.1
FK3410A	5	0–2	5.3	15.6	53.2	105.3	28.7		39.3	18.0	0.5	77.6
FK3410B	5	22–24	5.3	12.7	53.2	106.3	38.3		46.8	16.6	0.5	74.4
FK3410C	5	32–34	5.3	13.0	53.2	116.9	43.6		45.7	18.1	0.5	71.2
FK3410D	5	42–44	5.3	9.5	53.2	105.3	30.8		46.8	16.8	0.5	81.9
FK3410E	5	52–54	5.3	9.8	53.2	111.6	43.6		53.2	15.2	0.4	96.7
FK3410F	5	98–102	5.3	10.3	53.2	105.3	30.8		52.1	16.7	0.4	93.6
FK3410G	5	158–162	5.3	12.8	53.2	103.1	45.7		55.3	15.8	0.4	79.7
FK3410H	5	218–220	5.3	9.1	53.2	101.0	29.8		47.8	15.7	0.4	86.1
1903	6	0–10	5.0	16.4	50.2	14.1	5.0	10.0	1.0	6.6	0.4	11.1
1914	6	0–10	5.1	6.7	51.1	12.3	9.2	20.4	1.0	6.3	0.4	14.3
1917	6	0–10	5.0	9.4	50.3	11.1	6.0	10.1	1.0	6.9	0.4	11.1
1925	6	0–10	5.5	10.7	54.8	75.7	19.7	11.0	24.1	14.0	0.4	58.1
1930	6	0–10	5.0	6.6	50.1	7.0	4.0	5.0	1.0	6.0	0.3	5.0
1947	6	0–10	5.0	12.6	50.1	14.0	10.0	5.0	1.0	7.1	0.4	18.0
1958	6	0–10	5.0	9.8	50.4	15.1	7.1	5.0	1.0	8.8	0.4	21.2
1982	6	0–10	5.4	9.8	53.8	67.8	24.8	43.0	24.8	14.1	0.5	49.5
1983	6	0–10	5.1	8.5	50.8	52.8	15.2	30.5	12.2	11.4	0.4	40.6
1995	6	0–10	5.2	9.3	52.0	109.2	36.4	31.2	80.0	15.8	0.5	82.1
1997	6	0–10	5.7	21.8	57.2	74.3	27.5	22.9	33.2	16.4	0.6	78.9
2000	6	0–10	5.1	12.2	50.8	47.7	18.3	5.1	49.7	9.5	0.4	19.3
2007	6	0–10	5.1	8.8	50.5	46.5	16.2	5.1	12.1	10.9	0.5	34.3
Number of samples			73	73	73	73	73	65	73	73	73	73

Sample ID	Group	Depth, cm	Fe	Al	Ca	S	Mn	% Mud (<60 µm)	% OM
FR-EB1-0	1	0–5	21 275	32 147	5 556	110	369	1.3	1.34
FR2	1	0–10	82 986	106 096	11 649	156	833		5.51
FR6	1	0–10	21 612	33 804	4 079	107	271		1.58
FR9	1	0–10	80 109	103 870	11 354	178	891		5.40
FR10	1	0–10	70 074	91 516	10 229	170	849		5.1
FR11	1	0–10	28 275	40 672	4 655	109	340		2.09
FR12	1	0–10	74 006	96 338	10 663	175	896		5.18
F1	1	0–10	53 526	100 096	7 371	430	723	84.9	
F2	1	0–10	60 173	108 138	7 353	249	911	85.6	
F3	1	0–10	59 598	109 684	6 622	491	908	95.1	
EPA1	2	0–10	42 576	79 753	11 052	5 067	442		2.58
EPA7	2	0–10	55 198	92 042	3 548	3 088	762		3.26
EPA19	2	0–10	31 904	62 625	14 635	2 018	694		1.82
EPA23	2	0–10	58 979	89 647	7 461	1 275	740		3.67
EPA25	2	0–10	37 767	71 663	12 314	2 626	975		2.74
EPA30	2	0–10	48 092	84 637	6 928	1 683	2 217		3.54
EPA31	2	0–10	45 527	73 021	5 815	1 072	765		2.86
EPA34	2	0–10	55 810	92 280	5 861	779	1 926		3.80
EPA36	2	0–10	73 330	101 033	8489	665	1 023		4.75
EPA42	2	0–10	65 597	97 440	8 079	736	1 175		4.55
E1	2	0–10	54 861	104 128	6 033	2 811	879	99.5	
E2	2	0–10	45 579	86 884	8 146	4 257	989	63.0	
E3	2	0–10	43 413	80 289	9 864	2 475	1 257	46.1	
E4	2	0–10	42 959	80 194	9 028	2 495	1 456	74.0	
E5	2	0–10	51 679	95 854	5 703	2 566	1 106	95.5	
E6	2	0–10	53 635	100 394	4 340	1 267	576	79.5	
N1	3	0–10	43 179	83 050	16 133	4 193	435	40.7	
N2	3	0–10	45 613	86 331	14 737	5 189	349	67.0	
N3	3	0–10	45 412	86 881	14 043	3 575	347	83.8	

Sample ID	Group	Depth, cm	Fe	Al	Ca	S	Mn	% Mud (<60 µm)	% OM
K1	4	0–3	33 534	68 226	33 504	3 636	547	43.6	1.83
K2	4	3–6	34 723	73 022	33 816	3 390	504	63.6	1.97
K3	4	6–9	36 196	73 093	34 961	3 902	551	70.9	1.80
K4	4	9–12	35 628	69 945	33 165	4 192	526	64.2	2.27
K5	4	12–15	35 182	71 666	29 382	3 659	446	90.7	1.83
K6	4	15–18	33 342	67 081	40 326	4 216	520	55.7	1.98
K7	4	18–21	31 870	66 728	38 182	3 502	454	62.0	1.83
K11	4	29.5–32.5	38 336	75 898	36 523	4 414	561	69.1	2.14
K15b	4	41.5–44.5	41 334	82 164	24 507	2 766	532	65.9	2.07
KB40	4	51–55	29 003	57 098	55 228	3 112	660	27.2	1.61
KB30	4	61–64	49 759	94 217	11 791	3 361	669	79.0	2.42
KB21	4	70–73	13 990	34 463	25 474	1 549	818	43.7	1.14
KB12	4	79–82	39 138	76 336	8 345	3 841	519	87.2	1.57
KB3	4	88–91	30 344	62 445	28 117	4 177	573	64.0	1.77
K18	4	100–103	25 685	53 958	13 111	2 798	524	58.9	2.92
K24	4	118–121	20 730	42 823	24 052	3 635	458	37.9	2.72
K30	4	138–141	25 278	43 175	17 861	2 857	590	24.3	1.30
K37	4	160–163	24 068	41 942	42 169	2 824	749	31.7	1.69
K43	4	179.5–182.5	46 796	82 384	12 734	4 127	686	92.8	2.27
KB204	4	200–204	38 880	78 017	14 659	4 128	431	87.1	1.94
KB224	4	220–224	41 714	77 001	14 803	3 776	580	72.4	2.21
KB243	4	240–243	31 275	60 407	20 904	3 508	514	70.8	1.65
KB260	4	255–260	42 096	81 996	11 799	4 013	599	85.9	1.66
FK3410A	5	0–2	54 388	92 596	7 735	3 495	338	59.8	
FK3410B	5	22–24	50 394	89 355	6 269	3 810	338	69.9	
FK3410C	5	32–34	53 295	91 161	9 855	2 461	387	64.6	
FK3410D	5	42–44	52 023	93 749	5 835	2 899	552	80.9	
FK3410E	5	52–54	56 262	100 928	5 190	3 717	782	99.2	
FK3410F	5	98–102	52 172	101 238	3 769	1 792	659	99.5	
FK3410G	5	158–162	49 056	90 699	7 173	2 925	642	97.0	
FK3410H	5	218–220	51 822	93 063	6 025	1 737	790	98.6	
1903	6	0–10	12 589	20 960	29 849	455	374		0.71
1914	6	0–10	11 267	17 943	42 179	589	269		0.95
1917	6	0–10	10 021	19 902	42 061	625	242		0.75
1925	6	0–10	35 995	67 758	32 884	2 253	340		3.53
1930	6	0–10	6 608	15 610	30 597	417	178		0.41
1947	6	0–10	14 240	21 305	20 339	381	489		0.53
1858	6	0–10	15 189	34 073	41 407	646	453		1.04
1982	6	0–10	33 354	68 108	33 550	1 784	383		2.49
1983	6	0–10	26 719	50 360	40 517	1 054	338		2.13
1995	6	0–10	48 322	88 497	5 319	2 960	507		4.52
1997	6	0–10	45 874	85 026	10 521	3 408	461		3.00
2000	6	0–10	17 231	38 855	92 101	1 386	621		1.36
2007	6	0–10	23 310	44 257	30 201	890	243		1.33
Number of Samples			73	73	73	73	73	44	53