



**Cooperative Research Centre for Coastal Zone, Estuary & Waterway Management**

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# **Metal and polycyclic aromatic hydrocarbon contaminants in benthic sediments of Port Curtis**

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Helen Morrison**

**June 2006**



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**June 2006**

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Cooperative Research Centre for Coastal Zone, Estuary and Waterway Management

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## Terms and acronyms used

<b>Al</b>	Aluminium
<b>Anthropogenic activities</b>	Any activities involving humans (as opposed to natural events)
<b>ANZECC</b>	Australian and New Zealand Environment and Conservation Council
<b>ARMCANZ</b>	Agriculture and Resource Management Council of Australia and New Zealand
<b>As</b>	Arsenic
<b>ASE</b>	Accelerated solvent extraction
<b>ASS</b>	Acid sulfate soils
<b>Ca</b>	Calcium
<b>Cd</b>	Cadmium
<b>Cu</b>	Copper
<b>Cr</b>	Chromium
<b>CRC</b>	Cooperative Research Centre
<b>CV-AAS</b>	Cold-vapour atomic absorption spectroscopy
<b>Detection limit</b>	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
<b>Fe</b>	iron
<b>GC-MS</b>	Gas chromatography-mass spectroscopy
<b>Guideline</b>	Numerical concentration limit or narrative statement recommended to support and maintain a designated water use
<b>Guideline trigger</b>	The concentrations (or loads) for each water quality parameter, below levels 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
<b>Hg</b>	mercury
<b>ICP-MS</b>	Inductively-coupled plasma-mass spectroscopy
<b>ICP-OES</b>	Inductively-coupled plasma – optical emission spectroscopy
<b>ISQG</b>	Interim sediment quality guideline
<b>Limit of detection (LOD)</b>	See <i>detection limit</i>
<b>Mn</b>	Manganese
<b>MW</b>	Molecular weight
<b>NAA</b>	Neutron activation analysis

<b>NATA</b>	National Association of Testing Authorities
<b>Ni</b>	Nickel
<b>PAHs</b>	Polycyclic aromatic hydrocarbons
<b>PASS</b>	Potential acid sulfate soils
<b>Pb</b>	Lead
<b>PbIR</b>	Lead isotope ratio
<b>QA</b>	Quality assurance: The implementation of checks on the success of quality control (e.g. replicate samples, analysis of samples of known concentration)
<b>QC</b>	Quality control: The establishment and implementation of procedures to maximise the integrity of monitoring data (e.g. cleaning procedures, contamination avoidance, sample preservation methods)
<b>S</b>	Sulfur
<b>Sediment</b>	Unconsolidated mineral and organic particulate material that has settled to the bottom of aquatic environments
<b>SEE</b>	Standard error of the estimate
<b>SLRA</b>	Screening level risk assessment
<b>STP</b>	Sewage treatment plant
<b>TOC</b>	Total organic carbon
<b>Trigger value</b>	A guideline value that if exceeded triggers further investigations
<b>UCC</b>	Upper continental crust
<b>UCI</b>	Upper confidence interval
<b>Zn:</b>	Zinc

## Executive summary

Fine sediments (mud-clay) are excellent repositories of contaminants from the water column, catchment surface run-off and atmospheric deposition.

Contaminants (metals, polycyclic aromatic hydrocarbons or PAHs, etc.) may be remobilised from sediments into the water column when environmental conditions change, and hence they pose potential threats to aquatic organisms and possibly humans. Estuarine and marine sediments serve as sinks for various contaminants transported from the land (catchment).

Metals may come from natural sources such as the continental crust/coastal bedrock. They are also introduced into the environment by various industrial and other anthropogenic activities. PAHs are organic compounds consisting of two or more fused rings in their chemical structure. They have natural origins, such as forest fires, and are natural constituents of fossil fuels. They are also produced in many industrial and anthropogenic activities, particularly during incomplete high-temperature combustion of pyrolytic (e.g. biomass) and petrogenic sources. Metals have different toxicities to biota and humans; many PAHs are toxic to aquatic organisms and a number have potentially carcinogenic, mutagenic or teratogenic impacts on humans.

In this study, benthic sediments and sediment cores from Port Curtis were analysed for 10 metals and 17 PAHs. The concentrations were compared to the ANZECC (2000) interim sediment quality guidelines. The study confirmed that intertidal (mangrove) sediments tended to collect fine sediments, which contained higher levels of metals and PAHs than did estuarine sediments. The top 28 cm of subsurface sediments at intertidal or subtidal sites were estimated to have been deposited since 1958 in Port Curtis, which is roughly the start of the industrialisation of Gladstone. The rate of sediment deposition was at least 0.6 cm/yr. The sediment depositional zones were demonstrated to be largely at the intertidal (mangrove) sites, particularly at the northern Narrows, lower Calliope River and South Trees Inlet–Boyne River areas.

Sediment cores exhibited fairly constant metal concentrations with depth. Stable lead isotope ratios suggested generally low lead contamination in the region.

ANZECC (2000) trigger values for nickel, arsenic and chromium were exceeded in many sediment samples. Background metal levels were established using a statistical elimination procedure. Concentrations of nickel, arsenic and chromium appeared to be related to local geology and not to contamination by anthropogenic sources. Linear regression models provided prediction equations

which modelled the natural variation of metal concentrations between sites. The observed metal concentrations and predicted values correlated reasonably well for chromium, copper, nickel, lead and zinc, but only moderately for the other metals tested. Natural levels of nickel, arsenic and chromium were confirmed to be fairly close to their respective ANZECC (2000) trigger values. This is important to remember when undertaking sediment quality assessments.

PAHs from combustion or pyrolytic sources were dominant around intertidal sites along the industrial area of Gladstone, particularly at the Clinton Coal Facility, QAL–Red Mud Dam outlet, Auckland Creek, Calliope River near NRG power station and at the marina. Perylene, a naturally-occurring PAH, dominated sediments in the northern Narrows. Naphthalene levels were below 5 µg/kg, in contrast to high levels (exceeding the ANZECC guideline of 160 µg/kg) reported in 2000.

In terms of the contaminants studied Port Curtis may be considered as still a relatively low to moderately polluted estuary. It would be important to monitor changes in levels of the metal and PAH contaminants and their ecological impacts in the estuary, especially with the continuing rapid industrialisation of Gladstone and the expansion of port activities in the harbour.

# 1 Introduction

Fine sediments (mud-clay) are excellent repositories of contaminants from the water column, catchment surface run-off and atmospheric deposition. Contaminants (metals, polycyclic aromatic hydrocarbons or PAHs, etc.) may be remobilised from sediments into the water column when environmental conditions change, and hence they pose potential threats to aquatic organisms and possibly humans.

The screening level risk assessment (SLRA) of contaminants in Port Curtis (Jones, 2003; Apte *et al.*, 2005) found elevated arsenic, nickel and chromium in benthic sediments of Port Curtis. It was suspected that the observed metal enrichment could be a natural phenomenon reflecting the local geology of the region, and further studies were recommended to substantiate this possibility. The SLRA also identified the polycyclic aromatic hydrocarbon (PAH), naphthalene, in sediment as a contaminant of potential concern. This finding was based on the results of a study conducted in 2000 where elevated concentrations of naphthalene (200–501 µg/kg) were found in 5 out of 20 sediment samples from Port Curtis (WBM Oceanics Australia, 2000). The samples exceeded the ANZECC & ARM CANZ (2000) sediment guideline for naphthalene of 160 µg/kg. Other PAHs were detected only at <10–20 µg/kg.

The current study sought to determine:

- the sources of arsenic, nickel and chromium in benthic sediments;
- the concentrations of PAH contaminants, particularly naphthalene in benthic sediments; and
- the main contaminant deposition zones in Port Curtis and the deposition rates of particulate contaminants.

To assist in the determination of sediment sources, stable lead isotope ratio ( $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{208}\text{Pb}/^{206}\text{Pb}$ ) measurements on sediment samples from Port Curtis, as well as some sediments from Fitzroy catchment, were performed. Lead isotope ratios have been successfully used to provide evidence of lead sources in sediments (Munksgaard *et al.*, 2003). Sediment geochronology using Pb-210 and Cs-137 gamma spectrometry was also pursued to help estimate the age of intertidal sediments and their deposition rates.

The SLRA study (Apte *et al.*, 2005) investigated metal concentrations in estuarine surficial sediments alone. Figure 1 shows the Port Curtis estuary and the geographical zones used in the SLRA study. In this study, sediment cores,

especially from intertidal mangrove sites, were collected and analysed, as well as additional grab samples. Mangroves or intertidal sites generally trap fine sediments and hence may exhibit higher metal concentrations than estuarine benthic sediments. Sediment cores can provide evidence and history of contaminant accumulation provided they are not substantially disturbed by natural forces (e.g. mixing or bioturbation) or human activities (e.g. dredging or infrastructure and development works).

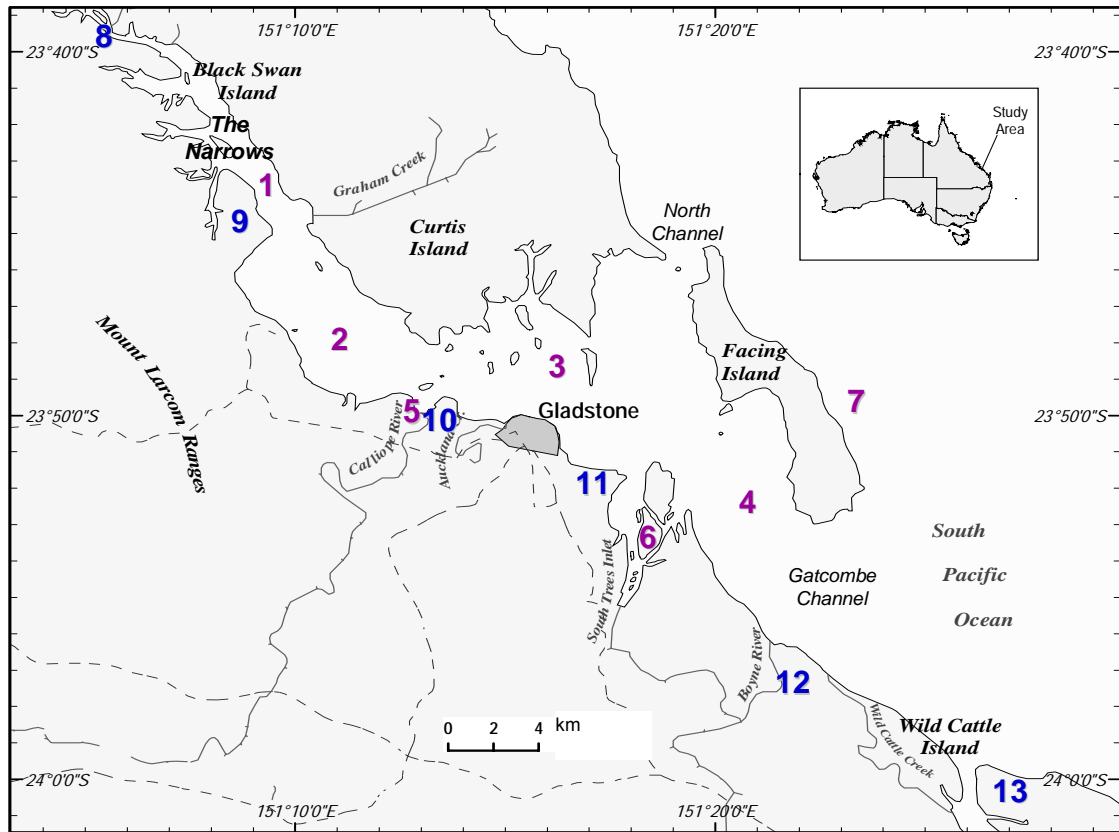
## 1.1 Description of the study area

The coastal area of Port Curtis is subject to tidal influence involving the waters of the interconnected Port Curtis and Fitzroy River estuaries and is protected from the open ocean by Curtis and Facing Islands. The area comprises a complex of inlets, channels, shoals, tidal marshes, river and stream mouths small islands and shorelines (Conaghan, 1966). The Boyne and Calliope rivers, as well Auckland Creek and several smaller creeks, drain the upper catchment and enter the estuary through its south-western coast near Gladstone Harbour. Boyne River flow, however, has been greatly altered since 1966 when the first stage of the Awoonga weir began. The original Awoonga Dam was completed in 1984 to meet the water demand of the community and industries in Gladstone, with the dam level subsequently raised by 10 metres in 2002 to meet the increasing domestic and industrial water demand (GAWB, 2005).

The Gladstone harbour is a significant port for several major exports of Queensland such as coal, magnesite, calcite and wood chips. Several industries operate in Gladstone including Queensland Alumina Limited, Boyne Smelters Limited, Orica Australia, Ticor Chemical Company Limited, Cement Australia Proprietary Limited, Queensland Energy Resources Ltd (formerly Southern Pacific Petroleum) and Comalco Alumina Refinery. The port facilities are currently undergoing expansion and new industries are being established at a very rapid pace in Gladstone.

Figure 1 shows the study area: zones 1–7 were used in the SLRA study (Apte *et al.*, 2005), while zones 8–13 are additional sites (largely mangrove or intertidal) used this study. Zone 13 is located at Rodds Harbour and may be considered as a reference site, since it is reasonably removed from the influences of the Fitzroy estuary and the industrial areas of Gladstone.

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Legend:

Zone	Name	Known major sources of chemical stressors
1	The Narrows	Horticulture
2	Targinnie section of the harbour	Oil shale, cement and cyanide industries, shipping, horticulture
3	Middle harbour	Shipping, urban run-off, downstream of other zones
4	Southern and outer harbour	Alumina industries, shipping, urban run-off
5	Calliope River	Catchment run-off, STP, urban run-off, power station
6	Boyne River and South Trees Inlet	Catchment run-off, STP, urban run-off, alumina industries
7	Eastern side of Facing Island	Control site
8-12	Largely mangrove sites	Various
13	Rodds Harbour	Reference mangrove site

Figure 1. Geographical zones of the Port Curtis Estuary and known major sources of chemical stressors (adapted from Apte *et al.*, 2005)

### 1.1.1 Physiography and hydrodynamics of Gladstone harbour

The physiography and hydrodynamics of the Gladstone harbour is complex and may be divided into three broad areas (Conaghan, 1966):

- *North-eastern shoals*—including the intertidal flats, mangrove swamps, salt pans, tidal creeks and marshes at the northern and eastern shores. This area includes Pelican Banks, Shoal Bay and the large intertidal area of the south coast of Curtis Island
- *Central channels and banks*—this zone is separated from the north-eastern shoal by the North Channel. The shipping channel (Gatcombe Channel) and its north-western extension towards The Narrows separate the zone from the south-western shoals. The physiography and bathymetry of this zone is the most complex of the three. It is characterised by deep tidal channels, numerous small islands, submerged areas of rocks and large sandbanks. Deep scour pits commonly occur in the confined parts of the channel.
- *South-western shoals*—this zone occurs along the mainland coastline. It exhibits intertidal elements similar to those found on the north-eastern shoals. Sandflats and mudflats occur between low and high tides. Mean high tide level is characterised by a prodigious growth of mangrove trees.

Port Curtis is a macrotidal estuary with tides up to 4 m (Conaghan, 1966). Tidal waters approaching Port Curtis through the southern channel are deflected into the estuary and enter the harbour from the south-south-east. Within the harbour, in the zone of the central channels and banks, a further deflection to the north-west occurs, reaching the south-west corner of Curtis Island. A north-north-west flow is maintained within the channel of The Narrows. Flood tide setting southward from the Fitzroy River estuary at Keppel Bay meets the northward flowing Port Curtis flood at the tidal watershed of The Narrows (Conaghan, 1966).

The hydrodynamics of the Port Curtis region was modelled by Herzfeld *et al.* (2004); however, the region at The Narrows where the Fitzroy River waters and Port Curtis waters meet was apparently not included. The model showed that currents in the estuary were predominantly due to the effects of the tide. The large tides mixed the water vertically so that any dissolved material would show little variation from the surface to the bottom. The flow regime within the estuary allowed dissolved material to be dispersed evenly throughout the estuary; however, material appeared to have difficulty leaving the estuary into the offshore environment.

### 1.1.2 Regional geology

Holmes (1984) and Kirkegaard *et al.* (1970) have described the geological units in the Gladstone 1:100 000 sheet area and are briefly summarised here. The Quaternary/Holocene (Cainozoic) age formations include sand dunes, estuarine deposits and beach ridges. The main rock types found are fill material, fine-grained quartz sand, shelly sand and mud. The Tertiary age formations include The Narrows beds consisting of claystone, oil shale and shale, calcrete and minor sandstone. There are intrusions of dolerite and diorite and volcanics consisting of olivine basalt and diorite. The Paleozoic age formations include: the Berserker beds, which consist of crystal and lithic tuff, lithic arenite, acid flows and mudstone; the Curtis Island group—Shoalwater, Wandilla and Doonside formations—consisting of quartz greywacke, mudstone, chert, arenite, limestone and minor basic volcanics; and the Calliope beds, which contain mainly volcanics and some coarse-grained feldspathic arenite, minor mudstone and a few lenses of limestone.

Conaghan (1966) described the basement of Port Curtis as consisting of Lower Paleozoic low grade metasediments (indurated argillites, arenites, cherts and jaspers), with the occasional occurrence of intrusive volcanic rocks. Extensive areas of Cainozoic sediments (gravels, sands and clays) also occur in some areas of lower relief. Rocks of Upper Paleozoic age—comprising greywacke, limestone, argillites and basic and intermediate volcanics—occur west of the coast-range in the catchment areas of the Boyne and Calliope rivers. These formations constitute the continental crust/coastal bedrock, which provide the natural geochemical characteristics of Port Curtis sediments.

### 1.1.3 Mineral resources

There are several mineral resources within Port Curtis catchment and the Central Queensland region in general which have been explored in the past, with some still ongoing and new ones being started. These workings result in erosion of disturbed land which contributes to siltation of rivers and estuaries, bringing metal-enriched sediments. The main resource areas of the coastal Central Queensland region as described above include important deposits of magnesite, limestone, salt, oil shale, nickel and cobalt, chrysophase, quarry rock and construction sand. Gold and manganese have been worked in the Targinnie area but do not have any significant economic importance (Holmes, 1984).

Numerous small deposits of chromite in the Rockhampton–Port Clinton areas (particularly Tungamull) were worked since 1907 but the average grade was only

about 28% chromic oxide, which is not high enough to make the deposit commercial (Kirkegaard *et al.*, 1970). The nickeliferous laterite on the ultramafic rocks has been explored since late 1960s (Kirkegaard *et al.*, 1970). There are continuing nickel explorations in Canoona–Marlborough, north of Rockhampton in the upper Fitzroy River catchment. Further north, high nickel values are associated with supratidal flats and coastal grasslands cracking clay in Broadsound, with a well defined nickel anomaly to the west of Herbert Creek with values up to 600 ppm in soils (Cook & Mayo, 1980). However this site is quite removed from Port Curtis and may not have any significant impact on Port Curtis. Arsenic anomalies have been reported in reefs in the Targinnie Field (Archer and Old Scottish) and Targinnie Creek. Arsenic in stream sediments showed strong association with the historical gold workings at Targinnie (Archer Reefs) and Targinnie Scottish (Pope, 1994).

Organic mineral resources include important coal deposits at Blackwater, Moura, Baralaba and in the Peak Downs area. Immense coal reserves occur in the Bowen Basin (Stevens, 1984; Day *et al.*, 1983). The Narrows beds consist dominantly of shale and oil shale, and minor argillaceous sandstone (Kirkegaard *et al.*, 1970). A typical oil shale consists dominantly of finely divided clay minerals but also contains elongated irregularly shaped reddish-brown organic masses derived from the decay of vascular plant tissues which form about 20% of the rock. Deposits of oil shale were proved at Rundle and Stuart (Holmes, 1984). Oil shale explorations began in 1973 and pilot scale production by Southern Pacific Petroleum (now Queensland Energy Resources Ltd) commenced in the late 1990s. These activities could be potential sources of polycyclic aromatic hydrocarbons (PAHs) in the Port Curtis estuary. PAHs are organic compounds with at least two fused benzene rings, which are toxic to many aquatic organisms; higher molecular weight PAHs are particularly of concern because they are potential carcinogens, mutagens and/or teratogens in humans (see Appendix 5).

#### 1.1.4 Acid sulfate soils

Ross (2002) reported a survey of acid sulfate soils (ASS) in the Central Queensland coast, from Tannum Sands to St Lawrence. ASS are soils containing sulfides or acid-producing soil layer resulting from the oxidation of sulfides. When exposed to air, sulfides are oxidised, producing sulfuric acid. Disturbed or excavated acid sulfate land can also release iron, aluminium, and other heavy metals into drainage waters and affect aquatic plants and animals. Ross (2002) found high occurrence of these soils on the coastal plain along the Curtis and Capricorn coasts, near Shoalwater Bay and Broadsound. The semi-tropical/

tropical climate combined with the high tides apparently favour the formation of ASS or potential ASS (PASS). Very high levels of oxidisable sulfur of up to 6.1% were recorded on supratidal flats or salt pans, while levels of up to 5.1% were recorded for intertidal flats or mangrove mudflats. Very high levels of sulfur at shallow depth were associated with the mangrove genus *Rhizophora*, which is quite dominant in Port Curtis (Houston, 1999).

## 1.2 Potential sources of metals and polycyclic aromatic hydrocarbons

### 1.2.1 Natural sources

The international literature identifies several natural and anthropogenic sources of metals and polycyclic aromatic hydrocarbons (PAHs).

Natural and diffuse sources of metal contaminants include rock formations which undergo weathering, assisted by semi-tropical humid climatic conditions and high tidal action (such as found in the Central Queensland coast). These natural processes are continuous but may be heightened by episodic storm events. PAHs on the other hand are known to enter the atmosphere and the aquatic environment from forest fires and volcanic activity (Kennish, 1997; Connell, 1997).

As mentioned above, acid sulfate soils could generate acidity and cause leaching of metals from rocks, soils and contaminated sediments. Illustrative data from a few sites located near the coastal areas of concern in this study are summarised in Table 1.

**Table 1. Acid sulfate soils in Port Curtis region** (Source: Ross, 2002)

Location	Depth (m)	Landform	Acid sulfate hazard*
South Trees Inlet	0.2–0.3	Intertidal flat	Very high to extreme
Tannum	0.4–0.5	Tidal flat	Very high
Calliope River	0.4–0.5	Supratidal flat	Extreme
Fisherman's Landing	0.5–0.6	Intertidal flat	Extreme
Kangaroo Island	0.3–0.4	Intertidal flat	Extreme
Wiggins Island	0.3–0.5	Intertidal flat	Extreme
Curtis Island	0.5–0.7	Supratidal flat	Very high

\* For this survey area only: Very high: Peroxide oxidisable sulfur content ( $S_{POS}$ ) >0.9%, total potential acidity (TPA) = 600–1000 mol  $H^+$  per tonne of soil; Extreme:  $S_{POS}$  >1.5%, TPA >1000 mol  $H^+$  per tonne of soil.

### 1.2.2 Anthropogenic sources

Metals are released into the environment in many industrial operations such as mining, metal production and refining, power generation and manufacturing. Similarly, PAHs are produced by coal-fired electricity power plants, incinerators, open burning and motor vehicle emissions. The industrial city of Gladstone produces significant emissions (air, land and water) from fossil fuel electricity production, coal and ash handling and storage (see Table 2) which include both types of contaminants. Diffuse sources of metals and PAHs reportedly also include sewage treatment plant discharges and run-off, especially during storm events (Kennish, 1997).

The continuing port development and expansion of Gladstone harbour has seen the loss of large mangrove areas due to both port reclamation and natural infilling of coastal wetland areas (Duke *et al.*, 2003). Mangroves have significant ecological roles; as well, they can trap fine sediments and hence act as natural filters of the estuary. The Gladstone Harbour's shipping channel is dredged periodically (about every 2–3 years), to restore the channel depth to safe levels for ships which use the port daily. There are also two spoil grounds in Port Curtis located east and south-east of Facing Island, with the latter no longer in use. The most recent dredging occurred in early 2002 and dredged materials were pumped into the Port Authority's port development site near the Clinton Coal Facility. Dredging can expose metal sulfides to air, causing their oxidation and the release of metals and acidity into the water column (Kennish, 1997), similar to what occurs in acid mine drainage.

Central Queensland also has a substantial cattle industry. Arsenic compounds (e.g. arsenic trioxide), together with other organochlorine or organophosphorus pesticides, have been used in cattle dips to control ticks. Other consumer products containing arsenic include fungicides, weed killers, preserved wood and wood treatment products. These represent potential diffuse sources of arsenic; for example, amended soil from an ex-cattle dip site in Stanwell in the lower Fitzroy catchment was still found to contain 229–354 mg/kg arsenic (S. Hanggi, N. Aswath and V. Vicente-Beckett, unpublished data).

PAHs generally enter the air, and are produced through incomplete burning of organic substances such as coal, oil and gas, garbage and other substances like tobacco or charbroiled meat. They can be produced by forest fires caused by humans, coal-fired electricity power plants, petrol and diesel combustion engines, incineration and burning of wood and coal. PAHs can attach to dust particles in the air. They can enter water through discharges from industrial and wastewater

treatment plants (ATSDR, 1996). They can also enter the aquatic environment as a result of oil spills from tankers, refineries or offshore drilling sites, as well as from run-off. PAHs (except naphthalene) have limited solubility in water, hence they are readily taken up by solid particles such as sediments (Kennish, 1997; Connell, 1997).

The coal facility in the Gladstone harbour area handles coal for export and is one of the largest coal facilities in Australia. There are anecdotal accounts that coal dusts are observed by local residents to be blown intermittently from the coal stockpiles into Port Curtis waters and other parts inland, even affecting some residential houses in Gladstone.

Significant concentrations of PAHs and hydrocarbon have been reported elsewhere in soil, beneath asphalt cover at sites which had not received any significant inputs from internal combustion vehicles, suggesting the contaminants may have originated through leaching from the asphalt surface (Sadler *et al.*, 1999). Run-off may carry these leachates (especially low molecular weight PAHs such as naphthalene) into waterways. Car exhausts, rubber tires and the asphalt material itself are all probable emission sources (Norin & Strömvall, 2004).

The SLRA study (Jones 2003; Apte *et al.*, 2005) developed conceptual models of sources (both point and diffuse) and stressors in the three major areas of Port Curtis estuary: the Fisherman's Landing section, Auckland Creek and Calliope River section, and the Boyne River and South Trees Inlet section. The contaminants of interest in the present study and the possible sources (mostly diffuse) within the Port Curtis–Gladstone area are summarised in Appendix 1.

The total emissions (air, land and water) reported to the National Pollutant Inventory (NPI) for the Gladstone area (postcode 4680) for 2003–2004 are summarised in Table 2. The main sources appear to be basic non-ferrous metal manufacturing and electricity supply. Particulate emissions are very high and the contaminant levels in particulate matter are of interest. Untrapped (fugitive) fine particulate emissions can provide active surface sites for adsorption of PAHs and other volatile air contaminants, which can eventually enter the atmosphere and waterways.

**Table 2. Total emissions in the Gladstone area** (source: NPI, 2004)

<b>Substance</b>	<b>Total emission (kg/year)</b>
Antimony and compounds	0.79
Arsenic and compounds	340
Cadmium and compounds	19
Chromium (III and VI) compounds	411
Copper and compounds	340
Lead and compounds	160
Mercury and compounds	230
Nickel and compounds	370
Zinc and compounds	1 100
Polycyclic aromatic hydrocarbons	30 000
Particulate matter (10.0 µm)	2 700 000

This study considered measuring atmospheric particulates but abandoned the idea due to constraints in time and resources. To date, there is no known documented contaminant data on atmospheric particulate emissions within the region. Industries in the area that monitor their atmospheric emissions measure only the quantities of particulate emissions and do not undertake analyses of the particulates for presence of metals or PAH contaminants. Some idea of the contribution of airborne contaminants to sediment load may be obtained from a recent study which found that the fraction of metal contaminants in lake sediments attributed to atmospheric fallout into Lake Moondarra in western Queensland was found to be <2% (Biffra, 2005).

## 2 Methods

### 2.1 Sampling

Benthic sediment samples were collected using a Van Veen grab sampler, which is designed for the collection of fine sediments from soft-bottomed locations (Mudroch & Azcue, 1995). The samples were kept frozen until analysis. Sediment cores were collected using 50 mm id x1 m PVC pipes. They were pushed manually through intertidal or subtidal sediment beds. The sediment cores were extruded from the pipes and sliced into two 1 cm slices from the top of the core, followed by 2 cm slices for the next 8 cm, then 4 cm slices until the end of the core. The slices were kept frozen until analysis.

The list of samples (see Appendix 2) for this study included 28 sediment grab samples and 31 push cores (depths varying between 14 and 45 cm). Archived benthic sediments from the SLRA surveys (2001-2002; Apte *et al.*, 2005) were also included in measurements of stable lead isotope ratios.

### 2.2 Analysis of metals and stable lead isotopes in sediments

Frozen sediment samples were thawed at room temperature shortly before analysis. Particle size distribution was determined gravimetrically on oven-dried (at 40°C) fractions following wet-sieving through a 1 mm or 60 µm nylon sieve.

Dried sediments of particles  $\leq 1$  mm in size were subjected to hot multi-acid digestion and analysed for total metals using ICP-OES (Cu, Ni, Zn, Al, Ca, S) or ICP-MS (Ag, Cd, Pb), CV-AAS (Hg) and NAA (As, Cr, Fe and Sb). The ICP-OES and ICP-MS analyses were performed by NATA-accredited laboratory, Genalysis Laboratory Services (Gosnells, Western Australia), while NAA were done by Becquerel Laboratories (Lucas Heights, NSW). PACS-2 and BCSS-1 (both from National Research Council Canada, Ottawa) were marine sediment reference materials used in the analysis of trace metals. Spiked recoveries were 87–107% for most metals in identified quality control samples, except in the case of chromium using ICP-MS (see Appendix 3).

For the analysis of stable Pb isotope ratios (PbIRs), sediments  $< 60$  µm size were digested in 1 mL concentrated nitric acid + 4 mL concentrated perchloric acid in an open tube block digester at 200°C for 6 h. PbIRs were analysed as  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  calibrated to NIST standard reference material 981 (common lead); the digests were also used to determine pseudo-total analyses of other

metals using ICP-MS. Experimental procedures used were similar to those given in Munksgaard *et al.* (2003), and were carried out at the Environmental Analytical Chemistry Unit, School of Science, Charles Darwin University in Darwin.

Appendix 3 provides quality assurance (QA) data for the analytical methods used.

## 2.3 Sediment geochronology

Sediment cores were sliced into 2 cm slices and dried at 40°C. Unfractionated bulk dry sediment from each depth section was ground in a ring mill and a known weight (50–150g, depending on density of particles) was pressed into a sealed container of known geometry. Sediment core samples were analysed for  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$  and  $^{137}\text{Cs}$  by gamma-ray spectrometry using the methods of Murray *et al.* (1987).  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  were determined from their direct decay lines, whereas  $^{226}\text{Ra}$  was determined from its daughter products after allowing 3 weeks for ingrowth of  $^{222}\text{Rn}$ . Measurements were performed in the laboratories of CSIRO Land and Water in Canberra.

The fundamentals of  $^{210}\text{Pb}$  geochronology are described in Robbins (1978). Briefly,  $^{210}\text{Pb}$  is continually deposited from the atmosphere in association with rainfall and dust, and is seen as 'excess'  $^{210}\text{Pb}$  in surface soils and sediments; the excess component being determined by the difference between the activities  $^{210}\text{Pb}$  and  $^{226}\text{Ra}$  in the soil/sediment. In water bodies, the accumulation of sediment laden with excess  $^{210}\text{Pb}$  results in high activities at the sediment surface, decreasing with depth. The rate of decrease is determined by the rate of sediment accumulation and the radioactive half-life of  $^{210}\text{Pb}$  (22.3 years). Under favourable conditions the decay profile of excess  $^{210}\text{Pb}$  can be modelled to provide estimates of sediment accumulation and sediment age over a time frame corresponding to 4–5  $^{210}\text{Pb}$  half-lives (90–110 years).

In the absence of an interpretable  $^{210}\text{Pb}$  profile, or where corroboration of modelled  $^{210}\text{Pb}$  ages is required, the  $^{137}\text{Cs}$  activity profile is often utilised.  $^{137}\text{Cs}$  is a man-made (anthropogenic) nuclide originating from atmospheric nuclear weapons testing in the mid-1950s to early 1970s. In the Australian landscape the presence of measurable  $^{137}\text{Cs}$  in the sediment profile dates that sediment horizon as being post ~1958 (Olley *et al.*, 1990).

## 2.4 Analyses of 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 spectroscopy (GC-MS) for PAHs, using either a DB5 or HT8 column.

Each batch of samples included a solvent blank and a sample spiked with a mixture of PAHs. All samples and 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.

All sample preparations and analyses were performed by the NATA-accredited analytical laboratories of the Queensland Health & Pathology Scientific Services in Brisbane.

## 2.5 Total organic carbon in sediments

Sediments were prepared according to the Standards Australia method AS4479. Sediments <2.00 mm fraction were ground to fine powder in a TEMA swing mill (Fe/Cr or zirconia). An accurately weighed portion of the sample was pretreated 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.

The analyses were performed by the analytical laboratories of the Queensland Health & Pathology Scientific Services in Brisbane.



## 3 Results and discussion

### 3.1 Metals in surficial sediments and sediment cores

The SLRA study (Apte *et al.*, 2005) investigated metal levels in estuarine surficial sediments in Port Curtis, whereas this study looked at sediment cores, especially from intertidal mangrove sites. Mangroves or intertidal sites generally trap fine sediments and hence may exhibit higher metal concentrations than subtidal or estuarine benthic sediments. Sediment cores can provide evidence and history of contaminant accumulation provided they are not disturbed by natural forces (such as mixing or bioturbation) or human activities (e.g. dredging, port infrastructure and other development works).

The study obtained several push cores from mangrove sites around the Port Curtis area, with the majority taken from the Gladstone side of the port. Details about the sediment cores and other grab samples are given in Appendix 2. The analyses of the core slices are summarised in Table 3, together with the mean data for surficial sediments from the main estuary obtained during the SLRA surveys (Apte *et al.*, 2005). Zones 1–7 represent sections of the estuary, as designated in the two SLRA surveys (see Figure 1). New zone designations in Table 3 are zones 8–13 which include additional sites largely at mangrove sites, plus a few subtidal/estuarine sites from Boyne River and one site at Awoonga Dam (upstream Boyne River). The concentration of other elements (Fe, Al, Ca, S) and sediment parameters (mud fraction or sub-60 µm particles, % organic matter) are also included in the table. Altogether, 245 samples (sediment grabs and core slices) were analysed, although the analyses for some metals and other sediment parameters were not completed for some samples due to limited time or funds. The full dataset are given in Appendix 4. Because of the varying number of samples or core slices, the standard error of the mean is presented in Table 3.

Table 3 shows the wide range of metal concentrations and other parameters obtained at each zone. Notably, Ag and to a lesser degree Cd showed several high readings, with the highest registered by the freshwater grab sample from Awoonga Dam, although the levels were still below ANZECC ISQG-low criteria (trigger values). Ni, As and Cr exceeded the ANZECC trigger values in 91, 63 and 39 samples (grabs or core slices), respectively.

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**Table 3. Metal concentrations ( $\mu\text{g}/\text{kg}$ , dry weight for Ag, Cd and Hg;  $\text{mg}/\text{kg}$  d w for all others ) in Port Curtis sediments.**

Zone	Sample Description	Total no. samples		Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn
1	grabs; subtidal	10	mean	<b>69</b>	<b>20.3</b>	<b>52.7</b>	<b>59.7</b>	<b>24.6</b>	<b>16.7</b>	<b>20.2</b>	<b>11.7</b>	<b>0.672</b>	<b>63.0</b>
			std. error	8.0	2.8	0.5	7.4	3.3	3.6	2.9	1.1	0.060	8.3
			min	51	6.0	50.5	22.0	8.4	2.1	7.0	5.8	0.380	19.5
			max	108	38.0	55.0	85.0	36.0	31.2	35.0	15.5	1.09	99.0
2	grabs; subtidal	15	mean	<b>98</b>	<b>14.7</b>	<b>52.2</b>	<b>54.2</b>	<b>21.5</b>	<b>19.4</b>	<b>17.3</b>	<b>11.7</b>	<b>0.579</b>	<b>62.6</b>
			std. error	16	0.9	0.3	4.1	2.7	3.4	2.3	0.66	0.025	6.4
			min	50	6.0	50.0	26.0	5.0	4.0	6.0	6.0	0.430	23.0
			max	215	21.0	53.7	74.0	35.0	55.3	32.0	15.0	0.750	98.9
3	grabs; subtidal	15	mean	<b>91</b>	<b>15.7</b>	<b>51.3</b>	<b>42.3</b>	<b>14.7</b>	<b>9.1</b>	<b>12.1</b>	<b>9.2</b>	<b>0.484</b>	<b>46.5</b>
			std. error	29	2.0	0.2	4.3	1.9	1.7	1.3	0.68	0.040	4.2
			min	50	5.0	50.4	16.0	4.0	1.7	4.0	3.0	0.200	19.0
			max	496	33.0	53.5	69.0	31.4	23.4	23.0	12.3	0.760	74.8
4	grabs; subtidal	27	mean	<b>53</b>	<b>20.9</b>	<b>51.1</b>	<b>40.3</b>	<b>12.7</b>	<b>5.4</b>	<b>10.6</b>	<b>10.0</b>	<b>0.479</b>	<b>39.7</b>
			std. error	1.9	4.1	0.2	4.1	1.9	0.66	1.0	0.64	0.033	4.4
			min	50	5.0	50.0	8.0	3.3	1.6	4.0	5.7	0.200	13.0
			max	101	122.0	54.0	73.0	35.0	12.9	20.0	18.0	1.030	95.0
5	grabs; subtidal	14	mean	<b>92</b>	<b>16.5</b>	<b>52.9</b>	<b>58.6</b>	<b>27.7</b>	<b>18.3</b>	<b>19.3</b>	<b>13.0</b>	<b>0.603</b>	<b>71.3</b>
			std. error	31	1.6	0.4	5.6	3.6	3.2	2.3	0.90	0.038	7.7
			min	50	5.0	50.2	13.0	7.4	1.7	5.0	6.7	0.320	20.4
			max	493	24.0	55.0	80.0	45.2	38.2	32.0	19.0	0.820	113.0
6	grabs; subtidal	11	mean	<b>66</b>	<b>17.6</b>	<b>73.7</b>	<b>45.6</b>	<b>16.7</b>	<b>12.9</b>	<b>14.2</b>	<b>11.1</b>	<b>0.465</b>	<b>48.4</b>
			std. error	7.4	2.3	17.1	6.3	3.6	3.0	2.7	1.2	0.050	7.5
			min	50	6.0	50.2	8.0	2.7	0.90	2.0	3.7	0.100	8.4
			max	107	36.0	236.0	77.0	36.0	25.4	27.0	16.8	0.600	81.2
7	grabs; subtidal	8	mean	<b>51</b>	<b>18.6</b>	<b>51.3</b>	<b>63.5</b>	<b>13.1</b>	<b>1.7</b>	<b>10.6</b>	<b>10.0</b>	<b>0.489</b>	<b>41.1</b>
			std. error	0.73	2.6	0.7	28.5	5.2	0.24	3.0	1.9	0.088	13.5
			min	50	10.0	50.0	5.0	1.0	0.90	2.0	3.0	0.100	6.4
			max	55	31.0	55.0	250.0	43.0	2.9	26.0	18.0	0.770	113.0
8	Narrows; intertidal	50	mean	<b>82.9</b>	<b>21.3</b>	<b>59.3</b>	<b>79.7</b>	<b>30.3</b>	<b>40.6 (n=47)</b>	<b>38.4 (n=45)</b>	<b>17.7</b>	<b>0.631 (n=47)</b>	<b>69.8 (n=44)</b>
			std. error	15.1	0.6	3.9	1.9	0.7	1.2	1.0	0.3	0.012	1.1
			min	51.0	8.7	51.0	36.1	17.3	30.0	7.0	11.4	0.430	45.3
			max	618.0	30.7	216.0	90.5	40.7	70.0	50.9	22.6	0.750	84.1
9	Targinnie Ck, Graham Creek, BS,SB, BC intertidal	14	mean	<b>226.6</b>	<b>19.5</b>	<b>61.0</b>	<b>38.6</b>	<b>31.2</b>	<i>nd</i>	<b>27.1</b>	<b>13.7</b>	<i>nd</i>	<b>83.5</b>
			std. error	44.7	1.5	13.8	2.8	0.7		1.2	0.3		2.3
			min	50.0	12.6	22.0	28.2	25.4		20.3	10.8		67.0
			max	526.0	34.8	226.0	58.5	36.3		40.3	15.6		104.0

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Table 3. (continued)

Zone	Sample Description	No. of samples		Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn		
10	Calliope River-CCF-Marina-AC; intertidal or subtidal	31	mean	226.2	11.9	43.0	30.3	35.7	nd	21.2	11.6	nd	80.3		
			std. error	25.8	0.5	3.3	1.7	1.2		0.6	0.3		2.1		
			min	50.0	6.4	25.0	14.4	27.9		15.7	7.0		49.5		
			max	544.0	20.0	117.0	49.4	54.2		28.4	14.6		108.0		
11	QAL/RMDO- Spillway Creek; intertidal	9	mean	164.7	12.1	31.1	36.8	17.5	nd	14.0	9.2	nd	57.7		
			std. error	41.0	1.3	5.2	2.3	0.8		1.2	0.5		5.0		
			min	50.0	7.9	22.0	29.2	14.4		9.8	7.5		43.3		
			max	343.0	18.2	72.0	48.2	22.4		19.5	11.6		92.6		
12	Boyne River (subtidal); Awoonga Dam - freshwater	6	mean	165.7	11.9	31.9	43.1	14.9	nd	11.8	9.9	nd	43.4		
			std. error	115.7	1.2	6.9	7.3	2.8		1.2	1.3		5.2		
			min	50.0	8.0	25.0	20.4	8.2		8.2	5.8		30.3		
			max	744.0	15.0	66.2	67.1	27.1		16.6	15.0		64.4		
13	Rodds Harbour; intertidal	35	mean	51.0	13.2	52.5	50.4	13.9	26.0	13.0 (n=33)	10.7	0.463	38.0 (n=34)		
			std. error	0.1	0.5	1.5	1.8	0.6	1.1	0.4	0.3	0.015	1.2		
			min	50.0	9.0	50.0	39.6	8.1	20.0	9.1	7.0	0.310	24.2		
			max	54.0	23.3	104.0	84.7	22.4	40.0	21.9	14.1	0.640	67.4		
			<b>Total samples</b>	<b>245</b>	mean	<b>106.0</b>	<b>16.9</b>	<b>52.6</b>	<b>52.2</b>	<b>22.8</b>	<b>21.8 (N=182)</b>	<b>20.5 (N=241)</b>	<b>12.4</b>	<b>0.543</b>	<b>58.8 (N=241)</b>
					std. error	7.6	0.58	1.5	1.7	0.73	1.1	0.74	0.25	0.011	1.5
					min	50	5	22	5	1.0	0.90	2.0	3.0	0.10	6.4
		max	744	122	236	250	54.2	70.0	50.9	15.0	1.09	113.0			
		<b>ANZECC ISQG-low</b>		<b>1000</b>	<b>20</b>	<b>1500</b>	<b>80</b>	<b>65</b>	<b>21</b>	<b>20</b>	<b>50</b>	<b>2</b>	<b>200</b>		
		<b>No. of exceedances</b>			63		39			91					

nd = no data

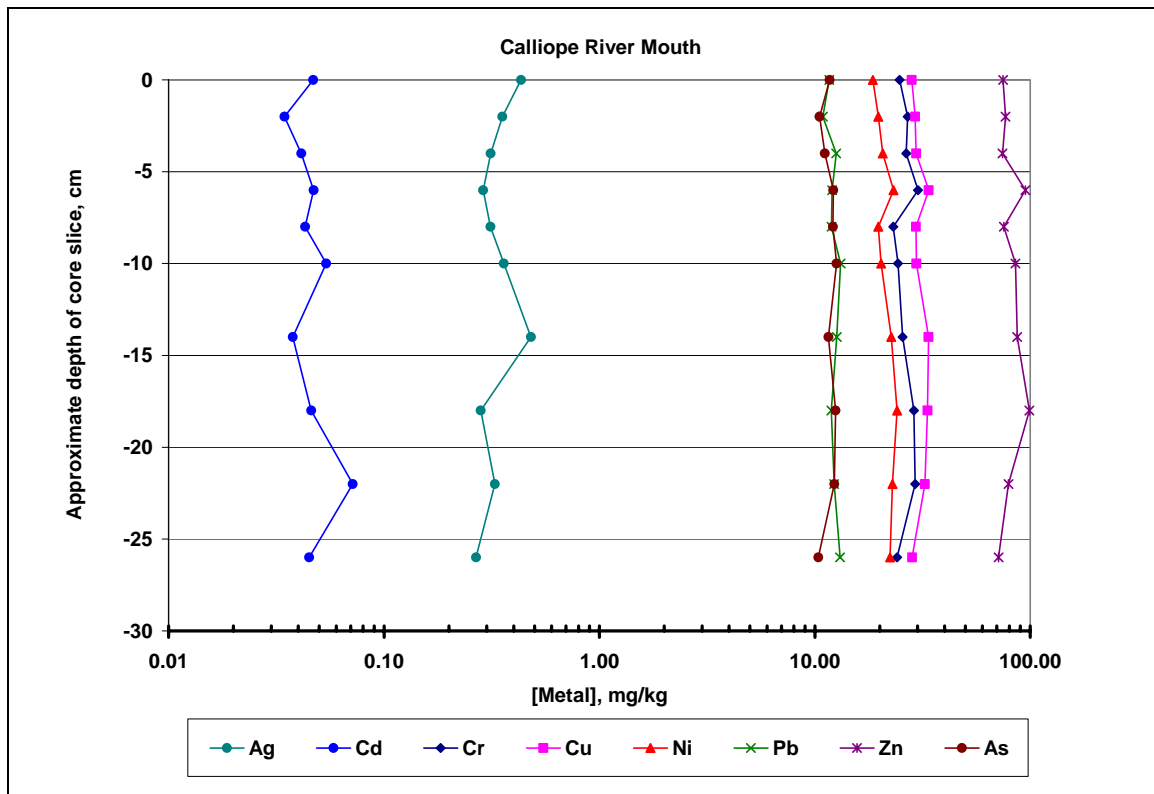
n, N = number of data

Four replicate cores each were taken at The Narrows (northern end of the Port Curtis estuary) and at Rodds Harbour (southern end of the estuary). The slices showed reasonably constant concentrations with depth. Unusually high Ni (130–176 mg/kg) and Zn (321–380 mg/kg) were initially reported in five slices of 5 cores from these two sites at depths between 6 cm and 8 cm (Vicente-Beckett & Shearer, 2005). However, unreported NAA data taken at the time on the same cores indicated that Zn levels in all slices were <100 mg/kg. Recent recheck analyses by AAS of one slice from each site concerned gave much lower levels of Ni (13–31 mg/kg) and Zn (36–58 mg/kg), suggesting that the high values reported earlier may have been due to sample contamination in the laboratory and were therefore deleted from the dataset. Insufficient remaining sample material prevented reanalysis of the other suspect slices.

The push cores (depths varied between 14 and 45 cm) taken from mangrove sites generally showed constant metal concentration levels with depth, as illustrated in Figure 2 for the Calliope River mouth core. The relatively constant concentration–depth profile does not indicate accumulation in the upper layers of the core. The mangroves sites are also subjected to strong mixing by tidal and natural wave action, possibly enhanced by shipping and other marine activities around the main port area, as well as bioturbation, resulting in sediment mixing.

A comparison of the average metal concentrations of sediments from the mangrove cores with the average concentration of estuarine surficial sediments from the main estuary given in Table 3 using one-way ANOVA suggests that there was generally no significant difference ( $p < 0.05$ ) between samples, with a few exceptions in some zones in the case of Ag, As, Cr, Cu, Ni and Pb.

As mentioned in section 1.1.3 there are Ni resources in the Fitzroy River catchment and in northern Queensland which are currently explored commercially. Surficial sediments from the Fitzroy River estuary were found to contain up to 0.5% chalcopyrite ( $\text{CuFeS}_2$ ) (L. Radke, personal communication, 2004), which may explain the high Cu contents in some sediments at The Narrows.



**Figure 2. Variation of metal concentration with depth (Calliope River mouth core)**

### 3.1.1 Sediment depositional zones

Bottom sediments consisting of fine particulates have highly reactive surfaces which lead to accumulation of contaminants (both metallic and organic). Table 4 gives the Pearson's correlation coefficients between the different metals and other sediment parameters. The table shows moderate to strong correlations exist between several metals, and between metals and the mud fraction (particle size <math><60 \mu\text{m}</math>) and organic content of sediments. Figure 3 shows the distribution of sediments of sub-

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**Table 4. Pearson correlations between metal concentrations and other sediment parameters.**

	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn	Fe	Al	Ca	S	% Mud	% OM
<b>N</b>	245	245	182	245	182	245	245	245	245	245	245	245	245	180	238
<b>Ag</b>	.430**	.871**	.687**	.602**	.344**	.610**	.651**	.532**	.617**	.574**	.560**	-.228**	.518**	.474**	.278**
<b>As</b>		.393**	.624**	.265**	.320**	.547**	.618**	.460**	.332**	.507**	.404**		.346**	.207**	
<b>Cd</b>			.682**	.622**	.350**	.601**	.656**	.555**	.677**	.599**	.605**	-.269**	.475**	.561**	.340**
<b>Cr</b>				.812**	.621**	.845**	.895**	.647**	.810**	.781**	.624**	-0.169	.688**	.730**	
<b>Cu</b>					.470**	.695**	.662**	.496**	.884**	.777**	.680**	-0.504	.457**	.715**	.466**
<b>Hg</b>						.634**	.612**	.276**	.343**	.274**	.267**		.603**	.386**	-.395**
<b>Ni</b>							.865**	.519**	.691**	.655**	.664**	-0.184	.652**	.582**	
<b>Pb</b>								.593**	.684**	.657**	.674**		.647**	.589**	
<b>Sb</b>									.535**	.579**	.519**	-.214**	.395**	.448**	.234**
<b>Zn</b>										.877**	.689**	-0.528	.406**	.735**	.579**
<b>Fe</b>											.677**	-.476**	.318**	.596**	.548**
<b>Al</b>												-.274**	.421**	.524**	.289**
<b>Ca</b>														-.308**	-0.664
<b>S</b>														.428**	
<b>% Mud</b>															.393**

N = number of samples.

\*\*Correlation is significant at the 0.01 level (2-tailed).

\*Correlation is significant at the 0.05 level (2-tailed).

Non-significant correlations and redundant cells have been excluded.

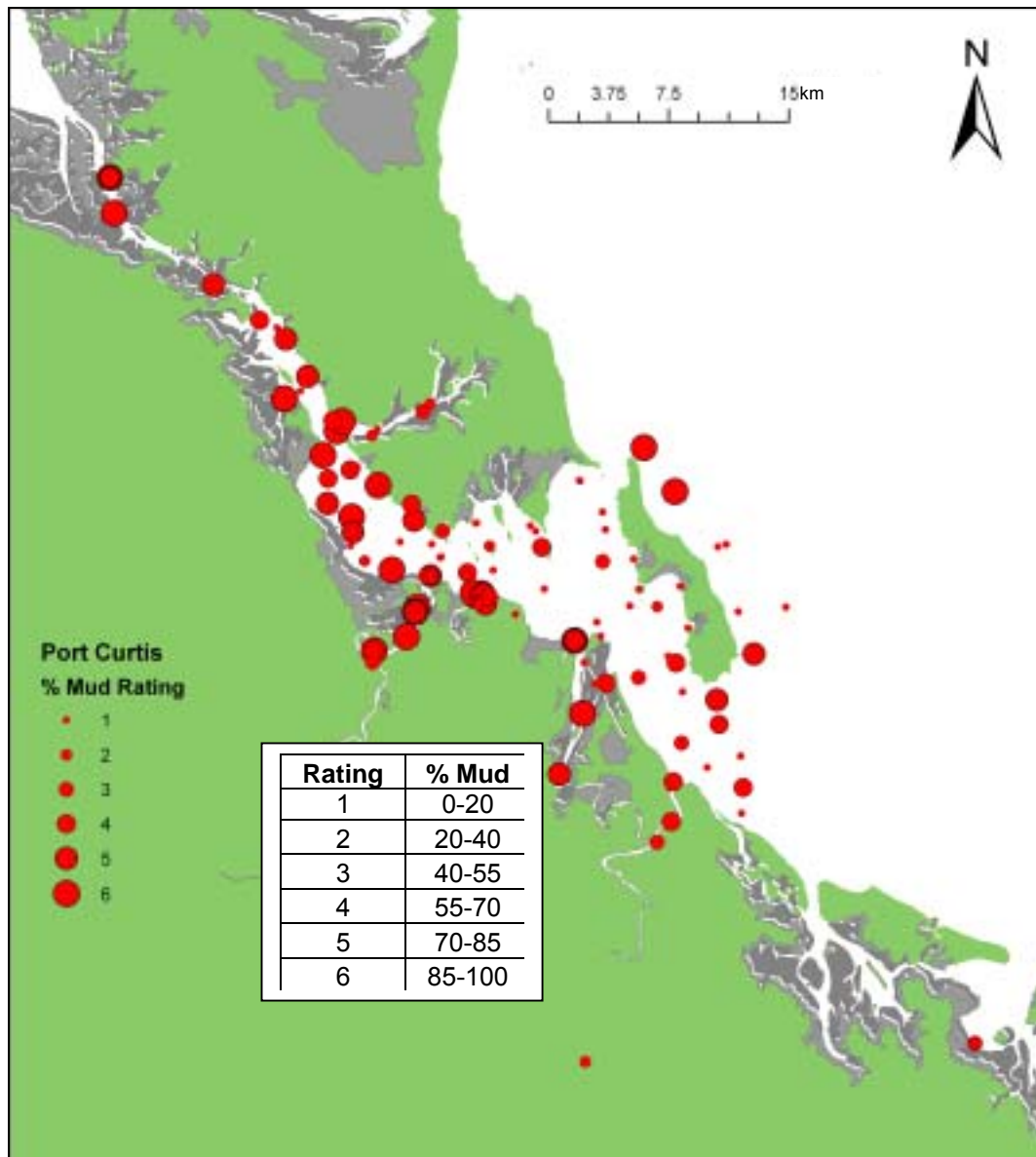


Figure 3. Distribution of sediments showing their particle size fraction <60  $\mu\text{m}$  (% Mud)

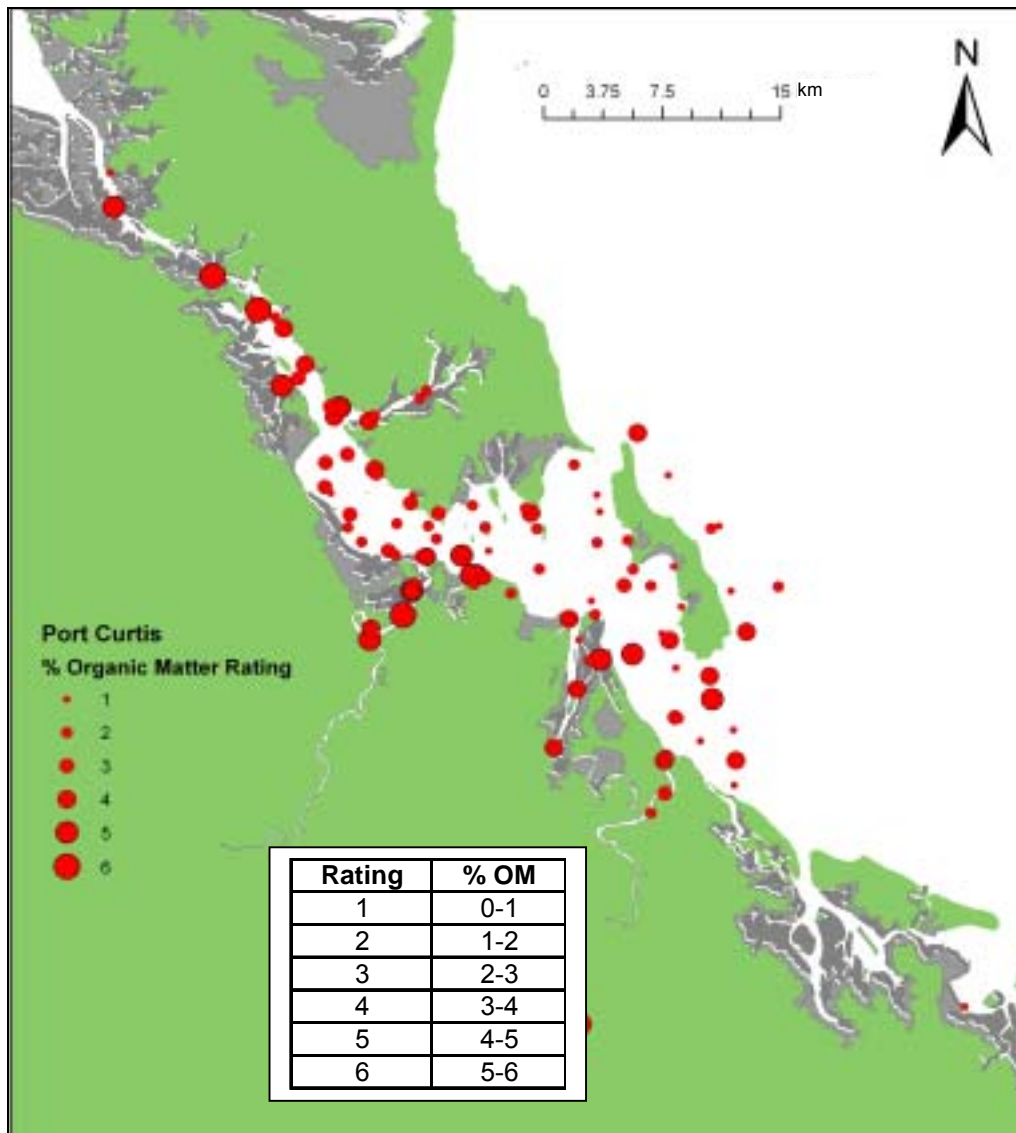


Figure 4. Distribution of sediments showing their organic matter content (% OM)

### 3.1.2 Estimates of background metal concentrations in sediments

To determine whether sediments (from either the main estuary or mangrove sites) are enhanced or enriched in metals (or other contaminants) by anthropogenic influences and to verify contaminant depositional zones, knowledge of background metal concentrations in sediments is needed. The ANZECC (2000) guidelines do not give much detail on how to measure background sediment concentrations. There are at least three possible approaches:

- (1) Measure the metal concentrations in adjacent areas not affected by industry.
- (2) Study sediment core profiles from quiescent environments and use bottom-of-core metal concentrations.
- (3) Use a statistical approach on a dataset from a relatively unpolluted site (see for example Roussiez *et al.*, 2005; Doherty *et al.*, 2000a,b; Liu *et al.*, 2003).

With the first approach, the recent estimate by Kamber *et al.* (2005) of the elemental composition of the earth's upper continental crust (UCC) from alluvial sediments of Queensland, or shale composition (Liaghati *et al.*, 2003; Reimann & de Caritat, 2005; Selvaraj *et al.*, 2004) may be used as background reference level. However, this approach would not be altogether valid because of variations in bedrock mineralogy and other sediment geochemical properties between the reference and the study area, as well as local catchment properties that further contribute to the complexity and heterogeneity of sediments. As this study did not have any sediment cores from quiescent environments, the third option was pursued, that is, using a statistical elimination method to derive background concentrations.

The statistical approach involved elimination of outliers, which was adopted (with modification) from those reported in the literature (e.g. Roussiez *et al.*, 2005; Doherty *et al.*, 2000a,b; Liu *et al.*, 2003) and applied to the dataset on the Port Curtis estuarine surficial sediments reported in the SLRA study (Apte *et al.*, 2005). Data on mangrove/intertidal sites reported in this study could have some influential values (as gleaned from Table 3) and hence were excluded in the statistical analysis. The mean metal concentrations (and other sediment parameters) were calculated from the Port Curtis dataset (N=100). Samples whose concentrations exceeded the upper 95% confidence interval (UCI) of the mean of this original dataset were removed. A new mean value was calculated from the reduced dataset, giving a new UCI; any outliers (values exceeding UCI)

were again removed. The elimination process was repeated until there were no more outliers compared to the UCI of the final dataset.

Table 5 gives the mean values of this final dataset (reduced to n=11), which represent estimates of the background levels of the Port Curtis estuarine surficial sediments. Also included in Table 5 for comparison are some historical data for Calliope and Boyne Rivers (which contribute to the Port Curtis estuary), the most recent estimate of the composition of the upper continental crust of Queensland (UCC-MUQ) based on 25 river and 30 alluvial sediments around Queensland (Kamber *et al.*, 2005), the mean levels found in the reference mangrove site (Rodds Harbour), and estimates of background concentrations of Fitzroy estuary sediments (Vicente-Beckett *et al.*, 2006a).

The Port Curtis background estimates are seen to be consistent with the range of reported values for UCC-MUQ, the Calliope and Boyne Rivers, and the reference mangrove site (Rodds Harbour), indicating that the statistical approach used in this study was reasonable. The UCC-MUQ values are greater than the estimated background Ni and Pb concentrations, suggesting that the upper catchment or upstream sources (particularly Calliope River) could be potential sources of these metals.

It is noted that the background levels obtained for As and Ni are very close to the lower trigger values of ANZECC (2000) interim sediment quality guidelines, which must be taken into consideration when undertaking sediment quality assessments. The estimated background concentrations in Fitzroy estuary sediments (Vicente-Beckett *et al.*, 2006a) on the other hand gave slightly lower levels of As, Cu, Hg, Sb and Zn than in Port Curtis sediments. The statistical procedure used has provided likely background levels of Ag, As, Cd, Hg and Sb in Port Curtis sediments, which are lacking in the UCC-MUQ dataset.

**Table 5. Metal concentrations (mg/kg dry wt) in sediments from various locations**

	<b>Ag</b>	<b>As</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Hg</b>	<b>Ni</b>	<b>Pb</b>	<b>Sb</b>	<b>Zn</b>
Estimated background levels, Port Curtis Estuary; <1mm fraction	0.054	20.4	0.052	65.3	29.4	0.0135	19.7	13.7	0.642	70.1
MUQ-upper continental crust; <150 µm fraction (Kamber <i>et al.</i> , 2005)	nd	nd	nd	64.5	32.4	nd	31.57	20.44	nd	73.47
Calliope River; <150 µm fraction (Kamber <i>et al.</i> , 2005)	nd	nd	nd	37.21	59.0	nd	19.4	8.25	nd	73.47
Boyne River, South Trees Inlet 1970–1992 data (min–max); <63 µm fraction (Semple & Williams, 1998)	nd	nd	<1-10	15-100	13-66	<0.1	7-38	<10-38	nd	19-140
Rodds Harbour (reference mangrove site); <1 mm fraction (see Table 3)	0.051	13.2	0.052	50.4	13.9	0.026	20.7	10.7	0.46	46.1
Estimated background levels, Fitzroy estuary; <1 mm fraction (Vicente-Beckett <i>et al.</i> , 2006a)	0.0056	6.87	0.052	66.1	17.1	0.0065	31.8	11.6	0.56	47.9
ANZECC (2000) ISQG-low	1	20	1.5	80	65	0.15	21	50	2	200

nd = no data

### 3.1.3 Predicting the natural gradient of metal concentration in sediments

Preda and Cox (2002) reported a baseline study of the trace metal distribution in the Pumicestone coastal area of south-east Queensland. They showed that regardless of the sample origin and composition, metal accumulation appeared systematic, suggesting relationships between metals and certain sediment parameters (e.g. Fe and Al contents, or particle size). Liaghati *et al.* (2003) showed that natural processes were more dominant than anthropogenic inputs in concentrating metals. The spatial variability exhibited by the metal data probably reflects the influence of other sediment variables such as Fe and/or Al contents, organic matter content, particle size etc. on the metal concentration.

Such influences are indicated by the Pearson's correlations shown in Table 4. To minimise variability of analytical data, as well as to obtain a better estimate of the maximum potentially labile metal, the common practice involves using only the fine sediment fractions (i.e. <63  $\mu\text{m}$ ) for chemical analysis. However, this procedure of size normalisation cannot fully deal with the variability due to complex interactions within the sediment. Linear regression models have been used to describe the natural gradient (i.e. the natural variation between sites) of metal concentration in sediments as well as to minimise the effects of multiple sources of variance (Doherty *et al.*, 2000a,b; Roussiez *et al.*, 2005; Liu *et al.*, 2003) in sediments from different sites.

A multivariate analysis was undertaken on the combined sediment dataset of the SLRA study (Apte *et al.*, 2005) and this study, to model the natural variation in metal concentration of Port Curtis sediments. The procedure is discussed in detail elsewhere (Vicente-Beckett *et al.*, 2006a,b). Table 6 summarises the unique prediction equations obtained for each metal, showing the different predictors (or independent variables) which influence the metal concentration in the sediments. Log-transformed data were used for the analysis to reduce skewness. These regression equations were used to predict metal concentrations of the sediment samples using the measured values of the corresponding predictors.

Figure 5 shows typical plots of the predicted concentration versus the observed sediment metal concentrations for four of the 10 metals analysed, together with their respective ANZECC (2000) trigger values. The UCI line defines the upper limit of the natural variation of sediment concentration. The adjusted correlation coefficients obtained for these plots are also given in Table 6, as well as the standard error of the estimate (SEE), which is a measure of the variation in the predicted value that is analogous to the standard deviation of a variable around its mean (Hair *et al.*, 1998). It is seen that good correlations between the predicted

metal concentration and the observed values were obtained for Zn, Cr, Ni, Cu and Pb, while only weak-to-moderate correlations were obtained for As, Sb, Hg, Ag and Cd. The limits of detection for Hg, Ag and Cd analyses probably contributed to the limitations of the models obtained. The regression analysis has confirmed that the *natural* levels of Ni, Cr and As are very close to the ANZECC (2000) trigger values, and may actually exceed the guideline (i.e. the samples falling below the UCI but above the trigger values).

In their study on Cleveland Bay (northern Queensland) sediments, Doherty *et al.* (2000a,b) considered all observed values exceeding the UCI as sediments with *enhanced* metal concentrations, although they may still fall below the ANZECC (2000) guidelines. The enhanced metal concentrations may be indicative of: anthropogenic inputs, the presence of sediments which are not typical of the modelled gradient, or of sediments which contained some irregular predictor(s) not accommodated within the regression model (Doherty *et al.*, 2000b). More sediment data (e.g. from less contaminated sites upstream of the two major tributaries, the Calliope and Boyne Rivers, additional mangrove sites and deeper sediment cores) are needed to resolve these questions and to improve the regression models.

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**Table 6. Regression models to predict sediment metal concentration**

Element	Prediction equation	Adjusted R <sup>2</sup>	SEE	N
<b>Ag</b>	$\log \text{Ag} = 1.56 + 0.011 \cdot \log \text{Fe} + 0.015 \cdot \log \text{Al} + 0.01 \cdot \log \text{S} + 0.002 \cdot \log \text{OM}$	0.477	0.00689	245
<b>As</b>	$\log \text{As} = -2.471 + 0.597 \cdot \log \text{Fe} + 0.095 \cdot \log \text{S} + 0.179 \cdot \log \text{Ca} - 0.075 \cdot \log \text{OM}$	0.452	0.115	245
<b>Cd</b>	$\log \text{Cd} = 1.542 + 0.009 \cdot \log \text{Fe} + 0.02 \cdot \log \text{Al} + 0.011 \cdot \log \text{S} + 0.003 \cdot \log \text{OM}$	0.493	0.00717	245
<b>Cr</b>	$\log \text{Cr} = -1.111 + 0.719 \cdot \log \text{Fe} - 0.244 \cdot \log \text{Al} + 0.094 \cdot \log \text{S} + 0.056 \cdot \log \text{Ca} - 0.053 \cdot \log \text{OM} + 0.142 \cdot \log \text{Mud}$	0.859	0.0783	245
<b>Cu</b>	$\log \text{Cu} = -3.098 + 0.508 \cdot \log \text{Fe} + 0.436 \cdot \log \text{Al} + 0.137 \cdot \log \text{S} - 0.154 \cdot \log \text{Ca} + 0.159 \cdot \log \text{Mud}$	0.843	0.111	245
<b>Hg</b>	$\log \text{Hg} = 0.706 + 0.605 \cdot \log \text{Fe} - 0.652 \cdot \log \text{Al} + 0.399 \cdot \log \text{S} - 0.157 \cdot \log \text{Ca} - 0.233 \cdot \log \text{OM} + 0.123 \cdot \log \text{Mud}$	0.458	0.306	182
<b>Ni</b>	$\log \text{Ni} = -4.582 + 0.812 \cdot \log \text{Fe} + 0.286 \cdot \log \text{Al} + 0.208 \cdot \log \text{S} - 0.077 \cdot \log \text{OM} + 0.076 \cdot \log \text{Mud}$	0.844	0.107	245
<b>Pb</b>	$\log \text{Pb} = -2.641 + 0.452 \cdot \log \text{Fe} + 0.245 \cdot \log \text{Al} + 0.086 \cdot \log \text{S} + 0.044 \cdot \log \text{Ca} - 0.045 \cdot \log \text{OM} + 0.025 \cdot \log \text{Mud}$	0.759	0.0724	245
<b>Sb</b>	$\log \text{Sb} = -2.276 + 0.216 \cdot \log \text{Fe} + 0.205 \cdot \log \text{Al} + 0.042 \cdot \log \text{Mud}$	0.469	0.0800	182
<b>Zn</b>	$\log \text{Zn} = -2.006 + 0.072 \cdot \log \text{Fe} + 0.104 \cdot \log \text{Al} + 0.047 \cdot \log \text{S} - 0.071 \cdot \log \text{Ca} + 0.108 \cdot \log \text{Mud}$	0.894	0.0712	245

SEE = standard error of the estimate

N = number of samples

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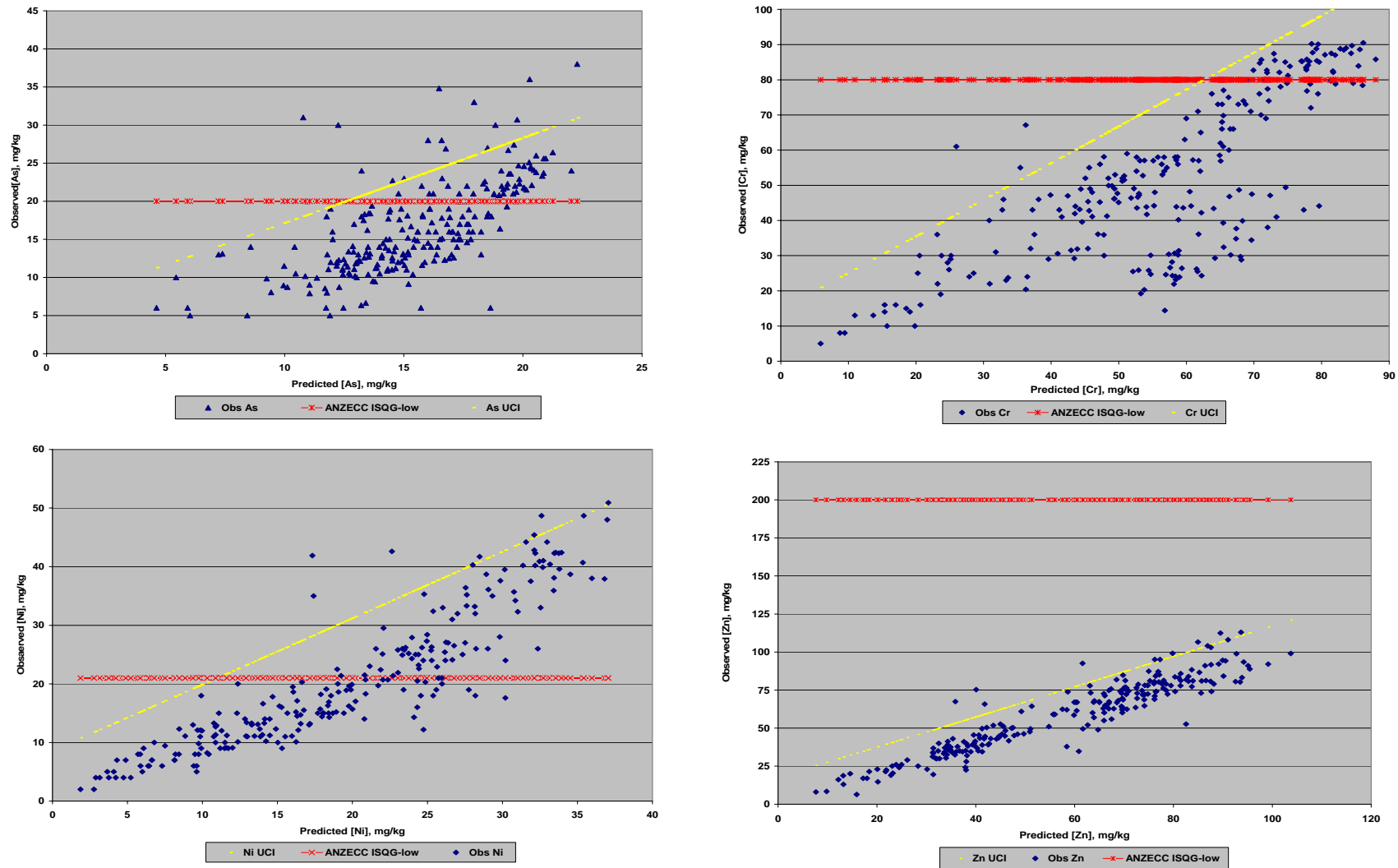


Figure 5. Plots of observed metal concentrations versus predicted concentrations for As, Cr, Ni and Zn

### 3.2 Sediment geochronology and sedimentation rate

Studies on chronology and/or sedimentation rate are often based on excess or unsupported  $^{210}\text{Pb}$  activity. The natural fallout radionuclide  $^{210}\text{Pb}$ , a member of the uranium decay series, is found on all surfaces exposed to the atmosphere. This atmospherically derived excess  $^{210}\text{Pb}$  is scavenged from the atmosphere by both wet and dry processes, subsequently being incorporated in sedimentary deposits and decaying with a half-life of about 22 years (Madsen *et al.*, 2005). The unsupported  $^{210}\text{Pb}$  activity or excess  $^{210}\text{Pb}$  is the measured activity of  $^{210}\text{Pb}$  which exceeds the activity in equilibrium with  $^{226}\text{Ra}$  in the sediment.  $^{137}\text{Cs}$  fallout resulted from nuclear bomb detonations in 1945–1980 and is globally distributed (Pfitzner *et al.*, 2004). Using several cores from northern Queensland, Pfitzner *et al.*, (2004) demonstrated that  $^{137}\text{Cs}$  is also a useful independent tracer for sediment dating purposes.

In this study four sediment cores from intertidal mangrove sites spread across the harbour were taken for dating and the results are shown in Figure 6. No pronounced  $^{210}\text{Pb}$  excess or  $^{137}\text{Cs}$  activity was observed particularly at the top sections (0–10 cm) of all cores, although somewhat higher activity at depths below 10 cm was observed. The lack of  $^{210}\text{Pb}$  excess count in the upper layers of the cores may be attributed to sediment mixing, a phenomenon which has been observed in estuarine sediment cores (Pfitzner *et al.*, 2004). This mixing may be gleaned from the fluctuating activities of either radionuclide with depth of core slice. Longer cores would have provided better estimates of the sedimentation history. Taking a much deeper core further out in the estuary using divers was considered but was not carried out due to time and budget limitations, lack of effective equipment for underwater coring and anticipated problems of visibility for the divers at the water depths involved. A research vessel such as that used by Geoscience Australia would be ideal but could not be organised due to time and budget limitations, although it may also be unsuitable for the relatively low water depths near the intertidal sites.

The Narrows and Calliope River cores exhibited  $^{210}\text{Pb}$  excess activity which decreased with depth of core; such trend was reasonably apparent only in  $^{137}\text{Cs}$  activity observed in the Calliope River core. Taking the year 1958 as the time when  $^{137}\text{Cs}$  activity above background levels was detected in the southern hemisphere (Pfitzner *et al.*, 2004), it appears that 28 cm of sediments were deposited over the past 47 years (core sampled in 2005). This gives an estimated sediment accumulation rate of *at least* 0.60 cm/yr. Table 7 shows the range of linear sedimentation rates observed at other estuaries for comparison. In particular, sedimentation rate of about 1.9 cm/yr (based on  $^{137}\text{Cs}$  activity) for a

1.2 m sediment core from offshore Keppel Bay, Central Queensland sampled in 2000 (V. Vicente-Beckett, unpublished data) is about threefold higher. This difference is not surprising considering the differences in the catchment size, the nature of land use, flow volume and hydrodynamics between the two locations. The sedimentation rate is highly variable both spatially and temporally as demonstrated by another Coastal CRC study, which found recently that the average sedimentation rates in the Fitzroy River estuary within the last 100–200 years were: 1 mm/year at the floodplains, 1.5 cm/year at the mangroves and tidal creeks at the river mouth, and 0.13 cm/year within the inner Keppel Bay (Helen Bostock, personal communication, 2006).

**Table 7. Linear sedimentation rates measured in sediment cores from various estuaries**

Location	Sedimentation rate, cm/year	Reference
Port Curtis	>0.6	This study
Fitzroy Estuary (core 3419)	1.9	V. Vicente-Beckett, unpublished data
Crescent Lagoon (Fitzroy Estuary)	1.3	G. Hancock, personal communication, 2005
Upstart and Rockingham Bays (northern Queensland), core 1241	~0.9	Pfitzer <i>et al.</i> , 2004
Hong Kong SAR, mangrove swamps	0.4–0.5	Ke <i>et al.</i> , 2005
Jiulongjiang estuary (China)	1.75	Alongi <i>et al.</i> , 2005
French Guiana coast	0.7	Allison and Lee, 2004
Wadden Sea (Denmark)	1.2	Madsen <i>et al.</i> , 2005

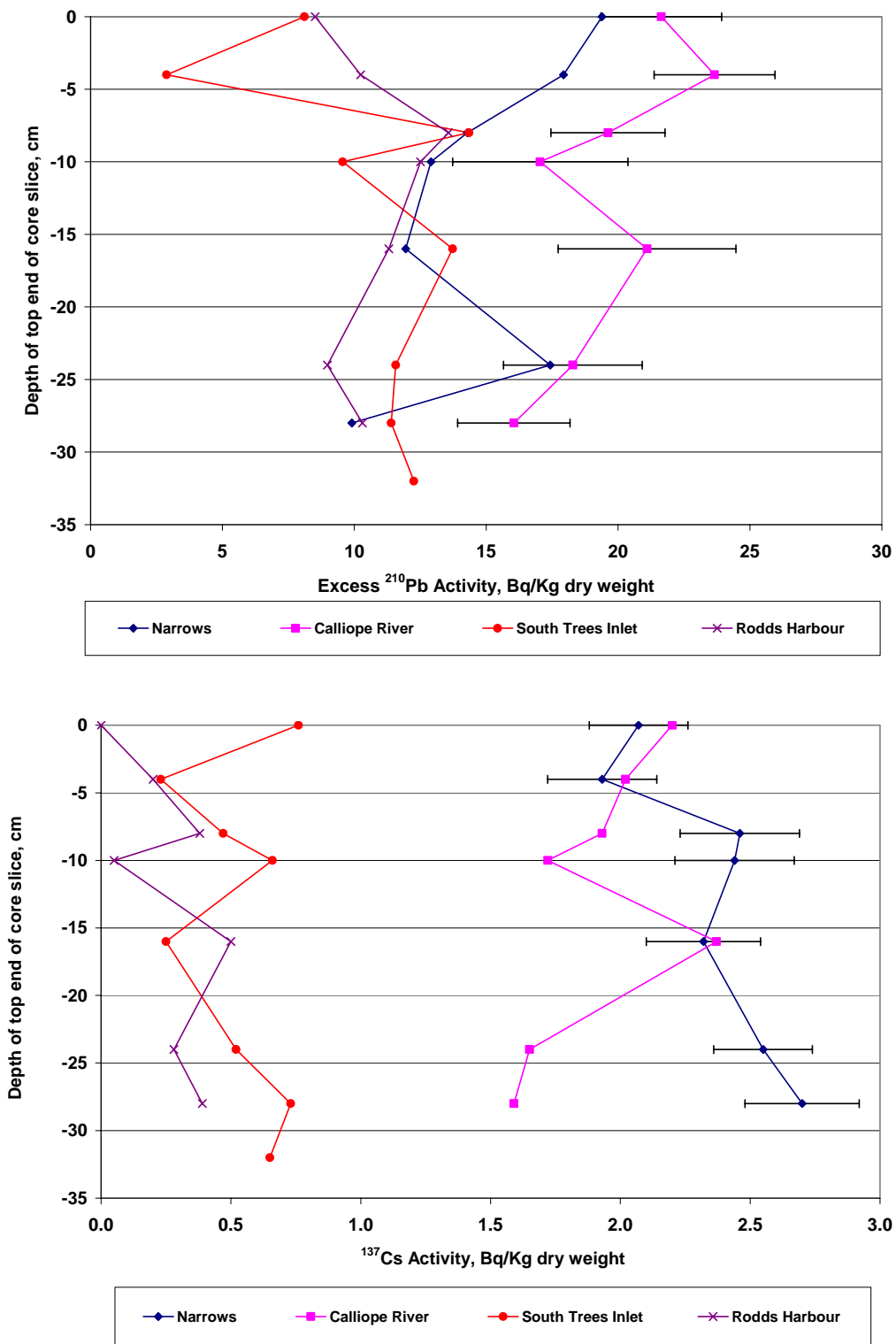


Figure 6. Excess <sup>210</sup>Pb activity (top) and <sup>137</sup>Cs activity (bottom) in Port Curtis sediment cores (indicative error bars (± standard error) are shown)

### 3.3 Stable lead isotope ratios (PbIRs)

The variety of lead ores used in various industrial applications has led to the introduction of lead in the environment with distinct relative isotope abundance. The relative ratios of the four stable lead isotopes  $^{206}\text{Pb}$  (from radioactive decay of  $^{238}\text{U}$ ),  $^{207}\text{Pb}$  (from  $^{235}\text{U}$  decay),  $^{208}\text{Pb}$  (from  $^{232}\text{Th}$  decay) and  $^{204}\text{Pb}$  (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, New South Wales, contain small amounts of radiogenic Pb isotopes; younger ores derived from high U/Pb sources such as mined in Missouri have much higher proportions of  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  relative to  $^{204}\text{Pb}$  (Chillrud *et al.*, 2003). Muñoz *et al.* (2004) used the stable lead isotope ratios ( $^{206}\text{Pb}/^{207}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$ ) to trace main Pb sources to coastal sediments considering various forms of environmental samples (e.g. industrial effluents, leaded petrol, riverine and marine suspended particulate materials). Gallon *et al.* (2005) have tracked the sources and chronology of atmospheric lead deposition using stable PbIRs.

PbIRs of sediments from Port Curtis estuary (plus a grab from Awoonga Dam) and a few soils and sediments from the lower Fitzroy catchment are plotted in Figure 7. The mean Pb content found for Port Curtis estuarine and intertidal sediments was  $12.4 \pm 3.9$  mg/kg dry wt. Among the cores, The Narrows registered Pb concentration which was significantly different ( $p < 0.05$ ) from those in the other mangrove zones. The mean PbIRs for all Port Curtis sediments were  $^{208}\text{Pb}/^{206}\text{Pb} = 2.0758 \pm 0.0111$  and  $^{207}\text{Pb}/^{206}\text{Pb} = 0.8368 \pm 0.0068$ . These ratios were not significantly correlated ( $p < 0.05$ ) to the Pb concentration, which is evident from Figure 7 (bottom plot). Plots of the PbIRs against Pb concentration also showed little correlation; the y-intercepts of these plots may be taken as the background values:  $^{208}\text{Pb}/^{206}\text{Pb} = 2.0711$  and  $^{207}\text{Pb}/^{206}\text{Pb} = 0.8333$ . The observed mean  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio is comparable to the value of 2.0635 measured for near-pristine estuarine and marine tropical northern Australia, bordering the Timor and Arafura Seas and the Gulf of Carpentaria (Munksgaard & 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 crustal value of these ratios was reported by Stacey and Kramers (1975) as  $^{208}\text{Pb}/^{206}\text{Pb} = 2.0606$  and  $^{207}\text{Pb}/^{206}\text{Pb} = 0.8357$  (converted values from other stable Pb isotope ratios reported). This point was included in Figure 7, as well as the Pb isotope ratios for Mount Isa (Queensland) Pb deposits and those for oceanic sediments (Atlantic and Pacific) (Stacey & Kramers, 1975). Also included in the figure are the measured ratios from an

upstream Fitzroy River sediment, three samples of contaminated soils (former cattle dip) and a wastewater sludge sample from the Fitzroy catchment (Pb concentration range for these samples was 30–153 mg/kg, indicating Pb contamination), with the sludge sample showing the highest PbIRs.

The plot shows that the Port Curtis sediments fall within a linear trend ( $r^2 = 0.6497$ ) starting from average modern or present-day Pb and ending at the most radiogenic Mount Isa Pb (Munksgaard *et al.*, 2003), with the Port Curtis 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) and other anthropogenic inputs, 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 (Bollhöfer & Rosman, 2000). The lower observed ratio ( $^{208}\text{Pb}/^{206}\text{Pb} = 2.0711$ ) in Port Curtis appears to reflect the decrease in these ratios which started in the 1970s (when leaded petrol was outlawed). Such decrease was clearly demonstrated elsewhere, for example, in the top 2.5 cm layer of sediments from a fairly isolated Canadian lake (Gallon *et al.*, 2005). Sediment mixing in the Port Curtis mangrove cores may have caused dispersal of lead, obviating any evidence of decreasing PbIRs with depth of core.

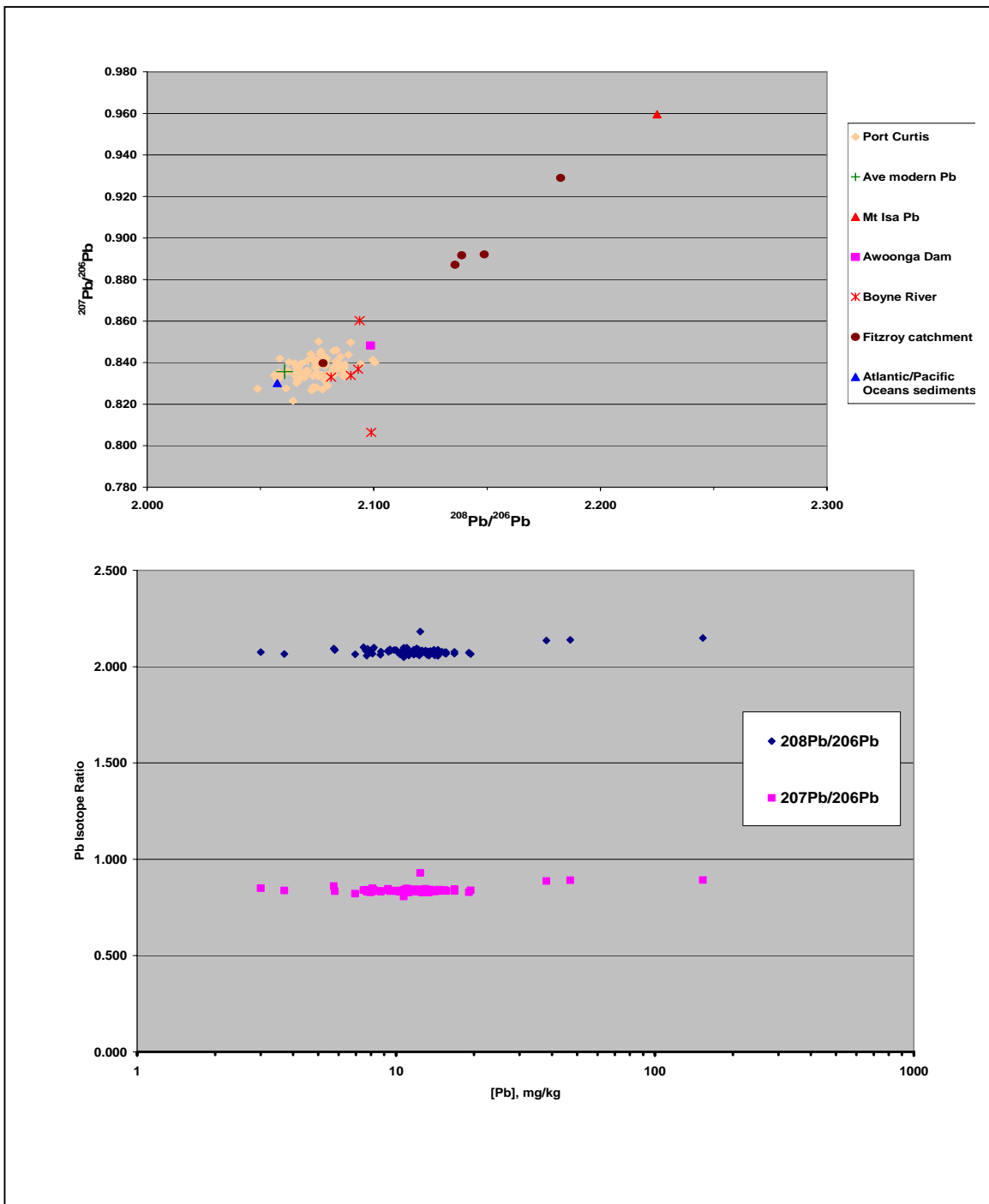


Figure 7. Pb isotope ratios in Port Curtis sediments and other samples (top) and the relationship of PbIRs with Pb concentration (bottom)

### 3.4 PAHs in sediments

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds consisting of at least two fused aromatic rings (see Appendix 5). They are natural constituents of crude oils, accounting for about 20% of total hydrocarbons (Kennish, 1997). They are of concern because of their potential carcinogenicity, mutagenicity and teratogenicity, particularly of the higher molecular weight (MW) PAHs (PAHs containing four rings or more), and the toxicity of the lower MW PAHs (2–3 rings) to aquatic animals. PAHs are the most biologically toxic of all hydrocarbon compounds (Haynes & Johnson, 2000). Their low solubility in water makes them attractive to hydrophobic organic matter, suspended particulates and sediments where they may remain for extended periods. They appear to degrade only very slowly, mainly by microbial action and photodegradation (Kennish, 1997).

Seventeen polycyclic aromatic hydrocarbons, representing mainly the priority pollutants identified in the ANZECC/ARMCANZ (2000) interim sediment quality guidelines, were tested in 25 sediment grabs and in one shallow core. Appendix 2 summarises the locations and descriptions of the samples and Appendix 5 gives the list of acronyms used for the PAHs and some information on their carcinogenicity potential and toxicity. Appendix 6 provides all the PAH data obtained in this study.

Figure 8 plots the PAH data for samples taken from the northern end of Port Curtis (left side of the figure) to the southern end of the estuary (right side of the figure). The highest concentrations of the different PAHs were clearly found near the industrial centre of Gladstone, that is, along Calliope River and its mouth and the South Trees Inlet. Sediments from the Clinton Coal Facility (CCF) contained the greatest amount of PAHs, followed by sediments from Red Mud Dam Outlet (RMDO), Auckland Creek (AC), downstream of the NRG Power Station (CR-NRG) and the marina (M). Sediments from the northern and southern ends of the estuary contained relatively low PAHs and only a few types of PAH; no detectable levels of PAHs were found at Boyne River and Rodds Harbour.

Figures 9 and 10 show detected levels of naphthalene (which has known toxicity to aquatic organisms; see Appendix 5) and of benz[b+k]fluoranthene (which has low-to-moderate carcinogenicity potential; see Appendix 5), respectively.

Figure 11 maps the total PAHs detected in the estuary. The ANZECC trigger values for PAHs were not exceeded in any of the samples. The naphthalene levels were  $\leq 5 \mu\text{g}/\text{kg}$ , in contrast to 200–501  $\mu\text{g}/\text{kg}$  reported earlier (WBM Oceanics Australia, 2000). Naphthalene constitutes a significant fraction of crude

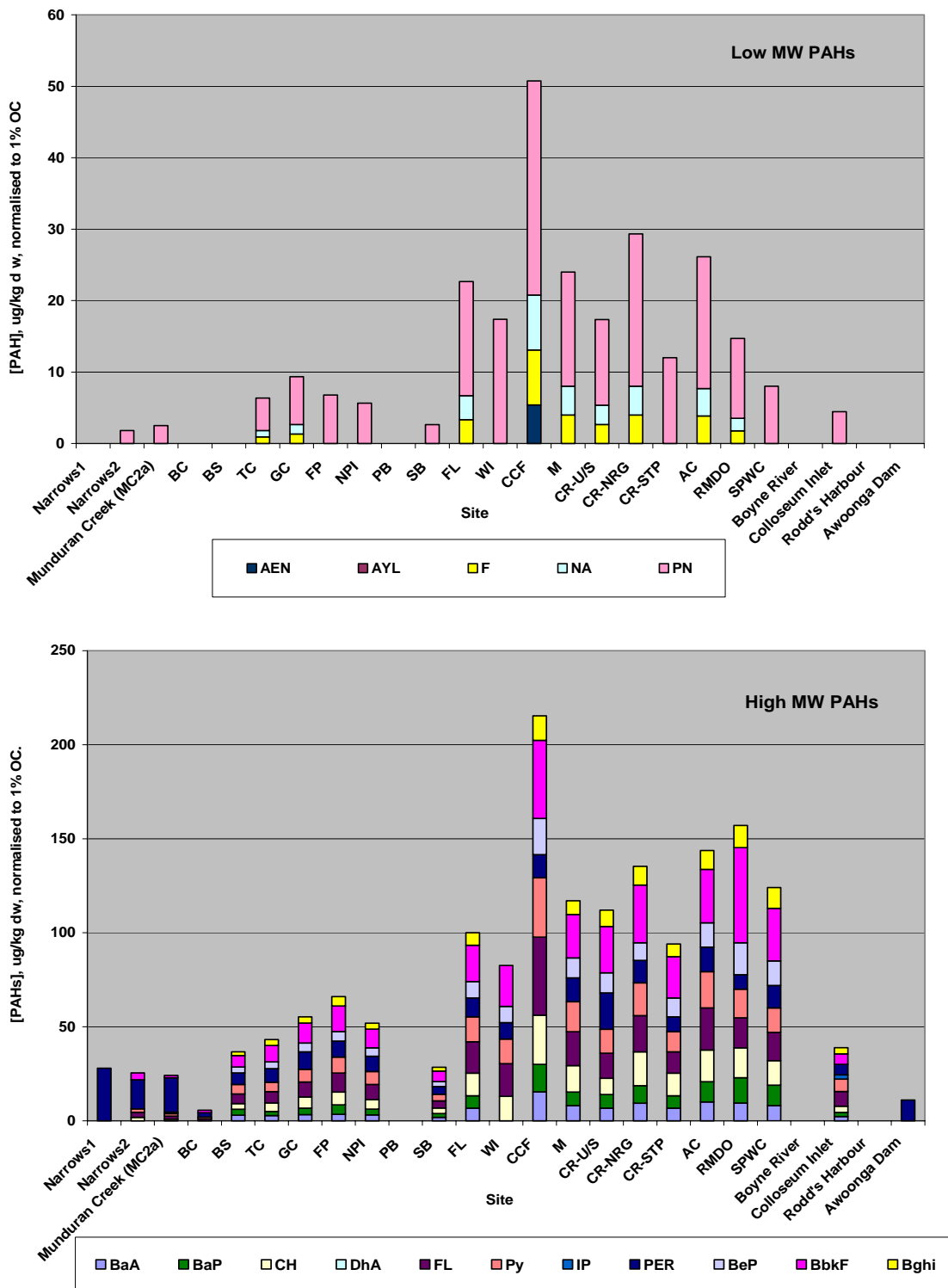
oils and petroleum products with lighter fractions. The high levels reported in 2000 (WBM, Oceanics Australia, 2000) could be indicative of the presence of a petroleum-source PAH contamination at the time the study was performed (Tam *et al.*, 2001).

Sediment from The Narrows and Munduran Creek and from Awoonga Dam (upstream Boyne River) contained high levels of perylene (53–99% and 79%, respectively); other grab samples (except QAL-RMDO) likewise contained significant levels of perylene (mean  $\pm$  sd for all grabs =  $91 \pm 27\%$ ). Figure 12 shows the PAHs found in a short core (core #1, 18-cm long) from Munduran Creek, which is seen to predominantly contain perylene.

Perylene is not included in the ANZECC (2000) sediment quality guidelines. It appears to be produced naturally although the process is not yet fully understood. It is largely viewed that perylene is diagenetic in origin, being formed after the sediments have been buried. It has been suggested that fungi are major precursor carriers for perylene in sediments (Jiang *et al.*, 2000), that diatom decomposition is the origin of perylene in marine sediments (Venkatesan, 1988), and that perylene is formed from non-specific precursor materials by biotic or abiotic transformation processes (Silliman *et al.*, 2001). It is also claimed that high concentrations of perylene are often associated with anoxic marine sediments and/or terrigenous peaty deposits (Dahle *et al.*, 2003).

The concentration of perylene in sediments is thought to be proportional to the amount of terrestrial input (Jiang *et al.*, 2000). It has been observed to be present at higher concentrations in deeper sediment core sections taken from various locations in the world (Jiang *et al.*, 2000), as well as from some cores (2.2–2.6 m long) in the Fitzroy Estuary (Vicente-Beckett *et al.*, 2006a). Silliman *et al.* (1998) argued that the low-to-absent perylene concentrations in upper, oxic sediments and its increasing concentrations with depth indicate that *in situ* diagenesis is responsible for the formation of perylene.

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**Figure 8. Distribution of low-MW (top) and high-MW (bottom) PAHs in Port Curtis benthic sediments**

(AEN = Acenaphthene; AYL = Acenaphthylene; BbkF = Benzo[b+k]Fluoranthene; BaA = Benz[a]Anthracene; BaP = Benz[a]Pyrene; BeP = Benz[e]Pyrene; Bghi = Benzo[ghi]Perylene; CH = Chrysene; DhA = Dibenz[ah]Anthracene; F = Fluorene; FL = Fluoranthene; IP = Indeno[123cd]Pyrene; NA = Naphthalene; PN = Phenanthrene; PER = Perylene; PY = Pyrene)

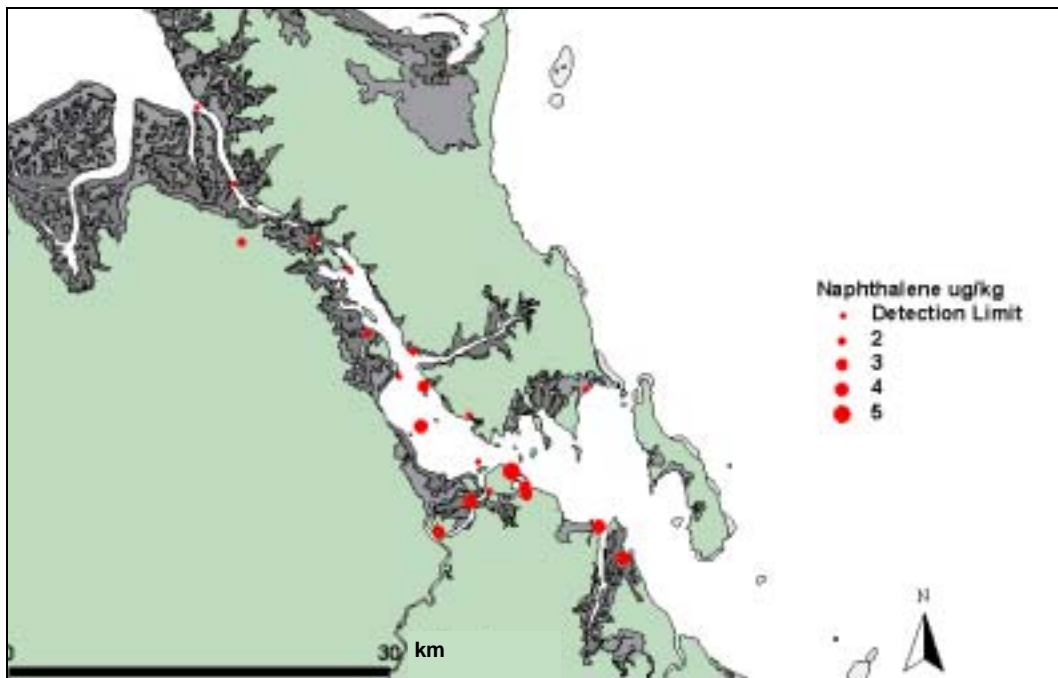


Figure 9. Naphthalene in Port Curtis benthic sediments

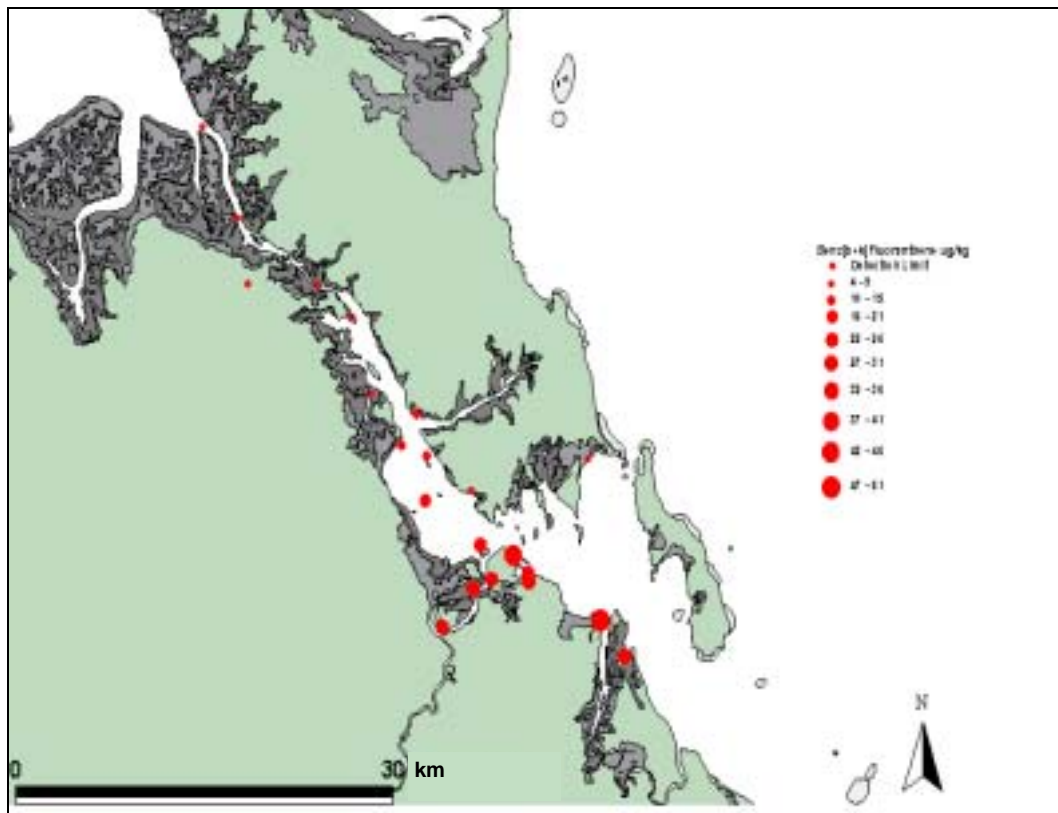


Figure 10. Benzo[b+k]Fluoranthene in Port Curtis benthic sediments

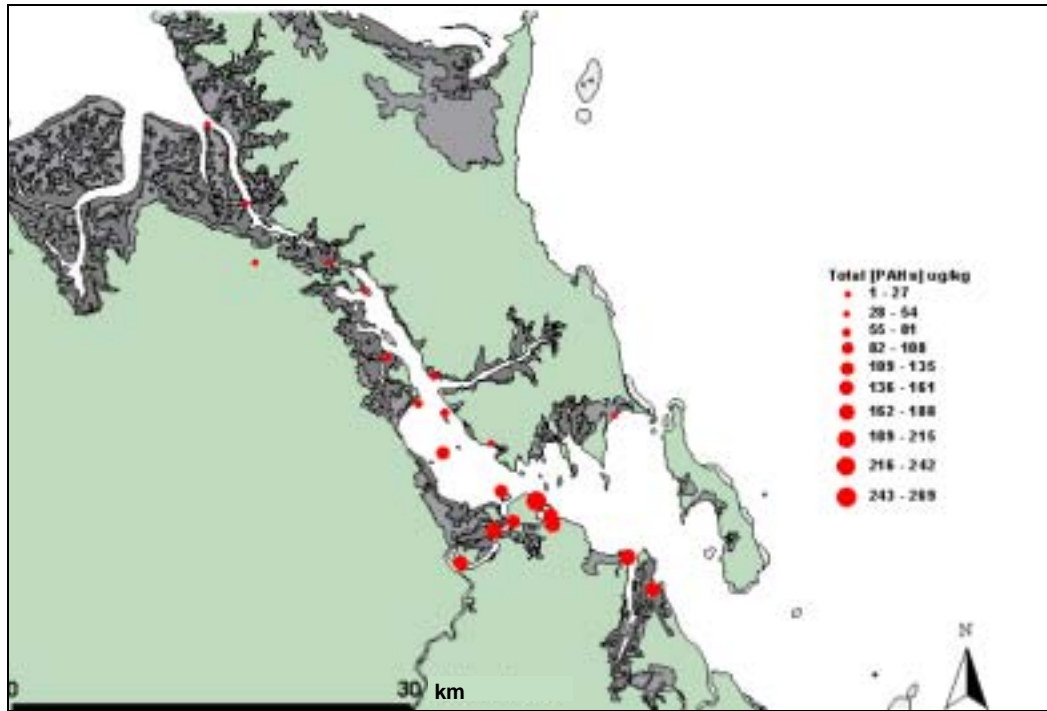


Figure 11. Total PAHs in Port Curtis sediments

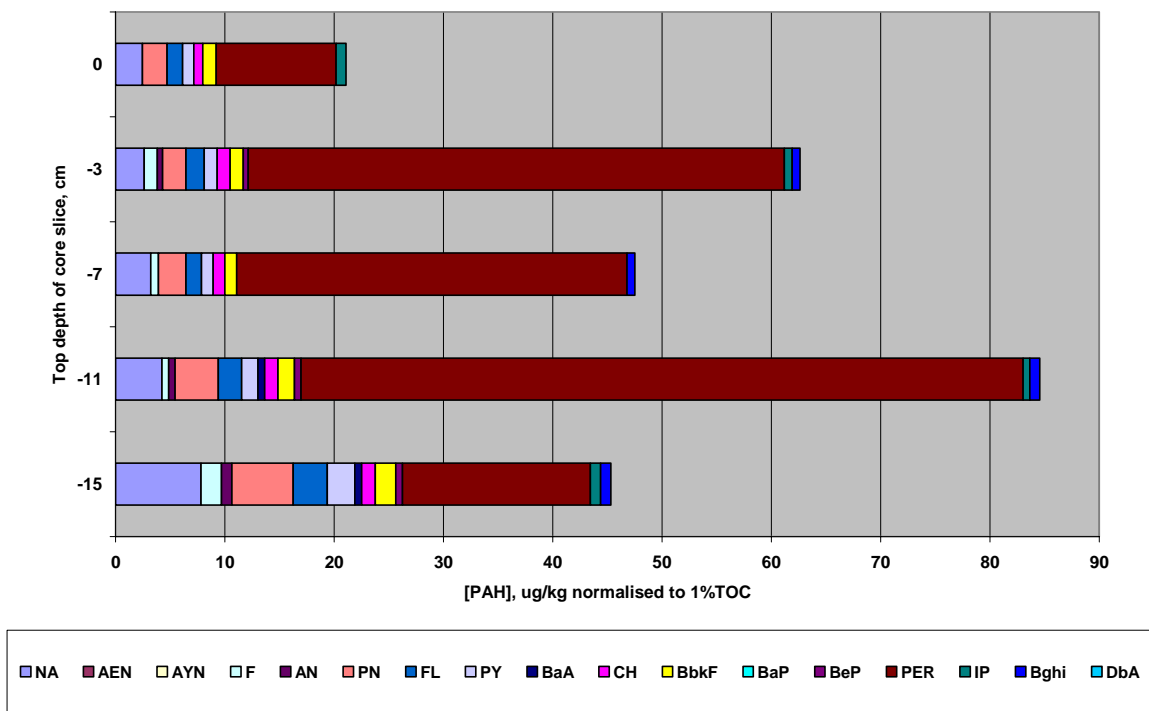


Figure 12. Depth profile of PAHs in Munduran Creek core

### 3.4.1 Sources of PAHs

PAH isomer ratios have been used to infer sources of PAHs in sediments. For example, for PAHs of MW= 178, a concentration ratio of anthracene to the sum of anthracene and phenanthrene <0.10 (both having MW = 178; see Appendix 5) is taken as an indication of petrogenic sources (e.g. fossil fuels), while a ratio >0.10 indicates a dominance of pyrolytic sources (i.e. PAHs formed from high-temperature and incomplete combustion of biomass or fossil fuels) (Yunker *et al.*, 2002). A third source category is diagenetic, such as the case of perylene (a 5-ring PAH). It has been suggested that concentrations of perylene which are higher than 10% of the total penta-aromatic isomers indicate a probable diagenetic input, whereas those in which perylene is less than 10% indicate a probable pyrolytic origin of the compound (Readman *et al.*, 2002).

Table 8 lists the PAH isomer ratios observed in Port Curtis benthic sediments, and reported empirical ratios for the three types of PAH sources. A colour code has been added to more easily differentiate the source types. It is seen from the table that combustion-derived PAHs were predominant in most samples, and perylene was consistently from a diagenetic source, except for one sample taken at red mud dam outlet which was of pyrolytic origin. The samples which indicated PAHs from petrogenic sources clustered around Fisherman's Landing, Calliope River, the marina and the red mud dam outlet.

The potential human health effects and toxicity of PAHs to aquatic organisms are briefly indicated in Appendix 5. Other aquatic organisms such as mussels and scallops are used as biomonitors for PAH contamination (Boehm *et al.*, 2005; Pan *et al.*, 2005). It would be important to monitor the presence of PAHs in Central Queensland coastal waters especially in the Gladstone area in view of its rapidly increasing industrialisation and urbanisation, as well as to investigate the impacts of PAHs on aquatic organisms in Port Curtis. PAHs have been consistently shown to increase in levels in industrialised and urbanised areas, in addition to sites which receive oil spills (Law *et al.*, 2002). There is high potential for PAH contamination from fossil fuel sources (particularly coal, which is continually being transported to the port area). The coal facility at the Gladstone harbour also stockpiles coal (while awaiting loading onto ships for export), which could be blown by wind into the harbour; indeed a few sediment grab samples were observed to contain some tiny particles of coal in them.

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Table 8. PAH isomer ratios and origins.

Sample ID	PAH Ratios							PER/(sum 5-rings)
	AN/(AN+PH)	FL/(FL+PY)	BaA/(BaA+CH)	IP/(IP+Bghi)	PN/AN	FL/PY	BaA/CH	
Narrows1								1.00
Narrows2		0.600				1.50		0.81
MunduranCk2a		0.571		1.00		1.33		0.94
BC		0.500				1.00		0.64
BS		0.500	0.500			1.00	1.00	0.29
TC		0.545	0.375			1.18	0.60	0.30
GC		0.533	0.333			1.20	0.56	0.30
FP		0.556	0.300			1.20	0.50	0.24
NPI		0.533	0.375			1.18	0.63	0.28
PB								
SB		0.500	0.400			1.08	0.60	0.25
FL	0.059	0.567	0.368		12	1.25	0.56	0.19
WI		0.567				1.33		0.22
CCF	0.063	0.568	0.366		13	1.32	0.59	0.12
M	0.111	0.529	0.364		8	1.13	0.57	0.21
CR-U/S	0.077	0.500	0.350		9	1.05	0.77	0.28
CR-NRG		0.528	0.333		16	1.12	0.52	0.17
CR-STP		0.500	0.368			1.06	0.56	0.15
AC	0.100	0.537	0.370		12	1.16	0.59	0.17
RMDO	0.083	0.516	0.360		9.5	1.04	0.59	0.08
SPWC		0.536	0.381			1.15	0.62	0.17
Boyne River								
Colloseum Inlet		0.538	0.400	0.40		1.17	0.67	0.36
Awoonga Dam								1.00
Rodd's Harbour								
<b>Pyrolytic sources</b> (high-T combustion of fossil fuels and biomass)	<b>&gt; 0.10</b>	<b>&gt; 0.5</b>	<b>&gt; 0.35</b>	<b>&gt; 0.5</b>	<b>&lt; 10</b>	<b>&gt; 1</b>	<b>&gt; 0.9</b>	<b>&lt; 0.1</b>
<b>Petrogenic sources</b> (eg fossil fuels, petroleum, shale oil etc)	<b>&lt; 0.10</b>	<b>&lt; 0.5</b>	<b>&lt; 0.2</b>	<b>&lt; 0.2</b>	<b>&gt; 15</b>	<b>&lt; 1</b>	<b>≤ 0.4</b>	
<b>Diagenetic sources</b> (formed from plant or biogenic precursors)								<b>&gt; 0.1</b>

## 4 Conclusions and recommendations for further study

The study confirmed that intertidal (mangrove) sites collect fine sediments, which contained higher concentrations of metals and PAHs than did estuarine sediments. Using radiochemical dating methods ( $^{210}\text{Pb}$  or  $^{137}\text{Cs}$  activity), the upper 28 cm of subsurface sediments were found to have been deposited since 1958, which is roughly the start of the industrialisation of Gladstone. The rate of sediment deposition was at least 0.60 cm/year. The sediment depositional zones identified were: the northern Narrows, lower Calliope River and South Trees Inlet–Boyne River areas. Stable lead isotope ratios in Port Curtis sediments were consistent with those reported for other sediments from northern Queensland and indicated no significant lead pollution sources.

Mangrove cores showed relatively constant metal concentrations with depth. Estimates of background metal levels in Port Curtis estuarine sediments were consistent with the latest reported estimates of the upper continental crust in Queensland (Kamber *et al.*, 2005). The estimated background levels of As, Cr and Ni were found to be very close to the ANZECC ISQG-low guidelines, which was further corroborated by a multivariate analysis to determine the natural gradient of metals in sediments from different sites of the estuary. These lines of evidence indicated that particulate arsenic, chromium and nickel are related to the local geology and do not reflect metal contamination by anthropogenic sources. It would be important to consider this when undertaking sediment quality assessments. PbIR data indicated no significant lead pollution in Port Curtis. However, there is still a need to investigate the role of acid sulfate soils in enhancing sediment metal concentrations, particularly at the mangrove sites.

PAH contaminants in sediments were highest around the industrial area of Gladstone with hardly any detected at Rodds Harbour, indicating that the latter site has relatively limited anthropogenic impacts. Several types of PAHs characteristic of pyrolytic or combustion sources were detected at the middle harbour largely at the Clinton Coal Facility, along Calliope River, at the marina and the South Trees Inlet–Boyne River area. Naturally occurring perylene was found in all sediments and were highest at The Narrows and Munduran Creek. Several types of PAHs, characteristic of combustion sources, were detected at the middle harbour, Calliope River, South Trees Inlet–Boyne River. The presence of these PAHs (although still below ANZECC trigger values) signals the need to monitor aquatic organisms (e.g. bivalves, crustaceans and fish) for any PAH ecological impacts. PAHs believed to be petrogenic in origin have been found in

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several aquatic organisms in the more highly urbanised Brisbane River estuary (Kayal & Connell, 1989, 1995).

There is very little information on both metal and PAH contaminants in particulate atmospheric industrial emissions in Port Curtis. This gap needs to be addressed, especially in view of the current rapid growth of industries in Port Curtis.

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## Appendixes

### Appendix 1: Sources of chemical stressors in Port Curtis estuary (modified from Apte *et al.*, 2005)

Source	As	Cd	Cu	Pb	Zn	Ni	Sb	Hg	Cr	PAHs
Weathering of rock formation	1	1	1	1	1	1	1	0	1	0
Geographical – adjacent catchment	?	?	?	?	?	?	?	?	?	?
Motor vehicle emissions	0	0	0	1	0	0	0	0	0	1
Clearing of vegetation	1	1	1	1	1	1	1	0	1	?
Fertiliser and pesticide application	1	0	1	0	0	0	0	0	0	0
Fish farm effluent	0	0	1	0	0	0	0	0	0	0
Stormwater	1	1	1	1	1	1	0	1	1	1
Sewage treatment plants	1	1	1	1	1	1	1	0	1	1
Waste disposal	?	1	1	1	1	1	1	1	1	?
Foreshore development	?	0	0	0	0	?	0	0	?	?
Industry	1	1	1	1	1	1	0	1	1	1
Shipping	0	0	1	0	1	0	0	0	0	1
Boating and fishing	0	0	1	1	1	0	0	0	0	1
Land reclamation – landfill	?	0	?	0	?	?	0	0	0	?

0 = not likely to occur, 1 = likely to occur, ? = unknown

## Appendix 2: Sediment samples (2003–2005)

Date sampled	Sample ID	Lat.	Long.	Location	No of grabs	No of cores
Dec 2003	N	S 23°35.925	E 151°02.343	Narrows		4
Dec 2003	RH	S 24°05.088	E 151°31.509	Rodds Harbour		4
7/12/04	N1	S 23°33.898	E 151°00.940	Narrows, near mouth of Fitzroy River	1	
7/12/04	N2	S 23°37.136	E 151°02.482	Narrows near mouth of Fitzroy	1	
28/02/05	SPWC	S 23°52.948	E 151°19.069	Spillway Creek	1	2
28/02/05	RMDO	S 23°51.629	E 151°18.006	QAL red mud dam outlet	1	2
28/02/05	PB	S 23°45.825	E 151°17.506	Pelican Bank	1	2
28/02/05	CR-U/S	S 23°51.863	E 151°11.249	Upstream Calliope River	2	2
28/02/05	CR-NRG	S 23°50.562	E 151°12.639	Calliope River, few kms downstream of NRG outlet	2	2
28/02/05	CR-STP	S 23°50.142	E 151°13.379	Calliope River, ~1 km downstream of STP outlet	2	2
28/02/05	FL	S 23°47.355	E 151°10.486	Fishermans Landing, close to outfall (Orica, QCL, QERL)	1	
28/02/05	BC	S 23°39.539	E 151°05.837	Northside Boatway Ck	1	
28/02/05	BS	S 23°40.726	E 151°07.396	Black Swan	1	
28/02/05	TC	S 23°43.376	E 151°08.216	Targinnie Ck	1	2
28/02/05	GC	S 23°44.135	E 151°10.178	Grahams Ck	1	2
28/02/05	FP	S 23°45.280	E 151°09.523	North Friend Point Flat	1	
28/02/05	NPI	S 23°45.682	E 151°10.604	North Passage Island	1	
28/02/05	SB	S 23°46.919	E 151°12.509	Stockyard Bay	1	
28/02/05	WI	S 23°48.936	E 151°12.865	Wiggins Island	1	
28/02/05	CCF	S 23°49.319	E 151°14.340	Clinton Coal Facility	1	
28/02/05	M	S 23°49.968	E 151°14.962	Marina	1	
28/02/05	AC	S 23°50.286	E 151°15.000	Auckland Ck	1	
April 2005	MC1, MC2	S 23°39.465	E 151°02.933	Mundurran Creek	2	2
Aug 2005	N	23.61954	151.04142	Narrows (for dating)		1
Aug 2005	CRM	23.82677	151.22049	Calliope River mouth (for dating)		1
Aug 2005	CRM	23.82244	151.21905	Calliope River mouth, subtidal (for metals)		1
Aug 2005	STI	23.85932	151.30191	South Trees Inlet (for dating)		1
Aug 2005	RH	24.04133	151.607	Rodds Harbour (for dating and PAHs analyses)	1	1
Aug 2005	CI	24.01597	151.442	Colloseum Inlet (for PAHs)	1	
Aug 2005	BR	23.94191	151.35429	Boyne River (for PAHs)	1	
Aug 2005	AD	24.0951	151.3062	Awoonga Dam (for PAHs and metals)	1	

### Appendix 3: Quality assurance: Analyses of certified sediment reference materials

(mg kg<sup>-1</sup> dry wt)

<b>Reference material: PACS-2</b>	<b>Sb</b>	<b>As</b>	<b>Ag</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Hg</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
Mean ( <i>n</i> = 3)	11.6	26	0.7	2.23	97	279	3.00	35	164	336
Standard deviation	2.6	1.5	0.14	0.15	4.6	12	0.15	2.3	8	23
Certified value	11.3	26.2	1.22	2.11	90.7	310	3.04	39.5	183	364
Standard deviation	2.6	1.5	0.14	0.15	4.6	12	0.19	2.3	8	23

<b>Reference material: BCSS-1</b>	<b>Sb</b>	<b>As</b>	<b>Ag</b>	<b>Cd</b>	<b>Cr</b>	<b>Cu</b>	<b>Ni</b>	<b>Pb</b>	<b>Zn</b>
Mean ( <i>n</i> = 3)	0.61	11	<0.1	0.33	131	16	50	22	104
Standard deviation	0.08	0.4	-	0.06	2	1	2	1	3
Certified value	0.59	11.1	-	0.25	123	18.5	55.3	22.7	119
Standard deviation	0.06	1.4	-	0.04	14	2.7	3.6	3.4	12

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

Metal and polycyclic aromatic hydrocarbon contaminants in benthic sediments of Port Curtis

**ICP-MS**

Quality control	Al	Ca	Cr*	Fe	Ni	Cu	Zn	Ag	Cd	Pb	Pb isotope ratios	
											208/206	207/206
MESS-3 av. (n=4)	84200	15300	37.9	42000	47.3	33.9	163	<DL	0.227	21.3	2.0322	0.8123
stdev.	1770	642	5.4	2150	3.4	0.6	14		0.019	0.4	0.0075	0.0022
RSD%	2.1	4.2	14.3	5.1	7.3	1.8	8.5		8.4	1.7	0.37	0.27
Certified value	85800	14700	105	43400	46.9	33.9	159	nc	0.240	21.1	nc	nc
NMI Biosoil av. (n=3)	35700	4820	43.3	26900	21.2	148	196	6.60	0.798	34.1	2.1486	0.8839
stdev.	2320	273	3.6	1690	0.6	6	5	0.27	0.115	0.9	0.0058	0.0016
RSD%	6.5	5.7	8.4	6.3	2.9	3.8	2.5	4.0	14.4	2.6	0.27	0.18
Certified value**	13100	4370	33.0	24900	16.6	150	182	5.63	0.770	31.4	nc	nc
Detection limit	80	100	1.00	100	0.050	0.200	0.300	0.100	0.050	0.030		
Digest blank av. (n=4)	<DL	<DL	1.70	<DL	0.422	0.225	1.55	<DL	<DL	0.079		

\*: Subject to interference (positive bias) in organic-rich sediments.

<DL: less than detection limit, nc: not certified

\*\* : Reference values based on aqua-regia extraction (excludes silicates)

Metal and polycyclic aromatic hydrocarbon contaminants in benthic sediments of Port Curtis

## Appendix 4: Metal concentrations and other sediment parameters

(nd = no data)

### A.4.1 Narrows sediment cores (metals data in mg/kg dry weight)

Core number	depth, cm	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn	Fe	Al	Ca	S	% Mud (<60 um)	% Organic Matter
1	0	0.054	22.10	0.216	84.10	35.60	0.065	44.20	22.60	0.55	76.50	39300	72030	28919	6542	nd	0.16
1	1	0.054	22.30	0.108	85.20	35.60	0.065	44.20	19.40	0.43	84.10	40700	74927	25755	5537	71.70	0.48
1	2	0.054	21.70	0.054	87.70	34.50	0.043	39.90	18.30	0.71	76.50	41600	73827	27258	4363	nd	0.12
1	4	0.053	23.60	0.053	83.80	33.10	0.043	39.50	18.10	0.51	76.90	40600	73629	28194	3366	nd	0.13
1	6	0.618	22.60	0.051	82.70	27.80	0.031	33.00	15.40	0.54	64.90	38800	66342	28677	2466	nd	0.16
1	8	0.051	17.90	0.051	69.80	26.50	0.041	29.50	15.30	0.60	59.00	32100	61960	36339	2163	nd	0.10
1	10	0.052	22.30	0.052	77.40	31.10	0.041	35.20	16.60	0.74	67.30	36700	68023	27856	3543	nd	0.12
1	14	0.052	18.40	0.052	82.10	34.40	0.042	nd	15.70	0.72	nd	33000	63018	33119	5621	nd	0.07
1	18	0.052	21.00	0.052	85.20	24.70	0.041	42.30	19.60	0.67	62.90	36100	69458	30655	6602	nd	0.08
1	22	0.053	22.90	0.053	90.10	23.30	0.042	42.30	19.00	0.67	62.40	38900	68407	24836	7044	nd	0.12
1	26	0.053	21.20	0.053	85.80	23.40	0.043	40.40	18.10	0.66	62.70	37200	71007	28205	6871	nd	0.09
2	0	0.054	26.40	0.054	78.40	33.70	0.044	35.90	18.50	0.70	69.60	39900	66152	39254	7250	67.80	0.23
2	1	0.054	21.00	0.054	79.70	32.20	0.043	37.50	17.20	0.60	72.90	37000	69299	33370	5613	71.70	0.12
2	2	0.055	25.10	0.055	87.50	34.10	0.044	40.70	19.80	0.69	78.10	40000	72466	29730	6904	63.30	0.13
2	4	0.055	20.90	0.055	87.40	36.50	0.044	38.70	17.70	0.72	76.20	37100	71311	26700	5999	61.40	0.50
2	6	0.052	27.40	0.052	79.00	33.30	0.042	39.60	19.80	0.49	78.10	40600	65851	30337	6373	61.50	0.15
2	8	0.052	30.70	0.052	88.60	40.70	0.052	42.80	20.90	0.64	76.20	44800	68611	27533	9165	66.60	0.15
2	10	0.057	24.10	0.057	90.50	34.10	0.045	38.70	18.20	0.67	73.90	42200	72160	31966	5120	69.50	0.15
2	14	0.053	18.00	0.053	87.10	23.30	0.042	40.20	19.00	0.67	63.40	37300	69546	30334	4722	69.90	0.10
2	18	0.056	22.30	0.056	89.00	24.50	0.033	42.30	20.10	0.75	63.50	38700	71712	33442	6087	71.80	0.13
2	22	0.053	21.80	0.053	87.00	27.50	0.032	48.70	18.00	0.66	71.90	38400	78531	28470	6537	72.60	0.11
2	26	0.053	20.80	0.053	88.50	24.40	0.042	42.40	19.10	0.68	64.60	39100	71678	26113	5792	73.20	0.12
2	30	0.051	21.50	0.051	83.90	39.00	0.041	38.00	16.40	0.70	68.70	39200	70260	28245	8350	65.50	0.13
2	35	0.051	14.60	0.051	78.80	31.60	0.031	35.70	15.30	0.70	66.30	34500	67670	26586	5546	71.10	0.08
2	40	0.051	15.80	0.051	89.70	30.70	0.031	37.90	15.40	0.65	74.80	38500	75937	16406	6679	90.80	0.08
3	0	0.054	11.80	0.054	48.90	34.40	0.043	41.90	17.20	0.60	75.20	18200	73676	28929	5047	nd	0.11
3	1	0.054	24.60	0.054	90.20	33.40	0.054	40.90	17.20	0.70	78.70	41900	73629	26791	4248	nd	0.13
3	2	0.053	20.10	0.053	80.00	31.00	0.043	36.40	16.00	0.50	72.70	37700	70313	29124	3185	nd	0.14
3	4	0.053	21.60	0.053	85.70	34.20	0.043	41.70	17.10	0.47	81.20	40300	76293	27116	3329	nd	0.28
3	6	0.052	24.30	0.052	87.50	31.90	0.041	38.10	18.50	0.57	72.10	42900	70750	26025	4577	nd	0.12
3	8	0.052	22.00	0.052	83.40	38.40	0.041	17.60	17.60	0.59	nd	39200	64561	24788	4520	nd	0.12
3	10	0.052	26.70	0.052	85.40	29.00	0.041	33.20	17.60	0.65	64.30	41100	58639	26632	3409	nd	0.16
3	14	0.052	24.00	0.052	81.20	32.00	0.041	36.10	17.50	0.70	68.10	40000	70484	28277	3080	nd	0.12
3	18	0.052	20.40	0.052	85.50	29.00	0.041	48.70	19.70	0.64	75.70	36300	79618	26442	5949	nd	0.09
3	22	0.053	21.80	0.053	82.80	24.40	0.042	42.40	19.10	0.75	66.80	37500	72232	28831	7403	nd	0.11
3	26	0.053	23.80	0.053	88.80	27.70	0.043	48.00	19.20	0.66	74.60	40200	81228	25862	7672	nd	0.11

Metal and polycyclic aromatic hydrocarbon contaminants in benthic sediments of Port Curtis

**A.4.1 Narrows sediment cores** (continued)

Core number	depth, cm	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn	Fe	Al	Ca	S	% Mud (<60 um)	% Organic Matter
4	0	0.053	12.90	0.053	58.10	31.80	0.042	35.00	15.90	0.54	65.70	19900	65750	37385	5944	nd	0.27
4	1	0.054	13.30	0.054	51.20	17.30	0.032	16.20	14.00	0.49	45.30	19400	55811	50022	3568	71.70	0.28
4	2	0.054	23.70	0.054	85.00	33.30	0.054	37.60	18.30	0.52	72.10	39900	69531	31729	6433	nd	0.57
4	4	0.053	19.30	0.053	85.30	31.00	0.032	34.20	16.00	0.58	67.30	37400	66937	28242	5367	nd	0.10
4	6	0.052	24.50	0.052	82.70	28.20	0.042	32.40	16.70	0.68	62.70	38000	61945	32868	6195	nd	nd
4	8	0.052	25.60	0.052	76.00	30.30	0.042	32.30	17.70	0.55	64.70	37800	64039	37762	6514	nd	0.15
4	10	0.057	25.60	0.057	85.80	38.70	0.045	nd	17.10	0.75	nd	40700	65260	35360	6595	66.30	0.15
4	14	0.053	24.70	0.053	82.50	25.40	0.032	40.20	19.00	0.62	63.40	38400	71644	37274	4699	65.00	0.10
4	18	0.053	23.60	0.053	82.10	26.30	0.042	41.00	20.00	0.71	62.00	37300	69193	32344	6198	65.00	0.11
4	22	0.053	18.90	0.053	83.50	26.40	0.042	45.40	19.00	0.62	68.60	35500	74742	25171	5649	75.70	0.10
4	26	0.053	20.50	0.053	88.80	29.70	0.042	50.90	19.10	0.66	80.60	38600	83551	25977	6745	82.20	0.10

**A.4.2 Other mangrove, subtidal and Boyne River sites** (Ag, Cd and Hg in µg/kg dry weight, other metals in mg/kg dry weight)

Sample ID	Depth, cm	Ag	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Al	Ca	S	% Mud (<60um)	% Organic Matter
SPWCK1	0-1	50	17.2	25	44.1	17.7	18.6	10.7	62.4	32300	46100	29800	2400	61.3	nd
	1-2	50	18.2	25	48.2	20.8	19.5	11.6	67	34200	50000	27800	1600	67.7	nd
QAL/RMDO1	0-1	50	10.5	72	35.9	16.3	12.9	9.35	50.3	23900	39800	12200	1000	73.0	1.60
	1-2	50	16.2	25	43.9	22.4	17.8	10.7	92.6	35300	45600	13700	857	60.6	1.94
	2-4	201	9.85	24	30.6	16.4	12.3	8.21	49.6	21600	33100	8730	652	78.8	1.52
	4-6	250	11.5	22	31.9	16.8	12.1	8.74	51.1	24100	36700	8500	772	80.7	1.52
	6-8	156	8.96	31	31.5	15.9	12.1	7.96	50.4	21500	34700	9710	1200	79.6	1.56
	8-10	332	7.9	26	36.1	16.4	11.3	7.96	52.6	23500	35100	11500	1500	81.6	nd
	10-14	343	8.73	30	29.2	14.4	9.8	7.49	43.3	20400	32700	10500	1700	76.2	nd
CRM/MC	0-2	433	11.7	47	24.7	28.2	18.6	11.7	74.8	35100	59500	7390	2900	41.2	nd
	2-4	328	10.5	33.9	25.5	27.9	18.2	10.6	73.2	34200	59000	8310	2500	33.6	nd
	4-6	312	11.1	41.3	26.6	29.6	20.7	12.6	74.4	36600	62700	7460	3400	47.6	nd
	6-8	289	12.2	47.2	30.2	33.8	23.2	12	95	41000	60100	8970	4700	50.5	nd
	8-10	312	12.1	43	23.2	29.5	19.7	12	75.5	36300	60700	7630	4700	41.8	nd
	10-14	360	12.6	53.9	24.3	29.6	20.3	13.2	85.3	37700	67900	7170	5900	57.4	nd
	14-18	481	11.6	37.7	25.5	33.7	22.6	12.6	87.1	40100	67600	7600	4800	44.5	nd
	18-22	281	12.5	45.9	28.8	33.3	24.1	11.9	99.1	41500	67100	10200	5600	57	nd
	22-26	327	12.3	71.5	29.3	32.4	22.9	12.3	79.2	39100	68200	10400	6400	50.9	nd
	26-30	268	10.4	44.9	24.1	28.3	22.4	13.1	71.3	33300	63700	11700	5700	49.3	nd
	30-34	544	9.13	45.3	26.2	30.5	21.4	13	69.6	34400	62900	10800	5700	61.8	nd

Metal and polycyclic aromatic hydrocarbon contaminants in benthic sediments of Port Curtis

**A.4.2 Other mangrove, subtidal and Boyne River sites (continued)**

Sample ID	Depth, cm	Ag	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Al	Ca	S	% Mud (<60um)	% Organic Matter
CR-US core1	0-1	50	9.53	25	39.3	37.5	20.7	12.3	83.7	39000	60800	6470	3200	94.6	3.72
	1-2	50	12.6	25	34.8	36	20.5	12	88.3	40300	63700	6030	3900	93.7	3.52
	2-4	177	10.3	37	20.3	33.2	19	11.7	74.2	33600	59100	4370	4400	91.8	3.57
	4-6	421	10.2	35	25.8	32.6	19.6	11.7	84.8	34700	59600	4780	3600	94.6	3.25
	6-8	158	11.3	37	24.3	35.7	20.7	13	87.4	37600	61400	4740	4500	90.9	3.80
	8-10	262	10.6	31	19.2	31.6	16.9	10.7	67.9	31300	53900	5500	4300	92.0	3.05
	10-14	146	9.45	46	26.4	28.5	15.7	9.31	77.8	32900	43000	7680	4000	92.3	2.77
CR-NRG core1	0-1	50	16.7	117	48.7	37.7	26.2	14.6	92.1	46300	76200	8710	2000	95.2	4.21
	1-2	50	16.3	25	47.1	38.5	25.8	14.5	94.5	48500	60000	7280	1600	93.6	3.66
	0-1	50	11.6	56	42.2	41.9	21.5	10.4	79	45000	58400	6630	1700	83.7	2.92
	1-2	340	11.2	63	30.7	44.3	21.4	10.3	78	43600	57300	6300	1500	84.1	3.16
	2-4	220	10.4	49	23.9	48.5	19.9	10	80.3	41600	59700	5050	1700	86.2	2.76
	4-6	274	11.1	47	24.6	39.5	19.1	9.83	72.4	40500	58100	5090	1300	85.7	3.08
	6-8	176	10.4	51	25.9	36.6	17.1	9.54	66.9	34600	51400	5590	1700	85.6	2.74
	8-10	228	6.35	40	21.9	48.9	15.7	6.95	60.2	34700	57600	6310	3200	90.7	2.31
	10-14	225	6.65	38	14.4	54.2	18.9	7.64	49.5	30200	50500	7140	5800	94.1	nd
CR-STP core1	0-1	50	11.6	56	42.2	41.9	21.5	10.4	79.0	45000	58400	6630	1700.0	83.7	2.92
	1-2	340	11.2	63	30.7	44.3	21.4	10.3	78.0	43600	57300	6300	1500.0	84.1	3.16
	2-4	220	10.4	49	23.9	48.5	19.9	10	80.3	41600	59700	5050	1700.0	86.2	2.76
	4-6	274	11.1	47	24.6	39.5	19.1	9.83	72.4	40500	58100	5090	1300.0	85.7	3.08
	6-8	176	10.4	51	25.9	36.6	17.1	9.54	66.9	34600	51400	5590	1700.0	85.6	2.74
	8-10	228	6.35	40	21.9	48.9	15.7	6.95	60.2	34700	57600	6310	3200.0	90.7	2.31
	10-14	225	6.65	38	14.4	54.2	18.9	7.64	49.5	30200	50500	7140	5800.0	94.1	nd
TC core1	0-1	434	18.6	71	39.9	31.2	25.4	13.6	80.3	46300	73700	5110	2800	93.0	4.14
	1-2	421	18.9	62	34.4	33.8	27.1	13.4	83.2	46600	69800	4860	3000	91.5	4.14
	2-4	526	19.4	30	31.4	32	26.2	13.2	80.7	45400	70900	3130	2600	94.1	4.57
	4-6	186	18.3	29	28.2	30	24.9	13.3	81.2	44300	71100	2930	2700	93.7	4.43
	6-8	192	18.4	34	30.2	31.3	27.9	14.5	104	44300	71000	2970	3000	93.1	4.12
	8-10	183	17.5	26	30.4	32.4	24.3	13.6	80.9	42900	72900	2880	3300	95.2	4.2
	10-14	169	14.1	22	30.1	31	25.8	13.2	77.9	39300	74500	2870	4000	92.7	4.01
GC core1	0-1	374	17.7	56	29.7	32.2	25.7	13.4	80.6	46200	72300	5460	2500	96.0	4.55
	1-2	382	18.4	59	32.4	31.9	26.3	13.7	93.4	45800	75800	4140	2500	95.5	4.84
N1	0-10	328	16.4	56	37.7	17.5	35.3	13.2	60.2	36200	61100	25500	6800	nd	nd
N2	0-10	360	17.6	53	40.2	22.5	42.6	15.6	72.3	43700	78300	7480	1500	nd	nd
MC1	0-10	396	8.73	147	36.1	35.3	18.3	11.4	52.6	40000	53400	2890	10800	69.7	5.04

Metal and polycyclic aromatic hydrocarbon contaminants in benthic sediments of Port Curtis

**A.4.2 Other mangrove, subtidal and Boyne River sites (continued)**

Sample ID	Depth, cm	Ag	As	Cd	Cr	Cu	Ni	Pb	Zn	Fe	Al	Ca	S	% Mud (<60um)	% Organic Matter
SB	0-10	106	34.8	72	44.1	36.3	26.5	15.4	91.7	47000	56800	9420	8600	84.5	nd
BC	0-10	50	22.7	226	56.9	29.9	40.3	15.4	88.8	46700	77700	3570	4400	65.5	nd
BS	0-10	50	26.9	64	58.5	28.2	33.3	15.6	77.2	44100	68500	6130	6700	38.3	nd
CCF	0-10	50	12.6	25	41	40.2	28.4	12.2	94.2	51300	68800	11600	1700	79.2	3.81
M	0-10	50	20	25	49.4	42.3	27.3	14.1	108	51200	69000	13200	1700	91.8	4.42
FL	0-10	50	18.1	25	47.5	33.6	25.1	12	83.9	44300	58700	9280	2000	88.9	4.07
FP	0-10	50	12.6	78	47.6	25.4	20.3	10.8	67	34600	46200	7820	2900	23.5	3.42
NPI	0-10	50	15.2	25	46.8	31.6	25.2	12.9	81.8	42100	65500	8020	3300	77.8	4.49
AC	0-10	50	17.8	25	43.4	28.3	22.5	12.1	81.8	39200	57700	22200	1700	65.2	3.39
BR1	0-10	50	12.6	25	51.5	9.94	11.1	7.76	37.5	19800	23100	48900	2100	nd	2.08
BR4	0-10	50	13.9	25	52	12.1	12.7	9.47	45.4	22000	32500	45000	2500	nd	2.47
BR8	0-10	50	15	25	43.6	16.3	16.6	10.7	49.9	27800	36300	55100	3200	nd	3.11
BR12	0-10	50	8.56	25	67.1	8.16	8.21	5.75	30.3	16600	14200	44300	1900	nd	1.11
BR16	0-10	50	13.1	25	23.7	15.9	9.42	11	32.6	14600	30000	4720	2300	nd	2.38
Awonga Dam	0-10	744	8.04	66.2	20.4	27.1	13	15	64.4	28600	52200	4660	328	29.9	nd

Metal and polycyclic aromatic hydrocarbon contaminants in benthic sediments of Port Curtis

**A.4.3. Rodds Harbour sediment cores (metal data in mg/kg dry weight)**

Core	Depth, cm	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Zn	Fe	Al	Ca	S	% Mud	% OM
1	0	0.0510	11.5	0.0510	45.2	14.3	0.040	13.3	10.2	0.378	36.7	17044	47037	44189	2534	nd	0.050
1	1	0.0517	14.5	0.0517	52.7	16.5	0.030	15.5	12.4	0.424	44.5	21714	54158	41438	2937	nd	0.084
1	2	0.0516	13.1	0.0516	49.1	15.5	0.030	14.5	10.3	0.403	41.3	20246	52940	40638	3167	nd	0.062
1	4	0.0510	11.1	0.0510	46.1	14.3	0.020	13.3	9.2	0.377	39.8	19170	47260	33243	2504	nd	0.079
1	6	0.0504	13.4	0.0504	46.6	18.1	0.020	nd	8.1	0.514	24.2	18732	44595	32805	3710	nd	0.041
1	8	0.0503	9.9	0.0503	41.1	12.1	0.020	10.1	14.1	0.352	33.2	16281	42056	33542	2641	nd	0.061
1	10	0.0503	10.2	0.0503	39.6	11.1	0.020	9.1	7.0	0.403	31.2	14902	39565	34267	2802	nd	0.055
1	14	0.0503	9.0	0.0503	42.8	11.1	0.020	9.1	8.1	0.372	30.2	15295	40352	35272	2678	nd	0.040
2	0	0.0510	20.0	0.0510	78.8	14.3	0.040	12.2	11.2	0.408	34.7	37964	47377	44366	2477	43.5	0.068
2	1	0.0512	11.1	0.0512	47.2	13.3	0.030	13.3	11.3	0.410	40.0	16390	46800	40852	2264	35.3	0.299
2	2	0.0514	13.4	0.0514	47.7	14.4	0.030	11.3	10.3	0.422	35.0	19234	47042	42665	2108	40.3	0.049
2	4	0.0514	11.0	0.0514	49.0	13.4	0.030	13.4	9.3	0.452	37.0	17472	46336	41760	2286	33.1	0.047
2	6	0.0506	11.8	0.0506	49.8	13.2	0.030	11.1	9.1	0.466	33.4	18834	43790	42398	2359	35.3	0.056
2	8	0.0505	11.4	0.0505	45.3	12.1	0.030	11.1	9.1	0.323	34.3	17971	43989	36836	2378	25.6	0.051
2	10	0.0508	12.7	0.0508	46.2	12.2	0.040	10.2	8.1	0.467	34.5	18693	43803	41211	3756	32.9	0.090
2	14	0.0505	13.3	0.0505	41.2	11.1	0.030	15.2	11.1	0.424	35.4	18595	49996	51494	5792	20.0	0.047
2	18	0.0539	15.1	0.0539	48.0	10.8	0.030	16.2	11.9	0.464	39.9	21145	54130	55274	7390	26.3	0.052
2	22	0.0508	13.1	0.0508	43.6	9.1	0.030	13.2	11.2	0.406	34.5	19194	48222	48319	6450	30.4	0.056
3	0	0.0511	21.7	0.0511	76.8	14.3	0.020	14.3	11.2	0.573	37.8	34976	48835	39428	2705	nd	0.061
3	1	0.0511	12.3	0.0511	49.9	13.3	0.020	12.3	11.3	0.522	37.8	18307	48273	38603	2232	nd	0.047
3	2	0.0511	12.4	0.0511	43.2	13.3	0.020	11.2	9.2	0.337	35.8	17485	44358	43933	2743	nd	0.381
3	4	0.0513	12.0	0.0513	45.1	13.3	0.020	12.3	10.3	0.431	39.0	16617	46862	40704	3473	nd	0.022
3	6	0.0503	12.3	0.0503	43.9	12.1	0.020	11.1	10.1	0.583	35.2	18609	42857	34653	4928	nd	0.053
3	8	0.0503	12.0	0.0503	41.7	12.1	0.020	12.1	10.1	0.312	38.2	18392	42446	30380	6318	nd	0.061
3	10	0.0505	12.7	0.0505	44.2	13.1	0.020	10.1	8.1	0.445	34.4	19406	42995	36260	4837	nd	0.055
4	0	0.0511	12.2	0.0511	52.7	21.4	0.020	11.2	13.3	0.521	67.4	17870	47045	52146	3269	49	0.063
4	1	0.0520	23.3	0.1041	84.7	20.8	0.030	21.9	13.5	0.406	48.9	38920	56742	43735	4002	nd	nd
4	2	0.0513	13.5	0.0513	55.0	16.4	0.030	14.4	11.3	0.585	43.1	21864	54358	45118	3306	54.2	0.061
4	4	0.0524	13.4	0.0524	57.1	16.8	0.030	14.7	12.6	0.639	42.9	22514	56000	45948	3285	56.9	0.271
4	6	0.0508	12.2	0.0508	58.0	16.3	0.030	16.3	13.2	0.529	43.7	22568	53115	41908	3645	57.7	0.081
4	8	0.0508	10.9	0.0508	57.2	16.2	0.030	15.2	12.2	0.620	44.7	22242	53993	37729	4195	57.4	0.067
4	10	0.0508	14.5	0.0508	57.2	22.4	0.020	13.0	11.2	0.610	36.0	23875	52375	44736	5195	nd	0.090
4	14	0.0505	11.2	0.0505	41.9	9.1	0.020	13.1	11.1	0.485	33.4	16776	47551	49519	4171	18.7	0.047
4	18	0.0508	14.8	0.0508	47.2	8.1	0.020	13.2	11.2	0.569	32.5	19289	44668	57132	5909	25.1	0.048
4	22	0.0511	15.0	0.0511	46.4	10.2	0.020	14.3	11.2	0.572	36.8	20742	48615	64455	7570	22.1	0.062

## Appendix 5: Polycyclic aromatic hydrocarbons and their properties

<b>List of PAHs and Some Properties</b> (source: Kennish, 1997)					
<b>PAH</b>	<b>Acronym</b>	<b>MW</b>	<b>Number of rings</b>	<b>Relative carcinogenicity index (a)</b>	<b>Toxic to aquatic organisms (b)</b>
<b>Naphthalene</b>	NA	128	2	?	Y
<b>Acenaphthylene</b>	AYL	152	3	?	?
<b>Acenaphthene</b>	AEN	154	3	?	?
<b>Fluorene</b>	F	166	3	?	Y
<b>Anthracene</b>	AN	178	3	?	?
<b>Phenanthrene</b>	PH	178	3	?	Y
<b>Fluoranthene</b>	FL	202	4	?	Y
<b>Pyrene</b>	PY	202	4	?	?
<b>Benz[a]Anthracene</b>	BaA	228	4	1	?
<b>Chrysene</b>	CH	228	4	?	Y
<b>Benz[a]Pyrene</b>	BaP	252	5	3	Y
<b>Benz[e]Pyrene</b>	BeP	252	5	?	?
<b>Benzo[b+k]Fluoranthene</b>	BbkF	252	5	2	?
<b>Perylene</b>	PER	252	5	?	?
<b>Benzo[ghi]Perylene</b>	Bghi	276	6	?	?
<b>Indeno[123cd]Pyrene</b>	IP	276	6	1	?
<b>Dibenz[ah]Anthracene</b>	DbA	278	5	1	Y

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

Metal and polycyclic aromatic hydrocarbon contaminants in benthic sediments of Port Curtis

## Appendix 6: Concentration of PAHs in Port Curtis sediments

(µg/kg dry weight normalised to 1% TOC)

### A.6.1 Mangroves and other sites

Sample ID	AEN	AYL	AN	F	NA	PN	IP	PER	BaA	BaP	BeP	BbkF	Bghi	CH	DhA	FL	Py	Total [PAHs]
Narrows grab 1 (N1)	<2	<2	<2	<2	<2	<2	<2	28	<2	<2	<2	<2	<2	<2	<2	<2	<2	28
Narrows grab 5 (N2)	<2	<2	<2	<2	<2	2	<2	15	<2	<2	<2	4	<2	2	<2	3	2	28
Munduran Creek (MC2a)	<2	<2	<2	<2	2.5	2.5	0.8	18	<2	<2	<2	1.3	<2	0.8	<2	2	1	29
BC	<2	<2	<2	<2	<2	<2	<2	2	<2	<2	<2	1	<2	<2	<2	1	1	5
BS	<2	<2	<2	<2	<2	<2	<2	6	3	3	3	6	2	3	<2	5	5	36
TC	<2	<2	<2	1	2	5	<2	7	3	2	4	9	3	5	<2	6	5	52
FP	<2	<2	<2	<2	<2	7	<2	8	3	5	5	14	5	7	<2	10	8	72
GC	<2	<2	<2	1	2	7	<2	9	3	3	5	11	3	6	<2	8	7	65
FL	<2	<2	1	3	4	16	<2	10	7	7	9	19	7	12	<2	17	13	125
NPI	<2	<2	<2	<2	3	6	<2	8	3	3	4	10	3	5	<2	8	7	60
CR-U/S	<2	<2	1	3	3	12	<2	19	7	7	11	25	9	13	<2	13	13	136
SB	<2	<2	<2	<2	<2	3	<2	4	2	2	3	6	2	3	<2	4	4	33
CR-NRG	<2	<2	<2	4	4	21	<2	12	9	9	14	31	10	18	<2	19	17	168
WI	<2	<2	<2	<2	<2	17	<2	9	<2	<2	9	22	<2	13	<2	17	13	100
CR-STP	<2	<2	<2	<2	<2	12	<2	8	7	7	10	22	7	12	<2	11	11	107
CCF	5	<2	2	8	5	30	<2	12	15	15	19	42	13	26	<2	42	32	266
M	<2	<2	2	4	3	16	<2	13	8	7	11	23	7	14	<2	18	16	142
AC	<2	<2	2	4	3	18	<2	13	10	11	13	28	10	17	<2	22	19	170
RMDO	<2	<2	1	2	4	11	<2	8	9	14	17	51	12	16	<2	16	15	176
SPWC	<2	<2	<2	<2	4	8.0	<2	12	8	11	13	28	11	13	<2	15	13	136
PB	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	
Colloseum Inlet	<2	<2	<2	<2	4	4	2	5	2	2	<2	6	3	3	<2	8	7	48
Awoonga Dam	<2	<2	<2	<2	3	<2	<2	11	2	2	<2	6	3	3	<2	8	7	48
Boyne River	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	
Rodd's Harbour	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	

Metal and polycyclic aromatic hydrocarbon contaminants in benthic sediments of Port Curtis

**A.6.2 Munduran Creek (core 1)**

Top depth of core slice, cm	NA	AEN	AYN	F	AN	PN	FL	PY	BaA	CH	BbkF	BaP	BeP	PER	IP	Bghi	DbA
0	2.45	<2	<2	<2	<2	2.3	1.4	1.03	<2	0.82	1.23	<2	<2	11.0	0.92	<2	<2
-3	2.6	<2	<2	1.2	0.48	2.1	1.7	1.2	<2	1.2	1.2	<2	0.48	49.0	0.71	0.71	<2
-7	3.2	<2	<2	0.71	<2	2.5	1.4	1.1	<2	1.1	1.1	<2	<2	35.7	0.00	0.71	<2
-11	4.2	<2	<2	0.61	0.61	3.9	2.1	1.5	0.61	1.2	1.5	<2	0.61	66.1	0.61	0.91	<2
-15	7.8	<2	<2	1.9	0.94	5.6	3.1	2.5	0.63	1.3	1.9	<2	0.63	17.2	0.94	0.94	<2