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A risk assessment approach to contaminants in Port Curtis, Queensland, Australia

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Abstract

Port Curtis is one of Australia's leading ports for which substantial industrial expansion is proposed over the next decade. However, there has been little attempt to date to assess the extent of contamination in waters, sediments and biota or to characterize the potential impacts of contaminants on aquatic biota. Contaminants of potential concern to biota and human health were investigated in the Port Curtis estuary using a screening-level risk assessment approach. Dissolved metal concentrations in waters were below [ANZECC/ARMCANZ, 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Vol. 1. The Guidelines, Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand] trigger values, suggesting low risk of these contaminants. In sediments, arsenic, nickel and chromium concentrations exceeded interim sediment quality guidelines-low (ISQG-low), but were also high in the reference zone suggesting a natural origin. Historical data on naphthalene in Harbour sediments showed that it was also of potential concern. Bioaccumulation of contaminants in a range of biota was also used as an indicator of contaminant exposure. Biota were generally enriched in metals and tributyltin, which was also elevated in water and sediments. Although not unique to Port Curtis, mercury in barramundi was identified as a potential risk to human health.

Keywords: Port Curtis estuary; Ecological risk assessment; Contaminants; Human health risk assessment; Metals; TBT

1. Introduction

The Port Curtis estuary (Fig. 1) is an area on the eastern coast of Australia where releases of chemical contaminants to air, land and water from various anthropogenic activities have taken place over the last century. Historically, extensive mangrove and salt marsh areas have been reclaimed for port infrastructure, marina, industrial and urban development. Port Curtis is one of Australia's leading ports, particularly for the export of coal, for which substantial industrial expansion is proposed over the next decade. Heavy industry including the world's largest alumina refinery, aluminium smelters, a cement kiln, a 1680-MW coal-fired power station and chemical plants line the foreshore. An area adjacent to the estuary has shale oil reserves worth millions of dollars, resulting in exploratory mining and processing in the last decade. Gladstone, the major town, now supports a population of over 44,000. Cattle grazing and fruit growing are land uses in the rural surrounds, while gold and copper mining

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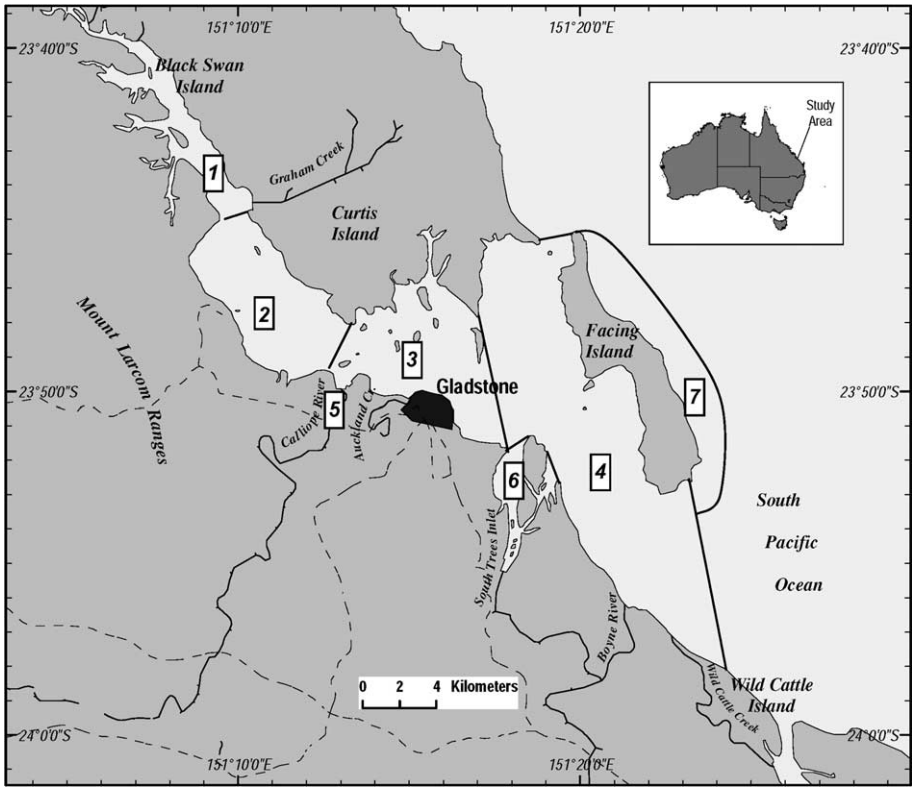

Fig. 1. Map of the study area—the Port Curtis estuary, Australia showing the seven zones used in the study of the Port Curtis estuary, 2001–2002: The Narrows (Zone 1); Targinnie section of the harbour (Zone 2); middle harbour (Zone 3); southern and outer harbour (Zone 4); Calliope River (Zone 5); Boyne River and South Trees Inlet (Zone 6); and eastern side of Facing Island (Zone 7).

had historical importance in the early development of the catchment. Port Curtis is also located adjacent to the World Heritage-listed Great Barrier Reef Marine Park.

As a consequence of increasing population and industrial activities, Port Curtis is expected to receive increasing quantities of contaminants from both diffuse and point sources. However, there has been little attempt to date to assess the extent of contamination in waters, sediments and biota or to characterize the potential impacts of contaminants on aquatic biota.

Ecological risk assessment (ERA) is a process that evaluates the likelihood that adverse ecological effects are occurring as a result of exposure to one or more stressors (US EPA, 1992). ERA may be effects driven e.g. an impact on a population or community is detected and the cause of the impact is subsequently investigated, or it may be stressor driven, where inputs into a system and how stressors interact within the system are used to prioritise issues (Munkittrick and McMaster, 2000).

This study aimed to identify contaminants of potential ecological concern by conducting a stressor-driven ecological risk assessment of contaminants in the Port Curtis estuary. Because of the limited historical data on contaminants in the estuary, a screening-level ecological risk assessment process was undertaken to objectively rank the risks of individual contaminants, before targeting specific contaminants for detailed investigation. The common approach to a screening-level ecological risk assessment of chemical contaminants in coastal environments is to examine concentrations of contaminants in water and sediments (Asante-Duah, 1998) and to compare these to guideline values using a hazard quotient approach. However, this study also included the measurement of contaminant concentrations in biota to assess contaminant bioaccumulation in the estuary. In addition, risk to humans through the ingestion of seafood was also determined in a screening-level human health risk assessment.

2. Materials and methods

2.1. Study area

The study area is a composite estuarine system located within latitudes 23°40′S and 23°59′S and longitudes 151°07′E and 151°25′E (Fig. 1). The major component estuaries, the Calliope and Boyne Rivers, The Narrows and Auckland Creek merge into a naturally sheltered 30 km long deepwater harbour, which is periodically dredged. The tidal range is 4.9 m at

mid-harbour and the estuary is thought to be well mixed. The Port Curtis region is important ecologically with a remaining 80 km^2 of mangroves and 100 km^2 of salt marsh, salt flats and mud flat communities (Saenger, 1995) sustaining significant fisheries. The sparse seagrass beds in the Port Curtis estuary (approximately 900 ha) support visiting and local populations of the vulnerable dugong (*Dugong dugon*) and the endangered green turtle (*Chelonia mydas*) (IUCN, 2003).

2.2. Problem formulation

Conceptual models of sources and fate of chemical contaminants in the Port Curtis estuary were developed, identifying multiple chemical stressors from diffuse and point sources of shipping, heavy and light industry, boating and fishing, landfill, sewage treatment plants, urban and agricultural runoff, aquaculture, motor vehicles and a sporadic connection with the adjacent Fitzroy catchment (Jones, 2003).

The deliberations of an expert panel and a survey of Port Curtis stakeholders defined the assessment endpoints for the screening-level risk assessment. These included:

- sustaining commercial fisheries;
- maintaining seagrass in richness/biomass and as feeding grounds for fisheries;
- maintaining health of mangrove and mud flats/banks communities;
- sustaining food sources and habitat for dugongs, turtles and dolphins.

These assessment endpoints could not be measured directly, so surrogate measures for assessing exposure were used. These included the measurement of contaminant concentrations in waters, sediments and biota, which were then compared to effects data using water and sediment quality guidelines (ANZECC/ARMCANZ, 2000).

The assessment endpoint for the human health risk assessment was that the health of the human population would not be adversely affected by exposure to contaminants via ingestion of seafood collected from this area. Human exposure via swimming and recreational activities was not considered.

A list of 61 possible chemical contaminants was recorded for the area, based on a rigorous appraisal of historical data. Using a decision tree approach, chemicals of low toxicity were eliminated if exposure was unlikely (e.g. manganese). Detailed rationale for the selection of contaminants included in the study is given in Jones (2003). The selected substances examined were Al, As, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Se, Zn, fluoride, cyanide, polycyclic aromatic hydrocarbons (PAHs) and tributyltin (TBT). Historical data for these chemicals were collated and where data gaps were identified, new data were collected. Several contaminants (aluminium, iron, selenium, fluoride and cyanide) were only measured in waters, not sediments, due to the absence of national and overseas sediment quality guidelines for comparison (ANZECC/ARMCANZ, 2000; CCME, 2001). Because mercury and PAHs strongly partition to sediments (ANZECC/ARMCANZ, 2000), these contaminants were not measured in waters. Fluoride, cyanide and PAHs were not measured in biota due to expected poor accumulation in soft tissues (CCME, 1999; Sijm and Hermens, 2000; NPI, 2001).

Contaminants examined in the human health risk assessment were the same as that measured for biota in the screening-level risk assessment, except that TBT was only measured in the flesh of mud crabs.

As sources of potential contaminants were spread across a wide area, a regional scale assessment was carried out, with the study area divided into seven zones for the screening-level risk assessment (Fig. 1): The Narrows (Zone 1); Targinnie section of the harbour (Zone 2); middle harbour (Zone 3); southern and outer harbour (Zone 4); Calliope River (Zone 5); Boyne River and South Trees Inlet (Zone 6); and eastern side of Facing Island (Zone 7). Because fish and shellfish from the area are likely to move between these zones, the study area was not divided into geographical zones for the human health risk assessment.

2.3. Existing data

Little data on chemical contaminants in the Port Curtis estuary were available. Data from Queensland Alumina Limited on metals and fluoride in the water column of the Boyne River and South Trees Inlet from surveys in February and September 1993 were incorporated into the risk analysis, together with data on cyanide and fluoride, collected in 2000 by South Pacific Petroleum (SPP)/Central Pacific Minerals (CPM) in the Fisherman's Landing area of Port Curtis estuary. Data relating to contaminants in benthic sediments were included from a survey of the Gladstone Harbour shipping channel in 2000 (WBM Oceanics Australia, 2000). Pesticides examined in sediments and biota have been reported to be below guideline concentrations in the study area (Mortimer, 2000; Haynes and Johnson, 2000).

In biota, previous studies have shown that concentrations of copper and selenium were high in mud crabs (*Scylla serrata*) of the Port Curtis region compared to other areas in Queensland (Mortimer, 2000; Andersen and Norton, 2001), while copper and iron were high in seagrasses (*Zostera capricorni*) compared to Moreton Bay, Queensland (Prange and Dennison, 2000). There were only a few data on chemical contaminants in

seafood species from Port Curtis and these were not incorporated.

2.4. Collection of new data

New data on chemical contaminants in waters and sediments were obtained in two surveys, a winter dry season (August–October 2001) and a summer wet season (February 2002) survey, applying a coarse grid with 50 sampling points distributed across seven zones of the study area. Four of these 50 sampling points were upstream of Zone 3 in areas regarded as possible sources of contamination, i.e. Gladstone marina and Auckland Creek. Because Port Curtis is considered to be a well-mixed estuary, only surface water samples were collected. Duplicates were taken from five sites in each survey. To obtain a better indication of temporal variation in dissolved metal concentrations in surface waters, additional monitoring was undertaken at Clinton Coal Wharf (Zone 3), Fisherman's Landing (Zone 2), Calliope River (Zone 5) and Grahame Creek (Zone 1) in April 2003. A nested sampling design was used, comprising weekly sampling over one month, daily sampling within one week and hourly sampling within one day.

Samples for metal analyses were taken at all site locations whereas water samples for analysis of cyanide, fluoride and TBT were only collected at locations likely to be influenced by a source(s), for example, near wharfs and chemical manufacturing plants. Salinity and pH measurements for the Port Curtis estuary were recorded at all sampling sites during the water surveys. Sediment samples were collected using a Van Veen grab. A detailed description of the methods for water and sediment collection and analyses is given in Jones (2003).

Biota, including seagrass *Z. capricorni*, oysters *Saccostrea amasa*, *S. echinata* and *S. glomerata*, and mud whelks *Telescopium telescopium* were collected within the same winter dry season to reduce variability due to spawning and seasonal differences. Three separate species of oysters of the genus *Saccostrea* were examined due to variation in species with habitats in the study area. These species are often cross referenced in the literature, confusion mostly being due to the plasticity of morphology with habitat adaptation and similar morphological characteristics in these oysters. For this study, it was assumed differences in net accumulation between these species were small and that concentrations were comparable with that in other studies with these species.

Eleven samples of oysters and mud whelks were collected from four study sites (one each in Zone 2, 3, 5 and 6) and a reference site. Due to funding constraints, only five samples of seagrass were collected from one study site (Zone 3) and a reference site. Reference sites, located in areas of low human use, were at northeastern Facing Island (23°76′S, 151.34′E) for oysters; Yellowpatch on northern Curtis Island (23°27′S, 151°04′E) for mud whelks; and the adjacent Rodds Bay (24°02′S, 151°39′E) for seagrass.

Mud whelks were of equivalent size. An individual, depurated and shucked, comprised the 9 g of sample required for the various analyses. As individual oysters were small, a composite sample of 9 g of soft tissue was used. Leaf material of seagrass was randomly chosen, washed but not scraped, according to the methods detailed in Jones (2003).

For the human health risk assessment, adult individuals of sea mullet (*Mugil cephalus*) ($n = 12$), barramundi (*Lates calcarifer*) >58 cm ($n = 9$), banana prawns (*Penaeus merguiensis*) ($n = 12$) and male mud crabs (*S. serrata*) with carapace >15 cm ($n = 12$), were randomly chosen from commercial and amateur catches in the region. Samples were collected between November 2001 and March 2002. Supply of barramundi flesh was limited to "wings" (muscle associated with pectoral fins) with only nine samples available due to high demand and low availability of this fish (a consequence of a series of dry seasons preceding the study). All specimens were caught in coastal waters of the region. Samples were taken of flesh with skin removed from the pectoral muscle of the barramundi and the anterior dorsal muscle block of the sea mullet. Abdominal tissue was sampled from prawns with shell and digestive tract removed, while muscle tissue of the mud crab body was sampled. Length of individual barramundi was measured. Detailed sampling and preparation procedures are given in Jones (2003).

2.5. Analytical methods

All water samples were collected using trace-analysis sampling and analysis techniques similar to those of Apte and Day (1998). The metals Cd, Cu, Ni, Pb and Zn were analysed by solvent-extraction graphite furnace atomic adsorption spectroscopy (SE GFAAS) (Apte and Day, 1998). Al and Fe were analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Spectroflame EOP). Analyses of As and Se were performed by hydride-generation atomic fluorescence spectrometry (AFS) using standard analytical conditions recommended by the manufacturer (Merlin Analyser, PSA analytical, UK). TBT was analysed by gas chromatography atomic absorption spectrometry (GC-AAS) following aqueous phase derivatisation with sodium tetraethylborate (Bowles et al., 2003). Fluoride was analysed using a colorimetric method (APHA, 1998). Total cyanide was analysed by AGAL (Pymble NSW) using a Lachat flow injection analyser according to the standard method of the American Public Health Association (APHA, 1998). Spiked recoveries were between 93% and 114% for most metals in identified quality control samples of the August 2001 and February

2002 surveys. Lead spike recoveries in the February 2002 survey were slightly lower and ranged from 81% to 96%.

Sediments (particle size $\leqslant$1 mm) were analysed for total metals in triplicate using inductively coupled plasma optical emission spectroscopy (ICP-OES) for Cu, Ni and Zn, inductively coupled plasma mass spectrometry (ICP-MS) for Cd and Pb and neutron activation analyses (at Becquerel Laboratories, Lucas Heights, NSW) for As and Cr. Mercury was analysed by AFS using the techniques of Bowles et al. (2001). Certified marine reference sediments (PACS-2 and BCSS-1) were used. Spiked recoveries were 87–107% for most metals in quality control samples. TBT was analysed by GC-AAS following extraction into HCl/methanol (Bowles et al., 2004). Sediments were analysed for PAHs by CSIRO Marine Research, Melbourne, Australia. TBT and PAH concentrations in sediments were normalised to 1% organic carbon, according to sediment quality guidelines (ANZECC/ARMCANZ, 2000).

Metals in biota were determined following microwave-assisted acid digestions (nitric:hydrochloric:hydrogen peroxide, 3:1:1). Cd, Pb, Cr and Ni were analysed by GFAAS; Al, Cu, Fe and Zn by ICP-AES and As and Se by hydride-generation AAS (Jones, 2003). For mercury, homogenised samples of oyster and mud whelk were acid-digested and analysed using the same procedure as that used for sediments. Certified reference materials (TORT 2, DORM 1, DORM 2, NIST2976, BCR279, NBS1575) were used for quality assurance purposes. Butyltins were extracted from homogenised soft tissue samples using a potassium hydroxide, thermally assisted digestion procedure. The butyltin species were ethylated and trapped onto Tenax. The ethylated butyltin species were thermally desorbed from the Tenax and analysed by gas GC-AAS (Method CAAC/AA02). Spike recoveries of butyltins in oysters (MBT = 74%, DBT = 37%, TBT = 113%) and in mud whelks (MBT = 47%, DBT = 90%, TBT = 91%) were used to correct tissue concentrations of MBT, DBT and TBT.

For the human health risk assessment, analytical methods were the same as for biota. Spike recoveries of butyltins in mud crab muscle tissue (MBT = 67%, DBT = 102%, TBT = 101%) were used to correct tissue concentrations of MBT, DBT and TBT.

2.6. Risk calculations for contaminants in waters and sediments

For waters, the expected environmental concentration (EEC) for each contaminant (the upper 95% confidence limit of the mean of the monitoring data) was divided by the ANZECC/ARMCANZ (2000) trigger value (to protect 95% of species with 50% confidence for slightly–moderately disturbed systems) to calculate the Hazard Quotient (HQ). If the HQ was <1 that contaminant was considered to be of low risk and was not considered further. If the HQ was >1, the contaminant was identified as a contaminant of potential ecological concern.

For arsenic and fluoride in waters, overseas guidelines (CCME, 1999; Ministry of Environment Lands and Parks, 2001) were used as ANZECC/ARMCANZ guidelines were either absent or required chemical speciation measurements for comparison.

For sediments, the EEC was the maximum contaminant concentration measured. This was divided by the low value of interim sediment quality guidelines (ISQG-low) (ANZECC/ARMCANZ, 2000). If the HQ was >1, then the contaminant was identified as a contaminant of potential ecological concern.

2.7. Contaminant enrichment in biota

As it was difficult to link adverse effects to bioaccumulation of contaminants in biota due to the lack of relevant tissue residue guidelines for these particular species, contaminant enrichment in biota (rather than contaminants of potential ecological concern) was determined. Concentrations in biota were used to determine contaminants requiring further investigation using the following methods.

Significant differences ($P = 0.05$) in metal concentrations between sites were determined using the Mann–Whitney U test for seagrass and Kruskal–Wallis non-parametric test followed by a post-hoc non-parametric comparison (Zar, 1999) for oysters and mud whelks. If a significant difference was found for a metal concentration between the study site and the reference site, data at the study site were compared to an upper tolerance level (UTL) that was the 95% upper confidence limit of the 95th percentile of that metal at the reference site. Contaminant enrichment was indicated when a study site displayed concentrations exceeding the UTL. Contaminant concentrations were also compared to benchmark concentrations in the literature including Generally Expected Levels for contaminants without dietary health risk (Scanes and Roach, 1999; ANZFA, 2001; Ministry of Environment Lands and Parks, 2001).

Concentrations of TBT in oysters and mud whelks were compared to concentrations cited in the literature (Jarvinen and Ankley, 1999; Meador, 1999).

2.8. Risk calculations for human health

For the human health risk assessment, screening for contaminants of potential concern involved comparing chronic daily intakes (CDIs) of fish/shellfish to threshold toxicity values (ATSDR, 2000; US EPA, 2001; JECFA, 2001) using the HQ method, i.e.

$$\mathrm{HQ} = \frac{\mathrm{CDI}}{\text{Threshold Toxicity Value}}$$

where

$$\text{CDI}\ (\text{mg kg}^{-1}\ \text{day}^{-1}) = \frac{\text{FT} \times \text{IR} \times \text{EF} \times \text{ED}}{\text{body weight} \times \text{average exposure years} \times 365\ \text{days yr}^{-1}}$$

and FT is the upper 95% CL of mean fish/shellfish tissue concentration (mg kg^{-1}), IR the kilograms of fish/shellfish ingested per day (FRDC, 1992; ABS, 1995), EF the exposure frequency (day year^{-1}) (ABS, 1995), ED the exposure duration, i.e. 65 years for adults, 5 years for children.

If the HQ was >0.1, the contaminant was identified as a contaminant of potential concern. The standard HQ value of one was divided by 10, to account for additivity of the contaminants (Hancock, 1976), in keeping with a conservative approach.

Tissue concentrations in barramundi, sea mullet, prawn and mud crabs were also compared to ANZFA food code standards (ANZFA, 2001) where available. Food code standards were $2\,\text{mg kg}^{-1}$ for inorganic arsenic, $0.5\,\text{mg kg}^{-1}$ for lead, $0.5\,\text{mg kg}^{-1}$ for mercury in fish and $1.0\,\text{mg kg}^{-1}$ for mercury in large predatory fish including barramundi.

3. Results and discussion

3.1. Screening-level risk assessment

3.1.1. Inorganics

The concentrations of metals, cyanide and fluoride in waters of the Port Curtis estuary were low during both dry and wet season surveys when compared to water quality guidelines (ANZECC/ARMCANZ, 2000). Due to the volatile nature of cyanide, its low persistence in the environment and its speciation at high pH and high temperatures (CCME, 1999; ANZECC/ARMCANZ, 2000; Ministry of Environment Lands and Parks, 2001), cyanide was not expected to be elevated in Port Curtis estuary. Indeed, cyanide was not detected in waters sampled in the Port Curtis estuary at the level of reporting ($<5.0\,\mu\text{g L}^{-1}$), while fluoride, though detectable ($0.8–1.1\,\text{mg L}^{-1}$), did not exceed the guideline value of $1.5\,\text{mg L}^{-1}$ (Ministry of Environment Lands and Parks, 2001).

Concentrations of dissolved metals in surface waters are shown in Table 1. All HQs for metals in water were <1. However, the mean dissolved copper concentration in Port Curtis ($0.34\,\mu\text{g L}^{-1}$) was about 10-fold higher than typical copper concentrations found in clean NSW coastal waters ($0.031 \pm 0.006\,\mu\text{g L}^{-1}$) using the same techniques (Apte et al., 1998).

The water surveys in 2001–2002 were observations at points in time and may not have detected pulses of contaminant releases or fluctuations that occur over time, such as those caused by seasonal influences, circulation, tides, weather, effluent release or biogeochemical cycling. However, temporal sampling in April 2003 confirmed that the concentrations were lower than guidelines, as found in the previous surveys.

Metal concentrations in sediments were generally low (Table 2). Total organic carbon ranged from 0.07% to 2% and the <63 μm particle size fraction varied from 0.1% to 97%. The mean mercury concentration was $10 \pm 10\,\mu\text{g kg}^{-1}$ dry weight, well below the ISQG-low of $150\,\mu\text{g kg}^{-1}$ dry wt. For arsenic, 28 sediment samples (maximum = $36\,\text{mg kg}^{-1}$ dry wt.) exceeded the ISQG-low of $20\,\text{mg kg}^{-1}$ dry wt., giving HQs of 1–6.2. For chromium, five samples (maximum = $85\,\text{mg kg}^{-1}$ dry wt.) exceeded the ISQG-low of $80\,\text{mg kg}^{-1}$ dry weight, with HQs of 1–3.1. For nickel, 22 samples (maximum = $33\,\text{mg kg}^{-1}$ dry wt.) exceeded the ISQG-low of $21\,\text{mg kg}^{-1}$ dry weight (HQs of 1–1.7). The high concentrations of arsenic, chromium and nickel in sediments were possibly due to natural mineralogy, as high concentrations were also found in the reference zone (Zone 1). The results for metals in both water and sediments indicated a low risk of effects on assessment endpoints in the Port Curtis estuary.

Metal concentrations in biota at study sites were generally higher than concentrations at reference sites (Table 3) and comparisons with UTLs indicated enrichment of aluminium, arsenic, chromium, copper, iron, lead, mercury, nickel, selenium and zinc in biota of the Port Curtis estuary (Table 4).

For seagrass, concentrations of aluminium, arsenic, cadmium, copper, iron, selenium and zinc were significantly different ($P < 0.05$) between the mid-harbour study site (Zone 3) and the reference site and comparisons with UTLs indicated metal enrichment in seagrass at the study site.

Table 1
Dissolved metals ($\mu\text{g L}^{-1}$) and TBT ($\mu\text{g Sn L}^{-1}$) in waters of the Port Curtis estuary

	Al	As	Cd	Cu	Cr	Fe	Ni	Pb	Se	Zn	TBT
Mean	23	1.9	<0.005	0.34	<2	10	<0.28	<0.10	0.1	<0.33	<0.012
Max	46	10	0.013	1.18	<2	15	0.66	0.68	0.4	1.03	0.02
Trigger value	–	12.5[a]	5.5[b]	1.3[b]	4.4[b]	–	70[b]	4.4[b]	2[c]	15[b]	0.006[b]

[a] CCME (2001).
[b] ANZECC/ARMCANZ (2000).
[c] Ministry of Environment Lands and Parks (2001).

Table 2
Metals (mg kg^{-1} dry weight) and TBT (mg Sn kg^{-1} dry weight) in sediments of the Port Curtis estuary

	As	Cr	Cu	Ni	Pb	Zn	Cd	TBT[a]	Hg
Mean (S.D.)[b]	18(12)	50(29)	18(12)	14(8)	30(27)	32(29)	0.10(0.01)	0.05(0.04)	0.01(0.01)
Median	16	53	14	13	16	16	<0.10	0.03	0.01
Minimum	6	13	4	4	5	11	<0.10	<0.025	0.001
Maximum	36	85	44	33	18	113	0.24	0.655	0.055
Trigger value (low)[c]	20	80	65	21	50	200	1.5	0.005	0.150
Exceedances[d]	28	5	0	22	0	0	0	8	0
Trigger value (high)[c]	70	370	270	52	220	410	10	0.070	1

[a] TBT = Tributyltin, 56 samples analysed.
[b] Mean (Standard deviation).
[c] Sediment quality guideline trigger values (ANZECC/ARMCANZ, 2000).
[d] Number of values exceeding trigger values (100 samples).

Table 3
Range of concentrations of metals in biota (mg kg^{-1} wet weight) at study sites and reference sites

Biota	Al	As	Cd	Cr	Cu	Fe
Seagrass						
Study	185–286	0.4–1.4	0.02–0.03	0.6–1.1	1.8–2.2	242–634
Reference	97–191	0.2–0.3	0.01–0.02	0.4–0.7	0.3–0.5	103–162
Oysters						
Study	26–248	3.3–6.9	0.14–0.42	0.2–9.4	114–363	35–252
Reference	10–37	11.2–15.7	0.14–0.26	<0.1–1.5	93–186	26–56
Whelks						
Study	5–199	2.0–4.2	0.03–0.37	0.1–15.4	13–53	59–423
Reference	4–77	1.7–4.4	0.01–0.08	0.1–3.8	24–48	42–228

Biota	Hg	Ni	Pb	Se	Zn
Seagrass					
Study	–	0.2–0.6	0.1–0.2	0.006–0.010	7–8
Reference	–	0.2–0.3	0.07–0.12	0.002–0.004	2–3
Oysters					
Study	0.03–0.09	<0.2–9.3	<0.04–0.09	0.3–1.5	463–1400
Reference	0.03–0.07	<0.2–0.9	<0.04–0.18	0.4–0.7	187–388
Whelks					
Study	0.01–0.37	0.3–15	<0.04–0.60	0.2–1.3	26–340
Reference	0.02–0.18	0.6–4.0	<0.04–0.07	0.2–0.4	14–67

Aluminium, chromium, copper, iron, nickel, selenium and zinc were enriched in oysters at two or more study sites, based on comparisons with UTLs (Table 4) and benchmarks in the literature. Although not significantly different between sites ($P = 0.058$), nearly half of the 55 oyster samples had mercury concentrations (median = 0.05 mg Hg kg^{-1} wet wt. (0.20 mg Hg kg^{-1} dry wt.)) exceeding the 85th percentile of world recordings for oysters (0.19 mg Hg mg kg^{-1} dry wt.) and concentrations reported for estuaries adjacent to Sydney, Australia (0.01–0.03 mg kg^{-1} wet wt.) (Scanes and Roach, 1999). Copper concentrations in oysters from all sites (93–363 mg kg^{-1} wet wt. (389–1530 mg kg^{-1} dry wt.)) were higher than national (29 mg kg^{-1} wet wt.) and international (280 mg kg^{-1} dry wt.) benchmark concentrations for oysters reported in Scanes and Roach (1999), as well as the Australian Food Code Generally Expected Level (30 mg kg^{-1} wet wt.) for copper (ANZFA, 2001).

The Targinnie harbour site (Zone 2) and the mid-harbour site (Zone 3) had the most oyster samples with concentrations above UTLs for metals and with concentrations significantly different between the study site and the reference site. Oysters were generally the same size (average size = width 35 mm, length 50 mm) across sites except those from mid-harbour, which were smaller (average size = width 20 mm, length 30 mm). The relationship between oyster size and tissue metal concentrations is unclear (Mackay et al., 1975; Talbot, 1985) and there appears to be no consistent relationship for molluscs generally (Langston et al., 1998). It is possible that the higher metal concentrations in oysters at mid-harbour could be influenced by size as well as location.

In Zone 3, enrichment of aluminium, chromium, lead, iron, mercury, selenium and zinc was found in mud whelks based on UTL comparisons (Table 4). Lead, iron, selenium and zinc were enriched in mud whelks at the adjacent study site in Zone 5. Samples of

Table 4
Samples of biota above UTLs at sites significantly different from the reference site

Biota	Metals (no. of samples above UTL)										
	n	Al	As	Cd	Cr	Cu	Hg	Fe	Pb	Ni	Se	Zn
Seagrass												
Zone 3	5	4	4	5	ns	5	–	5	ns	ns	5	5
Oysters												
Zone 2	11	11	ns	ns	4	8	ns	11	ns	ns	11	11
Zone 3	11	11	ns	ns	6	11	ns	11	2	3	ns	11
Zone 5	11	11	ns	ns	6	9	ns	9	ns	6	ns	11
Zone 6	11	11	ns	10	ns	ns	ns	10	ns	ns	11	11
Whelks												
Zone 2	11	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	10
Zone 3	11	5	ns	11	5	ns	7	11	11	ns	11	11
Zone 5	11	ns	ns	ns	ns	ns	ns	8	7	ns	9	9
Zone 6	11	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	11

ns = no significant difference between study site and reference site.

mud whelks at all study sites had zinc concentrations significantly higher ($P < 0.05$) than reference site samples and UTL comparisons indicated general enrichment of zinc.

Our observation of metal enrichment in Port Curtis estuary is supported by other studies of this area (Mortimer, 2000; Andersen and Norton, 2001). Andersen and Norton (2001) found that concentrations of copper in hepatopancreas of mud crabs at Port Curtis (mean = 198 mg kg^{-1} wet wt. in 1999, $n = 20$; mean = 311 mg kg^{-1} wet wt. in 2000, $n = 45$) were approximately threefold higher than the concentrations in mud crabs at Ayr (mean = 83 mg kg^{-1} wet wt. in 1999, $n = 10$; mean = 96 mg kg^{-1} wet wt. in 2000, $n = 30$). In addition, Mortimer (2000) recorded higher copper concentrations in the hepatopancreas of Port Curtis mud crabs (mean = 637 mg kg^{-1} dry wt.; $n = 10$) than in mud crabs at other Queensland locations, i.e. Ayr, Brisbane River, Maroochy River, Oxley Creek and Pine River (range of means = 42.6–334 mg kg^{-1} dry wt.).

In reference to concentrations linked to effects, oyster concentrations at study sites greatly exceeded that associated with reduced survival in other bivalves, i.e. 5 mg kg^{-1} Cu wet wt. in saltwater bivalve *Cerastoderma edule* and 130 mg kg^{-1} Zn wet wt. in saltwater blue mussel *Mytilus edulis* (Jarvinen and Ankley, 1999). However, further research is needed to determine whether toxic effects are associated with tissue metal concentrations in biota of the Port Curtis area.

On the basis of the current data, it is difficult to single out a major source for any of the metal contaminants in Port Curtis, particularly as there are possibly several interacting hydrological circulations occurring. Potential sources of metal contamination to the estuary are numerous and are spread across the study area. They include air and water emissions from several industrial sources, shipping and handling, coal stockpiles, power station corrosion products, leachate from landfill, urban development, sewerage treatment, historical copper mining, oil shale exploration and natural elements in the landscape.

3.1.2. TBT and PAHs

Water column TBT concentrations were above the trigger value of 0.006 μg Sn L^{-1} (Table 1). TBT was identified as a contaminant of potential ecological concern for Zones 2, 3 and 4 (Fisherman's Landing, mid- and southern harbour), areas traversed by the shipping channel, with HQs for TBT in water of >1 (i.e. 1.5–3.3).

TBT was detected in 8 out of 56 sediment samples with a maximum concentration of 0.66 mg Sn kg^{-1} dry wt. detected in Auckland Creek, a wharfing and docking area for sea vessels. Seven sediment samples from the marina, Auckland Creek and Fisherman's Landing (Zone 2) exceeded the ANZECC ISQG-low of 5 μg Sn kg^{-1} dry wt., with HQs ranging from 7 to 131. The high concentrations were similar to US harbours (average 0.41 and 0.82 mg Sn kg^{-1}) (Alzieu, 1998) and within the 1 mg Sn kg^{-1} expected in the vicinity of Australian marinas (Batley, 1995).

Enrichment of TBT in biota confirmed TBT as a contaminant of potential ecological concern. Oysters at Clinton Coal Wharf (Zone 3) and Fisherman's Landing (Zone 2) had concentrations ranging from 0.3 to 0.7 mg TBT kg^{-1} dry wt, while concentrations of TBT (0.5–1.5 mg TBT g^{-1} dry weight) in mud whelks from Calliope River mouth (Zone 5) exceeded the concentrations (0.5 mg TBT kg^{-1} dry weight) previously linked to imposex in gastropods in the same subclass, Prosobranchia (Meador, 1999) and were similar to extremely high concentrations of 0.3–1.6 mg TBT kg^{-1} dry wt and 0.9–2.0 mg TBT kg^{-1} dry wt. reported in gastropods of British estuaries (Alzieu, 1998). Further study to determine the extent of imposex in gastropods in Port Curtis is underway.

Concentrations of PAHs in all 23 sediment samples were below detection (<100 μg kg^{-1} dry wt.) although historical data with a lower detection level (<10 μg kg^{-1} dry wt.) (WBM Oceanics Australia, 2000) suggested HQs for naphthalene of 1.3–4 in Zones 2, 3 and 4 (Fisherman's Landing, mid- and southern Harbour). Elevated naphthalene concentrations in the Port Curtis estuary could be attributed to oil shale deposits underlying the region and the exposure of natural mineralogy through dredging of the shipping channels. Anthropogenic sources of PAHs are also widespread in the estuary, with potential sources including dust and runoff from coal stockpiles at Clinton Coal Wharf, Auckland wharf, the power station and the alumina refinery. Aluminium smelting contributes PAH emissions of 23000 kg per annum to the atmosphere (NPI, 2001). In addition, more than 45 oil spills were recorded by the Australian Maritime Safety Authority for the port between 1983 and 2000, another likely source of PAH contamination.

3.2. Human health risk assessment

Safe levels of most metals and TBT were found in all seafood collected. Tissue concentrations of arsenic (inorganic), lead and mercury did not exceed the Australian Food Code Standards for the relevant species. However, mercury in barramundi gave HQs >0.1 (HQ of 0.61 for adults and 0.41 for children), indicating mercury may be a contaminant of potential concern. As mercury concentrations are biomagnified along the food chain and accumulate in muscle tissue, elevated concentrations of mercury were expected in barramundi, a large predatory fish. Mercury in piscivorous fish has mostly been shown to be present as methylmercury, the most toxic form to humans (Bowles et al., 2001; Ministry of Environment Lands and Parks, 2001). Greater than 90% of total mercury in barramundi from a freshwater system was found to be present as methylmercury (Bowles et al., 2001). Speciation of mercury in barramundi tissue was not determined in the current study.

The current legal size for barramundi catches in Queensland is between 580 and 1200 mm. A linear relationship between mercury concentrations and length of barramundi has been evident in previous studies (Bowles et al., 2001). The relationship between length and total mercury concentration over the size range of the fish sampled in this study is shown in Fig. 2 where a linear relationship ([mercury concentration] = 0.9441 [length of barramundi] − 499.61 (r^2 = 0.95)) was found. Applying this relationship, a barramundi greater than 1060 mm would exceed the WHO guideline for mercury.

The barramundi are catadromous, the juvenile (male) fish inhabiting upstream freshwater bodies while the mature breeding adults move downstream to inhabit estuarine and coastal waters. The large barramundi are usually females, though size at which sex inversion occurs (about 870 mm) varies with individuals and populations (Bowles et al., 2001). Being migratory, movements of the barramundi of this study prior to being caught were unknown. It was assumed that they were from a population with a range covering the Port Curtis estuary, the adjacent Fitzroy River and estuary and the connecting Narrows, an assumption based on local tagging knowledge (Sawynok, B, Sunfish, pers. comm.). Concentrations of metals in barramundi were therefore likely to reflect values for the region, rather than specifically for Port Curtis. Barramundi from this region are not expected to exceed the Australian Food Code standard for barramundi of 1.0 mg kg^{-1} Hg wet weight, but may exceed the 0.50 mg kg^{-1} Hg wet weight for fish generally (ANZFA, 2001).

The implications for human health are that the larger the barramundi, the higher the tissue mercury, the higher the human exposure by ingestion and consequently the greater the potential for adverse effects on human health. Due to embryonic uptake of mercury, pregnant women are advised to restrict their consump-

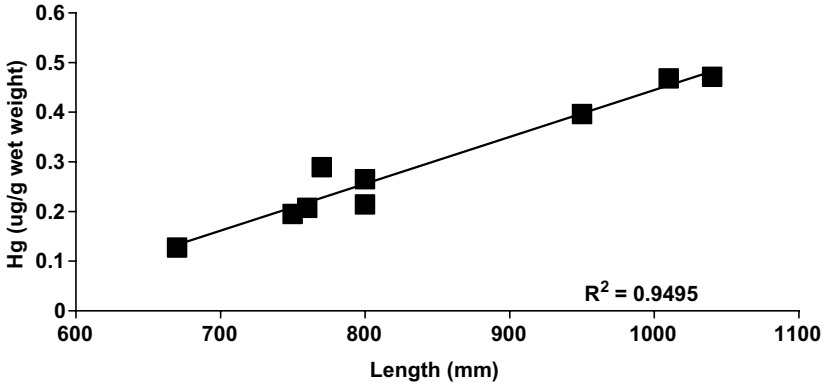

Fig. 2. Mercury in Barramundi from the Port Curtis region.

tion of higher trophic level fish such as barramundi (ANZFA, 2001).

4. Conclusions

Assessment endpoints may be potentially at risk from chemical contaminants in Port Curtis, given that enrichment of metals and TBT was found in biota, and TBT and naphthalene were identified as contaminants of potential ecological concern. The inclusion of bioaccumulation data as an additional line of evidence for exposure in the risk assessment was important, particularly as several metals were accumulating to high concentrations in biota, but were not accumulating in waters or sediments above guideline values. The ability of biota to integrate fluctuating concentrations of metals over time and to reflect exposure via dietary uptake meant that the inclusion of bioaccumulation data allowed a more thorough assessment of exposure of biota to contaminants in Port Curtis. The sources of the contaminants that are bioaccumulated may be further identified by carrying out field surveys over a wider geographical area and by modeling contaminant dispersion to differentiate natural and anthropogenic sources.

Further studies are in progress to determine the pathways by which metals are accumulated by biota of the Port Curtis estuary, e.g. via food, suspended particles and (or) passive uptake. The ecological health of organisms that have increased metal burdens is also being evaluated by measuring sublethal stress indicators (biomarkers) in selected biota. Future studies could also include an assessment of the risks associated with exposures to PCBs and dioxins (not assessed in this study) in the Port Curtis estuary.

Although there is a management issue for human consumption of large fish from the Port Curtis estuary in respect to mercury concentrations, this is not exclusive to Port Curtis. Attention to standards regulating the consumption of large predatory fish, particularly by pregnant women, is required.

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