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Abstract

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Keywords

spatial, queensland, estuary, curtis, port, australia, copper, variability, zinc, cadmium, nickel, manganese, CMMB

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Spatial variability of cadmium, copper, manganese, nickel, and zinc in the Port Curtis Estuary, Queensland, Australia

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Abstract Port Curtis is a rapidly growing industrialised and urbanised harbour in Central Queensland, Australia. Water sampling surveys were undertaken in late 2003 and 2004, accompanied by additional sediment sampling to investigate the sources and behaviour of trace metals, and the effects of pH on metal partitioning between dissolved and particulate forms. Sampling and analyses of trace metals in waters and suspended particulates were undertaken along axial transects extending away from possible point-sources within the harbour. Additional sampling was undertaken in selected inlets and major freshwater sources to Port Curtis, including the Fitzroy River. Most dissolved metal concentrations were significantly elevated in Port Curtis compared to the concentrations measured in the adjacent coastal waters. Dissolved cadmium did not exhibit any discernible spatial trend, with concentrations measured in Port Curtis in the range <1-38 ng/L. Dissolved copper and zinc concentrations ranged from <19 to 800 and <31 to 580 ng/L respectively, and maxima were observed in inner harbour waters adjacent to the southern entrance to the Narrows and in close proximity to anthropogenic sources. Dissolved nickel concentrations were measured in the range of 110 to 900 ng/L, and exhibited a maximum concentration in the central to northern Narrows, in an area that was not adjacent to anthropogenic sources. Dissolved manganese concentration maxima were measured in close proximity to the dissolved nickel maxima. Measurements of marginally lower pH and higher salinities in the inner harbour and Narrows may partially explain the trends in metal concentrations. By contrast, dissolved metal concentrations in oceanic waters adjacent to Port Curtis were low and comparable to those measured in the open Pacific Ocean and uncontaminated coastal sites around Australia. It appears likely that the elevated dissolved metal concentrations measured in Port Curtis and the Narrows were not caused by a single point source, and are the result of several factors, including extensive industrial activity around the foreshore, fluxes from sediment-porewater, low flushing durations, lower water pH, and possibly episodic inputs from the flooding of adjacent rivers.

Additional keywords: baseline study, spatial trends, copper, manganese, nickel, and zinc

Introduction

Port Curtis estuary is situated on the eastern coast of central Queensland, Australia, adjacent to the city of Gladstone and the World Heritage-listed Great Barrier Reef Marine Park (GBRMP) (Figure 1). Substantial industrialisation has occurred in the region over the last century, which has resulted in increased urbanisation, industrialisation, and shipping activities in the area. Port Curtis is one of Australia's largest ports for the export of raw materials such as coal. Its foreshore is lined with a number of heavy industries, including the world's largest alumina refinery, aluminium smelters, a 1680-megawatt coal-fired power station, and several chemical plants (Jones *et al*., 2005).

A recent screening-level risk assessment of metals in the Port Curtis estuary indicated that dissolved concentrations of metals in the waters were in the low- or sub-µg/L range and generally below levels of regulatory concern in Australia (ANZECC/ARMCANZ, 2000; Jones *et al*., 2005). However, the concentrations of many metals were elevated above background levels, and local seagrass, oyster, and mud whelk species were enriched in one or more of the metals cadmium, copper, nickel, and zinc (Andersen and Norton, 2001; Andersen, 2004; Jones *et al*., 2005). A shell disease in local mud crabs has also been shown to be associated with copper enrichment (Andersen and Norton, 2001). The pathways for metal enrichment were unclear, and further investigation of metal sources was recommended to improve the information available for environmental planning and decision making processes. Surprisingly, there are few data on trace metal concentrations in the adjacent Great Barrier Reef Marine Park (GBRMP), despite the acknowledged ecological significance of the location and the increased risk of contamination from anthropogenic activities in the region.

The aim of this study was to investigate trace metal behaviour and sources in Port Curtis and surrounding waters by characterising the spatial distributions of the cadmium, copper, nickel, and zinc. Two sampling surveys were undertaken, first along axial transects extending away from possible point sources within the harbour and through the Narrows, and then, following analysis of results, targeted sampling at selected sites (Figure 1). This included a repeat axial transect through Port Curtis, and temporal sampling at two selected locations having elevated metal concentrations. Laboratory experiments using sediment from the Narrows were conducted to investigate the effects of pH on metal partitioning between dissolved and particulate phases in sediment re-suspension and digestion tests.

Materials and methods

Study area

In Port Curtis, the major component estuaries, the Calliope and Boyne Rivers, the Narrows and Auckland Creek merge into a naturally sheltered 30 km long deepwater harbour protected by Curtis Island and Facing Island (Figure 1). The main entrances that the estuary has with the ocean are located either side of Facing Island, although the estuary is also connected to the ocean at Keppel Bay in the north-west via the Narrows. Most samples taken during this study were divided into one of either five zones, in order to make a statistical comparison of metal concentrations. These included Port Curtis (PC) and the Narrows (TN), and the Keppel Bay (KB), Facing Island (FI), and Rodd's Bay (RB) offshore sampling zones. The Keppel Bay, Facing Island, and Rodd's Bay offshore zones included sites from each respective transect, which were greater than 10 km from the mainland.

Water sample collection and treatment

Two water sampling surveys were conducted during December 2003 (axial transect survey) and 2004 (targeted and temporal sampling survey). The axial transect sampling was conducted in waters through the Port Curtis estuary and extending to surrounding coastal waters to identify trends in metal concentrations that may indicate possible metal sources and also characterise background trace metal concentrations in the adjacent coastal waters (Figure 1). Water samples were collected from 49 sites approximately 4 km apart, along 4 transects: (i) Keppel Bay through the Narrows and Port Curtis towards Rodd's Bay (samples A1.1 to A1.21), with most sites along this transect included in either the Port Curtis (PC) or the Narrows (TN) sample zones, (ii) continuing transect in point (i) east into Rodd's Bay, and then north-east into offshore waters (A2.1 to A2.8), with all sites included in the Rodd's Bay offshore area (RB), (iii) north-east from the seaward side of Facing Island into offshore waters (A3.1 to A3.10), with all but one site included in the Facing Island offshore area (FI), (iv) north east from the Keppel Bay into waters beyond Great Keppel Island (A2.1 to A2.10), with all but one site included in the Keppel Bay offshore area (KB). The offshore transects extended to approximately 45 km from the shore.

Targeted, transect, and temporal sampling was conducted during December 2004 in waters of Port Curtis, the Narrows, and the Fitzroy Estuary to aid the identification of metal sources. Water samples were collected from 51 sites and included: (i) an

approximate repeat of the Survey 1 transect (A1 series) through Port Curtis (PC) and the Narrows (TN) (B1.1 to B1.15), (ii) targeted sampling in selected inlets and creeks of Port Curtis and the Narrows (B2.1 to B2.9), (iii) targeted sampling of larger inlets in Keppel Bay between the entrance of the Fitzroy estuary and the northern entrance of the Narrows (B3.1 to B3.5), and the Fitzroy estuary and River (B4.1 to B4.8). Temporal sampling was also undertaken at a location approximately 3 km south of Ramsay's Crossing (December 7-8, 2004, site B1.6) and near Fisherman's Landing (December 8-9, 2004, site B2.4 - 5) at approximately hourly intervals for 7 h, and after 24 h.

To minimise sample contamination, all water samples were taken from the front of the boat while the boat was gently cruising forward into the current. On the vessel, care was taken to ensure that contamination was minimised at all times by ensuring that staff handling the samplers and sample bottles wore powder-free disposable vinyl gloves. Samples were taken from surface water at a single depth of 0.5 m because the waters of Port Curtis are considered well mixed (Herzfeld *et al*., 2003).
Low-density polyethylene (Nalgene) bottles were used for water sampling in the field and for holding filtrates in the laboratory. The bottles were cleaned rigorously before use using a three-stage sequential washing procedure, involving sequential soaking in 2% (v/v) Extran 300 detergent, 10% (v/v) high purity nitric acid (Merck Tracepur), and 1% high purity nitric acid (Merck Tracepur) and five rinses with deionised water (18 MΩ·cm, Milli-Q, Millipore) between different cleaning agents (Apte and Day, 1998). The bottles were placed in two zip-lock bags during transportation to the field. At each site the samples were collected by placing bottles into a holder installed on a purpose-built Perspex pole-sampler and using ultratrace sampling techniques (Ahlers *et al.* 1990; Apte and Day, 1998). During water sampling, for purposes of quality assurance and quality control (QA/QC), at least 10% site duplicates and 10% field blanks (air blanks from site filled with deionised water in the laboratory) were collected (USEPA 1996; Apte *et al*., 1998).

Following collection, samples were stored in ice-filled cooler boxes until return to the laboratory and were generally filtered within 8 h, and always filtered within 24 h of collection. Filtrations were undertaken using polycarbonate filtration units (Sartorius) which were acid-washed (10% HNO_3, Tracepur, 24 h), and fitted with pre-weighed 0.45 µm membrane filters (50 mm, type HA, Millipore) that were rinsed with 50 mL of 10% (v/v) HNO_3 (Merck, Tracepur) followed by two 100 mL volumes of deionised water before use (Hatje *et al*., 2001; Hatje *et al*., 2003; Teasdale *et al*., 2003).

The initial 50 mL of filtrate was used to rinse the 0.5 L acid-washed bottles (low-density polyethylene, Nalgene) and discarded, and the remaining filtrate was then transferred into these bottles. The filtrates were preserved by addition of concentrated HNO_3 (Merck Suprapur, 2 mL/L final concentration) in a class-100 clean laboratory. The filtration rig and filter were rinsed with deionised water and the suspended particulate matter (SPM) concentration was determined by drying and re-weighing the material retained on the filters. The total particulate metal concentrations were determined by digesting the dry material and filter in 120 mL polycarbonate vials according to the aqua-regia digestion method described by Simpson *et al*. (2004), and diluting with deionised water (18 MΩ·cm, Milli-Q, Millipore) to a 10% HNO_3 matrix.

The salinity of waters collected in Survey 1 was determined using the micro-scale chlorinity titration method of Grasshoff *et al*. (1983). A water quality analyser multi-probe (YSI 6600) was used in Survey 2 to determine water temperature, salinity, pH, and dissolved oxygen concentrations, which was calibrated immediately before use following the manufacturer's instructions. Both methods used to measure salinity were cross checked using a laboratory seawater sample of known salinity.

Sediment manipulations used to investigate metal partitioning

At low tide, sediment samples (~ 1 kg) were collected from the upper 10 cm of sediment at intertidal sites in the mid- and southern-Narrows to investigate metal partitioning in the laboratory. The sediment was collected with an acid-washed Teflon spatula and placed into double Zip-lock bags with the air squeezed out, and transferred to the laboratory in ice boxes. In the laboratory, the sediment was stored in a refrigerator (2-5 °C) for no more than two weeks before use to minimise physico-chemical changes. An aqua-regia digestion of these sediments was performed to measure particulate-bound metals at the different locations (Simpson *et al*., 2004).

The relationship between water pH and metal mobilisation from sediment-bound phases was investigated using sediments collected from the mid-Narrows and waters of pH 4 to 9. The sediment was homogenised with a clean plastic spatula in a nitrogen-filled glove box. Volumes of 0.5 L of filtered seawater (Stanwell Park beach, NSW) were adjusted to pre-determined pHs, by spiking with 1-10% NaOH or 1-10% HNO_3, so that the overlying water was at the desired pH 24 h after mixing the sediment with the water. The seawater was added to wet sediments 10 g/L (dry weight), shaken vigorously for 30 sec,

and allowed to stand at room temperature for 24 h. After 24 h a sub-sample of water was taken to measure pH, and the remaining water was filtered and acidified to 2 mL HNO_3/L (Merck, Tracepur), and retained for measurement of dissolved metals. A large water pH range and high sediment-to-water ratio were chosen to investigate metal mobilisation to reflect the conditions that may occur in areas such as sediment porewaters, organism burrows, salt marshes, and areas with hotspots of acid-sulfate soils.

Chemical analyses

The metal concentrations in filtered samples and particulate digests were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Spectroflame EOP, Spectro Analytical Instruments) calibrated with matrix-matched standards (QCD Analysts, Eaglewood, FL, USA). As concentrations of dissolved cadmium, copper, nickel, and zinc were below the detection limit of the ICP-AES in the filtered seawater samples, a dithiocarbamate complexation/solvent extraction method (Hatje *et al*., 2003) was used to concentrate metals and remove salt prior to analysis. The extraction solution (modified from Magnusson and Westerlund, 1981) combined sodium bicarbonate buffer, ammonium pyrrolidine dithiocarbamate (APDC) and diethyldithiocarbamic acid (DDC) complexing reagents, which were extracted into 1,1,1-trichloroethane in place of Freon (1,1,2-trichlorotrifluoroethane) (Apte and Gunn 1987; Hatje *et al*., 2003). The metals were back-extracted into 1 mL of concentrated nitric acid (Tracepur), diluted to a final volume of 10 mL with deionised water (18 MΩ·cm, Milli-Q, Millipore), and analysed by graphite furnace-atomic absorption spectrometry (GF-AAS) (Perkin Elmer, 4100ZL) using Zeeman effect background correction and operating conditions recommended by the manufacturer.

For purposes of quality assurance/quality control (QA/QC), method blanks, method duplicates and spike recoveries were performed on at least 10% of the filtered samples. The certified reference material (CRM) seawater (CASS-4) and particulate (PACS-2) (National Research Council of Canada) were processed as part of the routine quality control procedures.

Data analysis

Differences in the mean concentrations of dissolved and suspended solid-bound metals, pH, salinity, and suspended solids measured in the Port Curtis, the Narrows, and the Keppel Bay, Facing Island, and Rodd's Bay offshore sampling zones were examined using a one-way analysis of variance (ANOVA). For calculation purposes, samples that

had metal concentrations below the detection limit were assigned a value of half the detection limit. An analysis of variance in the mean concentrations of dissolved and particulate metals in Port Curtis and the Narrows between Survey 1 (December, 2003) and Survey 2 (December, 2004) was also performed. Student-Newman-Keuls test (SNK) was used as a post-hoc procedure to test for multiple comparisons upon means.

Results

General water quality parameters

The Port Curtis system was dominated by highly saline waters (Figure 2). The salinities were significantly ($p<0.05$) higher in the Narrows (mean ± SD = 38±1 PSU) and Port Curtis (37±1 PSU) sampling zones than in the Keppel Bay (36±1 PSU), Rodd's Bay (35±1 PSU), and Facing Island (35±1 PSU) offshore sampling zones in Survey 1. The only salinities that were lower than typical oceanic levels were measured in the Calliope River (22.8 PSU) and the Fitzroy River adjacent to the city of Rockhampton (<0.2-11.5 PSU).

During the targeted sampling (Survey 2), the pH of waters in Port Curtis, the Narrows, and adjacent inlets and Rivers ranged from 7.73-8.24 (Figure 3). The pH exhibited a broad minima in the range pH 7.95-8.05 between the Yarwun trade waste outlet at Fisherman's Landing in the inner harbour and Ramsay's Crossing in the Narrows. The lowest water pHs measured in this survey occurred in the Upper Fitzroy (pH 7.73-8.12) and Calliope Rivers (pH 7.95), that were the sites with the lowest salinities.

The concentrations of suspended particulate matter (SPM) in this study were in the range <0.5-89 mg/L (data not shown). They were highest in the Fitzroy River near the entrance to Keppel Bay, and decreased in the order: Keppel Bay > the Narrows > Port Curtis Harbour. The higher SPM measured in waters of the lower Fitzroy estuary and Keppel Bay (15-89 mg/L) were the result of the outflows of the Fitzroy River, which is known to have high and variable SPM concentrations (20-1000 mg/L) (Ford *et al*., 2005).

Dissolved metal concentrations

The analytical detection limits of dissolved cadmium, copper, nickel, and zinc were 1, 19, 48, and 31 ng/L (parts per trillion), respectively, and were similar to other ultratrace metal studies (Apte *et al*., 1998; Mackey *et al*., 2002). Concentrations of metals measured in the reference material CASS-4 were within 86 to 99% of the certified value for each metal, and spike recoveries were in the range 88-102%. The mean percentage relative standard deviations (RSDs) of site and method duplicates were typically 2-15%.

The concentrations of dissolved metals measured in the two surveys are shown in Tables 1 and 2, and also in Figures 4 and 5. The metal concentrations were generally lowest at offshore sites, particularly north-east of Facing Island, where the concentrations ranged from <1-1.5, <19-68, 120-160, and <31-130 ng/L, for Cd, Cu, Ni, and Zn, respectively. There were distinct gradients in trace metal concentrations with the highest concentrations being measured closest to Port Curtis and the Narrows.

The dissolved cadmium concentrations measured in the waters of Port Curtis, the Narrows, and the multiple inlets between the Fitzroy River and the northern mouth of the Narrows were in the range <1-38 ng/L, and did not exhibit an observable spatial trend (Table 1). In Survey 1, the mean dissolved cadmium concentrations measured in Port Curtis (7±5 ng/L) and the Narrows (4±1 ng/L) were significantly ($p<0.05$) higher than those measured in the offshore sampling zones (Figure 1) of Keppel Bay (2±1 ng/L), Rodd's Bay (3±3 ng/L), and Facing Island (1±0 ng/L) (Table 2).

Dissolved copper and nickel concentrations ranged between 270-740 and 120-910 ng/L, respectively (Table 1 and 2, and Figures 5 and 6). In Survey 2, the concentrations of dissolved copper and nickel measured in inlets adjacent to the Narrows were similar to those in the Narrows, which may indicate there was not a single point-source of copper and nickel in these inlets at the time of this survey. Similar trends in dissolved copper and nickel were measured in Port Curtis Harbour and the Narrows in Surveys 1 and 2. The mean dissolved copper concentrations measured in Port Curtis in surveys 1 and 2 (530±80 ng/L and 500±200 ng/L, respectively) and the Narrows (560±40 ng/L and 500±100 ng/L, respectively) were not significantly ($p<0.05$) different. However, the mean dissolved nickel concentrations measured in the Narrows in surveys 1 and 2 (730±140 ng/L and 600±200 ng/L) were nearly twice the concentrations found in Port Curtis (350±60 ng/L and 300±100 ng/L).

In Survey 1, the dissolved copper concentrations measured in the waters of Port Curtis and the Narrows were above 500 ng/L over a broad area, and exhibited a maximum of 640 ng/L in the southern Narrows. In Survey 2, the dissolved copper concentration measured along this transect exhibited a more pronounced trend, with a maximum concentration of 650 ng/L, in the area of the inner-harbour between Fisherman's Landing and the southern entrance to the Narrows (Figures 4 and 5).

Dissolved nickel and manganese measured along the transect through Port Curtis and the Narrows, exhibited similar pronounced concentration maxima in both surveys (Figures 4 and 5). The peak dissolved nickel concentrations measured along this transect were 910 ng/L (situated approximately 6 km north of Ramsay's Crossing) and 800 ng/L (situated approximately 2 km south of Ramsay's Crossing) during Surveys 1 and 2, respectively. Correspondingly, the peak dissolved manganese concentrations in Surveys 1 and 2 were 7000 (situated approximately 2 km north of Ramsay's Crossing) and 6400 ng/L (situated approximately 2 km south of Ramsay's Crossing), respectively. The dissolved manganese concentration measured at one location in the Targinie inlet in the southern Narrows was 19000 ng/L, which was nearly three times higher than the maximum concentration measured in the Narrows (6400 ng/L).

Dissolved zinc concentrations in Port Curtis Harbour and the Narrows ranged from 60-310 ng/L (Tables 1 and 2, and Figures 4 and 5). The dissolved zinc concentration was broadly elevated in waters between the outer harbour of Port Curtis and the southern entrance to the Narrows in Surveys 1 and 2 (Figures 4 and 5). There was no significant difference in the mean concentrations of dissolved zinc measured in Port Curtis (170±40 ng/L) and the Narrows (110±30 ng/L) during Survey 1. However, the mean dissolved zinc concentration measured in Port Curtis (170±90 ng/L) was significantly ($p<0.05$) higher than the Narrows (100±40 ng/L) during the Survey 2. In Survey 2, the concentrations of dissolved zinc measured in the Narrows and in adjacent inlets were similar, likely indicating there was not a single point-source of zinc in these inlets.

The dissolved copper and nickel measured in Survey 1 exhibited similar spatial trends between offshore sampling zones, with the Keppel Bay zone having significantly higher ($p<0.05$) dissolved concentrations than the Rodd's Bay zone, and both of these zones had significantly higher ($p<0.05$) dissolved concentrations than the Facing Island offshore zone. The higher mean dissolved copper and nickel concentrations measured in the Keppel Bay offshore sampling zone is probably due to water inputs from the Fitzroy River. The higher mean dissolved copper, nickel, and zinc measured in the Rodd's Bay offshore sampling zone than the Facing Island offshore sampling zone is likely due to tidal movement of waters in Port Curtis towards Rodd's Bay.

The site sampled in Boat Creek was in close proximity to the Clinton Coal Wharf and Fisherman's Landing in the inner harbour, and had marginally higher dissolved copper (770 ng/L) and the Calliope River had marginally higher dissolved copper (670-730 ng/L)

and zinc (340-500 ng/L) than the maximum concentration of these metals measured in the transect through waters of Port Curtis and the Narrows (Table 2). The highest concentrations of dissolved copper, nickel, and zinc were measured in the Fitzroy River adjacent to the city of Rockhampton during Survey 2, and ranged from 1200-1410, 1430-1760, and 140-580 ng/L, respectively (Table 2 and Figure 5), possibly due to anthropogenic sources from the city and surrounding agriculture and geological sources (such as derelict mines in the region) (Jones 2000; Jones *et al*., 2002; Moss and Costanzo, 1998; Rolfe *et al*., 2004). The concentrations of dissolved copper, nickel, and zinc in the lower estuary near the entrance to Keppel Bay were lower than upstream and ranged from 650-690, 980-1010, and 100-140 ng/L, respectively, probably due to dilution from tidal mixing (Baeyens *et al*., 2005), and scavenging of dissolved metals by SPM in the lower estuary (Ford *et al*., 2005; Sanudo-Wilhelmy *et al*., 1996; Teasdale *et al*., 2003).

Metals associated with suspended particulate matter

The concentrations of Al, Fe, and Mn bound to suspended particulate matter (SPM) measured in waters along the transect through Port Curtis and the Narrows ranged from 4400-9600 µg/g, 7050-16200 µg/g, and 190-950 µg/g, respectively (Table 1 and 2). The concentrations of suspended aluminium and iron (SPM-Al and SPM-Fe) did not exhibit a strong trend in Port Curtis and the Narrows, although SPM-Mn exhibited a broad concentration maximum in the inner harbour and the southern Narrows (Figure 4). The SPM-Cu and SPM-Zn concentrations were in the range of <3-50 µg/g and <3-230 µg/g, and did not exhibit strong trends in either survey. The SPM-Cd and SPM-Ni were below the analytical detection limit. The concentrations of SPM-bound metals were generally lower in the offshore sampling zones and often below detection limits.

The release of sediment-bound metals with changes in seawater pH

Results from aqua-regia metal digests of benthic sediments collected in Port Curtis and the Narrows indicated the central Narrows had significantly ($p<0.05$) higher concentrations of particulate copper and nickel than the mid-harbour. Concentrations in the central Narrows were approximately double those in the mid-harbour (data not shown). The concentrations of dissolved copper, nickel, and zinc released from the sediments re-suspended in seawater of varying pH are shown in Figure 6. As expected, the highest concentrations of dissolved copper, nickel, and zinc were measured following resuspension at pH 4 (Figure 6 A). The release of metals in resuspension tests in the pH 7.75-8.25 range (Figure 6 B) were more representative of waters in Port Curtis and the Narrows (pH 7.95-

8.20), although lower pH's may occur in the mud flats adjacent to the Narrows. Dissolved nickel and zinc increased by 58% and 34%, respectively, as the pH decreased from pH 8.25 to pH 7.75. In contrast, dissolved copper decreased as pH decreased from pH 8.25 to pH 7.75, and the copper concentration only increased significantly ($p<0.05$) above that measured for pH 8.25 waters in re-suspension treatments that employed waters with a pH equal to or less than pH 5.

Discussion

Port Curtis is different to many estuaries, as it is connected to the ocean at multiple locations (the Narrows and openings between Curtis and Facing Islands), and has highly variable, spasmodic inputs of freshwater due to the wet season/dry season climate dynamics of the catchment area (Ford *et al*., 2005; Jones *et al*., 2005). The hydrodynamics of water movement and the general water quality parameters (pH, salinity, SPM) in Port Curtis, the Narrows, and the Fitzroy River may have a significant influence on the concentrations of metals. A recent hydrodynamic model predicted that water in Port Curtis undergoes tidal movement over large distances, but little net displacement occurs, as the water returns close to its original location (Herzfeld *et al*., 2003). The model proposed a flushing duration in Port Curtis of 22-26 days, although poor tidal mixing in some protected inlets and bays of Port Curtis and the Narrows suggests that these waters have longer flushing durations. The model did not include all of the Narrows and it was not entirely clear whether hydrodynamic forces predominantly direct waters from Port Curtis north through the Narrows into Keppel Bay or from Keppel Bay south through the Narrows into Port Curtis. The direction of water flow in the Narrows fluctuates (north-west or south-east) through the tidal cycle making it difficult to predict metal dispersion from potential sources, such as the point sources from the Yarwun trade waste outlet and the Calliope Power Station, or diffuse sources from urban runoff and leaching from sediments.

The broad pH minimum measured between the inner harbour and Ramsay's Crossing in the Narrows was in agreement with past pH measurements (Apte *et al*., 2006). The position of the pH minimum was in close proximity to the entrance of the Calliope River and the Yarwun trade waste outlet, and both these areas may potentially contribute water of lower pH into Port Curtis. The lack of a decrease in salinity indicates that freshwater inputs were minimal during the sampling period. The discharges from the Yarwun Trade Waste outlet were not believed to be acidic (Leonie Anderson, Central Queensland University, personal communication), so the relatively small outflows (110 kg Cu per year,

410 kg Zn per year) of these waters were unlikely to have a significant influence on the water pH in Port Curtis Harbour (National Pollution Inventory, 2008).

The foreshore of the Narrows is predominantly lined with mangrove mud flats and salt marshes. The sediment surface area that comes into contact with water is relatively high because of the large tidal range (4-5 m, WBM Oceanics 1992) and flatness of the adjacent sediments. The water depth is also quite shallow in the Narrows and there is a relatively high ratio between the surface area of sediment that comes into contact with water and the volume of water. Several studies have reported lower pHs in waters lined with mangrove foreshores due to factors that result in the release of H^+ into waters including, mangrove systems having faster rates of diagenesis and organism-facilitated aerobic oxidation of organic matter because of the larger volumes of organic carbon (Clark *et al*., 1998; Kristensen, 2000; Otero and Macias, 2002; Van Cappellen and Wang, 1996). The lower pH of waters in the Narrows may also be generated by adjacent acid-sulfate soils (ASS), which are common along the east coast of Queensland and northern NSW, with hotspots of ASS activity identified in the vicinity of the Narrows (Powell and Martens, 2005; Ross, 2002). Mud flats and salt marshes often have higher water temperatures than the adjacent water column that may allow greater rates of chemically driven oxidation (e.g. air oxidation of sulfides), resulting in lower water pH (Otero and Macias, 2002).

The salinity of the waters of Port Curtis and the Narrows was in the range 33 to 39 PSU, and did not decrease at sites in the inner harbour and the Narrows where several creeks and rivers may potentially input fresh water into the system. On the contrary, the salinity was higher in the estuary near the outflows of these inlets than the offshore waters. Typical estuarine waters have salinities that increase as the estuary approaches the sea and are approximately 35 PSU at the seawater end-member (Hatje *et al*., 2003; Sanudo-Wilhelmy *et al*., 1996). The chemical analysis of major ions that may contribute to salinity indicated that the spatial trends in dissolved Ca, Mg, K, and Na were the same as salinity (data not shown), indicating no particular species were responsible for the increased salinity.

The mangrove mud flats and salt marshes along the foreshore of the Narrows and inner harbour are subject to evaporation (Saenger, 1995). It is likely that the hypersaline conditions measured in the Narrows and the inner harbour were the result of evaporative water losses. Average daily rainfall measurements in the catchment of Port Curtis (Calliope, Mount Larcon, and Gladstone Airport stations) in the thirty days before and

during the two surveys were <5 mm, and most days had <1 mm, indicating low freshwater inputs from rainfall into the estuary (Australian Bureau of Meteorology, 2008). Hypersaline conditions may be typical of many tropical Australian estuaries and may be assisted by evapotranspiration occurring in saline tolerant vegetation (water removed by plants leading to concentration of salt in estuarine system) (Largier *et al*., 1997; Ridd and Stieglitz, 2002; Wolanski, 1986).

Considering the ecological importance of the World Heritage listed GBRMP, there was surprisingly few data on the concentrations of trace metals in these waters. The increased industrial and shipping activity in this region of Australia also means that it is important to have knowledge of natural (baseline) concentrations for future comparison. A study by Denton and Burdon-Jones, (1986), that used Chelex-100 extraction and analysis of cadmium, copper, nickel, and zinc in waters of the GBRMP reported concentrations of <10-60, 110-240, 60-160 and 30-350 ng/L, respectively, but the results had high replicate variability and the method had poor extraction efficiencies.

The lowest concentrations of trace metals were measured in the Facing Island offshore sampling zone. This zone was considered the most representative of regional coastal water concentrations because Facing Island restricts water flow and thus, metal transfer from the harbour into these waters. The mean offshore concentrations of trace metals measured in this study were similar to those measured in offshore sites in Northern and Eastern Australia and the Western Pacific, and may be considered metal depleted relative to waters in the northern Atlantic which receive significantly greater inputs from atmospheric and riverine sources (Apte *et al*., 1998; Bruland *et al*., 1994; Kremling and Pohl, 1989; Jickells, 1995; Mackey *et al*., 2002; Williams *et al*., 1998) (Table 3). The similar concentrations of trace metal concentrations measured in offshore waters around Northern and Eastern Australia, indicate that the offshore metal concentrations measured in the current study are likely to be representative of those found in the GBRMP. The current study achieved relatively low detection limits and excellent quality control results, and to our knowledge, is the most recent and accurate data set of trace metal concentrations representative of those found in waters of the GBRMP.

The dissolved metal concentrations in Port Curtis did not exceed the current Australia and New Zealand water quality guideline trigger values for ecosystem protection (ANZECC/ARMCANZ 2000) (Table 3). The highest concentrations of dissolved Cd, Cu, Ni, and Zn measured in Port Curtis and the Narrows were 40, 740, 910, and 310 ng/L,

respectively. These concentrations are at the lower end of the concentration range of these metals measured in industrialised harbours around the world, indicating that Port Curtis was not contaminated to the same degree (Table 3). The level of metal enrichment in Port Curtis relative to regional concentrations was investigated by comparing mean metal concentrations from Port Curtis to those from the Facing Island offshore sampling zone. The ratios of Cd, Cu, Ni, and Zn measured in Port Curtis compared to the Facing Island offshore sampling zone were 2.4, 6.9, 3.0, and 1.7, respectively. The ratio of dissolved copper in Port Curtis compared to offshore sampling zones was larger than the other metals, indicating greater enrichment in the harbour. The copper concentrations were also higher than those measured in previous studies of pristine estuaries, such as Bathurst Harbour, Tasmania or Sea lochs in Scotland (Hall *et al*., 1996; Mackey *et al*., 1996).

The presence of a strong spatial separation of concentration maxima for dissolved copper, manganese, nickel, and zinc in this study is likely to indicate that there were multiple metal sources or parameters influencing metal concentrations. The dissolved copper and zinc concentration maxima were located in the inner harbour and southern Narrows. The foreshore of these waters was lined with urban, commercial, and industrial centres, which means there were likely to be multiple sources of metals (Comber *et al*, 1995; Hatje *et al*., 2003; Laslett and Balls, 1995; Owens and Balls, 1997). For instance, the National Pollution Inventory website of the Commonwealth of Australia reports that copper and zinc are discharged into waters of the Calliope River and the Yarwun trade waste outlet at Fisherman's Landing, by industries such as the Gladstone power station and sewage works (National Pollution Inventory, 2008). The leachate from reclaimed land containing fly ash from the nearby power station and antifouling paints from boats may also contribute to the higher concentrations of dissolved copper and zinc in the inner harbour (Jones *et al*., 2005; Warnken *et al*., 2004). The dissolved concentrations of Cu, Ni, and Zn exhibited low temporal variation at the Ramsay's Crossing and Fisherman's Landing sites over the 24-h duration of the sampling period (data not shown).

In contrast, the dissolved nickel concentration maximum was located in the central to northern Narrows and is not in close proximity to anthropogenic sources. The dissolved nickel concentration maximum of each survey was located within close proximity (2-4 km) to the dissolved manganese maxima, and strong correlations of 0.67 ($p<0.001$) and 0.92 ($p<0.0001$) were measured in Surveys 1 and 2, respectively (Figure 7). The close association of nickel and manganese has been shown in several previous studies, indicating

that the same process may be responsible for the release of dissolved manganese and nickel from soils and sediments (Hatje *et al*., 2003; Laslett and Balls, 1995; Sanudo-Wilhelmy and Gill, 1999).

Many trace metals are associated with manganese and iron (hydr)oxides in sediments. The chemically or bacterially driven reduction of manganese and iron (hydr)oxides may result in the release of manganese, iron, and trace metals into the dissolved phase, although iron would rapidly re-oxidise and be removed from the dissolved phase upon entering the overlying water (Laslett and Balls, 1995; Sanudo-Wilhelmy and Gill, 1999; Simpson and Batley, 2003; Zhang *et al*., 2002). The reduction of manganese and iron hydr(oxides) is a natural process that has been reported to be enhanced in warmer temperatures, when biological activity is increased and oxygen concentrations are generally lower (Laslett and Balls, 1995; Otero and Macias, 2002). Natural geochemical weathering and leaching processes may also release trace metals including nickel from particulate-bound forms into the dissolved phase, and these processes are likely to be facilitated in the Narrows because of ASS hotspots. Processes that cause the release of nickel from sediments into the dissolved phase are likely to have a greater influence on sources of nickel in the Narrows than Port Curtis, because of the higher particulate nickel in the sediments of the Narrows than the mid-harbour measured previously and in the current study (Vincente-Beckett and Shearer, 2005).

The water pH may also influence the behaviour of nickel in Port Curtis and the Narrows, as shown by the increase in dissolved nickel with decreasing water pH in re-suspension experiments (Figure 6 B). However, the results from these experiments were indicative of nickel release from SPM in highly turbid conditions or in the benthic water layer, as the SPM concentrations were approximately 3 orders of magnitude higher than the SPM measured in the Narrows. Therefore, the results are expected to greatly overestimate the nickel released from SPM due to the decreased pH of water in the overlying water of the Narrows, but may be representative of metal release in sediment porewater and the benthic water layer of mudflats in this area.

The Narrows was unlikely to act as a significant source of metals to Port Curtis Harbour because of the difference in concentrations was not particularly great, and the relatively small water volume in the Narrows compared with the harbour. The Calliope River may also contribute natural and/or anthropogenic metals to the waters of this area of the harbour, although rainfall was low before and during both surveys and it is unlikely

that outflows from this river had a significant influence on the concentrations during this study. The sites sampled in rivers, creeks, and inlets adjacent to Port Curtis and the Narrows had similar metal concentrations to those measured along adjacent transects, indicating that these waters were probably not acting as substantial metal sources at the time of the survey. It is unlikely that atmospheric deposition contributes significant inputs of metals to the waters sampled, as this would be expected to cause higher concentrations over a broad area (Jickells, 1995; Kremling and Pohl, 1989).

Conclusions

Overall, the waters of Port Curtis and the Narrows had a marginally lower water pH and higher salinity, and had elevated metal concentrations compared to the surrounding coastal waters. The concentrations measured in the GBRMP and adjacent waters were similar to concentrations measured in regional waters on the north east coast of Australia. Strong spatial separations of maxima for dissolved copper, manganese, nickel, and zinc were measured, indicating that there was not one particular source responsible for the elevated metal concentrations. Copper and zinc are likely to originate from anthropogenic sources, whereas, nickel and manganese are likely to be released by natural processes, such as reduction of manganese (hydr)oxides and leaching by the lower sediment and water pH. All metal concentrations measured in waters of Port Curtis were below regulatory guideline values. However, dissolved copper was significantly ($p<0.05$) elevated above the concentrations in the adjacent coastal waters and pristine estuarine systems, and may be of potential concern if the concentrations in Port Curtis and the Narrows continue to increase.

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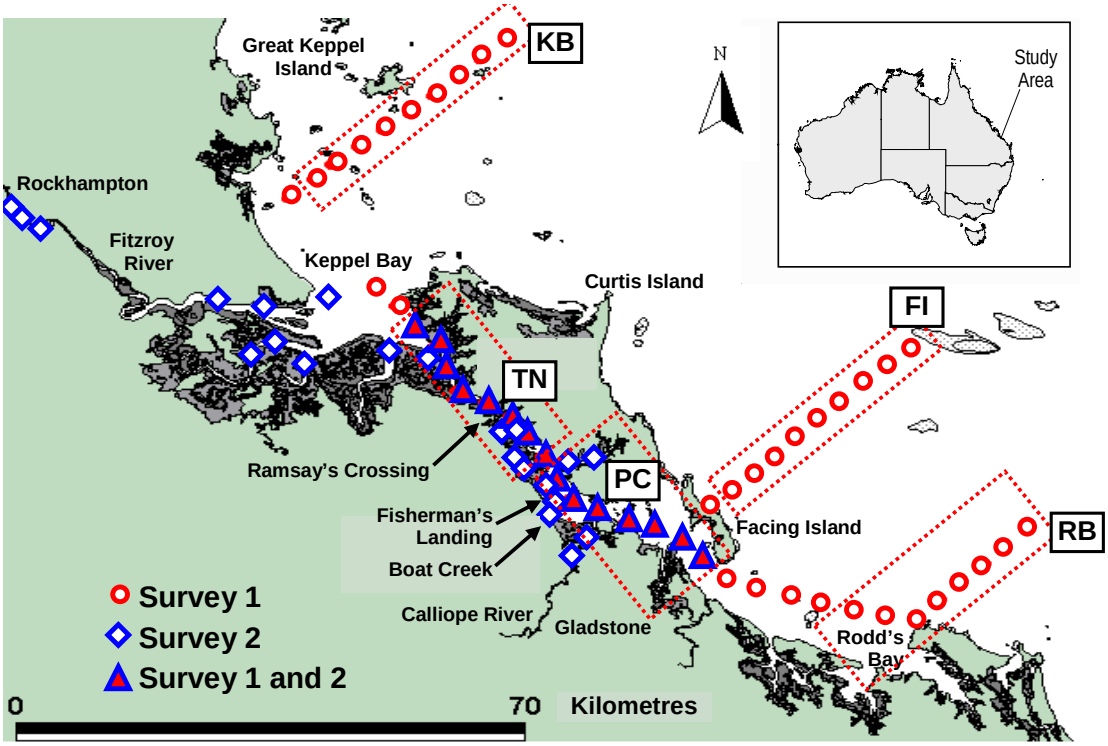

Fig. 1. Map of Port Curtis estuary and surrounding waters showing sampling sites for Survey 1 (○), Survey 2 (◇), and both surveys (▲). The different areas that were compared statistically were PC = Port Curtis, TN = The Narrows, KB = Keppel Bay offshore area, FI = Facing Island offshore area, and RB = Rodd's Bay offshore area.

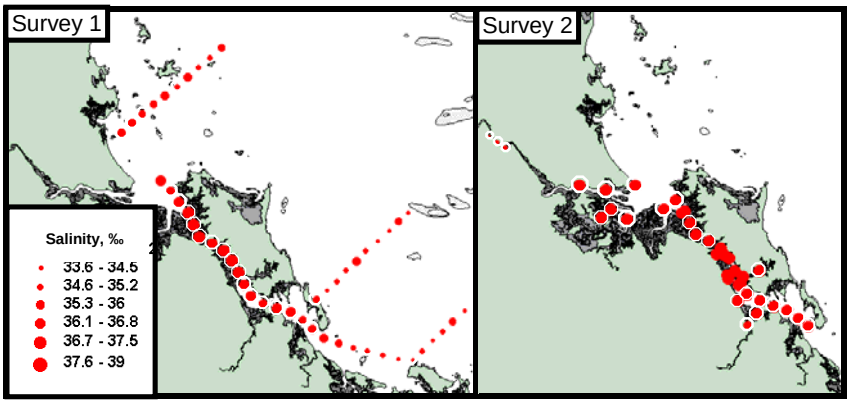

Fig 2. Measured salinity of Port Curtis and surrounding waters.

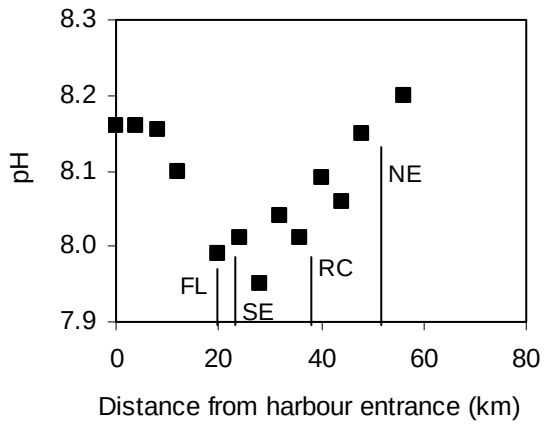

Fig 3. Measured pH of Port Curtis and surrounding waters during Survey 2, where the symbols FL, SE, RC, and NE refer to the locations of Fisherman's Landing, the southern entrance to the Narrows, Ramsay's Crossing, and the northern entrance to the Narrows, respectively. The entrance to the harbour was defined as site B1.15 (Survey 2).

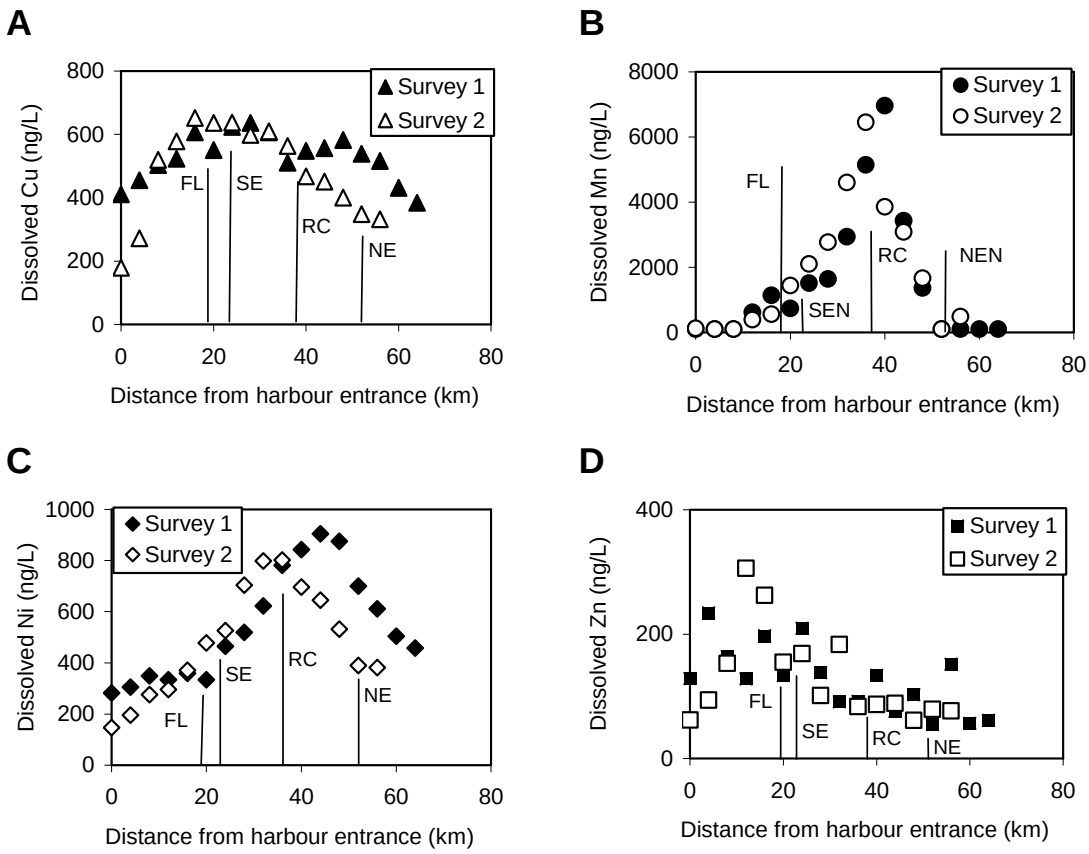

Fig 4. The concentrations of dissolved copper (▲△), manganese (●○), nickel (◇◆), and zinc (■□) measured along the transect direct from the outer harbour of Port Curtis into the Narrows during Survey 1 (▲●◆■) and Survey 2 (△○◇□). The entrance to the harbour was defined as site A1.17 (Survey 1) and site B1.15 (Survey 2). The symbols FL, SEN, RC, and NEN refer to the locations of Fisherman's Landing, the southern entrance to the Narrows, Ramsay's Crossing, and the northern entrance to the Narrows, respectively.

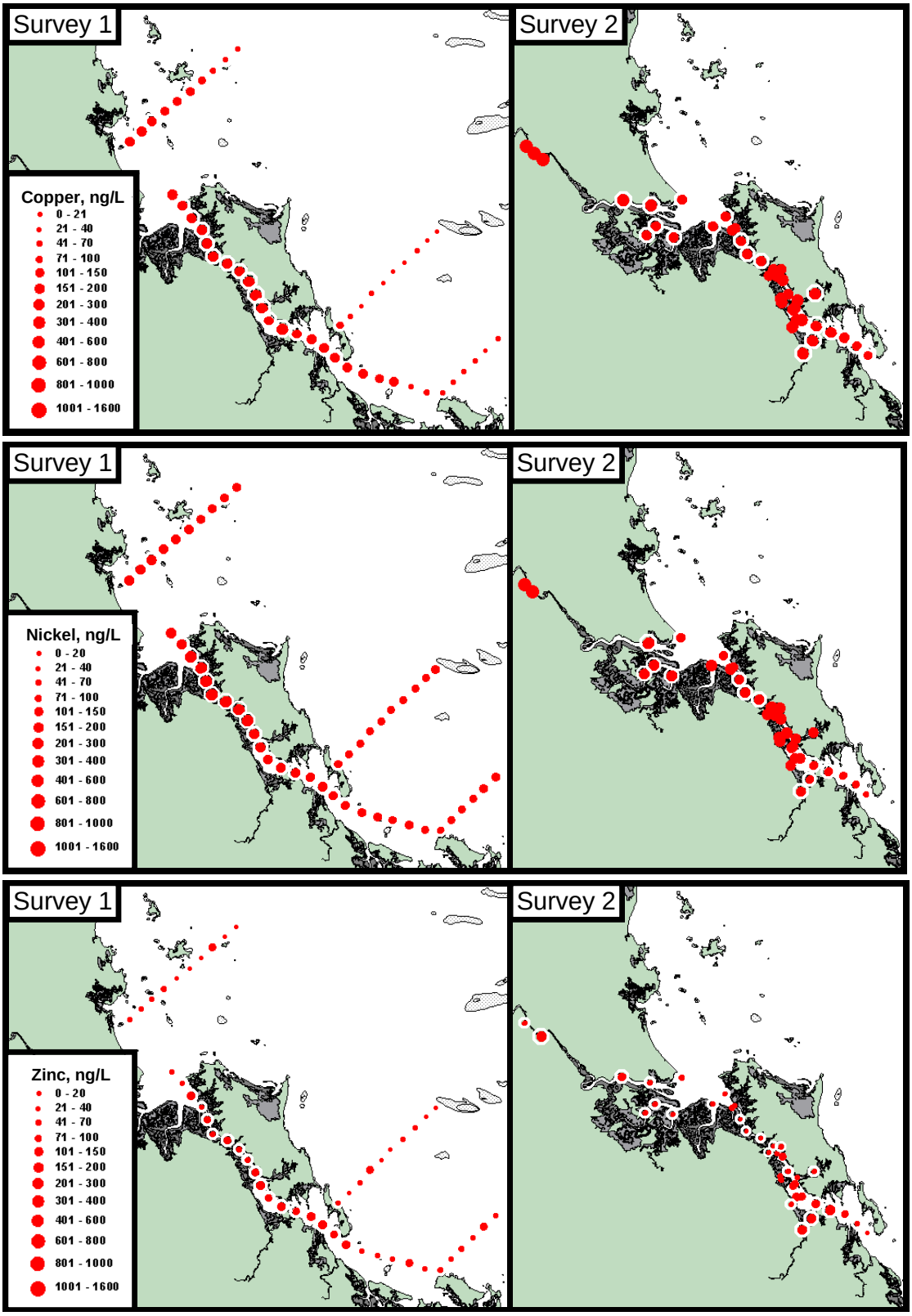

Fig 5. Dissolved copper, nickel and zinc concentrations (ng/L) in Port Curtis estuary and surrounding waters.

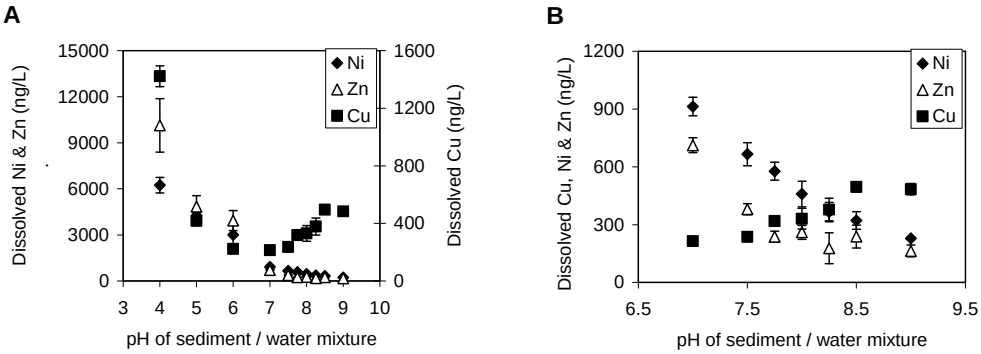

Fig 6. Dissolved (<0.45 µm) metals measured following re-suspension and 24-h storage of central Narrows (sampling site B1.5) sediment (10000 mg/L) for water pH in the range (A) pH 3.0-10.0 and (B) pH 6.5-9.5.

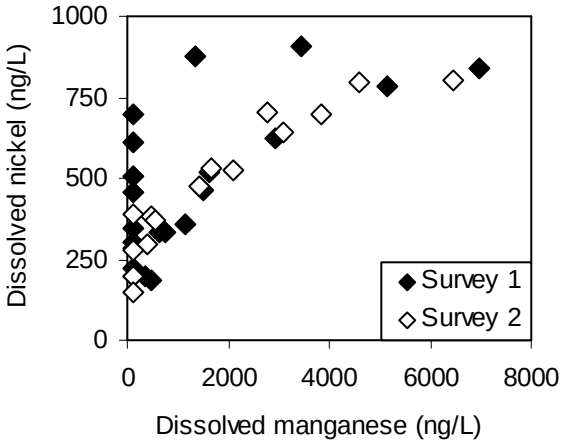

Fig 7. The relationship between dissolved manganese and nickel measured in Port Curtis and the Narrows in Surveys 1 and 2.

Table 1. Dissolved (<0.45 µm) and particulate metal concentrations in Port Curtis Estuary and surrounding waters in Survey 1

Site	Area		Dissolved metals (ng/L)					Suspended particulate metals (µg/g)				
			Cd	Cu	Mn	Ni	Zn	Al	Mn	Fe	Cu	Zn
		The Narrows and Port Curtis (Keppel Bay → Rodd's Bay)										
A1.1			3.0	380	<200	460	61	7000	420	12000	13	26
A1.2			3.5	430	<200	500	57	7000	400	12000	11	22
A1.3	TN	Keppel Bay	6.5	520	<200	610	150	4300	240	7000	7.7	19
A1.4	TN	northern Narrows	3.5	540	<200	700	55	6800	360	9500	8.8	26
A1.5	TN	↓	5.8	580	1400	880	100	7800	460	9700	9.2	32
A1.6	TN	↓	5.8	560	3400	910	76	8400	560	11000	5.8	44
A1.7	TN	Ramsay's Crossing	4.0	550	7000	840	130	8500	640	14000	9.4	43
A1.8	TN	↓	3.5	510	5200	780	92	9600	670	16000	14	55
A1.9	TN	↓	3.0	610	2900	620	91	8400	670	13000	17	57
A1.10	TN	southern Narrows	3.0	640	1600	520	140	9300	940	15000	19	55
A1.11	PC	↓	5.0	620	1500	470	210	8400	950	14000	14	61
A1.12	PC	Fisherman's Landing	2.0	550	740	330	130	7800	750	12000	16	30
A1.13	PC	mid-harbour	15	610	1100	360	200	8700	880	15000	22	56
A1.14	PC	↓	4.5	520	620	330	130	9200	920	15000	24	46
A1.15	PC	↓	4.5	500	<200	350	160	6300	600	11000	15	29
A1.16	PC	outer-harbour	15	460	<200	310	230	4500	480	8200	10	26
A1.17	PC	↓	6.3	410	<200	280	130	8800	770	14000	20	61
A1.18		↓	15	300	<200	230	190	2200	190	3600	46	27
A1.19		↓	2.0	250	<200	200	70	6300	470	8600	14	88
A1.20		↓	3.8	190	360	200	64	2400	170	2900	3.0	34
A1.21		Rodd's Bay	3.0	220	490	190	57	n/a	n/a	n/a	n/a	n/a
		Rodd's Bay → offshore										
A2.1	RB	Rodd's Bay	10	66	-	170	140	n/a	n/a	n/a	n/a	n/a
A2.2	RB	↓	1.8	84	-	140	61	6400	350	7500	<3	71
A2.3	RB	↓	3.0	70	-	120	92	2600	130	2500	16	19
A2.4	RB	↓	<1.5	69	-	150	42	500	90	600	4.2	53
A2.5	RB	↓	3.0	60	-	110	95	600	90	730	<3	44
A2.6	RB	↓	<1.5	41	-	120	68	370	50	510	<3	51
A2.7	RB	Offshore	2.0	39	-	160	140	n/a	n/a	n/a	n/a	n/a
A2.8	RB		<1.5	63	-	160	41	n/a	n/a	n/a	n/a	n/a
		Facing Island → offshore										
A3.1		Facing Island	<1.5	120	-	170	61	n/a	n/a	n/a	n/a	n/a
A3.2	FI	↓	1.5	68	-	150	<31	n/a	n/a	n/a	n/a	n/a
A3.3	FI	↓	1.5	38	-	150	41	n/a	n/a	n/a	n/a	n/a
A3.4	FI	↓	<1.5	51	-	120	130	230	160	400	<3	<3
A3.5	FI	↓	<1.5	19	-	140	<31	420	280	640	<3	<3
A3.6	FI	↓	<1.5	<19	-	130	37	n/a	n/a	n/a	n/a	n/a
A3.7	FI	↓	<1.5	30	-	140	67	n/a	n/a	n/a	n/a	n/a
A3.8	FI	↓	1.5	41	-	140	43	n/a	n/a	n/a	n/a	n/a
A3.9	FI	Offshore	<1.5	22	-	140	<31	n/a	n/a	n/a	n/a	n/a
A3.10	FI		<1.5	35	-	160	<31	n/a	n/a	n/a	n/a	n/a
		Keppel Bay → offshore										
A4.1		Keppel Bay	3.0	430	-	540	48	9300	410	14000	14	31
A4.2	KB	↓	3.0	370	-	440	64	4600	230	7100	7.5	26
A4.3	KB	↓	2.0	270	-	340	46	8000	510	12000	10	68
A4.4	KB	↓	<1.5	190	-	250	82	8300	460	11000	10	82
A4.5	KB	↓	<1.5	170	-	260	<31	7300	400	7600	7.9	80
A4.6	KB	↓	<1.5	160	-	260	<31	4200	460	4500	6.6	110
A4.7	KB	↓	<1.5	120	-	190	<31	1700	360	2300	<3	100
A4.8	KB	Offshore beyond	4.0	90	-	170	100	420	80	510	<3	18
A4.9	KB	Great Keppel	<1.5	60	-	160	<31	1700	260	2000	<3	69
A4.10	KB	Island	<1.5	70	-	180	33	n/a	n/a	n/a	n/a	n/a

Where, PC refers to Port Curtis, TN refers to The Narrows, RB refers to Rodd's Bay, FI refers to Facing Island, KB refers to Keppel Bay, "-" refers to data not measured, and "n/a" refers to SPM-bound metal concentrations that are not available because the amount of SPM recovered for digestion was too low.

Table 2. Dissolved (<0.45 µm) and particulate metal concentrations in Port Curtis estuary and surrounding waters in Survey 2

Site	Area		Dissolved metals (ng/L)					Suspended particulate metals (µg/g)				
			Cd	Cu	Mn	Ni	Zn	Al	Mn	Fe	Cu	Zn
		The Narrows and Port Curtis (Keppel Bay → the mid-harbour)										
B1.1	TN	Keppel Bay	9.6	330	490	380	76	5200	250	7800	8.8	69
B1.2	TN	northern Narrows	3.1	350	<200	390	79	-	-	-	-	-
B1.3	TN	↓	4.1	400	1700	530	61	4400	280	6200	7.3	75
B1.4	TN		38	450	3100	640	89	-	-	-	-	-
B1.5	TN	Ramsay's Crossing	4.8	470	3900	700	87	4700	290	6900	8.1	75
B1.6	TN	↓	15	560	6400	800	83	-	-	-	-	-
B1.7	TN		11	610	4600	800	180	5800	410	9700	11	68
B1.8	TN	southern Narrows	12	600	2800	700	100	-	-	-	-	-
B1.9	PC	↓	5.4	640	2100	530	170	4200	330	6800	11	77
B1.10	PC	Fisherman's Landing	13	640	1400	480	150	-	-	-	-	-
B1.11	PC	mid-harbour	6.4	650	560	370	260	4900	390	8600	13	78
B1.12	PC	↓	12	580	400	300	310	4600	300	7600	11	74
B1.13	PC		4.2	520	<200	280	150	3900	280	6300	12	78
B1.14	PC	outer-harbour	2.3	270	<200	200	94	-	-	-	-	-
B1.15	PC		2.3	180	<200	150	62	-	-	-	-	-
		Creeks and inlets in direction: Port Curtis → the Narrows										
B2.1		Boat Creek	5.6	770	-	480	140	-	-	-	-	-
B2.2		Caliope 1	5.6	670	-	330	340	5300	370	10000	17	78
B2.3		Caliope 2	9.2	730	6900	430	500	-	-	-	-	-
B2.4		Fishermans Landing 1	4.6	740	-	410	220	-	-	-	-	-
B2.5		Fishermans Landing 2	4.1	710	-	450	170	4800	470	8800	14	72
B2.6		Graham's Creek 1	3.9	630	-	510	94	-	-	-	-	-
B2.7		Graham's Creek 2	4.2	630	-	600	140	-	-	-	-	-
B2.8		Targinie Creek	5.5	610	19000	640	120	-	-	-	-	-
B2.9		Blackswan Creek	4.1	560	2500	790	84	-	-	-	-	-
		Delta of inlets in direction: northern end of the Narrows → mouth of Fitzroy estuary										
B3.1		Division Point	5.2	430	-	670	120	4500	300	6600	8.1	74
B3.2		Connors Creek	16	440	-	660	93	-	-	-	-	-
B3.3		Port Alma	6.8	530	-	760	90	5600	260	8100	12	67
B3.4		Casuarina 1	7.0	540	-	710	260	7400	430	13000	15	55
B3.5		Casuarina 2	20	570	-	770	120	-	-	-	-	-
B3.5		Cattle Point	8.8	410	-	470	120	6100	260	9000	10	71
		Fitzroy River / estuary and Dee River samples: in direction river → estuary										
B4.1		Fitzroy River 1	4.1	1200	-	1600	360	8500	2500	15000	22	160
B4.2		Fitzroy River 2	4.3	1300	-	1800	580	-	-	-	-	-
B4.3		Fitzroy River 3	2.0	1200	-	1400	140	10000	2700	18000	29	230
B4.4		Fitzroy estuary 1	7.2	690	-	1100	96	6700	440	11000	13	55
B4.5		Fitzroy estuary 2	8.9	650	-	980	140	-	-	-	-	-
B4.6		Dee River	22000	6E+06	-	65000	3E+06	-	-	-	-	-

Where, PC refers to Port Curtis, TN refers to The Narrows, and "-" refers to data not measured.

Table 3. Comparison of dissolved trace metal concentrations in Port Curtis with published data for other estuarine and marine waters

Location	Metal concentration, ng/L				Reference
	Cadmium	Copper	Nickel	Zinc	
Port Curtis, offshore	<1.5 (<1.5-4.0)	40 (<19-85)	150 (11-190)	40 (<30-140)	This study
Port Curtis Harbour	7.0 (2.0-15.0)	510 (410-620)	340 (280-470)	170 (130-230)	This study
The Narrows	8.0 (3.0-6.5)	530 (520-640)	650 (470-910)	110 (60-210)	This study
NSW coast	2.5	30	180	<22	Apte *et al*. 1998
Western Pacific Ocean	1-101	40-280	120-522	-	Mackey *et al*. 2002
North Pacific Ocean	0.3-112	-	-	15-520	Bruland *et al*. 1994
Great Barrier Reef	<10-60	110-240	60-160	30-350	Denton and Burdon-Jones. 1986
Bathurst Harbour, Tasmania	2.2	140	140	392	Mackey *et al*. 1996
North Atlantic	0.7	68	-	-	Kremling and Pohl. 1989
Scottish sea loch	<10	180	20	-	Hall *et al*. 1996
Port Jackson, Australia	6-104	932-2550	175-1610	3270-9660	Hatje *et al*. 2003
Torres Straight & Gulf of Papua	<1-29	36-986	940-4600	-	Apte and Day, 1998
Port Phillip Bay, Australia	<5-70	400-630	540-1100	250-1050	Fabris and Monahan, 1995
Nine estuaries, northern Australia	1.4-72	150-5500	120-4250	<10-11300	Munksguard and Parry, 2001
Tweed estuary, UK	7-33	490-4700	-	430-1900	Laslett 1995
Humber estuary, UK	80-450	180-10100	2500-12000	3000-20500	Comber *et al*. 1995
Mersey estuary, UK	10-110	800-4950	2000-10500	6500-28000	Comber *et al*. 1995
Tay estuary, Scotland	<3-85	250-1550	250-900	<100-3200	Owens and Balls, 1997
Forth estuary, Scotland	-	-	290-1470	460-10130	Laslett and Balls, 1995
Scheldt estuary, Netherlands	15-100	750-1800	1000-6800	1000-10000	Baeyens *et al*. 2005
San Francisco Bay estuary, USA	22-123	315-2230	140-2410	160-1960	Sanudo-Wilhelmy *et al*. 1996
Six estuaries, Texas, USA	-	100-3200	-	300-18000	Benoit *et al*. 1994
Australian Guideline values (95% protection)	700	1300	7000	15000	ANZECC/ARMCANZ 2000