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Metals in the Waters and Sediments of Port Curtis, Queensland

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CONTENTS

FIGURES

TABLES

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EXECUTIVE SUMMARY

Following recent concerns about the impacts of dredging in Gladstone Harbour, Gladstone Ports Corporation (GPC) requested assistance from CSIRO to accurately determine the concentrations of metals in the waters and sediments of Port Curtis.

The CSIRO group at Lucas Heights, Sydney has extensive experience in low level metals analysis and the assessment of contaminant impacts on aquatic systems. The CSIRO laboratory is fully equipped with state-of-the-art instrumentation and has a dedicated trace metals clean laboratory which is National Association of Testing Authorities, Australia (NATA) accredited. Its range of sensitive analytical techniques allows the accurate determination of dissolved metal concentrations in marine waters at sub-µg/L concentrations. There are few laboratories in Australia that possess this capability. The group has worked in Port Curtis previously as part of the Cooperative Research Centre (CRC) for Coastal Zone, Estuary and Waterway Management and has produced a number of peer reviewed publications which detail metal contaminant concentrations in Port Curtis (Jones *et al*., 2005, Angel *et al*., 2010).

This report describes a study of water and sediment quality within Port Curtis. The study was funded by GPC but conducted independently by CSIRO. Water and sediment samples were collected over the period 6-8 December 2011 at 21 sites across the Port Curtis region. The study design was based on a sampling campaign conducted by CSIRO in 2003 and 2004 (Angel *et al*. 2010). Sampling and analysis was conducted using internationally-accepted protocols and state-of-the art QA/QC procedures including the use of Certified Reference Materials.

The study gives a three-day snapshot of trace metal concentrations in Gladstone Harbour. A detailed interpretation of the data was provided including comparison to existing trace metals data for Port Curtis and other coastal locations impacted by anthropogenic activities. The data from the current study were also compared to water and sediment quality guidelines for marine waters (ANZECC/ARMCANZ 2000) that currently apply in Australia.

The findings of the study were as follows:

1. The concentrations of dissolved arsenic, cadmium, cobalt, chromium, copper, manganese, nickel, lead and zinc were below the ANZECC/ARMCANZ marine water quality guideline trigger values that apply in Australia at all 21 sites sampled and the concentrations were relatively low compared to other industrialised harbours.

2. Dissolved aluminium concentrations were above the ANZECC/ARMCANZ (2000) environmental concern level (ECL) of 0.5 µg/L at the majority of sites sampled. It should be noted that there is no reliable guideline value for aluminium in marine waters in Australia and the ECL value is a highly conservative value based on very limited toxicity data. There are no water quality guidelines that apply for aluminium in marine waters in Europe or North America. From the current data set, it was not possible to attribute a specific source of the dissolved aluminium.

3. The dissolved copper concentrations measured in Port Curtis in December 2011 were lower than the ANZECC/ARMCANZ guideline value of 1.3 µg/L. However, the dissolved copper concentrations were noticeably higher than the concentrations measured in the CSIRO surveys in December 2003 and 2004, indicating increased inputs of these metals from various sources, and the concentrations at some sites were only marginally lower than the ANZECC/ARMCANZ guideline value. Dissolved cadmium and zinc concentrations were comparable to those measured in 2003/2004 by CSIRO.

4. A comparison of some of the dissolved metals in Port Curtis and other industrialised harbours around the world (see Table 13 of the main report) shows that Port Curtis compares favourably with most other

harbours and has relatively low metal concentrations despite the large amount of industrial activity and shipping.

5. Apart from arsenic, the concentrations of particulate metals in benthic (seabed) sediments were below the ANZECC/ARMCANZ sediment quality guideline values. Particulate arsenic concentrations exceeded the ANZECC/ARMCANZ ISQG-low trigger value in two samples from the Narrows and one site off Quoin Island. Previous studies indicate that the source of this arsenic is natural (geological formation in the area) and is not associated with anthropogenic inputs.

6. Metal concentrations in suspended sediments were not elevated and were comparable to the concentrations of metals in the <63 µm (fine) fraction of benthic sediments. This is consistent with the resuspension of fine sediments into the water column.

7. The study did not detect any ‘hot spots’ of metal concentrations. There was no detectable elevation of metal concentrations at sites where dredging was being conducted.

Recommendations for future work are also provided in Section 6 of the report.

1 INTRODUCTION

Following recent concerns about the impacts of dredging in Gladstone Harbour, Queensland, Gladstone Ports Corporation (GPC) requested assistance from CSIRO to accurately determine the concentrations of metals in the waters and sediments of Port Curtis.

The CSIRO group at Lucas Heights, Sydney has extensive experience in low level metals analysis and the assessment of contaminant impacts on aquatic systems. The CSIRO laboratory is fully equipped with state-of-the-art instrumentation and has a dedicated trace metals clean laboratory. which is National Association of Testing Authorities, Australia (NATA) accredited. Its range of sensitive analytical techniques allows the accurate determination of dissolved metal concentrations in marine waters at sub-µg/L concentrations. There are few laboratories in Australia that possess this capability. The group has worked in Port Curtis previously as part of the Cooperative Research Centre (CRC) for Coastal Zone, Estuary and Waterway Management and has produced a number of peer reviewed publications which detail metal contaminant concentrations in Port Curtis (Jones *et al*. 2005, Angel *et al*. 2010).

This report describes a study of water and sediment quality in Port Curtis in December 2011 and gives a three-day snapshot of trace metal concentrations. The study was funded by GPC but conducted independently by CSIRO. The study design was based on a previous sampling by CSIRO in 2003 and 2004 (Angel *et al*. 2010). Sampling and analysis was conducted using internationally-accepted protocols and state-of-the art QA/QC procedures including the use of Certified Reference Materials. A detailed interpretation of the data is provided including comparison to existing trace metals data for Port Curtis and other coastal locations impacted by anthropogenic activities. The data from the current study were also compared to water and sediment quality guidelines for marine waters (ANZECC/ARMCANZ, 2000) that currently apply in Australia.

2 METHODS

2.1 BACKGROUND

The study design was based on the sampling campaigns conducted by Angel *et al*. (2010) in 2003 and 2004. Sites for water and sediment sample collection were chosen to cover the general area of Port Curtis, the southern Narrows and Rodds Bay, with more detailed sampling at sites close to the current dredging and liquefied natural gas (LNG) construction zones (Figure 1 and 2, Appendix A). Depth profile samples at various points in the water column (typically surface, mid-depth and near bottom) were collected at selected sites. We had initially planned to also sample two sites on the eastern side of Facing Island including the offshore dredge spoil dumping grounds, however, safety considerations arising from the poor weather conditions at the time of sampling prevented the sampling of these sites. Instead, additional samples were collected from within the Harbour.

The sampling program was executed by trained CSIRO staff with logistical support from staff from Central Queensland University (CQU). CSIRO provided ultraclean sampling bottles, filtration apparatus, and water sampling equipment. Two survey boats, a grab sampler for sediment collection and laboratory facilities for sample processing (e.g. filtrations) were provided by the Centre for Environmental Management, CQU.

The water and sediment sampling was performed between 6 and 8 December 2011. The sampling was conducted over a number of tidal cycles and there were periods of rainfall on 6 December whilst conditions were fine on 7 and 8 December. Full details of the sampling locations, water samples collected and sampling dates are given in Table 1. For the purpose of quality control, field blanks to assess background contamination and site duplicates were collected from at approximately 10% of the sample sites to assess background contamination and site variability respectively. Detailed descriptions of the field and laboratory protocols employed in the study are given in the ensuing sections.

Dissolved mercury was not included in this study as the concentrations in Port Curtis were expected to be very low (low ng/L) and would require costly specialist sampling and analysis. Mercury is known to biomagnify in food webs so measuring mercury concentrations in biota (Jones *et al*. 2005) is a far more effective means of assessing the risks posed by this metal.

2.2 GENERAL ANALYTICAL PROCEDURES

The analysis of trace metals at sub-µg/L concentrations in marine waters is acknowledged to be technically challenging and necessitates the application of rigorous protocols during sample container preparation, sample collection and analysis, to ensure the accuracy of results. State-of-the-art protocols, as outlined by USEPA (1996) and Apte *et al*. (2002) were used throughout this work. Full details of the methods used are given below.

All plastic ware was acid-washed prior to use with a minimum soak for 24 hours in 10% v/v nitric acid (Merck, analytical reagent grade). One-litre low-density polyethylene (Nalgene) bottles were used for water sample collection. Prior to use, the bottles were rigorously cleaned using a three-stage sequence. First, the bottles and caps were submerged for a minimum of two hours in 2% Extran detergent solution, followed by rinsing with copious amounts of deionised water (Milli-Q, 18 MΩ/cm, Millipore, Australia). The bottles were then soaked for a minimum of 24 hours in 10% nitric acid (Merck, AR grade) contained in a covered plastic tank. They were then rinsed five times with Milli-Q (MQ) high purity water and filled with 1% high purity nitric acid (Merck Tracepur) in MQ water, capped and left to stand for at least 48 hours. After this time, the bottles were rinsed five times with MQ water, 'double-bagged' in two polyethylene zip-lock bags, and stored in sealed containers to avoid contamination.

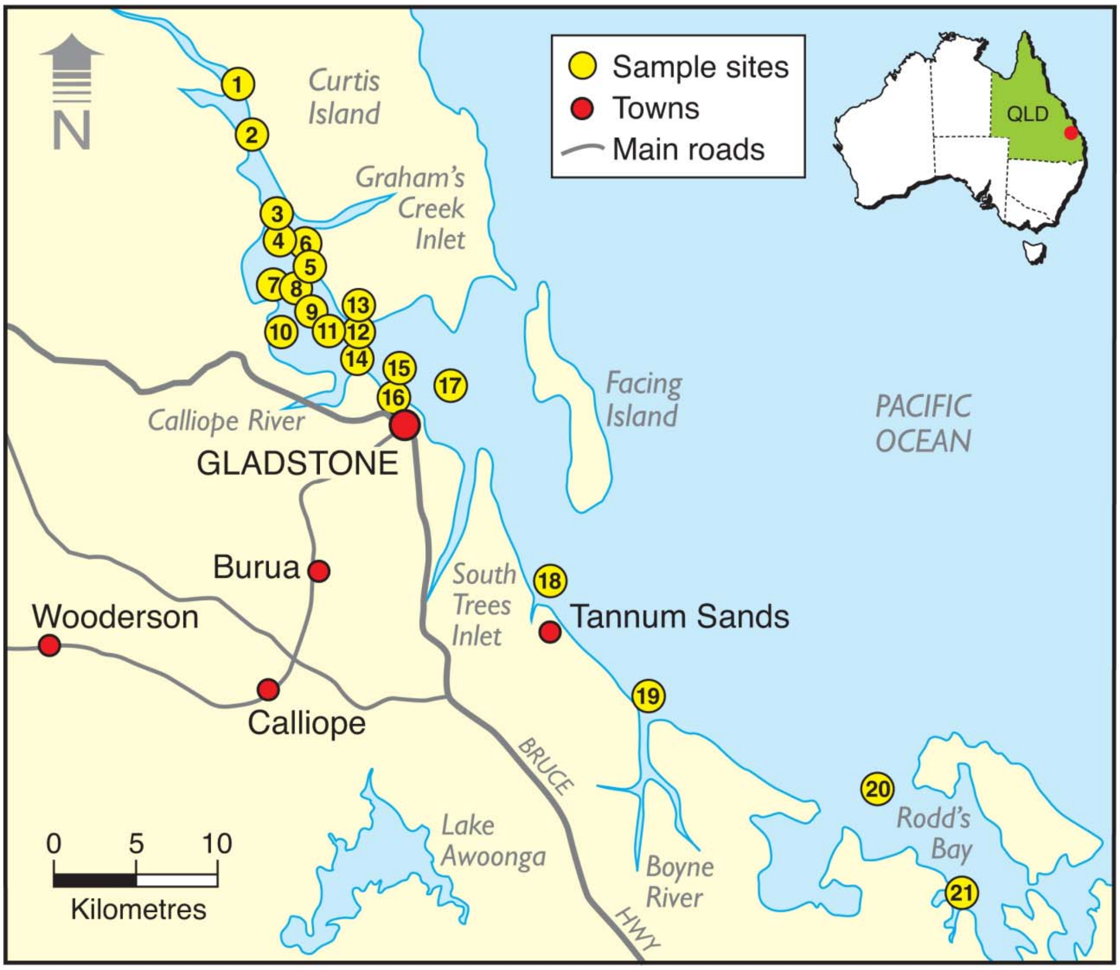

Figure 1. Sites in Port Curtis where water and sediment samples were collected (6-8 December 2011)

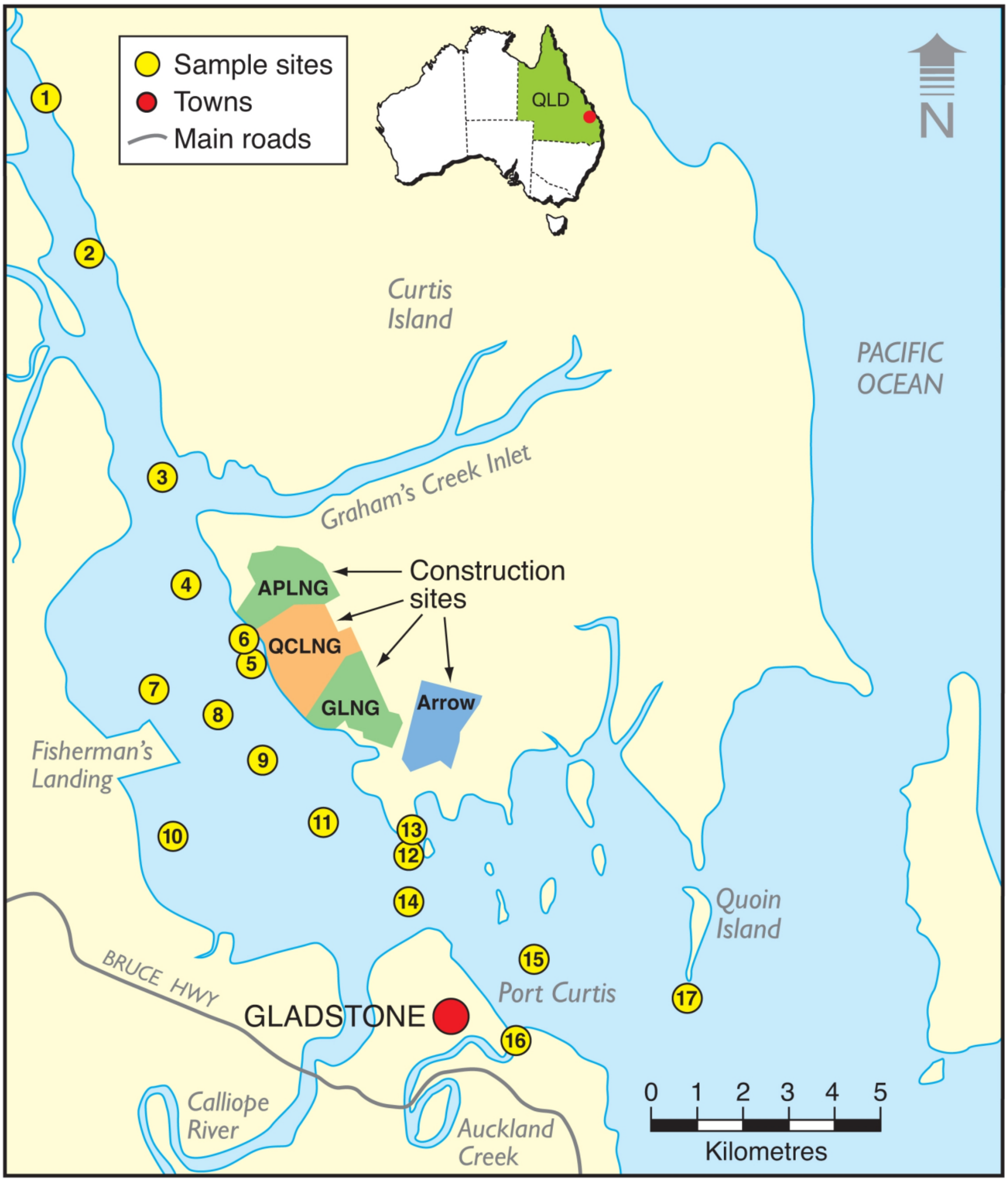

Figure 2. A more detailed map showing the main sampling sites in Port Curtis (6-8 December 2011) and their proximity to the LNG construction sites

2.3 SAMPLE COLLECTION PROCEDURES

2.3.1 Water sample collection

All water samples were collected by CSIRO staff using rigorous ‘clean hands/dirty hands’ sampling protocols to avoid sample contamination (USEPA 1996, Angel *et al*. 2010, Ahlers *et al*. 1990). This included the wearing of clean vinyl gloves for the handling of all sample bottles, and sampling equipment and storage of all equipment in zip-lock bags when not in use.

Surface water samples were collected from 31 sites using a purpose-built Perspex pole sampler. The ‘clean-hands’ person was responsible for handling the 1 L Nalgene bottles, which involved removing bottles from zip-lock bags and carefully placing them into a holder installed on the Perspex pole sampler. The ‘dirty hands’ person then used the pole sampler to collect samples by rapidly submerging the sample bottle on the pole to 0.5 m water depth to collect the sample. Each bottle was rinsed with the sample by first collecting an initial sample and then emptying it from the bottle by lifting the pole sampler and inverting. The submersion was then repeated to collect the actual sample. The ‘clean hands’ person then removed the bottle from the pole sampler, replaced the lid, replaced the bottle back into two zip-lock bags and stored them in the on-board laboratory refrigerator until sample processing and preservation.

Water samples from the middle and near-bottom water depth were collected at selected sites using a Niskin water sampler. The Niskin sampler had been previously cleaned by soaking in 2% nitric acid and washed with deionised water. The Niskin sampler was conditioned for at least 15 minutes at each depth of water collection. After this time the operator moved the sampler up one metre and back down to the sample depth and the messenger weight was deployed to trigger the closure of the sampler. The sampler was then returned to the deck of the boat and the ‘dirty hands’ operator activated the tap while the ‘clean hands’ operator rinsed the low density polyethylene bottles (Nalgene) with the dispensed sample and then filled them. The ‘clean hands’ person then replaced the bottles back into two zip-lock bags and transferred them into the on-board laboratory refrigerator until sample processing and preservation. When not in use (e.g. between sites and during overnight storage), the Niskin sampler was stored in a clean plastic bag housed within a plastic container.

Measurements of salinity, pH, and turbidity were performed on subsamples of waters collected with the pole- and Niskin- samplers immediately after water samples were collected onboard the boat. The salinity was measured using a LF 320 WTW conductivity meter (Weilheim, Germany) and electrode (TetraCon 325, WTW). The pH was measured using a Wissenschaftlich-Technische Werkstattan (WTW, Weilheim, Germany) meter equipped with a pH probe (Orion sure-flow combination pH 9165BN) calibrated at regular intervals with pH 4.0 and 7.0 buffer (Orion Pacific, Sydney, NSW, Australia) solutions. The turbidity was measured using an Analite 156 Turbidimeter (Mc Van Instruments, Victoria, Australia) equipped with a nephelometer probe, and calibrated daily using deionised water and a freshly prepared 40 NTU formazin standard.

Table 1. Details of samples collected

Site Name	Sample depth (m)		Date	Time	Site Coordinates	
	Water	Sediment			Southing	Easting
Site 1, 0.5 m	0.5	5	6-Dec-11	13:40	23.6713	151.12967
Site 1, 2 m, Site Duplicate 1	2	5	6-Dec-11	14:10	23.6713	151.12967
Site 1, 2 m, Site Duplicate 2	2	5	6-Dec-11	14:20	23.6713	151.12967
Site 1, 4 m	4	5	6-Dec-11	14:00	23.6713	151.12967
Site 2, 0.5 m	0.5	4.5	6-Dec-11	14:55	23.69922	151.14312
Site 3, 0.5 m	0.5	10.5	6-Dec-11	15:30	23.7391	151.1643
Site 3, 5 m	5	10.5	6-Dec-11	15:35	23.7391	151.1643
Site 3, 10 m	10	10.5	6-Dec-11	15:40	23.7391	151.1643
Site 4, 0.5 m	0.5	4	6-Dec-11	16:10	23.75898	151.17196
Site 4, 0.5 m	0.5	4	7-Dec-11	10:35	23.75898	151.17196
[1]Site 5, 0.5 m	0.5	6	7-Dec-11	14:35	23.76782	151.18552
Site 5, 1.5 m	1.5	6	7-Dec-11	14:43	23.76782	151.18552
Site 5, 3.5 m	3.5	6	7-Dec-11	14:48	23.76782	151.18552
Site 5, 5.5 m	5.5	6	7-Dec-11	14:52	23.76782	151.18552
Site 6, 0.5 m	0.5	7	7-Dec-11	15:03	23.7707	151.1876
Site 6, 6 m	6	7	7-Dec-11	15:03	23.7707	151.1876
Site 7, 0.5 m, Site Duplicate 1	0.5	4	7-Dec-11	15:26	23.77869	151.16849
Site 7, 0.5 m, Site Duplicate 2	0.5	4	7-Dec-11	15:30	23.77869	151.16849
Site 8, 0.5 m	0.5	4.5	6-Dec-11	16:40	23.78181	151.1823
Field blank 2 (Site 8)	-	-	6-Dec-11	16:50	23.78181	151.1823
Site 9, 0.5 m	0.5	7.5	7-Dec-11	10:55	23.78945	152.19295
Site 9, 3 m	3	7.5	7-Dec-11	11:05	23.78945	152.19295
Site 9, 6 m	6	7.5	7-Dec-11	11:10	23.78945	152.19295
Site 10, 0.5 m, Site Duplicate 1	0.5	4	7-Dec-11	9:55	23.8062	151.17707
Site 10, 0.5 m, Site Duplicate 2	0.5	4	7-Dec-11	10:00	23.8062	151.17707
Field blank 3 (Site 10)	-	-	7-Dec-11	10:15	23.8062	151.17707
Site 11, 0.5 m	0.5	6.5	6-Dec-11	11:55	23.79891	151.20704
[1]Site 12, 0.5 m	0.5	6	7-Dec-11	14:20	23.80333	151.22534
Site 13, 0.5 m	0.5	4	6-Dec-11	11:25	23.7993	151.22569
Field blank 1 (Site 13)	-	-	6-Dec-11	11:35	23.7993	151.22569
Site 14, 0.5 m	0.5	3.5	7-Dec-11	11:40	23.81188	151.22654
Site 15, 0.5 m	0.5	10.5	7-Dec-11	13:57	23.82026	151.25314
Site 16, 0.5 m, Site Duplicate 1	0.5	3.5	6-Dec-11	10:30	23.83427	151.26223
Site 16, 0.5 m, Site Duplicate 2	0.5	3.5	6-Dec-11	10:40	23.83427	151.26223
Site 17, 0.5 m	0.5	13.5	7-Dec-11	13:37	23.82202	151.28621
Site 18, 0.5 m	0.5	7	8-Dec-11	10:30	23.92665	151.36468
Site 19, 0.5 m	0.5	7.5	8-Dec-11	9:40	23.98	151.4342
Site 20, 0.5 m, Site Duplicate 1	0.5	5	8-Dec-11	8:26	24.06734	151.64541
Site 20, 0.5 m, Site Duplicate 2	0.5	5	8-Dec-11	8:29	24.06734	151.64541
Field blank 4 (Site 20)	-	-	8-Dec-11	8:29	24.06734	151.64541
Site 21, 0.5 m	0.5	11	8-Dec-11	8:54	24.01025	151.583

[1] No benthic sediment sample collected

2.3.2 Water sample pretreatment

On return to the Centre for Environmental Management (CEM) laboratory at the CQU Gladstone campus, water samples for trace metals analyses were filtered through acid-washed 0.45 µm Millipore membrane filters using polycarbonate filtration apparatus (Sartorius) using a vacuum generated by an electric pump. All filtration assemblies were rigorously cleaned before processing each sample by first filtering 100 mL volumes of 10% v/v nitric acid (Merck, Tracepur) solution followed by two volumes of approximately 150 mL of deionised water, and finally, a 50 mL volume of sample. The 50 mL volume of sample was swirled in the top and bottom compartments of the filtration rig to pretreat the filtration rig, before being poured into the filtrate receiving bottle, shaken to pretreat the bottle, and discarded to waste. The sample was then filtered and preserved by addition of 2 mL/L concentrated nitric acid (Merck, Tracepur). The volume of sample filtered through each filter depended on the turbidity and was generally between 450-800 mL.

Samples for suspended solids-bound metals and total suspended sediments (TSS) analyses were acquired by filtering known volumes of water through pre-weighed 0.45 µm Millipore membrane filters cleaned using the same procedure as above. The upper compartment of the filtration apparatus and the filter were then rinsed with approximately 20 mL of MQ water to remove salts and rinse suspended solids from the apparatus onto the filter. The filters were placed into acid-washed polycarbonate vials for transfer to CSIRO laboratories, Sydney, after which they were oven dried at 60°C, cooled to room temperature, and weighed to determine the mass of the dry filter and suspended solid. This procedure was repeated three times to ensure the mass was consistent, after which, the filters were stored at room temperature until required for analysis. The TSS concentration (mg/L) of the water samples was determined gravimetrically by dividing the difference in the mass of the filter before and after filtration by the volume of sample filtered.

2.3.3 Benthic sediment sampling

Benthic sediments were collected at each sample site (Table 1) using a stainless steel Van Veen grab sampler attached to an onboard winch system. The grab had an area of approximately 400 cm^2 (20 cm × 20 cm) and typical grab depth of 10 cm. Each of the sediments was collected after all water samples were collected at each site so that sediment disturbance would not affect the water samples. Approximately 300 g of sediment from the 0-2 cm surface layer was transferred from the grab sampler into zip-lock bags using a clean plastic spatula. Following collection, samples were 'triple-bagged' and placed in the onboard refrigerator to keep them cool in the field. Upon return to the CEM laboratory, the sediments were stored at 4 °C.

2.4 ANALYTICAL METHODS

Water and sediment samples were subsequently transported to the CSIRO laboratory at Lucas Heights, Sydney, by courier and analysed for a range of trace metals. Full details are given in the following sections.

2.4.1 Dissolved metals analyses

A sub-sample of each water sample was taken for direct metals analysis using inductively coupled atomic emission spectrometry (ICPAES) (Varian730 ES) (in-house method C-229) and operating instructions recommended by the manufacturer. The instrument was calibrated using matrix-matched standards.

The marine water samples were also subjected to complexation and solvent extraction prior to the analysis of cadmium, cobalt, copper, lead, nickel and zinc in order to achieve lower detection limits by removing the salt matrix and pre-concentrating the metals (in-house method C-208). The extraction procedure allowed the pre-concentration of metals by a factor of 25, making them easier to quantify. The method used a dithiocarbamate complexation/solvent extraction spectrometric method based on the procedure described by Magnusson and Westerlund (1981). The major differences were the use of a combined sodium bicarbonate buffer/ammonium pyrrolidine dithiocarbamate reagent (Apte and Gunn 1987) and 1,1,1-trichloroethane as the extraction solvent in place of Freon. In brief, sample aliquots (250 mL) were buffered to pH 5 by addition of the combined reagent and extracted with two X 10 mL portions of triple-distilled trichloroethane. The extracts were combined and the metals back-extracted into 1 mL of concentrated nitric acid (Merck Tracepur). The back extracts were diluted to a final volume of 10 mL by addition of deionised water and analysed by inductively coupled plasma-mass spectrometry (ICPMS) (Agilent, 7500CE) (in-house method C-209), using the operating conditions recommended by the manufacturer.

Dissolved arsenic concentrations were determined by hydride-generation atomic absorption spectrometry, using procedures based on the standard methods described by APHA (1998) (in-house method C-212). Samples were first digested by addition of potassium persulfate (1% mass/volume final concentration) and heating to 120 °C for 30 minutes in an autoclave. Hydrochloric acid (Merck, Tracepur), (3 M final concentration) was then added to the samples. Pentavalent arsenic was then pre-reduced to arsenic (III) by addition of potassium iodide (1% m/v final concentration) and ascorbic acid (0.2% m/v final concentration) and left standing for at least 30 minutes at room temperature prior to analysis. Arsenic concentrations were then measured by hydride-generation atomic absorbance spectrometry (AAS) using a Varian VGA system operating under standard conditions recommended by the manufacturer. Arsenic (III) in solution was reduced to arsine by borohydride, which was stripped with nitrogen gas into a silica tube, electrically heated at 925°C. Heating converted arsine into arsenic vapour whose atomic adsorption was measured. The analysis provides total dissolved arsenic concentrations in marine waters.

2.4.2 Total suspended solids analyses

The dry pre-weighed 0.45 µm filter membranes (Millipore) containing the suspended solids were subjected to a microwave-assisted aqua-regia digestion (in-house method C-223). This procedure involved the transfer of the dried filter membranes into pre-cleaned microwave accelerated reaction system (MARS) express digestion vessels to which 9 mL of concentrated nitric acid (Merck, Tracepur) and 3 mL of concentrated hydrochloric acid (Merck, Tracepur) were added. The digestion vessels were heated in a MARS digestion system (in-house method CE-223). Once cool, digests were diluted to a final volume of 40 mL with deionised water. The concentration of metals in the final digest solutions was analysed using a combination of ICP-AES (Varian 730 ES) and ICP-MS (Agilent 7500 CE) (in-house methods C-229 and C-209 respectively). The spectrometers were operated under the standard operating conditions recommended by the manufacturer.

2.4.3 Sediment fractionation

Each sediment sample was homogenised with a clean plastic spatula in a clean plastic container. A portion of known mass was then wet-sieved (<63 µm) into another clean plastic container so that there was two portions of each sample (total and <63 µm). Each portion was oven-dried at 90 °C for 48 hours, followed by 100 °C for 2 hours, cooled in a desiccator and weighed to determine the <63 µm sediment fraction. Then a mortar and pestle were used to grind each fraction of the sediments to a fine powder in preparation for analysis of sediment-bound metals.

2.4.4 Total particulate metals analyses in sediments

Approximately 0.5 g of each dry total and <63 µm sediment powder was accurately weighed and subjected to a microwave-assisted aqua-regia digestion (in-house method C-223). This procedure involved the dried powder being transferred into a pre-cleaned microwave-assisted reaction system (MARS, CEM Milestone) express digestion vessels to which 9 mL of concentrated nitric acid (Merck Tracepur) and 3 mL of concentrated hydrochloric acid (Merck Tracepur) was added. The digestion vessels were heated in the MARS digestion system using in-house method CE-223. Once cool, digests were diluted to a final volume of 40 mL with deionised water. The concentration of metals in the final digest solutions was analysed using a combination of ICP-AES (Varian 730 ES) and ICP-MS (Agilent 7500 CE) (in-house methods C-229 and C-209 respectively). The spectrometers were operated under the standard operating conditions recommended by the manufacturer. The concentrations of 21 trace elements were quantified in the sediment samples.

2.5 QA/QC

Rigorous field and laboratory quality assurance procedures were adopted in this study. Field blanks, field duplicate samples, method blanks, certified reference materials, spike recovery tests and method duplicates were an integral part of the field sampling and laboratory analysis quality control scheme. To check on the precision of the analytical procedures, at least 10% of the water and sediment samples were analysed in duplicate. To check on potential matrix interferences at least 10% of the filtered water samples had spike recoveries performed. Detection limits (3 sigma) were calculated using within-batch blank concentration data derived over the course of the sample analyses. This approach gives a more realistic assessment of limits of detection than reliance on historical data which is the approach used in the majority of routine analytical laboratories.

To confirm analytical accuracy, portions of certified reference materials from the National Research Council of Canada (NRC) were analysed with each batch of samples, whenever a suitable reference material was available. Reference standards have certified concentrations of elements for a range of sample matrices such as seawater and sediment, allowing the performance of the analytical procedures to be assessed by a comparison of the results obtained with the certified concentrations. The following reference materials were used: CASS-4 and CASS-5 for metals in saline waters, and PACS-2 for particulate metals in sediments.

3 RESULTS AND DISCUSSION

3.1 GENERAL WATER QUALITY PARAMETERS

General water quality parameter (total suspended solids, turbidity, pH and salinity) measurements are shown in Table 2. The pH of water samples in the study were in the narrow range of 7.80 to 8.21. Salinity also varied over a narrow range of 33.3 to 36.7 PSU. The turbidity varied from 1.2 to 22.5 nephelometric turbidity units (NTU) and was within the range reported by the Department of Environment and Resource Management (DERM) for Port Curtis (DERM 2012). Total suspended solids (TSS) concentrations were variable and in the range 3-74 mg/L. Turbidity and TSS are closely related physical variables and as expected, there was a statistically significant correlation between the two variables ($r=0.662$, $p<0.05$). TSS concentrations are depicted graphically in Figure 3. The highest TSS concentrations were observed in the dredge zone. TSS concentrations were generally higher than measured in the previous CSIRO field studies conducted in 2003 and 2004 (Figure 3) but this could be due to multiple factors such as different weather conditions, increased shipping activity in the Harbour and dredging. Apart from the depth profile taken at Site 9, there was little evidence of TSS increasing with depth.

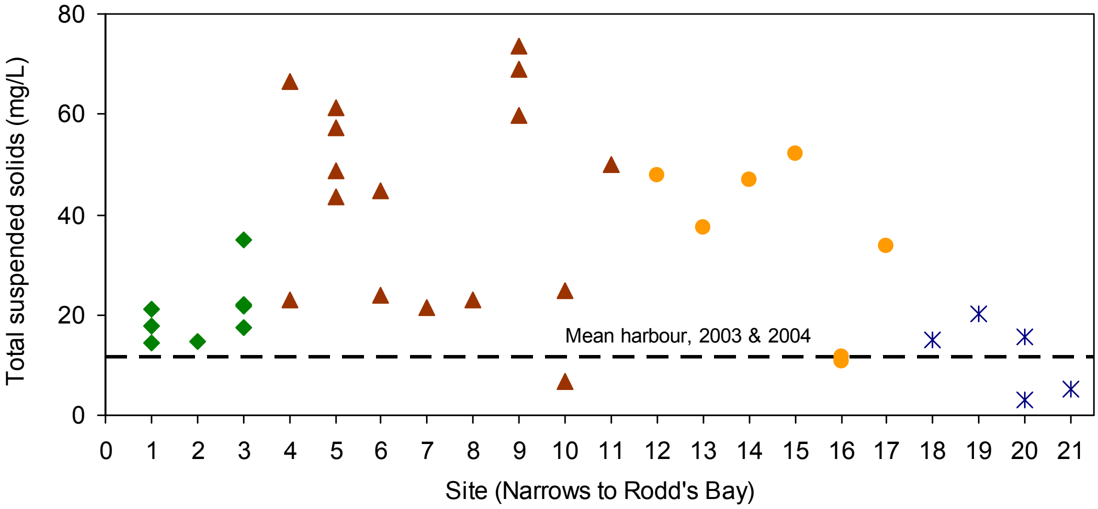

Figure 3. Total suspended sediment concentrations (TSS) at sites between the Southern Narrows and Rodds Bay, where, ◆ represents sites in the Southern Narrows, ▲ represents sites adjacent to the dredge and construction sites, ● represents sites in the outer harbour and, ✳ represents marine sites outside the harbour between the Boyne River and Rodds Bay

Table 2. Water samples: general data

Site Name	pH	Salinity (PSU)	Turbidity (NTU)	Suspended solids (mg/L)
Site 1, 0.5 m	7.81	34.1	7.3	14.4
Site 1, 2 m, Duplicate 1	7.88	34.3	12.0	21.1
Site 1, 2 m, Duplicate 2	7.89	34.5	9.0	17.7
Site 1, 4 m	7.85	34.2	8.2	14.9
Site 2, 0.5 m	7.94	34.1	6.9	34.8
Site 3, 0.5 m	8.00	33.8	13.0	17.5
Site 3, 5 m	7.98	33.8	12.0	22.0
Site 3, 10 m	7.97	34.1	11.5	21.7
Site 4, 0.5 m	8.03	36.6	8.5	22.9
Site 4, 0.5 m	7.97	34.7	20.5	66.6
Site 5, 0.5 m	7.98	36.6	17.3	61.3
Site 5, 1.5 m	7.98	36.7	17.5	57.3
Site 5, 3.5 m	7.97	36.7	21.4	43.5
Site 5, 5.5 m	7.95	36.5	21.6	48.8
Site 6, 0.5 m	7.92	36.6	20.1	44.9
Site 6, 6 m	7.93	36.5	20.4	24.0
Site 7, 0.5 m, Duplicate 1	8.03	36.5	9.5	21.5
Site 7, 0.5 m, Duplicate 2	8.03	36.4	8.0	-
Site 8, 0.5 m	8.01	37.1	8.7	23.0
Site 9, 0.5 m	8.00	35.7	15.1	59.8
Site 9, 3 m	8.01	35.8	22.5	69.1
Site 9, 6 m	8.02	35.7	17.5	73.6
Site 10, 0.5 m, Duplicate 1	8.00	34.5	13	6.7
Site 10, 0.5 m, Duplicate 2	8.02	34.7	13.4	24.8
Site 11, 0.5 m	8.00	33.6	13.9	49.9
Site 12, 0.5 m	8.00	36.3	14.0	47.9
Site 13, 0.5 m	8.05	33.3	10.6	37.5
Site 14, 0.5 m	8.04	35.6	18.2	46.9
Site 15, 0.5 m	7.93	35.9	9.2	52.0
Site 16, 0.5 m, Duplicate 1	7.80	33.5	15.2	11.6
Site 16, 0.5 m, Duplicate 2	7.83	33.6	15	10.7
Site 17, 0.5 m	8.05	35.7	7.9	33.7
Site 18, 0.5 m	8.20	34.0	4.3	15.1
Site 19, 0.5 m	8.19	33.9	3.0	20.3
Site 20, 0.5 m, Duplicate 1	8.16	33.5	1.8	15.6
Site 20, 0.5 m, Duplicate 2	8.16	33.5	1.2	3.1
Site 21, 0.5 m	8.21	33.4	1.7	5.2

3.2 DISSOLVED TRACE METALS

The results for field blanks and duplicates and full details of QA/QC for analyses are presented in Appendix B. The data for reference materials, spike recoveries and blanks were all within acceptable limits indicating satisfactory analytical performance.

Dissolved metals data are shown in Table 3 and are also presented graphically (see Appendix C and Figures 4, 5 and 6). The metal concentrations in all samples were below the ANZECC/ARMCANZ guideline trigger values that apply for 95% species protection in marine waters.

The following general trends were noted in the data:

(i) There was no consistent relationship between sample depth and concentration for any of the dissolved metals measured in the current study. This likely indicates that Port Curtis is well mixed by the strong tidal currents.

(ii) There was no indication of localised elevation of dissolved trace metal concentrations in the region of the Harbour that is currently being dredged.

(iii) Depth profile samples showed no consistent trends apart from at Site 3 (close to the mouth of Graham's Creek Inlet) where the concentrations of several metals (aluminium, cadmium, cobalt, copper, manganese, nickel, lead and zinc) were higher in the surface water sample compared to the middle and bottom samples. This trend may be caused by runoff from Graham's Creek.

(iv) The concentrations of dissolved aluminium, iron, lead and zinc displayed no discernible trends across Port Curtis. Dissolved nickel concentrations increased from south to north. Dissolved arsenic concentrations increased from north to south. The lowest cadmium and copper concentrations were observed at the southern-most sites.

(v) Dissolved cobalt and manganese concentrations were highest in the samples collected from the Narrows indicating a source of these metals in this region. This trend in manganese concentrations is consistent with data reported in the previous CSIRO study (Angel *et al*. 2010) which also indicated that the Narrows could be a source of dissolved nickel.

(vi) Dissolved aluminium concentrations were in the range 1.0-21.1 µg/L at all but one site (Site 3, 0.5 m), which had a suspected outlier concentration of 334 µg/L. The dissolved aluminium did not exhibit a clear trend in the study area. All dissolved aluminium concentrations were above 0.5 µg/L, which is the Environmental Concern Level (ECL) in the Australia/New Zealand marine water quality guidelines (ANZECC/ARMCANZ 2000). Note that the ECL is not formally considered as a guideline value because of its low reliability..

(vii) The dissolved copper was in the range 0.078-1.06 µg/L (Table 3 and 4, Appendix B and C). Dissolved copper concentrations were broadly elevated in the harbour compared to Sites 18-21 outside the harbour, probably because of multiple sources. The average (± standard deviation) dissolved copper concentration measured in Port Curtis in the current study was 0.82±0.0.09 µg/L, which was marginally higher than the concentrations of 0.53±0.08

and 0.50±0.20 µg/L measured in the harbour in 2003 and 2004, respectively (Angel *et al*., 2010). However, in the current study, more sites were sampled in the inner harbour and less in the outer harbour than the study by Angel *et al*. (2010), which may explain the higher average harbour concentration. Nevertheless, it is of note that dissolved copper appears to be higher in the current study than when measured in Port Curtis in December 2003 and 2004 and some concentrations were only marginally lower than the trigger value (Angel *et al*. 2010).

(viii) The concentration of dissolved nickel ranged from 0.16 to 0.82 µg/L. The dissolved nickel was lowest at Sites 18-21 outside the harbour, and exhibited a trend of increasing concentration as the sites were closer to the Narrows, with the highest concentration measured at the most northerly site in the Narrows. This trend is similar to that measured by Angel *et al*. (2010), and is likely to indicate a natural source of nickel in the Narrows. The average (± S.D.) dissolved nickel measured in the harbour in the current study was 0.52±0.10 µg/L, which was marginally higher than the concentrations of 0.35±0.06 and 0.33±0.14 µg/L measured in the harbour in 2003 and 2004, respectively (Angel *et al*. 2010). However, in the current study more sites were sampled in the inner harbour and less in the outer harbour than the study by Angel *et al*. (2010), which may explain the higher average harbour concentration.

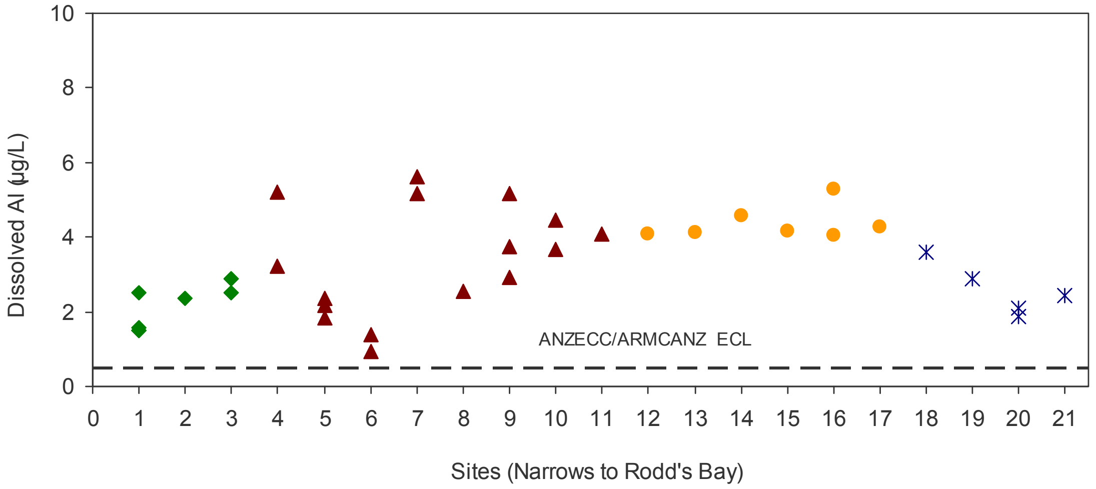

Figure 4. Dissolved aluminium concentrations from all depths at sites between the Southern Narrows to Rodds Bay. Note that an outlier concentration of 334 µg/L measured at 0.5 m depth at Site 3 is not plotted, where, ◆ represents sites in the Southern Narrows, ▲ represents sites adjacent to the dredge and construction sites, ● represents sites in the outer harbour and, ✱ represents marine sites outside the harbour between the Boyne River and Rodds Bay

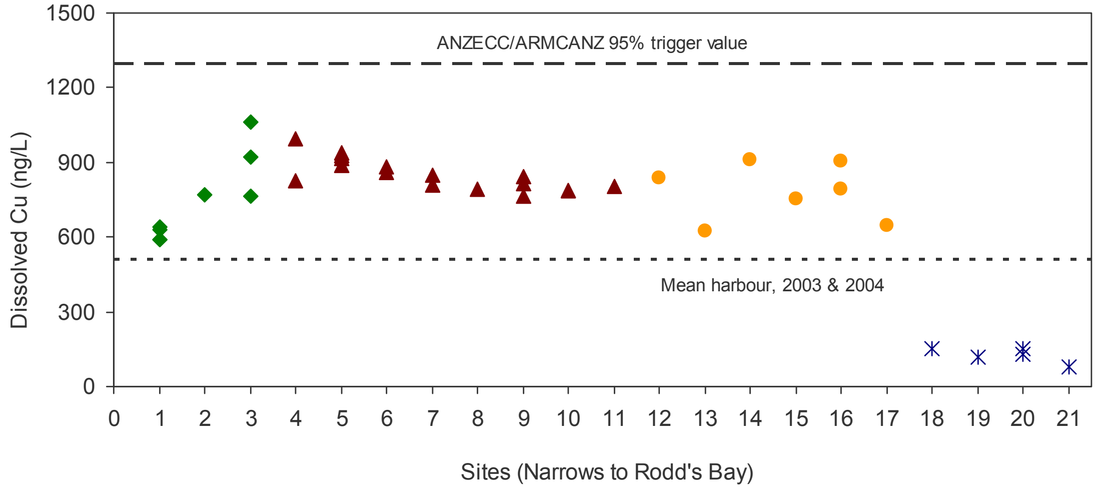

Figure 5. Dissolved copper concentrations from all depths at sites between the Southern Narrows and Rodds Bay, where, ◆ represents sites in the Southern Narrows, ▲ represents sites adjacent to the dredge and construction sites, ● represents sites in the outer harbour and, ✳ represents marine sites outside the harbour between the Boyne River and Rodds Bay

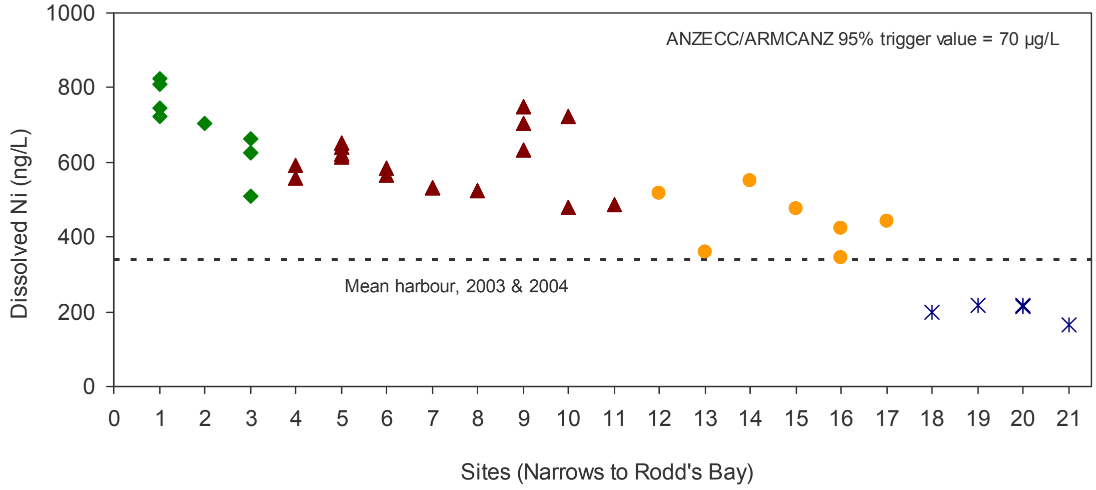

Figure 6. Dissolved nickel concentrations from all depths at sites between the Southern Narrows and Rodds Bay, where, ◆ represents sites in the Southern Narrows, ▲ represents sites adjacent to the dredge and construction sites, ● represents sites in the outer harbour and, ✳ represents marine sites outside the harbour between the Boyne River and Rodds Bay

3.3 TOTAL METAL CONCENTRATIONS IN WATERS

Total metal concentrations are presented in Table 4 and graphically in Appendix D. These data are included in this report to allow comparison with other studies that did not measure dissolved metal concentrations. Total metal concentrations are poor indicators of metal toxicity as they are largely determined by the particulate metals content of the sample which is generally far less bioavailable than metals that are in dissolved forms.

Calculations indicated that for aluminium, iron, manganese and lead, 98, 99, 89 and 94% respectively of the total metal concentration could be attributed to metals within the suspended sediment fraction. Cobalt, chromium and zinc had similar TSS contributions with mean percentages of 80, 75 and 77%, respectively. Arsenic, copper and nickel had the lowest partitioning to the TSS fraction with mean percentages of 29, 45 and 46%, respectively. The dependence of total metal concentrations on TSS is illustrated for the case of aluminium in Figure 13. As can be seen, there is a strong relationship between total aluminium concentration and TSS (r=0.84).

Table 3. Dissolved metal concentrations measured in the water samples

Sample description	Al (µg/L)	As (µg/L)	Cd (ng/L)	Co (ng/L)	Cr (µg/L)	Cu (ng/L)	Fe (µg/L)	Mn (µg/L)	Ni (ng/L)	Pb (ng/L)	Zn (ng/L)
Field blank 1 (Site 13)	<1	<0.09	<3	<2	0.4	<15	<1.5	<0.1	<32	<16	93
Field blank 2 (Site 8)	<1	<0.09	<3	<2	<0.4	<15	<1.5	<0.1	<32	<16	101
Field blank 3 (Site 10)	<1	<0.09	<3	<2	<0.4	46	<1.5	<0.1	36	<16	141
Field blank 4 (Site 20)	<1	<0.09	<3	<2	<0.4	<15	<1.5	<0.1	41	<16	170
Site 1, 0.5 m	2	0.79	3	153	<0.4	588	<1.5	5.4	746	<16	109
Site 1, 2 m, Duplicate 1	1	0.77	3	161	<0.4	630	<1.5	5.2	808	<16	139
Site 1, 2 m, Duplicate 2	2	0.68	5	144	<0.4	590	<1.5	4.3	725	<16	259
Site 1, 4 m	3	0.68	4	171	<0.4	643	<1.5	5.6	823	16	266
Site 2, 0.5 m	2	0.82	3	93	<0.4	769	1.5	2.2	706	<16	120
Site 3, 0.5 m	330	1.03	8	144	<0.4	1060	214	6.5	662	85	623
Site 3, 5 m	3	0.91	6	51	<0.4	921	1.6	0.8	626	16	152
Site 3, 10 m	3	0.79	3	50	<0.4	767	<1.1	0.6	508	<16	231
Site 4, 0.5 m	5	1.02	5	30	<0.4	995	<1.5	0.2	557	<16	1620
Site 4, 0.5 m	3	0.91	5	45	<0.4	824	<1.5	0.4	591	<16	225
Site 5, 0.5 m	2	0.84	4	72	<0.4	886	<1.5	2	612	<16	306
Site 5, 1.5 m	21	0.92	4	75	<0.4	938	12	2	640	17	504
Site 5, 3.5 m	2	0.82	4	68	<0.4	915	<1.5	2	651	20	406
Site 5, 5.5 m	2	0.90	5	66	<0.4	926	<1.5	1	621	<16	330
Site 6, 0.5 m	1	0.92	3	64	<0.4	880	<1.5	1	565	<16	303
Site 6, 6 m	1	0.97	6	62	<0.4	857	<1.5	1	584	<16	726
Site 7, 0.5 m, Duplicate 1	6	0.95	4	61	<0.4	849	<1.5	3	531	<16	261
Site 7, 0.5 m, Duplicate 2	5	1.04	5	55	<0.4	806	<1.5	2	533	<16	214
Site 8, 0.5 m	3	0.96	5	39	<0.4	790	<1.5	0.5	525	<16	200
Site 9, 0.5 m	5	0.92	5	29	<0.4	843	1.8	0.4	706	<16	348
Site 9, 3 m	4	0.94	4	24	<0.4	815	<1.5	<0.1	749	<16	365
Site 9, 6 m	3	0.90	6	22	<0.4	766	<1.5	<0.1	635	<16	265
Site 10, 0.5 m, Duplicate 1	4	1.00	4	51	<0.4	788	<1.5	1.7	479	<16	232
Site 10, 0.5 m, Duplicate 2	4	1.05	4	52	<0.4	786	<1.5	1.7	722	<16	353
Site 11, 0.5 m	4	1.06	9	24	<0.4	801	<1.5	<0.1	488	<16	201
Site 12, 0.5 m	4	0.98	4	53	<0.4	837	<1.5	1.9	516	<16	325
Site 13, 0.5 m	4	1.12	5	34	<0.4	625	<1.5	0.4	359	<16	149
Site 14, 0.5 m	5	1.00	4	35	<0.4	911	<1.5	0.9	552	<16	531
Site 15, 0.5 m	4	0.96	3	24	<0.4	752	<1.5	0.2	475	<16	243
Site 16, 0.5 m, Duplicate 1	5	1.00	6	35	<0.4	792	<1.5	1.7	345	<16	331
Site 16, 0.5 m, Duplicate 2	4	1.07	3	38	<0.4	907	<1.5	2.0	423	<16	255
Site 17, 0.5 m	4	1.05	3	24	<0.4	645	<1.5	0.8	443	<16	203
Site 18, 0.5 m	4	1.15	<3	23	<0.4	149	<1.5	0.1	200	<16	439
Site 19, 0.5 m	3	1.24	<3	25	<0.4	120	<1.5	<0.1	217	<16	18

Sample description	Al (µg/L)	As (µg/L)	Cd (ng/L)	Co (ng/L)	Cr (µg/L)	Cu (ng/L)	Fe (µg/L)	Mn (µg/L)	Ni (ng/L)	Pb (ng/L)	Zn (ng/L)
Site 20, 0.5 m, Duplicate 1	2	1.14	<3	37	<0.4	127	<1.5	1	212	19	27
Site 20, 0.5 m, Duplicate 2	2	1.27	<3	39	<0.4	151	<1.5	1	216	<16	40
Site 21, 0.5 m	2	1.03	<3	12	<0.4	78	<1.5	<0.1	163	<16	20
95% trigger value[1]	-	2.3-4.5	5500	1000	27.4	1300	-	802	70000	4400	15000

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[1] ANZECC/ARMCANZ, 2000 trigger value for 95% species protection in marine waters

Table 4. Total metal concentrations measured in the water samples

Sample name	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
						(µg/L)					
Field blank 1 (Site 13)	<8	<0.01	<0.02	<0.01	0.30	<0.17	2	<0.02	<0.03	<0.04	0.30
Field blank 2 (Site 8)	<8	<0.01	<0.02	<0.01	<0.04	<0.17	<1.7	<0.02	<0.03	<0.04	0.24
Field blank 3 (Site 10)	<8	<0.01	<0.02	<0.01	0.31	<0.17	<1.7	<0.02	<0.03	0.06	0.25
Field blank 4 (Site 20)	<8	<0.01	<0.02	<0.01	<0.04	<0.17	<1.7	<0.02	<0.03	<0.04	0.35
Site 1, 0.5 m	590	1.04	<0.02	0.34	1.09	0.90	581	16.2	1.21	0.18	1.08
Site 1, 2 m, Duplicate 1	790	1.10	<0.02	0.45	1.39	1.11	801	20.7	1.44	0.26	1.53
Site 1, 2 m, Duplicate 2	410	0.96	<0.02	0.34	0.99	0.90	551	16.5	1.14	0.17	1.00
Site 1, 4 m	850	0.94	<0.02	0.37	1.21	0.92	642	17.0	1.34	0.18	1.29
Site 2, 0.5 m	370	1.06	<0.02	0.31	0.89	1.07	482	13.5	1.02	0.15	0.95
Site 3, 0.5 m	950	1.30	<0.02	0.36	1.04	1.59	774	15.8	1.02	0.29	1.56
Site 3, 5 m	760	1.29	<0.02	0.36	1.26	1.54	792	15.6	1.10	0.24	1.55
Site 3, 10 m	930	1.18	<0.02	0.37	1.33	1.48	841	18.4	1.06	0.25	2.45
Site 4, 0.5 m	610	1.43	<0.02	0.35	1.12	1.68	771	17.8	1.01	0.24	2.95
Site 4, 0.5 m	1240	1.62	0.03	0.61	1.96	2.05	1350	25.9	9.49	0.45	3.34
Site 5, 0.5 m	1200	1.37	<0.02	0.49	1.71	1.89	1100	18.4	1.26	0.38	2.06
Site 5, 1.5 m	1530	1.41	<0.02	0.48	1.94	2.01	1190	19.1	1.39	0.40	2.40
Site 5, 3.5 m	1060	1.48	<0.02	0.55	1.70	2.14	1250	23.3	1.34	0.44	2.25
Site 5, 5.5 m	1310	1.66	<0.02	0.65	2.15	2.70	1500	27.8	1.41	0.70	2.74
Site 6, 0.5 m	1470	1.59	<0.02	0.61	2.04	2.18	1520	25.9	1.30	0.54	2.33
Site 6, 6 m	690	1.35	<0.02	0.35	1.16	1.54	751	13.4	0.98	0.27	1.91
Site 7, 0.5 m, Duplicate 1	420	1.28	<0.02	0.31	0.89	1.29	601	16.5	0.96	0.18	1.23
Site 7, 0.5 m, Duplicate 2	520	1.41	<0.02	0.33	1.09	1.36	651	17.1	0.92	0.20	1.50
Site 8, 0.5 m	980	1.39	<0.02	0.39	1.36	1.50	911	18.6	1.05	0.27	1.79
Site 9, 0.5 m	820	1.58	<0.02	0.51	1.59	1.79	1060	23.9	1.40	0.34	2.16
Site 9, 3 m	1680	1.83	<0.02	0.76	2.50	2.32	1720	36.0	1.83	0.55	3.65
Site 9, 6 m	2120	1.80	<0.02	0.74	2.62	2.21	1730	33.6	1.78	0.53	3.39
Site 10, 0.5 m, Duplicate 1	300	1.13	<0.02	0.15	0.61	0.99	291	7.4	0.63	0.07	0.59
Site 10, 0.5 m, Duplicate 2	320	1.22	<0.02	0.17	0.63	1.00	311	7.7	0.91	0.08	0.78
Site 11, 0.5 m	920	1.68	<0.02	0.51	1.50	1.80	1140	26.0	1.13	0.36	2.29
Site 12, 0.5 m	1360	1.52	<0.02	0.47	1.69	1.71	1070	21.9	1.17	0.32	2.21
Site 13, 0.5 m	870	1.53	<0.02	0.36	1.28	1.29	871	17.3	0.81	0.27	1.62
Site 14, 0.5 m	1050	1.53	<0.02	0.44	1.57	1.81	981	20.9	1.20	0.29	2.42

Sample name	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
						(µg/L)					
Site 15, 0.5 m	1200	1.46	<0.02	0.43	1.57	1.53	1000	19.4	1.06	0.27	1.81
Site 16, 0.5 m, Duplicate 1	430	1.24	<0.02	0.20	0.78	1.27	421	11.5	0.62	0.14	1.32
Site 16, 0.5 m, Duplicate 2	450	1.27	<0.02	0.19	0.75	1.28	421	11.7	0.65	0.14	1.04
Site 17, 0.5 m	590	1.32	<0.02	0.22	0.95	1.00	501	10.2	0.74	0.14	0.94
Site 18, 0.5 m	200	1.43	<0.02	0.13	0.70	<0.17	301	7.3	0.38	0.12	0.71
Site 19, 0.5 m	510	1.66	<0.02	0.17	1.03	<0.17	451	9.9	0.49	0.13	0.19
Site 20, 0.5 m, Duplicate 1	130	1.23	<0.02	0.08	0.48	<0.17	111	4.7	0.30	<0.04	<0.11
Site 20, 0.5 m, Duplicate 2	130	1.34	<0.02	0.08	0.47	<0.17	111	4.5	0.29	<0.04	<0.11
Site 21, 0.5 m	90	1.10	<0.02	0.04	0.40	<0.17	91	2.4	0.22	<0.04	<0.11

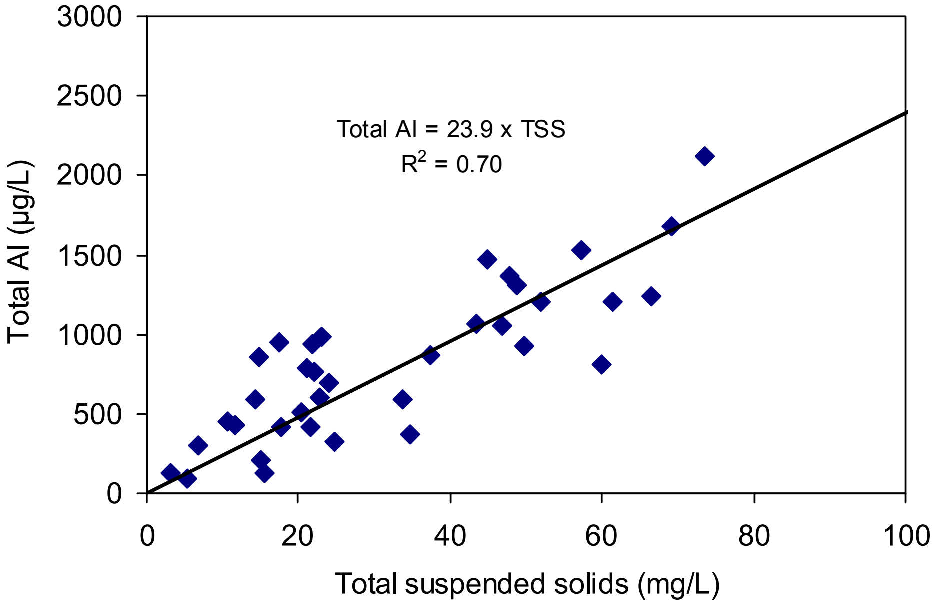

Figure 7. The relationship between the concentrations of total aluminium and total suspended solids measured in water samples.

3.4 METALS IN BENTHIC SEDIMENTS

The results for duplicates and full details of QA/QC for sediment analyses are given in Appendix B. The data for reference materials, spike recoveries and blanks were all within acceptable limits indicating satisfactory sampling and analysis.

Sediment grab samples were not obtained from Sites 5 and 12 owing to the rocky nature of the sea bed at these sites and lack of fine sediment. The percentage of silt in the sediments collected at each site is shown in Table 5. The silt content was very variable and ranged from 0.2-96% and indicated the heterogeneous nature of sediment content in the region, which ranged from very silty to very sandy. There was up to 15% relative standard deviation difference between sample duplicates highlighting the heterogeneity of sediments even at the same site.

Total particulate metal concentrations are presented in Table 7 and 8. Graphical plots of the particulate metals data are presented in Appendix F. For most metals there was no discernible trend between concentration and location. The exceptions were:

- Particulate cobalt – highest in samples collected from the Narrows
- Particulate barium – highest in the area of current dredging activities

Sediment quality guidelines (ANZECC/ARMCANZ 2000), based predominantly on ecotoxicological data are available for ten metals and are applied to metals in the total sediment fraction. Two guideline values exist for each metal: the ISQG-low trigger value (TV) and an ISQG-high values, where ISQG refers to the interim sediment quality guideline. Sediments that have metal concentrations exceeding the ISQG-low TV are deemed worthy of further investigation, as not all of the metals may be in bioavailable forms. The ISQG-high values give an indication of metal concentrations where toxic effects would be expected. All metals were below the guideline TV, except for arsenic which marginally exceeded the TV of 20 µg/g at three sites (two in the Narrows and one site off Quoin Island), but never exceeded the corresponding high value. The particulate arsenic data are presented graphically in Figure 8. The two sites in the Southern Narrows have previously been shown to exceed the TV and this is most likely a reflection of the local geology which is naturally-enriched in arsenic (Jones *et al*. 2005).

A comparison of the sediment-bound metal concentrations measured in Port Curtis in the current study and those reported by Jones *et al*. (2005) for studies in 2001 and 2002 are shown in Table 6. Most metals were either similar to or lower than those reported by Jones *et al*. (2005). Particulate cadmium concentrations were consistently higher in the current study, but were well below TV (ANZECC/ARMCANZ, 2000).

Particulate metal concentrations in the <63 µm sediment fractions are shown in Tables 9 and 10. Graphical plots of the particulate metals data are presented in Appendix F. For most metals there was no discernible trend between concentration and location. The exceptions were:

- Particulate barium – highest in the area of current dredging activities
- Particulate strontium – highest concentrations observed at the southern-most sites.

The particulate metal concentrations were nearly always higher in the <63 µm fraction because smaller sediment particles have a higher surface area and subsequent number of binding sites available for metals. A comparison of the particulate metal concentrations between the <63 µm and total fractions is illustrated for copper, lead, nickel and zinc in Figure 9.

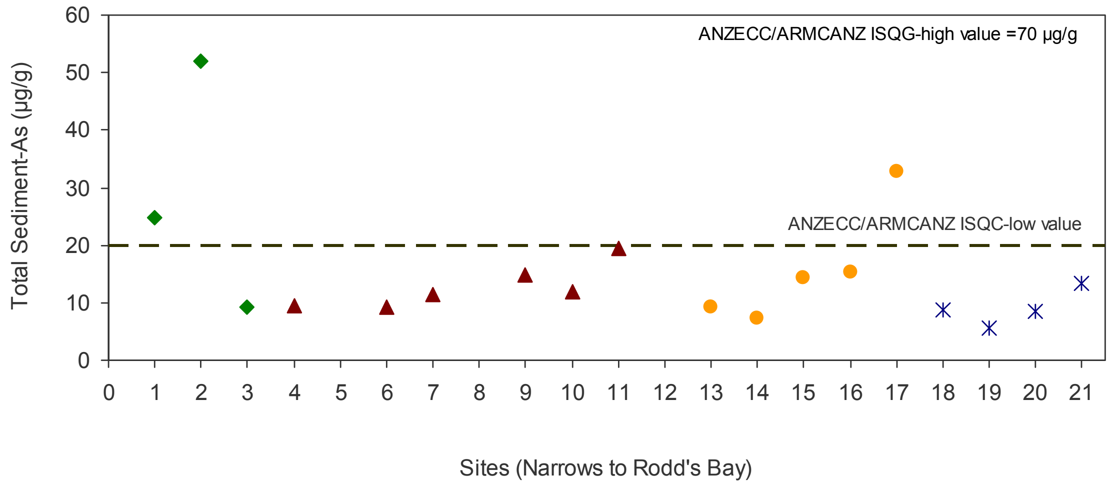

Figure 8. Total particulate arsenic concentrations of benthic sediment samples collected at sites between the Southern Narrows and Rodds Bay, where, ◆ represents sites in the Southern Narrows, ▲ represents sites adjacent to the dredge and construction sites, ● represents sites in the outer harbour and, ✳ represents marine sites outside the harbour between the Boyne River and Rodds Bay

Table 5. Percentages of silt (<63 µm) in the benthic sediment samples

Site	% silt (<63 µm)
Site 1	1.4
Site 2 site Duplicate 1	39
Site 2 site Duplicate 2	29
Site 3	50
Site 4	27
Site 6 site Duplicate 1	52
Site 6 site Duplicate 2	65
Site 7	96
Site 8	27
Site 9	3.0
Site 10 site Duplicate 1	20
Site 10 site Duplicate 2	14
Site 11	8.0
Site 13	5.4
Site 14 site Duplicate 1	28
Site 14 site Duplicate 2	14
Site 15	8
Site 16	87
Site 17	6.6
Site 18 site Duplicate 1	0.2
Site 18 site Duplicate 2	0.2
Site 19	8.7
Site 20	40
Site 21	43

Table 6. Comparison of total metal concentrations measured in benthic sediment samples from Port Curtis in the current study and reported previously by Jones *et al.* (2005)

Study		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
					(µg/g)				
Current study	Minimum concentration	7	0.11	7	4	0.02	4	3	8
Current study	Maximum concentration	33	0.44	32	22	0.05	16	12	57
Current study	**Mean**	**13**	**0.24**	**15**	**10**	**0.03**	**8**	**7**	**29**
Jones *et al.*, 2005	Minimum concentration	6	<0.1	13	4	0.001	4	5	11
Jones *et al.*, 2005	Maximum concentration	36	0.24	85	44	0.055	33	18	113
Jones et al., 2005	**Mean**	**18**	**0.10**	**50**	**18**	**0.01**	**14**	**30**	**32**
[1]Triggervalue		20	1.5	80	65	0.15	21	50	200
[1]ISQG high value		70	10	370	270	1	52	220	410

[1] ANZECC/ARMCANZ, 2000 ISQG values

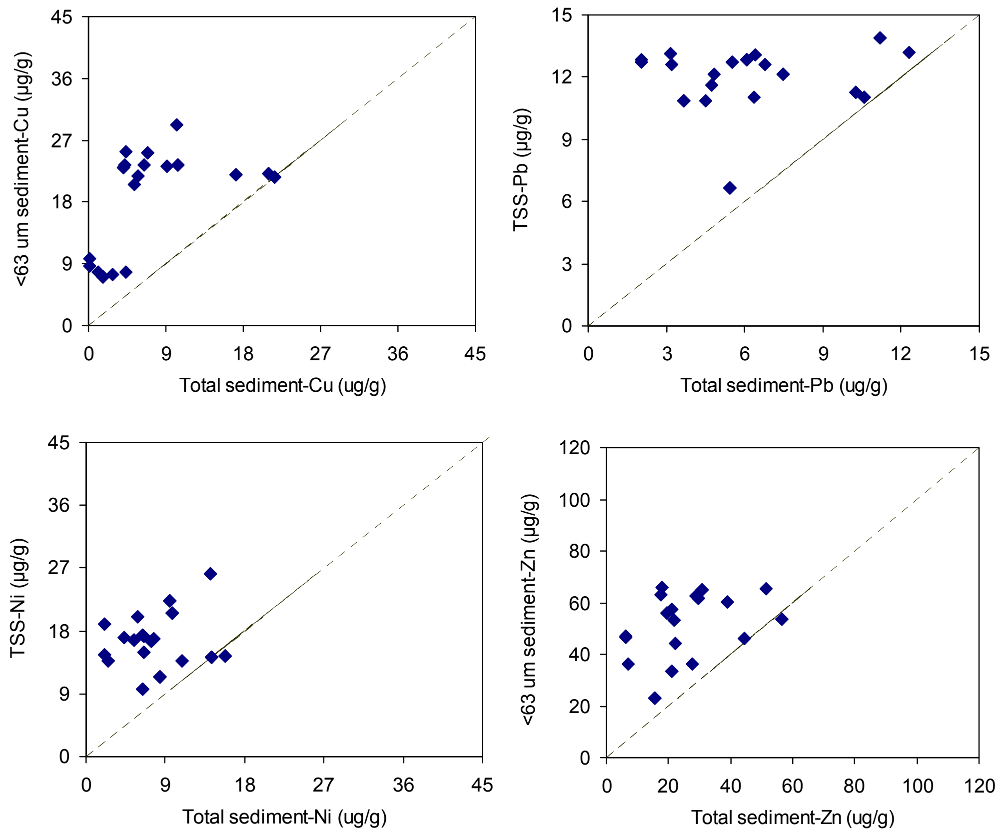

Figure 9. Graphs showing the relationship between copper, lead, nickel and zinc in the <63 µm and total fractions of benthic sediment samples

Table 7. Total metal concentrations in sediments

Site	Fraction	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Ga	Hg
		(µg/g)											
Site 1	Total	0.01	1720	25	13	0.22	0.16	19	13	2	19500	2	<0.02
Site 2 Duplicate 1	Total	0.04	8430	54	10	0.79	0.38	30	24	7	62600	8	<0.02
Site 2 Duplicate 2	Total	0.03	6370	50	10	0.71	0.35	31	22	5	58200	7	<0.02
Site 3	Total	0.03	9850	9	11	0.49	0.23	10	16	10	16900	5	<0.02
Site 4	Total	0.03	10800	7	14	0.36	0.20	8	13	7	14000	5	<0.02
Site 6 Duplicate 1	Total	0.02	9280	10	54	0.42	0.16	6	20	15	31900	6	<0.02
Site 6 Duplicate 2	Total	0.03	18600	8	64	0.48	0.19	6	22	19	25900	8	<0.02
Site 7	Total	0.06	21200	11	82	0.73	0.38	13	25	21	28600	8	<0.02
Site 8	Total	0.05	19800	12	31	0.56	0.30	11	21	11	23100	7	<0.02
Site 9	Total	0.02	4400	15	16	0.23	0.19	12	7	4	13500	2	<0.02
Site 10 Duplicate 1	Total	0.03	11600	12	21	0.49	0.27	18	17	7	24500	6	<0.02
Site 10 Duplicate 2	Total	0.03	6680	12	13	0.43	0.22	17	13	6	22300	5	<0.02
Site 11	Total	0.02	3820	20	9	0.26	0.30	10	8	4	18000	3	0.02
Site 13	Total	0.01	4050	9	9	0.22	0.11	8	7	4	12300	3	<0.02
Site 14 Duplicate 1	Total	0.03	9110	7	18	0.31	0.22	8	13	11	16900	5	<0.02
Site 14 Duplicate 2	Total	0.03	13400	7	26	0.31	0.23	7	14	9	16500	5	<0.02
Site 15	Total	0.02	4390	14	11	0.29	0.18	10	8	6	14400	2	0.02
Site 16	Total	0.07	26900	15	29	0.78	0.44	11	32	22	28900	10	0.05
Site 17	Total	0.03	6040	33	10	0.37	0.26	14	10	5	22400	4	<0.02
Site 18 Duplicate 1	Total	0.01	2150	9	4	0.17	0.08	3	5	0.1	4970	1	<0.02
Site 18 Duplicate 2	Total	0.01	2340	8	6	0.18	0.09	3	6	0.2	5180	1	<0.02
Site 19	Total	0.01	2960	6	4	0.18	0.09	3	7	1	5090	2	<0.02
Site 20	Total	0.03	9130	13	10	0.52	0.21	6	16	3	15300	4	<0.02
Site 21	Total	0.05	17800	9	17	0.63	0.29	6	25	4	16000	6	<0.02
Trigger value[1]		1	-	20	-	-	2	-	80	65	-	-	0.15
ISQG high value[1]		3.70	-	70	-	-	10	-	370	270	-	-	1

[1] ANZECC/ARMCANZ, 2000 ISQG values

Table 8. Total metal concentrations in sediments (continued)

Site	Fraction	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
					(µg/g)						
Site 1	Total	1130	1	8	5	0.28	0.08	76	0.03	59	16
Site 2 Duplicate 1	Total	535	2	14	13	0.25	0.17	224	0.05	112	53
Site 2 Duplicate 2	Total	522	2	14	12	0.24	0.15	267	0.04	114	50
Site 3	Total	400	1	10	6	0.17	0.15	83	0.06	36	31
Site 4	Total	358	0.4	7	5	0.08	0.12	59	0.06	30	25
Site 6 Duplicate 1	Total	74	1	6	12	0.19	0.42	28	0.05	66	18
Site 6 Duplicate 2	Total	104	1	7	10	0.18	0.51	34	0.09	52	24
Site 7	Total	365	1	14	10	0.17	0.20	50	0.10	52	45
Site 8	Total	484	1	12	6	0.19	0.16	202	0.09	50	34
Site 9	Total	1330	1	5	4	0.14	0.10	235	0.02	37	19
Site 10 Duplicate 1	Total	433	1	9	7	0.19	0.14	30	0.09	47	40
Site 10 Duplicate 2	Total	322	1	6	8	0.17	0.13	43	0.08	42	38
Site 11	Total	896	1	6	5	0.13	0.13	349	0.02	42	18
Site 13	Total	407	0.4	4	3	0.12	0.05	97	0.02	27	18
Site 14 Duplicate 1	Total	290	0.5	7	5	0.12	0.11	56	0.04	37	30
Site 14 Duplicate 2	Total	348	1	7	4	0.13	0.10	95	0.06	39	28
Site 15	Total	659	1	6	5	0.23	0.15	486	0.03	33	21
Site 16	Total	484	1	16	11	0.19	0.27	179	0.13	52	57
Site 17	Total	960	1	7	6	0.35	0.12	576	0.03	48	22
Site 18 Duplicate 1	Total	175	0.1	2	2	0.05	0.02	181	0.01	11	6
Site 18 Duplicate 2	Total	163	0.1	2	2	0.05	0.02	167	0.01	11	6
Site 19	Total	150	0.2	3	3	0.09	0.07	137	0.03	12	7
Site 20	Total	169	1	7	6	0.12	0.15	274	0.08	24	22
Site 21	Total	197	1	11	7	0.12	0.17	241	0.12	32	28
Trigger value[1]		-	-	21	50	2	-	-	-	-	200
ISQG high value[1]		-	-	52	220	25	-	-	-	-	410

[1] ANZECC/ARMCANZ, 2000 ISQG values

Table 9. Total metal concentrations in the <63 µm sediment fractions

Site	Fraction	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Ga	Hg
								(µg/g)					
Site 1	<63 µm	0.05	5275	15	9	0.36	1.68	18	13	7	14223	2	0.36
Site 2 Duplicate 1	<63 µm	0.08	35600	14	33	1.13	0.68	14	46	23	37400	13	0.08
Site 2 Duplicate 2	<63 µm	0.06	34400	13	31	1.02	0.84	13	44	21	34300	12	0.08
Site 3	<63 µm	0.07	28800	13	24	1.00	0.74	15	38	23	33800	8	0.11
Site 4	<63 µm	0.06	25900	9	28	0.90	0.79	13	34	22	30100	10	0.13
Site 6 Duplicate 1	<63 µm	0.03	23800	5	58	0.50	0.30	6	25	22	23700	9	0.06
Site 6 Duplicate 2	<63 µm	0.03	28500	8	68	0.61	0.39	8	29	22	28300	10	0.07
Site 7	<63 µm	0.04	21000	12	84	0.70	0.45	12	25	22	28900	8	0.05
Site 8	<63 µm	0.07	29100	14	25	1.05	0.74	16	38	24	36700	12	0.05
Site 9	<63 µm	0.06	19000	24	48	0.71	1.47	21	23	23	32800	9	0.31
Site 10 Duplicate 1	<63 µm	0.07	23000	10	23	0.83	0.94	12	30	24	28200	9	0.16
Site 10 Duplicate 2	<63 µm	0.05	23200	10	23	0.86	0.64	12	32	26	29600	10	0.14
Site 11	<63 µm	0.06	27600	12	28	0.89	0.78	16	34	25	31100	11	0.09
Site 13	<63 µm	0.06	26000	21	54	0.89	1.34	17	30	23	38400	10	0.32
Site 14 Duplicate 1	<63 µm	0.05	21800	10	28	0.72	0.79	14	25	31	31900	8	0.14
Site 14 Duplicate 2	<63 µm	0.05	23700	12	32	0.75	0.88	14	27	28	33000	10	0.17
Site 15	<63 µm	0.05	22700	14	30	0.81	0.82	14	29	23	28400	9	0.16
Site 16	<63 µm	0.04	16700	14	22	0.74	0.90	10	26	22	25900	8	0.17
Site 17	<63 µm	0.05	20900	15	25	0.75	0.67	12	27	21	26400	8	0.09
Site 18 Duplicate 1	<63 µm	0.04	16700	16	22	0.67	6.43	11	33	8.5	22600	10	1.92
Site 18 Duplicate 2	<63 µm	0.04	16400	13	17	0.76	1.94	10	33	8.8	21800	8	0.51
Site 19	<63 µm	0.06	29400	13	23	0.91	0.77	11	45	10	26800	10	0.13
Site 20	<63 µm	0.05	25300	14	22	0.95	0.53	8	37	7	26000	9	0.08
Site 21	<63 µm	0.03	14400	11	16	0.78	0.49	7	30	8	20500	6	0.10
Trigger value[1]		1.00	-	20	-	-	2	-	80	65	-	-	0.15
ISQG high value[1]		3.70	-	70	-	-	10	-	370	270	-	-	1

[1] ANZECC/ARMCANZ, 2000 ISQG values

Table 10. Total metal concentrations in the <63 µm sediment fractions (continued)

Site	Fraction	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
					(µg/g)						
Site 1	<63 µm	1654	2	11	7	0.17	0.90	136	0.05	42	23
Site 2 Duplicate 1	<63 µm	322	1	26	14	0.20	0.36	53	0.19	67	67
Site 2 Duplicate 2	<63 µm	260	1	26	13	0.23	0.35	53	0.18	61	64
Site 3	<63 µm	198	1	22	13	0.24	0.33	46	0.16	64	65
Site 4	<63 µm	221	1	19	12	0.20	0.32	49	0.15	59	59
Site 6 Duplicate 1	<63 µm	95	1	8	15	0.16	0.34	25	0.11	45	29
Site 6 Duplicate 2	<63 µm	172	1	12	13	0.17	0.45	32	0.14	52	38
Site 7	<63 µm	374	1	14	11	0.17	0.20	42	0.11	55	46
Site 8	<63 µm	309	1	22	13	0.24	0.35	55	0.14	65	64
Site 9	<63 µm	1520	2	17	11	0.22	0.71	122	0.10	80	56
Site 10 Duplicate 1	<63 µm	250	1	17	12	0.26	0.34	41	0.12	58	59
Site 10 Duplicate 2	<63 µm	263	1	17	13	0.27	0.33	43	0.14	64	62
Site 11	<63 µm	851	1	20	12	0.17	0.64	76	0.15	60	66
Site 13	<63 µm	798	1	17	13	0.28	0.35	108	0.11	77	63
Site 14 Duplicate 1	<63 µm	440	1	15	11	0.16	0.34	50	0.11	62	61
Site 14 Duplicate 2	<63 µm	551	1	15	11	0.18	0.30	69	0.11	65	64
Site 15	<63 µm	734	1	17	12	0.20	0.54	98	0.13	55	57
Site 16	<63 µm	427	1	14	11	0.17	0.24	137	0.11	47	54
Site 17	<63 µm	607	1	16	11	0.20	0.59	127	0.12	52	53
Site 18 Duplicate 1	<63 µm	912	1	15	13	0.21	0.36	230	0.11	45	53
Site 18 Duplicate 2	<63 µm	417	1	14	12	0.24	0.38	189	0.13	49	41
Site 19	<63 µm	298	1	19	13	0.23	0.47	184	0.17	59	46
Site 20	<63 µm	251	1	17	13	0.15	0.28	89	0.16	43	44
Site 21	<63 µm	226	1	14	13	0.04	0.30	214	0.14	42	36
Trigger value[1]		-	-	21	50	2	-	-	-	-	200
ISQG high value[1]		-	-	52	220	25	-	-	-	-	410

[1] ANZECC/ARMCANZ, 2000 ISQG values

3.5 METALS ASSOCIATED WITH SUSPENDED SOLIDS

The results for duplicates and full details of QA/QC for analyses of suspended solids are given in Appendix B. The data for reference materials, spike recoveries and blanks were all within acceptable limits and indicate satisfactory sampling and analysis.

Metals associated with suspended sediments may be potentially bioavailable to filter-feeding organisms and their concentrations give some indication of exposure.

The concentrations of metals in the suspended solids fraction of the waters sampled (TSS-metals) are shown in Tables 11 and 12 and graphically in Appendix E. The TSS- silver, cadmium and all but four mercury concentrations were below the limits of detection and are not discussed any further. The variation of TSS-metal concentrations across the sampling sites is illustrated for the cases of aluminium, copper, nickel and zinc in Figures 10 to 13 respectively.

In general, the TSS-metal concentrations were comparable to the particulate metal concentrations of the <63 µm fraction of benthic sediments (see Figure 14 for example data). This is consistent with a significant proportion of the suspended sediment pool originating from the resuspension of fine benthic sediments.

Most TSS-metals displayed no discernible trends across Port Curtis. However TSS-copper concentrations were lowest at the Southern-most sites, TSS- molybdenum, nickel, lead and zinc concentrations showed a gradual increase in concentration from south to north and TSS-Strontium showed a gradual increase in concentration from north to south.

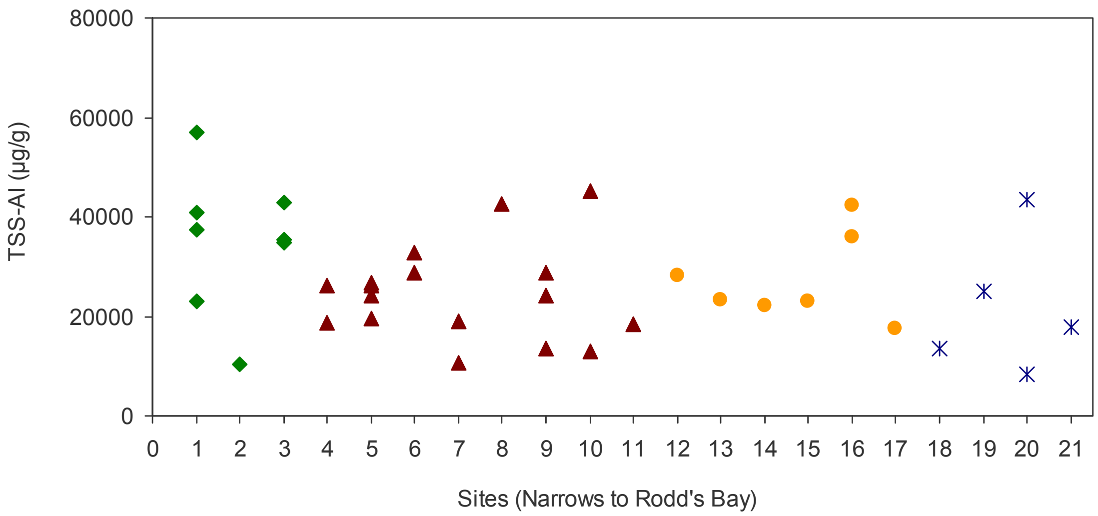

Figure 10. TSS-bound aluminium concentrations from all depths at sites between the Southern Narrows and Rodds Bay, where, ◆ represents sites in the Southern Narrows, ▲ represents sites adjacent to the dredge and construction sites, ● represents sites in the outer harbour and, ✳ represents marine sites outside the harbour between the Boyne River and Rodds Bay

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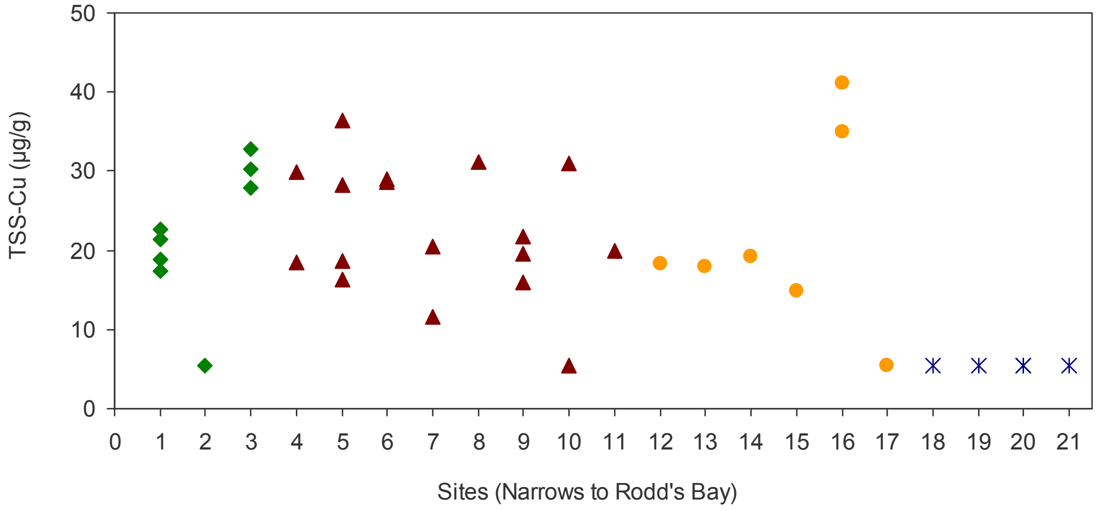

Figure 11. TSS-bound copper concentrations from all depths at sites between the Southern Narrows and Rodds Bay, where, ◆ represents sites in the Southern Narrows, ▲ represents sites adjacent to the dredge and construction sites, ● represents sites in the outer harbour and, ✳ represents marine sites outside the harbour between the Boyne River and Rodds Bay

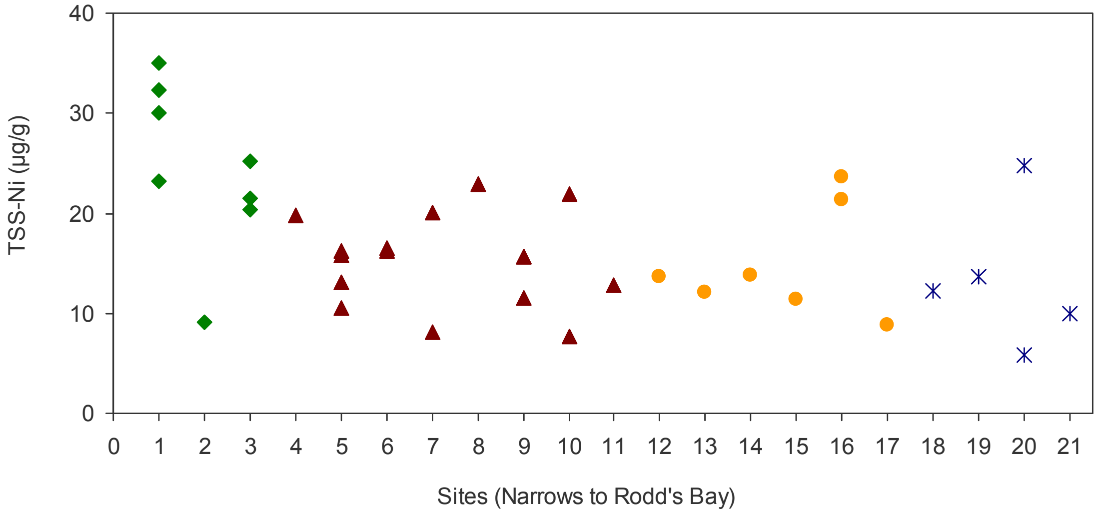

Figure 12. TSS-bound nickel concentration from all depths at sites between the Southern Narrows to Rodds Bay, where, ◆ represents sites in the Southern Narrows, ▲ represents sites adjacent to the dredge and construction sites, ● represents sites in the outer harbour and, ✳ represents marine sites outside the harbour between the Boyne River and Rodds Bay

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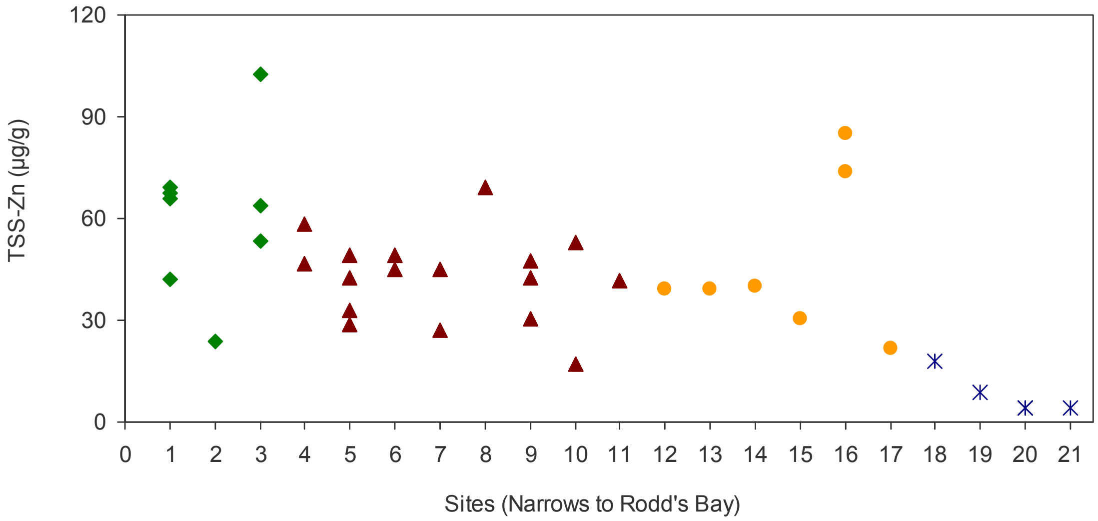


Figure 13. TSS-bound zinc concentrations from all depths at sites between the Southern Narrows and Rodds Bay, where, ◆ represents sites in the Southern Narrows, ▲ represents sites adjacent to the dredge and construction sites, ● represents sites in the outer harbour and, ✳ represents marine sites outside the harbour between the Boyne River and Rodds Bay

Table 11. Suspended sediments: particulate metals concentrations

Sample description	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe
	(µg/g)									
Field blank 1	<2.4	<310	<0.5	<2.5	<0.06	<1.1	<0.5	<2.5	<11	<69
Field blank 2	<2.4	<310	<0.5	<2.5	<0.06	<1.1	<0.5	<2.5	<11	<69
Field blank 3	<2.4	<310	<0.5	<2.5	<0.06	<1.1	<0.5	<2.5	<11	<69
Field blank 4	<2.4	<310	<0.5	<2.5	<0.06	<1.1	<0.5	<2.5	<11	<69
Site 1, 0.5 m	<2.4	40900	17	42	1.2	<1.1	13	58	21	39900
Site 1, 2 m, Duplicate 1	<2.4	37500	15	40	1.1	<1.1	14	54	23	37900
Site 1, 2 m, Duplicate 2	<2.4	23100	16	30	0.9	<1.1	11	41	17	31100
Site 1, 4 m	<2.4	56900	17	59	1.3	<1.1	14	64	19	43000
Site 2, 0.5 m	<2.4	10500	7	12	0.5	<1.1	6	18	<11	13700
Site 3, 0.5 m	<2.4	35500	15	49	0.8	<1.1	12	45	30	32100
Site 3, 5 m	<2.4	34700	17	46	0.8	<1.1	14	45	28	35900
Site 3, 10 m	<2.4	42900	18	49	0.9	<1.1	15	49	33	38900
Site 4, 0.5 m	<2.4	26100	18	34	0.7	<1.1	14	38	30	33600
Site 4, 0.5 m	<2.4	18600	11	27	0.7	<1.1	8	26	18	20200
Site 5, 0.5 m	<2.4	19600	9	28	0.5	<1.1	7	24	16	17900
Site 5, 1.5 m	<2.4	26300	9	35	0.7	<1.1	7	29	19	20700
Site 5, 3.5 m	<2.4	24300	15	46	0.7	<1.1	11	33	28	28800
Site 5, 5.5 m	<2.4	26700	16	53	0.9	<1.1	12	39	36	30800
Site 6, 0.5 m	<2.4	32800	15	52	1.1	<1.1	12	40	29	33800
Site 6, 6 m	3.3	28800	16	50	1.0	<1.1	12	38	29	31500
Site 7, 0.5 m, Duplicate 1	<2.4	19100	15	31	0.9	<1.1	12	30	20	28100
Site 7, 0.5 m, Duplicate 2	<2.4	10600	8	13	0.5	<1.1	6	17	12	13700
Site 8, 0.5 m	<2.4	42500	18	52	1.0	<1.1	15	48	31	39600
Site 9, 0.5 m	<2.4	13500	11	20	0.5	<1.1	8	22	16	17800
Site 9, 3 m	<2.4	24300	13	28	0.8	<1.1	11	32	22	24900
Site 9, 6 m	<2.4	28800	12	34	0.6	<1.1	10	32	20	23600
Site 10, 0.5 m, Duplicate 1	<2.4	45100	19	50	0.9	<1.1	15	52	31	44100
Site 10, 0.5 m, Duplicate 2	<2.4	13000	7	13	0.3	<1.1	5	15	<11	12600
Site 11, 0.5 m	<2.4	18400	13	23	0.6	<1.1	10	25	20	22800
Site 12, 0.5 m	<2.4	28300	11	34	0.7	<1.1	9	30	18	22400
Site 13, 0.5 m	<2.4	23300	11	27	0.6	<1.1	9	27	18	23300
Site 14, 0.5 m	<2.4	22300	11	25	0.5	<1.1	9	28	19	21000
Site 15, 0.5 m	<2.4	23000	10	28	0.4	<1.1	8	25	15	19200
Site 16, 0.5 m, Duplicate 1	<2.4	36100	20	44	1.0	<1.1	14	45	41	36100
Site 16, 0.5 m, Duplicate 2	<2.4	42400	19	49	1.3	<1.1	15	47	35	39300
Site 17, 0.5 m	<2.4	17600	8	18	0.5	<1.1	6	21	<11	14900
Site 18, 0.5 m	<2.4	13500	19	17	0.8	<1.1	7	30	<11	19600
Site 19, 0.5 m	<2.4	24900	21	25	0.8	<1.1	7	38	<11	22100
Site 20, 0.5 m, Duplicate 1	<2.4	8240	6	7	0.3	<1.1	3	14	<11	7300
Site 20, 0.5 m, Duplicate 2	<2.4	43500	24	40	1.2	<1.1	12	69	<11	35300
Site 21, 0.5 m	<2.4	17700	13	17	0.8	<1.1	6	28	<11	17000

Table 12. Suspended sediments: particulate metals concentrations continued

Sample description	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
						(µg/g)					
Field blank 1	<0.39	<0.7	<0.61	<2.5	<2.2	<0.10	<0.15	<0.4	<0.06	<0.8	<8.6
Field blank 2	<0.39	<0.7	<0.61	<2.5	<2.2	<0.10	<0.15	<0.4	<0.06	<0.8	<8.6
Field blank 3	<0.39	<0.7	<0.61	<2.5	<2.2	<0.10	<0.15	<0.4	<0.06	<0.8	<8.6
Field blank 4	<0.39	<0.7	<0.61	<2.5	<2.2	<0.10	<0.15	<0.4	<0.06	<0.8	<8.6
Site 1, 0.5 m	<0.39	747	1.9	32	12	0.1	0.3	72	0.2	81	68
Site 1, 2 m, Duplicate 1	<0.39	739	1.9	30	12	0.2	0.3	67	0.1	77	66
Site 1, 2 m, Duplicate 2	<0.39	688	1.5	23	9	0.2	0.3	56	0.1	60	42
Site 1, 4 m	<0.39	768	2.1	35	11	0.2	0.3	84	0.1	87	69
Site 2, 0.5 m	<0.39	326	0.7	9	4	<0.10	0.2	115	<0.06	31	24
Site 3, 0.5 m	0.6	525	1.9	20	12	0.4	0.2	63	0.3	72	53
Site 3, 5 m	0.4	672	1.5	21	10	0.2	0.3	46	0.2	74	64
Site 3, 10 m	<0.39	817	1.0	25	11	0.3	0.3	66	0.3	82	102
Site 4, 0.5 m	<0.39	773	1.0	20	10	0.2	0.5	59	0.2	70	58
Site 4, 0.5 m	<0.39	382	0.9	134	7	0.1	0.4	90	0.1	45	47
Site 5, 0.5 m	<0.39	267	0.8	11	6	0.1	0.3	101	0.1	40	29
Site 5, 1.5 m	<0.39	298	0.9	13	7	0.2	0.3	90	0.1	48	33
Site 5, 3.5 m	<0.39	498	1.3	16	10	0.2	0.3	54	0.1	60	42
Site 5, 5.5 m	<0.39	547	1.5	16	14	0.4	0.7	50	0.2	65	49
Site 6, 0.5 m	<0.39	558	1.3	16	12	0.3	0.5	58	0.2	69	45
Site 6, 6 m	<0.39	533	1.1	16	11	0.2	0.5	60	0.3	64	49
Site 7, 0.5 m, Duplicate 1	0.5	648	0.9	20	8	0.2	0.4	54	0.2	54	45
Site 7, 0.5 m, Duplicate 2	<0.39	326	<0.61	8	4	0.1	0.2	114	0.1	31	27
Site 8, 0.5 m	<0.39	791	1.4	23	12	0.2	0.6	59	0.2	80	69
Site 9, 0.5 m	<0.39	394	0.8	12	6	0.2	0.2	90	0.1	42	30
Site 9, 3 m	<0.39	521	1.1	16	8	0.2	0.3	91	0.1	58	48
Site 9, 6 m	<0.39	457	0.9	16	7	0.2	0.3	95	0.2	57	42
Site 10, 0.5 m, Duplicate 1	<0.39	852	1.5	22	9	0.2	0.2	83	0.2	83	53
Site 10, 0.5 m, Duplicate 2	<0.39	242	<0.61	8	3	<0.10	<0.15	115	<0.06	26	17
Site 11, 0.5 m	<0.39	521	0.8	13	7	0.1	0.4	87	0.1	49	42
Site 12, 0.5 m	<0.39	419	0.8	14	7	0.1	0.2	104	0.2	52	39
Site 13, 0.5 m	<0.39	449	0.9	12	7	0.2	0.3	96	0.1	48	39
Site 14, 0.5 m	<0.39	425	0.6	14	6	0.1	0.2	106	0.1	49	40
Site 15, 0.5 m	<0.39	369	0.8	11	5	0.1	0.2	106	0.1	45	30
Site 16, 0.5 m, Duplicate 1	<0.39	843	1.4	24	11	0.3	0.5	92	0.2	83	85
Site 16, 0.5 m, Duplicate 2	<0.39	912	1.0	21	12	0.3	0.8	89	0.1	82	74
Site 17, 0.5 m	<0.39	281	<0.61	9	4	0.1	0.3	118	0.1	35	22
Site 18, 0.5 m	<0.39	477	0.8	12	7	0.2	0.4	231	0.2	41	18
Site 19, 0.5 m	<0.39	486	1.1	14	6	0.2	0.6	255	0.3	45	9
Site 20, 0.5 m, Duplicate 1	<0.39	224	<0.61	6	<2.2	0.1	0.3	149	0.1	15	<8.6
Site 20, 0.5 m, Duplicate 2	<0.39	1070	2.5	25	10	0.1	0.8	174	0.4	70	<8.6
Site 21, 0.5 m	0.6	452	0.7	10	3	<0.10	0.8	242	0.3	33	<8.6

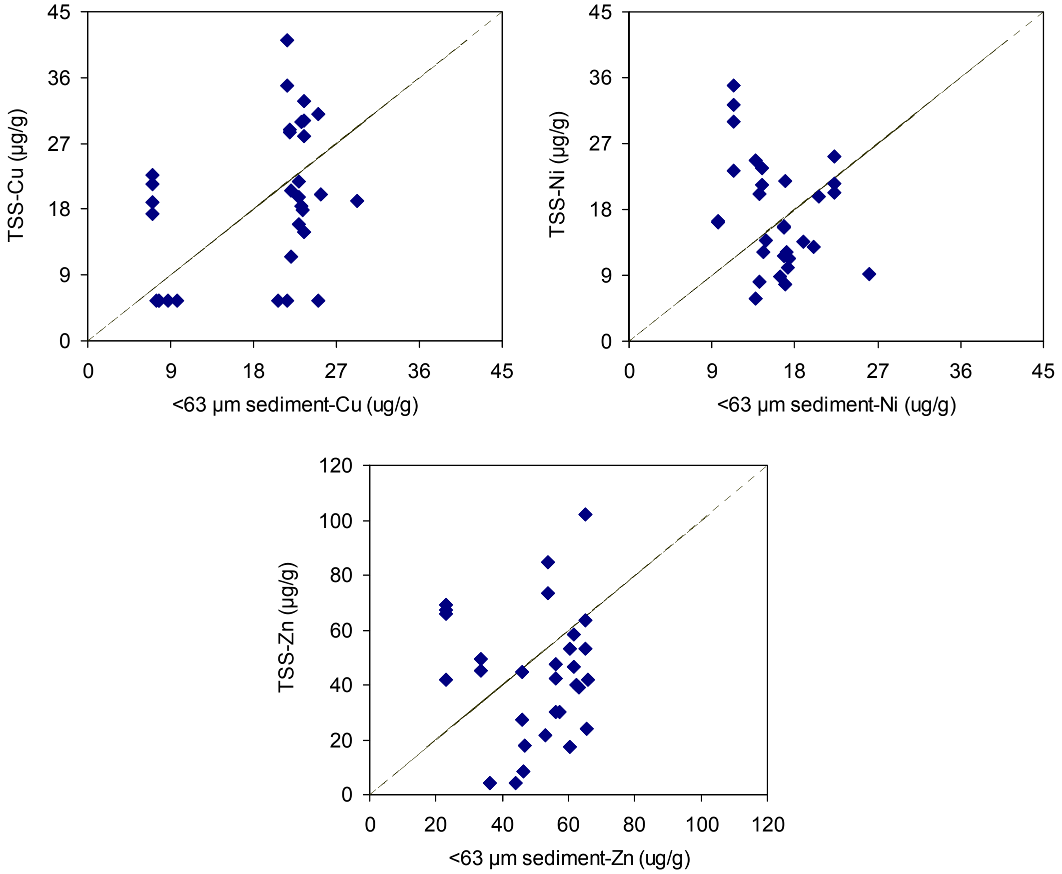


Figure 14. Graphs showing the relationship between copper, nickel and zinc bound to TSS and the <63 µm fraction of sediment

4 GENERAL DISCUSSION

4.1 DISSOLVED METALS

A comparison of some of the dissolved metals in Port Curtis and other industrialised harbours around the world is shown in Table 13. Port Curtis compares favourably with most other harbours and has relatively low metal concentrations despite the large amount of industrial activity and shipping.

The dissolved aluminium concentrations were nearly all above the ANZECC/ARMCANZ 2000 Environmental Concern Level (ECL) of 0.5 µg/L. It should be pointed out that this is a low reliability value derived from the most sensitive toxicity data divided by an arbitrary application factor of 200. It is not formally considered as a guideline value. As part of the current revision of the Australian Water Quality Guidelines the marine aluminium trigger value (TV) is being updated. There are no water quality guidelines that apply to aluminium in marine waters in Europe or North America (USA and Canada).

Dissolved aluminium concentrations have previously been reported to be variable in Port Curtis and in exceedance of the ECL. CSIRO measured dissolved metal concentrations in 2003 and 2004 (Angel unpublished data) and found dissolved aluminium concentrations that ranged from <0.6 to 83 µg/L in the southern part of the Narrows and from <0.6 to 44 µg/L in mid Port Curtis Harbour. These data indicate that high and variable levels of dissolved aluminium have occurred for some time in the area. There are several potential sources of aluminium in the harbour including tidal and/or dredging-induced resuspension of sediments containing aluminosilicates and nearby aluminium industries. One possibility for the high and variable dissolved aluminium concentrations is the resuspension of colloids containing aluminium that were less than the 0.45 µm pore size used to filter samples for dissolved metals analyses. Ultrafiltration or dialysis measurement techniques could be performed to exclude such colloids.

No fish toxicological data was used in the derivation of the marine ECL for aluminium and very few studies are available in the literature. Fish are also generally more sensitive to aluminium than freshwater aquatic invertebrates because it acts as a gill toxicant causing both ionoregulatory and respiratory effects (Gensemer and Playle, 1999). A study by Hyne and Wilson, (1997) using the Australian Bass, *Macquaia novemaculeata* in estuarine water (20-25 PSU) found aluminium toxicity was strongly pH dependent between pH 4 and 8. No juvenile mortality was detected for dissolved aluminium concentrations up to 10 mg/L at water pH's above pH 6, but 500 µg/L caused significant mortality at pH 4. Another previous study in seawater showed that aluminium was only toxic to a variety of fish species when the pH of the seawater was less than 6.7 at concentrations of 18 mg/L or greater (Pulley, 1950). It should also be noted that toxicity tests measure the toxicity soon after addition of aluminium and freshly prepared solutions have been shown to be more toxic (Pulley, 1950). Therefore, marine waters at approximately pH 8 may be much less toxic to fish than freshwaters at lower pH, which dominate the aluminium toxicological literature.

As noted earlier, of the dissolved metals measured, copper was closest to its ANZECC/ARMNCANZ trigger value. The relatively high concentrations observed are consistent with our previous observations (Angel *et al*. 2010). There are a number of sources of copper in Port Curtis including release from antifouling paints applied to boats. Given the increased shipping activity in the Harbour it is likely that this source of copper has increased over recent years. It is therefore advisable to monitor copper speciation and assess the bioavailability of this metal. A number of speciation methods are available for this purpose.

The current study has provided a useful snapshot of metal concentrations in waters and sediments of the Port Curtis region. However there is a need to characterise how water quality changes with time. It must be stressed that variations in water quality in tropical and sub-tropical systems often occur as pulse events. Event-related sampling is required to capture information from these events.

It is evident from the absence of any localised elevation in the metal concentrations within the vicinity of the dredging area that the current dredging operations have not elevated dissolved metal concentrations in Port Curtis. This is most likely because the sediments being dredged have a relatively low metal content which is not mobilised into solution during dredging operations. It would be useful to conduct some follow-up laboratory studies on dredge material to further examine the mobility of metals when dredge material is suspended in seawater. This work could also cover the likelihood of contaminant mobilisation during dredge spoil disposal.

Table 13 Comparison of dissolved metal concentrations measured in the current study with previous data from Port Curtis and with other locations.

LOCATION	DISSOLVED METAL CONCENTRATION, ng/L				REFERENCE
	Cadmium	Copper	Nickel	Zinc	
Port Curtis, Dec 2011	4	717	538	306	This study
Port Curtis Harbour	7.0	510	340	170	Angel *et al*., 2010
The Narrows	8.0	530	650	110	Angel *et al*., 2010
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
Humber estuary, UK	80-450	180-10100	2500-12000	3000-20500	Comber *et al*. 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
NSW coast	2.5	30	180	<22	Apte *et al*. 1998
North Pacific Ocean	0.3-112	-	-	15-520	Bruland *et al*. 1994
Australian Guideline values (95% species protection)[1]	5500	1300	70000	15000	ANZECC/ARMCANZ 2000

[1] ANZECC/ARMCANZ (2000) 95% values with 50% confidence

5 CONCLUSIONS

1. The concentrations of dissolved arsenic, cadmium, cobalt, chromium, copper, manganese, nickel, lead and zinc were below the ANZECC/ARMCANZ marine water quality guideline trigger values that apply in Australia at all 21 sites sampled and the concentrations were relatively low compared to other industrialised harbours.

2. Dissolved aluminium concentrations were above the ANZECC/ARMCANZ (2000) environmental concern level (ECL) of 0.5 µg/L at the majority of sites sampled. It should be noted that there is no reliable guideline value for aluminium in marine waters in Australia and the ECL value is a highly conservative value based on very limited toxicity data. There are no water quality guidelines that apply for aluminium in marine waters in Europe or North America. From the current data set, it was not possible to attribute a specific source of the dissolved aluminium.

3. The dissolved copper concentrations measured in Port Curtis in December 2011 were lower than the ANZECC/ARMCANZ guideline value of 1.3 µg/L. However, the dissolved copper concentrations were noticeably higher than the concentrations measured in the CSIRO surveys in December 2003 and 2004, indicating increased inputs of these metals from various sources, and the concentrations at some sites were only marginally lower than the ANZECC/ARMCANZ guideline value. Dissolved cadmium and zinc concentrations were comparable to those measured in 2003/2004 by CSIRO.

4. A comparison of some of the dissolved metals in Port Curtis and other industrialised harbours around the world (Table 13) shows that Port Curtis compares favourably with most other harbours and has relatively low metal concentrations despite the large amount of industrial activity and shipping.

5. Apart from arsenic, the concentrations of particulate metals in benthic sediments were below the ANZECC/ARMCANZ sediment quality guideline values. Particulate arsenic concentrations exceeded the ANZECC/ARMCANZ ISQG-low trigger value in two samples from the Narrows and one site off Quoin Island. Previous studies indicate that the source of this arsenic is natural (geological formation in the area) and is not associated with anthropogenic inputs.

6. Metal concentrations in suspended sediments were not elevated and were comparable to the concentrations of metals in the <63 µm (fine) fraction of benthic sediments. This is consistent with the resuspension of fine sediments into the water column.

7. The study did not detect any 'hot spots' of metal concentrations. There was no detectable elevation of metal concentrations at sites where dredging was being conducted.

6 RECOMMENDATIONS

1. The forms of dissolved aluminium (speciation) in the waters of the Port Curtis region and their bioavailability/toxicity should be examined. It is possible that a large proportion of the dissolved aluminium is present in a non-bioavailable form, but this needs to be investigated.

2. Given that the dissolved copper concentrations were only marginally lower than the ANZECC/ARMCANZ guideline value at some sites in Port Curtis and have previously been measured above the guideline by DERM (November 2011), it is advisable to follow the ANZECC/ARMCANZ framework for metals in aquatic systems and characterise the chemical forms of dissolved copper (speciation) and their bioavailability/toxicity. It is likely that a significant proportion of the copper is associated with organic matter and will not exert toxic effects on marine life.

3. It is recognised that the current study only provides a snapshot of water quality as it was conducted over a period of three days. It is desirable to characterise temporal variations in dissolved metal concentrations (e.g. pulse events) by conducting regular surveys ideally under different tidal and climatic conditions.

4. Given the public concerns around fish disease in the Gladstone region, it is recommended that tissue metal concentrations in fish are analysed. This should be conducted on both healthy and diseased specimens, if available.

5. Previous water quality programs in the Port Curtis region have used total metal concentrations. It is strongly recommended in the ANZECC/ARMCANZ decision tree framework that dissolved metals be used for monitoring of trace metals. Dissolved concentrations give a better indication of metal bioavailability and toxicity. Monitoring of dissolved concentrations should be adopted in Port Curtis. We note that Vision Environment QLD have recently commenced monthly water quality surveys to address these issues.

7. The actual dissolved trace metal concentrations at the dredge spoil dumping sites should be characterised.

7 REFERENCES

Ahlers, W.W., Reid, M.R., Kim, J.P. and Hunter, K.A. (1990). Contamination-free sample collection and handling protocols for trace elements in natural waters. *Australian Journal of Marine and Freshwater Research* 41, 713-720.

Angel, B., Hales, L.T., Simpson, S.L, Apte, S.C, Chariton, A., Shearer, D. and Jolley, D.F. (2010). Spatial variability of cadmium, copper, manganese, nickel and zinc in the Port Curtis Estuary, Queensland, Australia. *Marine and Freshwater Research* 61, 170-183.

ANZECC/ARMCANZ (2000). Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Volume 1. The Guidelines, Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, ACT, Australia.

Apte, S.C. and Gunn, A.M. (1987). Rapid determination of copper, nickel, lead and cadmium in small samples of estuarine waters by liquid/liquid extraction and electrothermal atomic absorption spectrometry. *Analytica Chimica Acta* 193, 147-156.

Apte, S. C., Batley, G. E., Szymczak, R., Rendell, P. S., Lee, R. and Waite, T. D. (1998). Baseline trace metal concentrations in New South Wales coastal waters. *Marine and Freshwater Research* 49, 203-214.

Apte, S.C. and Day, G.M. (1998). Dissolved metal concentrations in the Torres Strait and Gulf of Papua. *Marine Pollution Bulletin* 30, 298-304.

Apte, S.C., Batley, G.E. and Maher, W.A. (2002). Monitoring of trace metals and metalloids in natural waters. In: Handbook of Environmental Monitoring. Burden, F., Forstner, U., Guenther, A., and McKelvie, I., Eds, McGraw Hill, New York, Chapter 6.

Baeyens, W., Goeyens, M., Monteny, F. and Elskens, M. (1998). Effect of organic complexation on the behaviour of dissolved cadmium, copper, and zinc in the Scheldt estuary. *Hydrobiologia* 366, 15-43.

Bruland, K.W., Orians, K.J. and Cowen, J.P. (1994). Reactive trace metals in the stratified central North Pacific. *Geochimica et Cosmochimica Acta* 58, 3171-3182.

Comber, S.D.W., Gunn, A.M. and Whalley, C. (1995). Comparison of the partitioning of trace metals in the Humber and Mersey Estuaries. *Marine Pollution Bulletin* 30, 851-860.

DERM (2011). Water Quality of Port Curtis and Tributaries. Supplementary Report based on data collected in the week of 26th September 2011. Queensland Department of Environment and Resource Management report, 39 pages.

Fabris, G.L. and Monahan, C.A. (1995). Characterisation of toxicants in waters from Port Phillip Bay: metals. Technical Report No. 18, CSIRO Port Phillip Bay Environmental Study. Technical Report No. 18, Melbourne, Australia.

Gensemer, R. W., Playle, R. C., (1999). The bioavailability and toxicity of aluminium in aquatic environments. *Critical Reviews in Environmental Science and Technology* 29, 315–450.

Hatje, V., Apte, S.C., Hales, L.T. and Birch, G.F. (2003). Dissolved trace metal distributions in Port Jackson estuary (Sydney Harbour), Australia. *Marine Pollution Buletin* 46, 719-730.

Hyne, R. V., Wilson, S. W., (1997). Toxicity of acid-sulphate soil leachate and aluminium to the embryos and larvae of Australian Bass, *Maquaria Novemaculeata* in estuarine water. *Environ. Poll*. 97. 221-227.

Jones, M-A., Stauber, J.L., Apte, S.C., Simpson, S.L., Vincente-Beckett, V., Johnson, R. and Duivenvoorden, L. (2005). A risk assessment approach to contaminants in Port Curtis, Queensland, Australia. *Marine Pollution Bulletin* 51, 448-458.

Magnusson, B. and Westerlund, S. (1981). Solvent extraction procedures combined with back-extraction for trace metal determinations by atomic absorption spectrometry. *Analytica Chimica Acta* 131, 63-72.

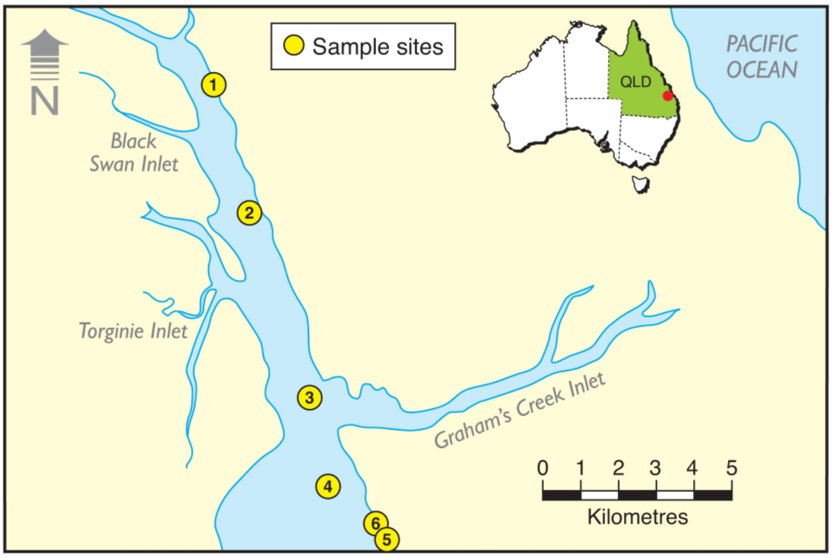
Munksgaard, N.C. and Parry, D.L. (2001). Trace metals, arsenic and lead isotopes in dissolved and particulate phases of North Australian coastal and estuarine seawater. *Marine Chemistry* 75, 165-184.

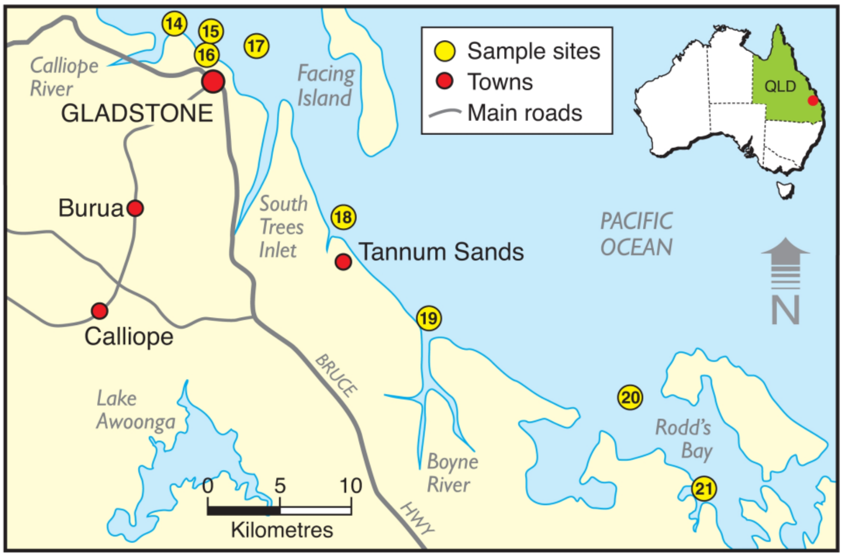
Pulley, T. E., (1950). The effect of aluminium chloride in small concentration on various marine organisms. *The Texas Journal of Science 2,* 405-411.

Sanudo-Wilhelmy, S.A., Rivera-Duarte, I. and Flegal, A.R. (1996). Distribution of colloidal trace metals in the San Fransisco Bay estuary. *Geochimica et Cosmochimica Acta* 60, 4933-4944.

USEPA (1996). Sampling ambient water for trace metals at EPA water quality criteria levels. Method 1669. US Environmental Protection Agency, Office of Water Engineering and Analysis Division (4303), Washington DC 20460.

Appendix A Maps showing the site sampled in the Southern Narrows and marine sites south-east of Port Curtis





Appendix B Quality Control Data

Table B1: Limits of detection for dissolved metals

LABORATORY I.D.	Al (µg/L)	As (µg/L)	Cd (ng/L)	Co (ng/L)	Cr (µg/L)	Cu (ng/L)	Fe (µg/L)	Mn (µg/L)	Ni (ng/L)	Pb (ng/L)	Zn (ng/L)
Limit of Detection (3σ)	1	0.09	3	2	0.4	15	1.5	0.1	32	16	9

Table B2: Certified reference material (CASS-4) for dissolved metals analyses

LABORATORY I.D.	**As (µg/L)**	**Cd (ng/L)**	**Co (ng/L)**	**Cu (ng/L)**	**Mn (µg/L)**	**Ni (ng/L)**	**Pb (ng/L)**	**Zn (ng/L)**
CASS-4, 14/12/11	---	---	---	---	2.8	---	---	---
CASS-4, 14/12/11	---	---	---	---	2.8	---	---	---
CASS-4, 14/12/11	---	---	---	---	2.8	---	---	---
CASS-4, 14/12/11	---	24	25	535	---	275	<16	347
CASS-4, 11/01/11	---	25	25	532	---	284	<16	370
CASS-4, 14/02/12	1.14	---	---	---	---	---	---	---
CASS-4, 14/02/12	1.18	---	---	---	---	---	---	---
CASS-4, 14/02/12	1.04	---	---	---	---	---	---	---
CASS-4, 15/02/12	1.16	---	---	---	---	---	---	---
CASS-4, 15/02/12	0.90	---	---	---	---	---	---	---
Mean CASS-4 (n=5)	1.09	---	---	---	---	---	---	---
Mean CASS-4 (n=2)	---	24	25	533	---	279	<16	359
Mean CASS-4 (n=3)	---	---	---	---	2.8	---	---	---
Certified value - CASS-4	1.11	26	26	592	3	314	<16	381
% recovery	98	94	96	90	101	89	-	94

Table B3: Certified reference material (CASS-5) for dissolved metals analyses

LABORATORY I.D.	**Cd (ng/L)**	**Co (ng/L)**	**Cu (ng/L)**	**Ni (ng/L)**	**Pb (ng/L)**	**Zn (ng/L)**
CASS-5, 14/12/11	21	85	347	305	<16	691
CASS-5, 23/01/12	17	87	351	336	<16	623
CASS-5, 24/01/12	21	90	371	333	<16	726
Mean CASS-5 (n=3)	19	88	356	325	<16	680
Certified value - CASS-5	22	95`	380	330	<16	719
% recovery	90	92	94	98	-	95

Table B4: Dissolved metals analyses: replicate determinations

Site	**Al (µg/L)**	**As (µg/L)**	**Cd (ng/L)**	**Co (ng/L)**	**Cr (µg/L)**	**Cu (ng/L)**	**Fe (µg/L)**	**Mn (µg/L)**	**Ni (ng/L)**	**Pb (ng/L)**	**Zn (ng/L)**
Site 16, 0.5 m, Site Dup 1	---	1.05	---	---	---	---	---	---	---	---	---
Site 16, 0.5 m, Site Dup 1	---	0.96	---	---	---	---	---	---	---	---	---
Site 16, 0.5 m, Site Dup 1	---	*1.00*	---	---	---	---	---	---	---	---	---
Site 13, 0.5 m	---	---	6	34	---	638	---	---	373	13	163
Site 13, 0.5 m	---	---	5	34	---	611	---	---	345	13	136
Site 13, 0.5 m	---	---	*5*	*34*	---	*625*	---	---	*359*	*13*	*149*
Site 11, 0.5 m	4	---	---	---	<1	---	1.8	<0.1	---	---	---
Site 11, 0.5 m	4	---	---	---	<1	---	1.8	<0.1	---	---	---
Site 11, 0.5 m	4	---	---	---	<1	---	1.8	<0.1	---	---	---
Site 3, 5 m	---	0.94	---	---	---	---	---	---	---	---	---
Site 3, 5 m	---	0.88	---	---	---	---	---	---	---	---	---
Site 3, 5 m	---	0.91	---	---	---	---	---	---	---	---	---
Site 10, 0.5 m, Site Dup 1	5	---	---	---	<1	---	1.9	1.7	---	---	---
Site 10, 0.5 m, Site Dup 1	4	---	---	---	<1	---	1.4	1.7	---	---	---
Site 10, 0.5 m, Site Dup 1	4	---	---	---	<1	---	1.7	1.7	---	---	---
Site 9, 6 m	---	0.88	---	---	---	---	---	---	---	---	---
Site 9, 6 m	---	0.92	---	---	---	---	---	---	---	---	---
Site 9, 6 m	---	0.90	---	---	---	---	---	---	---	---	---
Site 6, 6 m	1	---	---	---	<1	---	0.9	0.7	---	---	---
Site 6, 6 m	1	---	---	---	<1	---	1.1	0.7	---	---	---
Site 6, 6 m	1	---	---	---	<1	---	1.0	0.7	---	---	---
Site 6, 0.5 m	---	0.89	---	---	---	---	---	---	---	---	---
Site 6, 0.5 m	---	0.96	---	---	---	---	---	---	---	---	---
Site 6, 0.5 m	---	0.92	---	---	---	---	---	---	---	---	---
Site 20, 0.5 m, Site Dup 2	2	---	---	---	<1	---	0.9	1.2	---	---	---
Site 20, 0.5 m, Site Dup 2	2	---	---	---	<1	---	0.8	1.2	---	---	---
Site 20, 0.5 m, Site Dup 2	2	---	---	---	<1	---	0.8	1.2	---	---	---
Site 19, 0.5 m	---	---	<1.3	25	---	121	---	---	221	11	19
Site 19, 0.5 m	---	---	<1.3	25	---	120	---	---	213	11	17
Site 19, 0.5 m	---	---	<1.3	25	---	120	---	---	217	11	18
Site 18, 0.5 m	---	---	1.3	23	---	152	---	---	204	11	445
Site 18, 0.5 m	---	---	1.3	23	---	147	---	---	197	11	432
Site 18, 0.5 m	---	---	1.3	23	---	149	---	---	200	11	439

Table B5: Spike recovery data for the dissolved metals analyses

Site	Al	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
						Recovery (%)					
Site 16, 0.5 m, Dup 2	---	87	---	---	---	---	---	---	---	---	---
Site 1, 0.5 m	96	---	96	96	100	99	100	96	97	104	95
Site 8, 0.5 m	95	---	94	95	98	97	100	98	93	104	91
Site 14, 0.5 m	---	100	---	---	---	---	---	---	---	---	---
Site 12, 0.5 m	93	---	---	---	100	---	98	98	---	---	---
Site 7, 0.5 m, Dup 1	---	88	---	---	---	---	---	---	---	---	---
Site 7, 0.5 m, Dup 2	---	---	106	103	---	104	---	---	99	102	108
Site 20, 0.5 m, Dup 1	105	---	99	98	107	94	102	105	96	102	102
Site 20, 0.5 m, Dup 2	---	---	97	96	---	98	---	---	93	100	100
Site 21, 0.5 m	---	---	102	99	---	99	---	---	95	101	99
Field Blank 3		100	---	---	---	---	---	---	-	-	-

Particulate Metals QC Data

Table B6: Limits of detection for sediment analyses

	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Ga	Hg
						(µg/g, dry weight)						
LOD (3σ)	0.002	10	1	0.1	0.02	0.03	0.02	0.4	1	4	1	0.02

	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
LOD (3σ)	0.3	0.04	1	1	0.004	0.04	0.1	0.01	0.3	1

Table B7. Sediment metals PACS-2 certified reference material analyses

Sample ID/digestion ID:	**Ag**	**Al**	**As**	**Ba**	**Be**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Hg**
	µg/g dry weight										
PACS-2 (CUR-2-4)	1.26	19500	24	484	0.46	2.46	8.7	52	295	30700	3.19
PACS-2 (CUR-2-5)	1.11	15600	24	407	0.38	2.22	8.6	47	292	29100	3.06
PACS-2 (CUR-3-4)	1.15	16200	24	450	0.39	2.43	8.2	47	295	30100	3.01
PACS-2 (CUR-3-5)	1.21	15400	23	354	0.38	2.46	8.3	46	297	29900	3.40
PACS-2 (CUR-4-4)	1.17	14600	24	369	0.35	2.43	8.0	45	290	29800	3.21
PACS-2 (CUR-4-5)	1.20	17900	24	437	0.39	2.62	8.7	49	289	30300	3.19
PACS-2 (CUR-5-4)	1.30	18200	24	461	0.42	2.48	8.8	49	292	30500	2.74
PACS-2 (CUR-5-5)	1.22	14600	23	332	0.35	2.42	8.5	46	295	29400	2.88
PACS-2 Average (n=8)	1.20	16500	24	412	0.39	2.44	8.5	48	293	29975	3.08
In-house reference value	1.16	16700	26	---	0.43	2.45	9.5	51	299	31200	2.91
% Recovery	104	99	92	---	91	100	89	93	98	96	106

Sample ID/digestion ID:	**Mn**	**Mo**	**Ni**	**Pb**	**Sb**	**Se**	**Sr**	**Tl**	**V**	**Zn**
	µg/g dry weight									
PACS-2 (CUR-2-4)	255	4.9	32	168	8.34	1.01	69	0.46	81	343
PACS-2 (CUR-2-5)	238	4.8	30	169	7.36	0.98	61	0.42	71	333
PACS-2 (CUR-3-4)	241	4.9	31	170	6.98	0.98	62	0.42	72	338
PACS-2 (CUR-3-5)	238	5.0	31	168	8.11	1.03	60	0.44	70	338
PACS-2 (CUR-4-4)	235	5.0	31	165	8.25	0.90	59	0.40	70	336
PACS-2 (CUR-4-5)	245	5.1	32	166	7.85	0.96	65	0.42	75	332
PACS-2 (CUR-5-4)	249	5.1	32	167	9.02	0.93	70	0.44	77	339
PACS-2 (CUR-5-5)	234	5.0	30	164	8.10	0.93	62	0.43	68	334
PACS-2 Average (n=8)	242	5.0	31	167	8.00	0.96	64	0.43	73	337
In-house reference value	253	5.0	32	170	8.01	0.99	69	---	82	345
% Recovery	96	100	97	98	100	97	92	---	89	98

Table B8. Total sediment metals replicate analyses

Site	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Ga	Hg
						(µg/g, dry weight)						
Site 2	0.04	8450	53	10	0.78	0.39	31	24	7	62300	8	<0.02
Site 2	0.04	8400	54	11	0.80	0.37	29	24	7	62900	8	<0.02
Site 2	0.04	8430	54	10	0.79	0.38	30	24	7	62600	8	<0.02
Site 4	0.03	12800	6	15	0.37	0.21	8	14	7	14400	5	<0.02
Site 4	0.03	8850	7	12	0.35	0.19	8	12	8	13600	4	<0.02
Site 4	0.03	10800	7	14	0.36	0.20	8	13	7	14000	5	<0.02
Site 6	0.03	17200	9	65	0.5	0.21	6	21	19	25700	7	<0.02
Site 6	0.03	17100	8	64	0.5	0.18	6	21	19	25200	7	<0.02
Site 6	0.04	21500	8	64	0.5	0.19	6	24	19	26900	8	<0.02
Site 6	0.03	18600	8	64	0.5	0.19	6	22	19	25900	8	<0.02
Site 7	0.05	17000	11	81	0.7	0.36	13	23	20	27500	7	<0.02
Site 7	0.06	23300	12	83	0.7	0.38	13	26	21	29300	9	<0.02
Site 7	0.06	23200	11	83	0.7	0.39	13	26	21	28900	9	<0.02
Site 7	0.06	21200	11	82	0.7	0.38	13	25	21	28600	8	<0.02
Site 10	0.06	20100	10	21	0.79	0.86	12	28	24	26500	9	0.17
Site 10	0.08	25800	10	25	0.87	1.02	13	32	24	29900	10	0.15
Site 10	0.07	23000	10	23	0.83	0.94	12	30	24	28200	9	0.16
Site 11	0.01	3310	19	9	0.25	0.29	11	8	4	18300	3	<0.02
Site 11	0.02	3330	20	9	0.30	0.31	10	8	4	18200	2	0.02
Site 11	0.02	4820	19	10	0.24	0.30	10	8	5	17600	3	<0.02
Site 11	0.02	3820	20	9	0.26	0.30	10	8	4	18000	3	0.02
Site 14	0.03	13300	8	26	0.31	0.23	7	14	9	16500	5	<0.02
Site 14	---	13400	7	26	---	---	---	14	9	16500	5	---
Site 14	0.03	13400	7	26	0.31	0.23	7	14	9	16500	5	<0.02
Site 15	0.02	4790	14	11	0.3	0.18	9	9	6	14600	3	<0.02
Site 15	0.02	3980	14	11	0.3	0.17	10	8	7	14100	2	0.02
Site 15	0.02	4390	14	11	0.3	0.18	10	8	6	14400	2	0.02
Site 17	0.03	5330	34	8	0.4	0.28	15	10	6	23100	4	<0.02
Site 17	0.02	6750	32	11	0.3	0.24	13	11	5	21600	4	<0.02
Site 17	0.03	6040	33	10	0.4	0.26	14	10	5	22400	4	<0.02
Site 18	0.01	2030	8	5	0.2	0.09	3	6	0.3	5070	1	<0.02
Site 18	0.01	2640	9	6	0.2	0.09	3	6	0.1	5300	1	<0.02
Site 18	0.01	2340	8	6	0.2	0.09	3	6	0.2	5180	1	<0.02

Table B9. Total sediment metals, replicate analyses

Site	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
					(µg/g, dry weight)					
Site 2	531	2	14.5	12	0.24	0.18	224	0.05	112	53
Site 2	539	2	14.3	13	0.25	0.17	225	0.05	113	53
Site 2	535	2	14.4	13	0.25	0.17	224	0.05	112	53
Site 4	343	0.4	7.6	5	0.04	0.13	61	0.06	31	26
Site 4	373	0.4	6.9	4	0.12	0.11	57	0.05	29	24
Site 4	358	0.4	7.2	5	0.08	0.12	59	0.1	30	25
Site 6	105	1	7.3	10	0.18	0.50	33	0.08	52	23
Site 6	103	1	6.7	10	0.16	0.51	33	0.08	51	23
Site 6	106	1	7.5	11	0.20	0.51	34	0.10	54	26
Site 6	104	1	7.2	10	0.18	0.51	34	0.09	52	24
Site 7	365	1	13.1	9	0.19	0.18	47	0.08	50	42
Site 7	365	1	15.2	11	0.16	0.21	51	0.11	54	46
Site 7	363	1	14.6	11	0.16	0.20	51	0.10	53	46
Site 7	365	1	14.3	10	0.17	0.20	50	0.10	52	45
Site 10	243	1	16.0	11	0.25	0.32	39	0.1	54	56
Site 10	256	1	17.4	12	0.27	0.36	42	0.1	62	61
Site 10	250	1	16.7	12	0.26	0.34	41	0.1	58	59
Site 11	897	1	5.9	5	0.10	0.13	339	0.02	42	18
Site 11	900	1	5.9	5	0.12	0.13	340	0.02	42	18
Site 11	891	1	5.9	4	0.16	0.13	369	0.02	43	18
Site 11	896	1	5.9	5	0.13	0.13	349	0.02	42	18
Site 14	346	1	6.5	4	0.13	0.10	95	0.06	39	28
Site 14	349	---	6.7	4	---	---	96	---	39	28
Site 14	348	1	6.6	4	0.13	0.10	95	0.06	39	28
Site 15	646	1	6.5	5	0.21	0.16	468	0.03	35	21
Site 15	671	1	6.2	4	0.24	0.13	503	0.03	32	21
Site 15	659	1	6.4	5	0.23	0.15	486	0.03	33	21
Site 17	1258	1	7.9	6	0.39	0.12	595	0.03	49	22
Site 17	661	1	6.9	7	0.30	0.12	557	0.03	47	22
Site 17	960	1	7.4	6	0.35	0.12	576	0.03	48	22
Site 18	157	0.1	2.0	2	0.05	0.02	168	0.01	11	6
Site 18	169	0.1	2.1	2	0.06	0.02	166	0.02	12	6
Site 18	163	0.1	2.0	2	0.05	0.02	167	0.01	11	6

Table B11 Sediment metals in the <63 µm fraction, replicate analyses: (Sites 2 to 8)

(

Site	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Ga	Hg
						(µg/g, dry weight)						
Site 2	0.08	38400	15	36	1.18	0.62	15	48	23	37800	14	0.08
Site 2	0.08	38700	14	36	1.17	0.63	15	48	24	38000	14	0.08
Site 2	0.09	32400	14	30	1.03	0.77	14	44	23	36600	13	0.07
Site 2	---	32800	14	31	---	---	---	45	22	37300	12	---
Site 2	0.08	35600	14	33	1.13	0.68	14	46	23	37400	13	0.08
Site 3	0.06	28500	14	23	0.99	0.62	15	38	23	33400	11	0.11
Site 3	0.08	29100	13	25	1.01	0.86	16	38	24	34100	5	0.11
Site 3	0.07	28800	13	24	1.00	0.74	15	38	23	33800	8	0.11
Site 4	0.06	18000	10	22	0.86	0.88	13	29	21	26700	8	0.13
Site 4	0.06	35800	10	35	1.00	0.77	14	40	23	33900	13	0.13
Site 4	0.05	23900	9	26	0.85	0.73	12	33	22	29700	10	0.13
Site 4	0.06	25900	9	28	0.90	0.79	13	34	22	30100	10	0.13
Site 8	0.05	21200	13	19	0.94	0.58	15	32	24	32300	9	0.07
Site 8	0.09	32900	13	28	1.17	0.90	16	41	25	38700	13	0.04
Site 8	0.07	33100	14	28	1.05	0.74	16	41	25	39000	13	0.05
Site 8	0.07	29100	14	25	1.05	0.74	16	38	24	36700	12	0.05
Site 6	0.03	23900	5	59	0.50	0.28	6	25	22	23700	9	0.05
Site 6	0.03	23600	6	58	0.50	0.33	6	25	21	23600	9	0.06
Site 6	0.03	23800	5	58	0.50	0.30	6	25	22	23700	9	0.06
Site 6	0.03	31000	9	69	0.65	0.39	8	31	23	29300	11	0.07
Site 6	0.03	26100	8	67	0.58	0.39	7	28	22	27300	9	0.06
Site 6	0.03	28600	8	68	0.61	0.39	8	29	22	28300	10	0.07
Site 7	0.04	23800	12	86	0.73	0.49	13	26	22	29300	9	0.06
Site 7	0.04	18100	12	82	0.67	0.42	12	24	22	28500	7	0.05
Site 7	0.04	21000	12	84	0.70	0.45	12	25	22	28900	8	0.05

Table B11 Sediment metals in the <63 µm fraction, replicate analyses: (Sites 2 to 8)

Site	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
(µg/g, dry weight)										
Site 2	322	1	27.2	14	0.20	0.39	54	0.2	69	69
Site 2	325	1	27.0	14	0.20	0.36	54	0.2	70	70
Site 2	319	1	25.4	14	0.20	0.32	52	0.2	65	64
Site 2	322	---	25.6	14	---	---	52	---	66	65
Site 2	322	1	26.3	14	0.20	0.36	53	0.2	67	67
Site 3	198	1	22.5	13	0.24	0.34	45	0.2	64	65
Site 3	197	1	22.1	13	0.24	0.32	46	0.2	64	65
Site 3	198	1	22.3	13	0.24	0.33	46	0.2	64	65
Site 4	211	1	16.5	11	0.21	0.31	46	0.1	52	53
Site 4	235	1	21.5	13	0.19	0.35	53	0.2	67	67
Site 4	218	1	18.8	12	0.20	0.30	48	0.1	57	57
Site 4	221	1	18.9	12	0.20	0.32	49	0.1	59	59
Site 8	295	1	19.6	13	0.23	0.35	52	0.1	56	58
Site 8	315	1	23.5	14	0.26	0.36	57	0.2	69	66
Site 8	317	1	23.6	14	0.24	0.35	57	0.1	69	67
Site 8	309	1	22.2	13	0.24	0.35	55	0.1	65	64
Site 6	95	1	7.9	15	0.16	0.34	26	0.11	46	29
Site 6	95	1	7.7	15	0.15	0.35	25	0.11	45	29
Site 6	95	1	7.8	15	0.16	0.34	25	0.11	45	29
Site 6	175	1	12.2	13	0.17	0.46	33	0.15	54	40
Site 6	169	1	10.9	12	0.16	0.44	31	0.13	50	37
Site 6	172	1	11.5	13	0.17	0.45	32	0.14	52	38
Site 7	370	1	14.9	13	0.17	0.22	43	0.12	57	47
Site 7	377	1	13.6	10	0.17	0.18	41	0.10	53	45
Site 7	374	1	14.2	11	0.17	0.20	42	0.11	55	46

Table B12. Sediment metals in the <63 µm fraction, replicate analyses: (Sites 11-18)

(

Site	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Ga	Hg
					(µg/g, dry weight)							
Site 11	0.06	26400	12	27	0.87	0.75	16	33	26	31000	10	0.09
Site 11	0.05	26200	12	27	0.92	0.78	17	33	25	30900	11	0.10
Site 11	0.06	30200	12	30	0.88	0.80	15	35	25	31300	11	0.09
Site 11	0.06	27600	12	28	0.89	0.78	16	34	25	31100	11	0.09
Site 13	0.05	26700	22	54	0.89	1.28	17	30	24	38100	11	0.31
Site 13	0.07	25300	21	54	0.90	1.40	16	29	23	38700	10	0.33
Site 13	0.06	26000	21	54	0.89	1.34	17	30	23	38400	10	0.32
Site 14	0.04	16400	13	27	0.73	0.84	13	24	26	30200	8	0.19
Site 14	0.04	16200	13	27	0.71	0.82	14	24	26	30100	8	0.19
Site 14	0.08	40600	13	46	0.85	1.05	15	36	30	39600	14	0.18
Site 14	0.05	24400	13	33	0.76	0.91	14	28	27	33300	10	0.18
Site 15	0.04	16900	13	26	0.82	0.75	13	26	23	26000	8	0.16
Site 15	0.06	28500	14	34	0.80	0.89	14	33	24	30900	11	0.15
Site 15	0.05	22700	14	30	0.81	0.82	14	29	23	28400	9	0.16
Site 16	0.04	15100	14	21	0.71	0.84	11	25	21	24900	8	0.17
Site 16	0.05	18400	14	22	0.78	0.95	10	27	22	26900	9	0.18
Site 16	0.04	16700	14	22	0.74	0.90	10	26	22	25900	8	0.17
Site 17	0.05	20700	15	25	0.73	0.67	12	27	21	26300	8	0.09
Site 17	0.05	21100	15	25	0.76	0.68	12	28	21	26500	8	0.08
Site 17	0.05	20900	15	25	0.75	0.67	12	27	21	26400	8	0.09
Site 18	0.04	13800	15	20	0.65	4.50	10	29	8	20200	10	1.26
Site 18	0.04	17700	12	16	0.81	0.69	9	35	9	22600	7	0.15
Site 18	0.04	17700	12	16	0.82	0.64	9	35	9	22600	7	0.13
Site 18	0.04	16400	13	17	0.76	1.94	10	33	9	21800	8	0.51

Table B13. Sediment metals in the <63 µm fraction: replicate analyses: (Sites 11-18) Mn to Zn (All concentrations are in units of µg/g)

Site	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
					(µg/g, dry weight)					
Site 11	859	1	20.0	12	0.21	0.63	75	0.1	59	66
Site 11	853	1	19.6	12	0.21	0.65	75	0.1	58	65
Site 11	841	1	20.6	12	0.07	0.63	78	0.2	63	67
Site 11	851	1	20.1	12	0.17	0.64	76	0.1	60	66
Site 13	799	1	17.4	13	0.27	0.37	109	0.1	77	64
Site 13	796	1	16.8	13	0.30	0.33	106	0.1	77	62
Site 13	798	1	17.1	13	0.28	0.35	108	0.1	77	63
Site 14	581	1	13.1	10	0.19	0.28	72	0.1	61	60
Site 14	576	1	13.2	12	0.18	0.30	72	0.1	60	60
Site 14	608	1	19.7	12	0.20	0.29	82	0.1	76	73
Site 14	588	1	15.3	11	0.19	0.29	75	0.1	66	64
Site 15	727	1	15.9	11	0.19	0.57	96	0.1	50	53
Site 15	741	1	18.8	12	0.20	0.52	100	0.1	60	62
Site 15	734	1	17.4	12	0.20	0.54	98	0.1	55	57
Site 16	428	1	13.9	11	0.17	0.24	138	0.1	45	52
Site 16	426	1	15.0	11	0.17	0.24	136	0.1	48	55
Site 16	427	1	14.5	11	0.17	0.24	137	0.1	47	54
Site 17	609	1	16.3	11	0.19	0.59	127	0.1	53	53
Site 17	605	1	16.6	11	0.21	0.59	127	0.1	52	53
Site 17	607	1	16.4	11	0.20	0.59	127	0.1	52	53
Site 18	681	1	12.4	11	0.22	0.34	211	0.09	42	45
Site 18	283	1	15.0	12	0.24	0.39	178	0.14	52	39
Site 18	285	1	15.0	13	0.25	0.41	178	0.14	52	39
Site 18	417	1	14.1	12	0.24	0.38	189	0.13	49	41

Table B15. Sediment-bound metals, spike recovery analysis: Ag to Hg

Site	Fraction	Ag	As	Ba	Be	Cd	Co	Cr	Cu	Ga	Hg
						Recovery (%)					
Site 1	<63µm	97	95	88	92	101	93	94	95	91	106
Site 1	Total	94	96	95	101	100	93	95	95	95	97
Site 6	Total	90	98	97	92	90	107	100	102	96	102
Site 7	Total	84	98	96	94	90	108	100	102	96	97
Site 13	<63µm	95	96	90	96	101	102	96	98	93	104
Site 13	Total	95	99	96	103	101	101	97	98	96	97
Site 14	<63µm	101	97	93	103	104	100	97	100	96	97
Site 14	Total	92	99	95	101	100	102	97	99	96	97
Site 15	<63µm	102	97	93	92	103	98	97	100	94	98
Site 18	<63µm	99	97	93	95	108	94	98	100	95	101

Sediment-bound metals spike recovery analysis: Mn to Zn

Site	Fraction	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
							Recovery (%)				
Site 1	<63µm	---	113	92	92	106	83	94	99	88	96
Site 1	Total	---	106	94	94	102	91	93	95	96	96
Site 6	Total	101	107	99	99	96	105	103	100	92	100
Site 7	Total	90	112	98	98	96	98	103	95	92	100
Site 13	<63µm	---	112	95	95	107	97	89	89	90	97
Site 13	Total	87	111	96	96	104	90	95	94	98	98
Site 14	<63µm	88	110	97	97	106	100	89	96	91	100
Site 14	Total	91	107	96	95	100	91	98	94	98	97
Site 15	<63µm	85	108	95	96	107	91	88	94	91	98
Site 18	<63µm	88	114	97	96	115	90	86	95	91	100

TSS Metals QC DATA

Table B16. TSS-bound metals PACS-2 certified reference material recovery analysis

LABORATORY I.D.	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Hg
						(µg/g, dry weight)					
PACS-2 (PT-1-9)	1.40	19300	28	509	0.44	2.15	9.0	58	279	30300	3.03
PACS-2 (PT-1-10)	1.28	20600	28	515	0.44	2.14	8.9	59	276	30100	2.96
PACS-2 (PT-2-4)	1.27	19200	26	489	0.42	2.08	8.7	56	272	29900	2.90
PACS-2 (PT-2-4)	1.30	19300	27	489	0.41	2.04	9.0	58	283	29800	3.03
PACS-2 (PT-2-5)	1.37	15800	27	425	0.38	2.21	8.9	54	283	28500	3.09
PACS-2 (PT-3-4)	1.20	18800	27	512	0.40	2.00	8.6	55	265	30000	2.99
PACS-2 (PT-3-5)	1.40	17300	27	480	0.41	1.99	8.8	56	282	29800	3.09
PACS-2 average (n=7)	1.32	18600	27	488	0.42	2.09	8.9	56	277	29800	3.01
PACS-2 in-house value	1.16	16700	26	-	0.43	2.45	9.5	51	299	31200	2.94
% recovery	113	111	107	-	97	85	93	111	93	95	102

LABORATORY I.D.	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
						(µg/g, dry weight)				
PACS-2 (PT-1-9)	253	5.1	34	172	8.6	1.00	63	0.44	89	311
PACS-2 (PT-1-10)	252	5.1	33	171	8.7	1.00	65	0.44	92	311
PACS-2 (PT-2-4)	250	4.9	32	172	7.5	0.95	63	0.44	86	296
PACS-2 (PT-2-4)	250	5.1	34	174	7.8	0.96	63	0.45	90	307
PACS-2 (PT-2-5)	236	5.1	32	173	8.1	1.01	57	0.43	82	310
PACS-2 (PT-3-4)	249	5.1	32	165	7.2	0.99	61	0.45	85	304
PACS-2 (PT-3-5)	247	5.3	33	179	8.3	1.01	59	0.45	85	314
PACS-2 average (n=7)	248	5.1	33	172	8.0	0.99	61	0.44	87	308
PACS-2 in-house value	253	5.0	32	170	8.0	0.99	69	-	82	345
% recovery	98	102	102	101	100	100	89	-	107	89

Table B17. TSS-bound metals replicate analysis: Ag to Hg

Sample	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Hg
						(µg/g, dry weight)					
Site 16, 0.5 m, Dup 2	<2.4	42500	20	49	1.2	<1.1	15	47	36	39100	<0.39
Site 16, 0.5 m, Dup 2	<2.4	42200	17	49	1.3	<1.1	15	46	34	39500	<0.39
Site 16, 0.5 m, Dup 2	<2.4	42400	19	49	1.3	<1.1	15	47	35	39300	<0.39
Site 1, 4 m	<2.4	56600	17	59	1.3	<1.1	13	64	19	43200	<0.39
Site 1, 4 m	<2.4	57200	18	58	1.2	<1.1	14	65	19	42900	<0.39
Site 1, 4 m	<2.4	56900	17	59	1.3	<1.1	14	64	19	43000	<0.39
Site 3, 5 m	<2.4	35000	18	46	0.8	<1.1	14	47	29	36000	0.40
Site 3, 5 m	<2.4	34400	17	46	0.7	<1.1	14	44	27	35900	0.49
Site 3, 5 m	<2.4	34700	17	46	0.8	<1.1	14	45	28	35900	0.44
Site 9, 6 m	<2.4	28800	12	34	0.6	<1.1	10	32	19	23500	<0.39
Site 9, 6 m	<2.4	28800	12	34	0.6	<1.1	10	32	20	23600	<0.39
Site 9, 6 m	<2.4	28800	12	34	0.6	<1.1	10	32	20	23600	<0.39
Site 6, 6 m	3.29	28700	16	50	1.0	<1.1	12	38	29	31400	<0.39
Site 6, 6 m	3.41	28800	16	50	1.0	<1.1	12	38	28	31600	<0.39
Site 6, 6 m	3.35	28800	16	50	1.0	<1.1	12	38	29	31500	<0.39
Site 7, 0.5 m, Dup 1	<2.4	19300	16	30	0.8	<1.1	12	30	20	27700	<0.39
Site 7, 0.5 m, Dup 1	<2.4	18900	14	31	1.1	<1.1	12	30	21	28600	<0.39
Site 7, 0.5 m, Dup 1	<2.4	19100	15	31	0.9	<1.1	12	30	20	28100	0.51

Table B18. TSS-bound metals replicate analysis: Mn to Zn

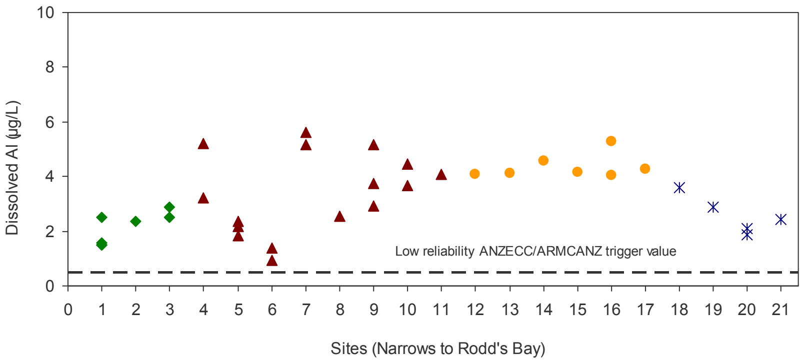
Sample	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
					(µg/g, dry weight)					
Site 16, 0.5 m, Dup 2	912	0.7	23	12.0	0.27	0.44	89	0.09	84	75
Site 16, 0.5 m, Dup 2	913	1.4	20	11.6	0.34	1.14	89	0.10	80	72
Site 16, 0.5 m, Dup 2	912	1.0	21	11.8	0.30	0.79	89	0.10	82	74
Site 1, 4 m	764	2.1	35	11.3	0.21	0.30	84	0.15	88	65
Site 1, 4 m	772	2.1	35	11.1	0.21	0.35	84	0.10	86	73
Site 1, 4 m	768	2.1	35	11.2	0.21	0.32	84	0.12	87	69
Site 3, 5 m	675	1.9	22	10.6	0.17	0.36	46	0.20	73	64
Site 3, 5 m	668	1.1	21	10.1	0.18	0.15	46	0.21	75	63
Site 3, 5 m	672	1.5	21	10.3	0.18	0.25	46	0.21	74	64
Site 9, 6 m	458	0.9	15	7.0	0.15	0.26	95	0.16	57	43
Site 9, 6 m	456	1.0	16	7.1	0.16	0.26	95	0.15	57	42
Site 9, 6 m	457	0.9	16	7.1	0.15	0.26	95	0.15	57	42
Site 6, 6 m	535	1.0	17	11.1	0.19	0.61	60	0.31	65	50
Site 6, 6 m	531	1.1	16	10.4	0.27	0.41	60	0.25	63	48
Site 6, 6 m	533	1.1	16	10.8	0.23	0.51	60	0.28	64	49
Site 7, 0.5 m, Dup 1	638	1.0	19	8.1	0.23	0.40	53	0.24	54	43
Site 7, 0.5 m, Dup 1	659	0.7	21	7.9	0.20	0.42	54	0.21	54	47
Site 7, 0.5 m, Dup 1	648	0.9	20	8.0	0.21	0.41	54	0.22	54	45

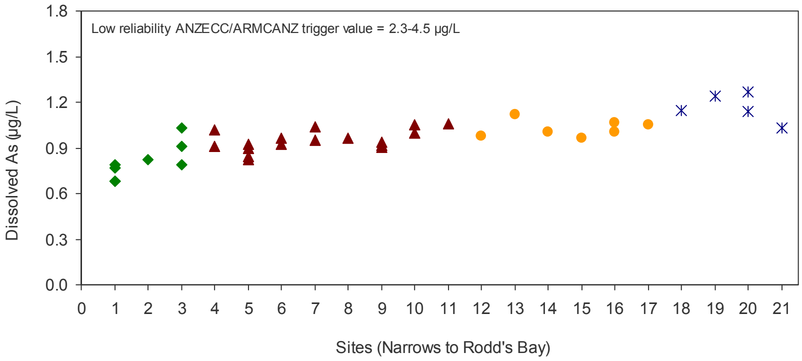
Table B19. TSS-bound metals: spike recovery analysis

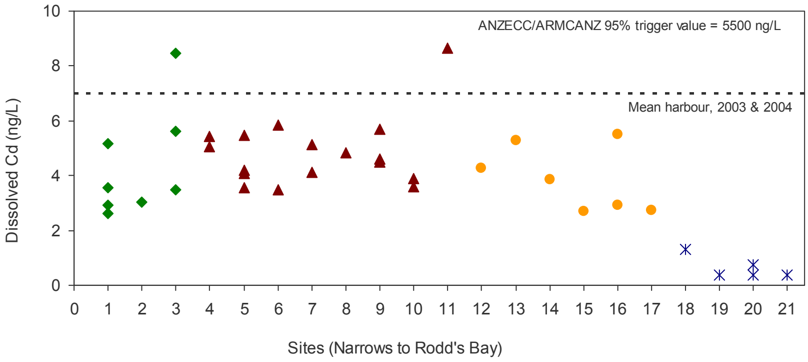
Site	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Hg
						Recovery (%)					
Site 1, 0.5 m	91	87	106	96	113	106	105	106	110	86	107
Site 3, 0.5 m	90	91	104	96	102	104	103	101	104	88	103
Site 9, 3 m	93	---	107	95	104	108	107	105	106	---	106
Site 5, 5.5 m	90	---	106	96	100	105	105	103	104	---	102
Site 6, 0.5 m	93	---	105	96	98	104	104	102	105	---	103

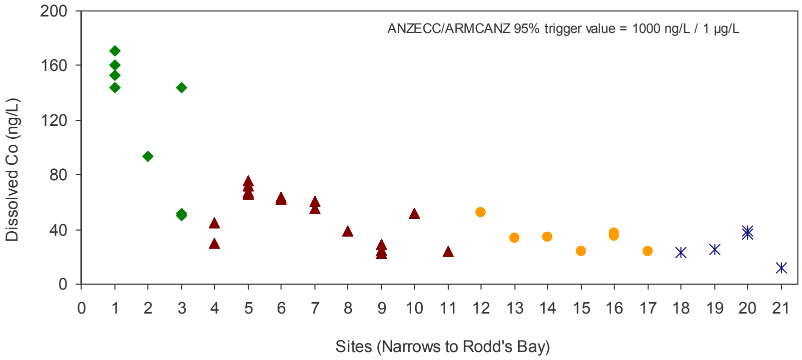
Site	Mn	Mo	Ni	Pb	Sb	Se	Sr	Tl	V	Zn
						Recovery (%)				
Site 1, 0.5 m	100	104	106	102	105	107	94	103	105	111
Site 3, 0.5 m	99	101	104	98	102	101	93	97	102	106
Site 9, 3 m	98	104	106	97	105	103	91	99	105	105
Site 5, 5.5 m	100	102	105	97	100	102	90	99	104	101
Site 6, 0.5 m	99	103	102	98	102	102	92	99	102	105

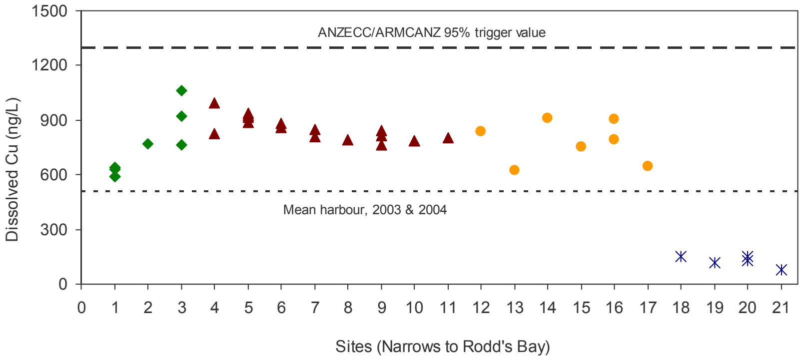
Appendix C Dissolved metal concentrations in waters between the Southern Narrows and Rodds Bay

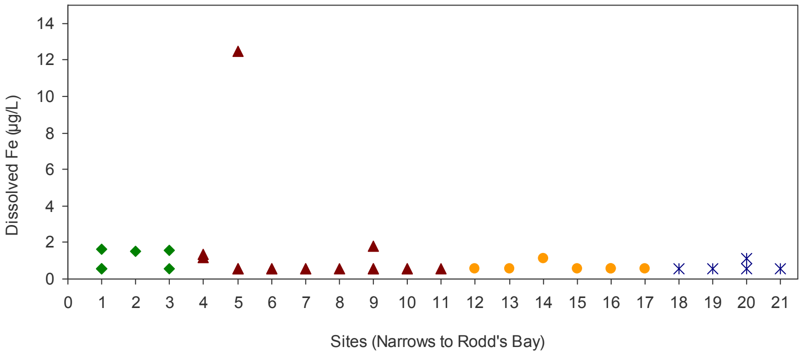


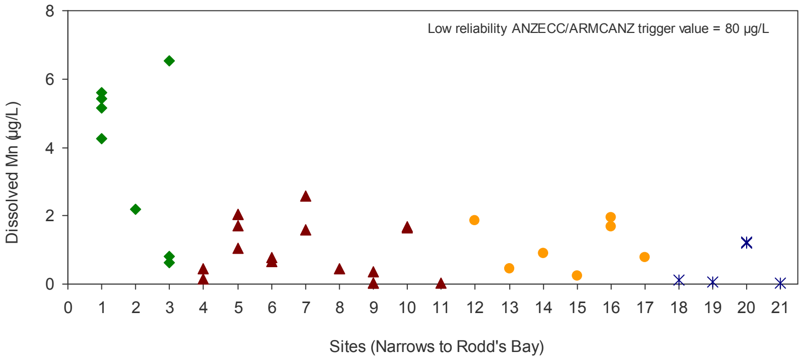


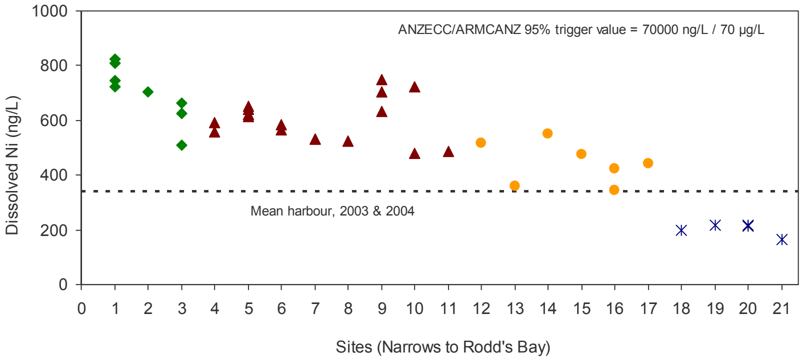


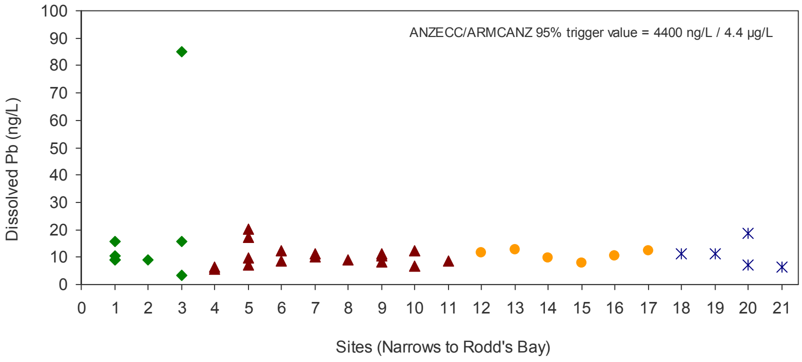

ANZECC/ARMCANZ 95% trigger value = 1000 ng/L / 1 µg/L
Dissolved Co (ng/L)
200
160
120
80
40
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

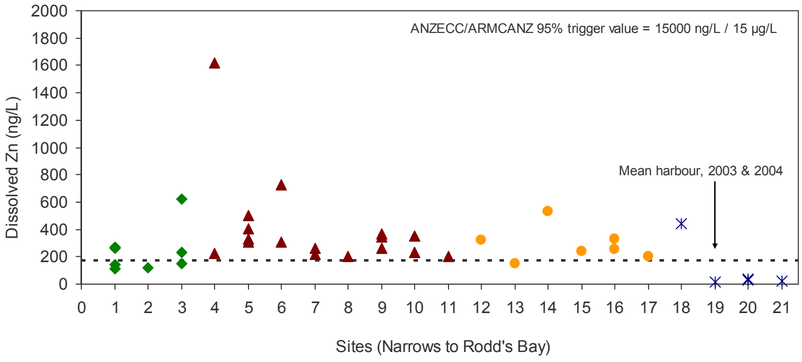

ANZECC/ARMCANZ 95% trigger value
Mean harbour, 2003 & 2004
Dissolved Cu (ng/L)
1500
1200
900
600
300
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)


Dissolved Fe (µg/L)
14
12
10
8
6
4
2
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

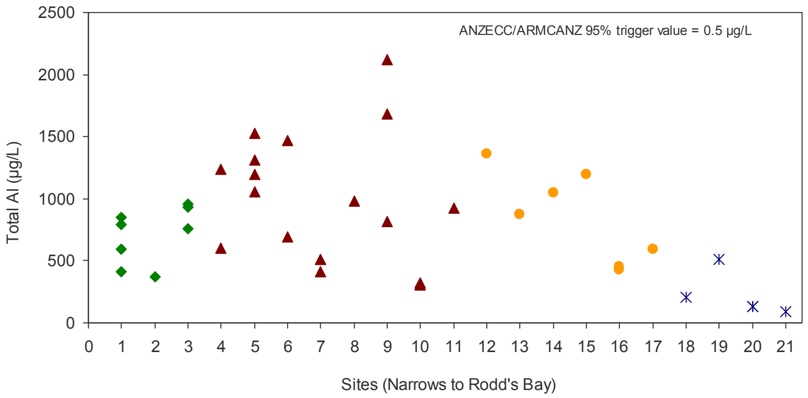

Low reliability ANZECC/ARMCANZ trigger value = 80 µg/L
Dissolved Mn (µg/L)
8
6
4
2
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

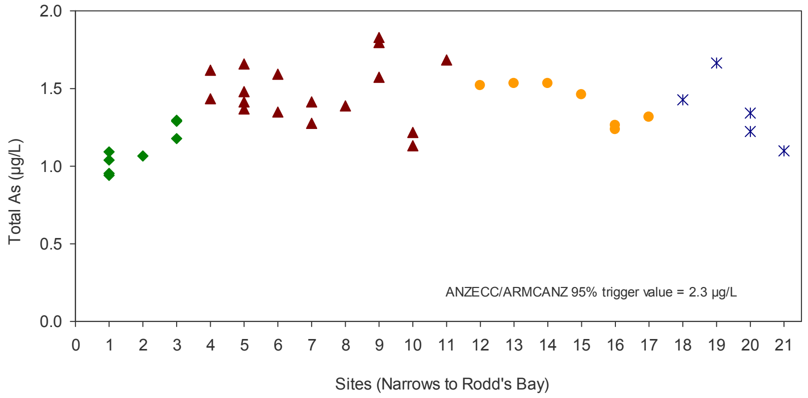

ANZECC/ARMCANZ 95% trigger value = 70000 ng/L / 70 µg/L
Mean harbour, 2003 & 2004
Dissolved Ni (ng/L)
0
200
400
600
800
1000
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

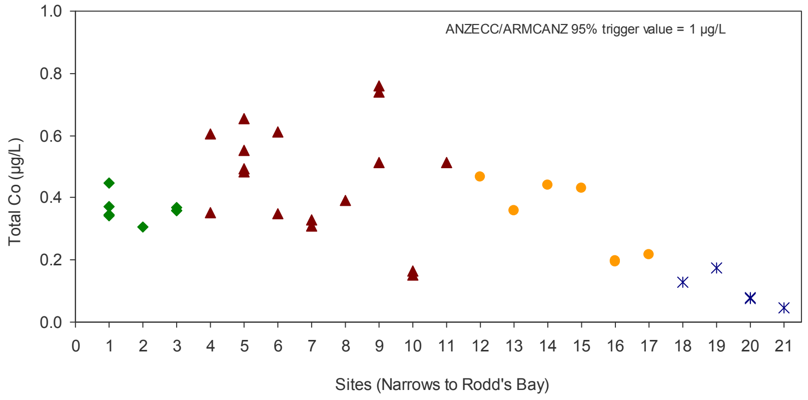

ANZECC/ARMCANZ 95% trigger value = 4400 ng/L / 4.4 µg/L
Dissolved Pb (ng/L)
0
10
20
30
40
50
60
70
80
90
100
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

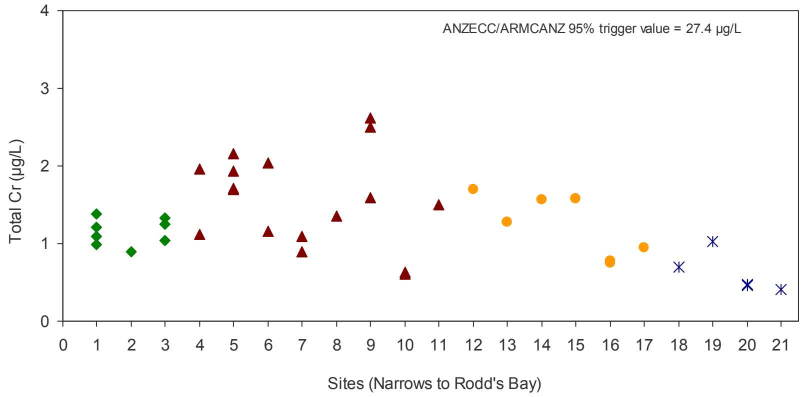

ANZECC/ARMCANZ 95% trigger value = 15000 ng/L / 15 µg/L
Mean harbour, 2003 & 2004
Dissolved Zn (ng/L)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

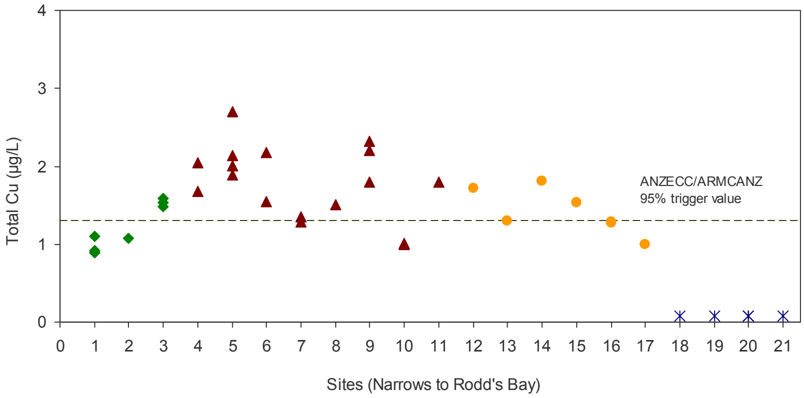
Appendix D Total metal concentrations in waters between the Southern Narrows and Rodds Bay

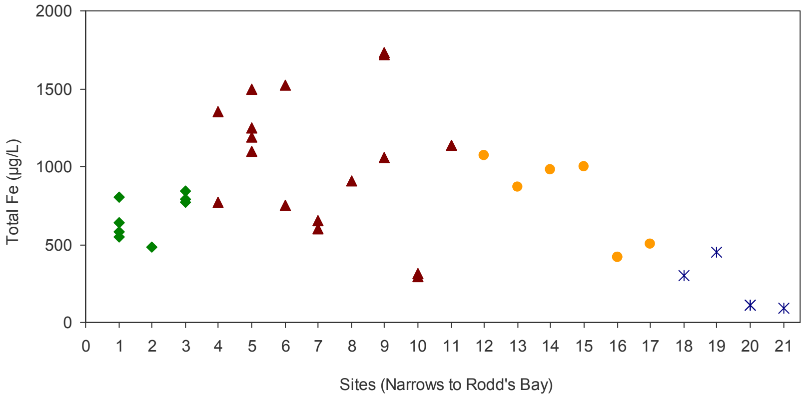


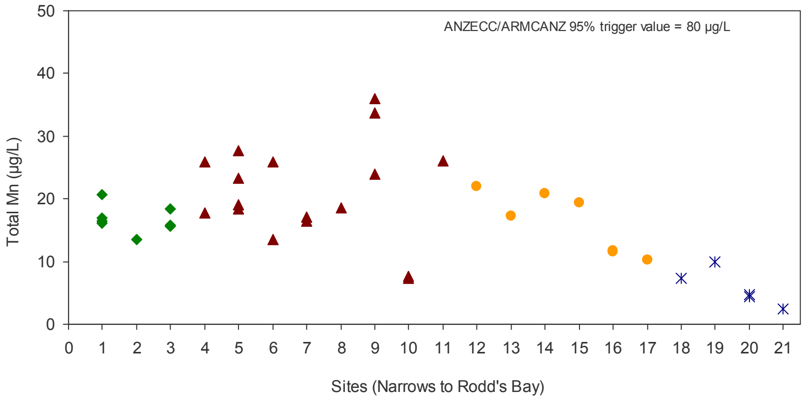


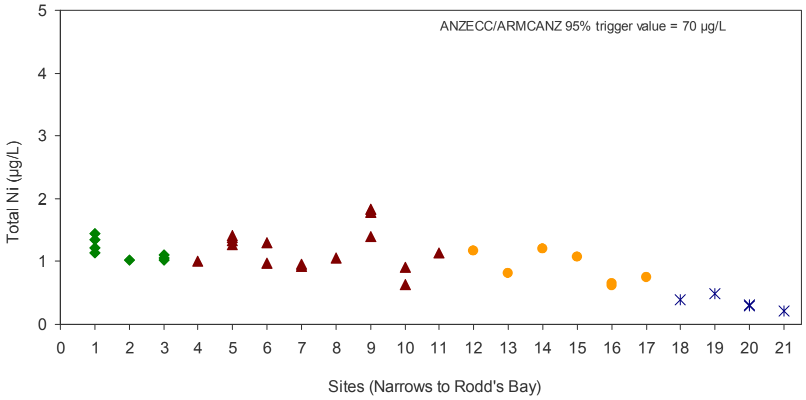


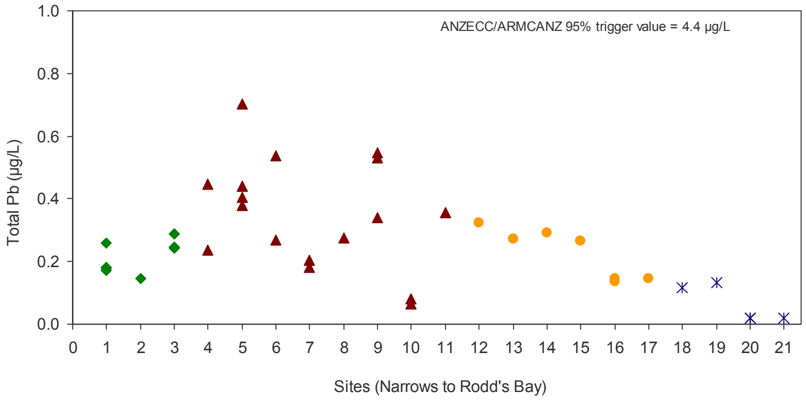

ANZECC/ARMCANZ 95% trigger value = 27.4 µg/L
Total Cr (µg/L)
0
1
2
3
4
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

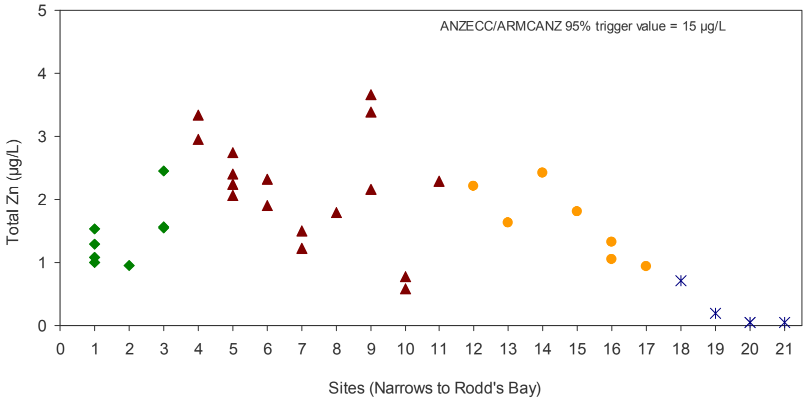

ANZECC/ARMCANZ
95% trigger value
Total Cu (µg/L)
0
1
2
3
4
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)


Total Fe (µg/L)
0
500
1000
1500
2000
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

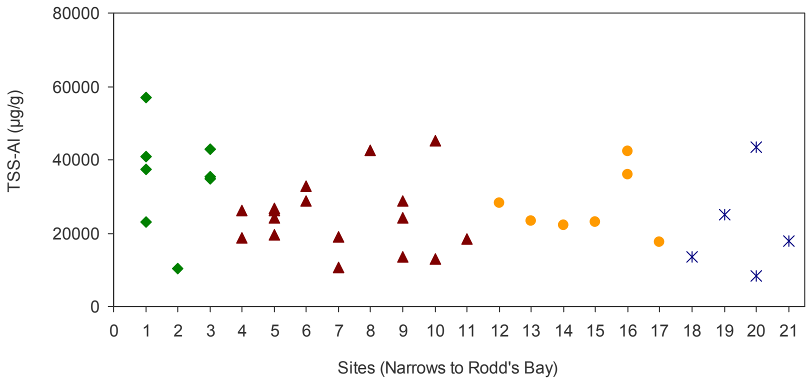

ANZECC/ARMCANZ 95% trigger value = 80 µg/L
Total Mn (µg/L)
0
10
20
30
40
50
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

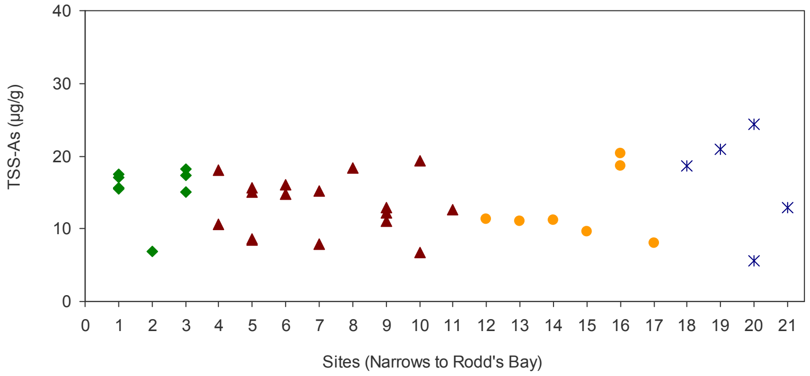

ANZECC/ARMCANZ 95% trigger value = 70 µg/L
Total Ni (µg/L)
0
1
2
3
4
5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

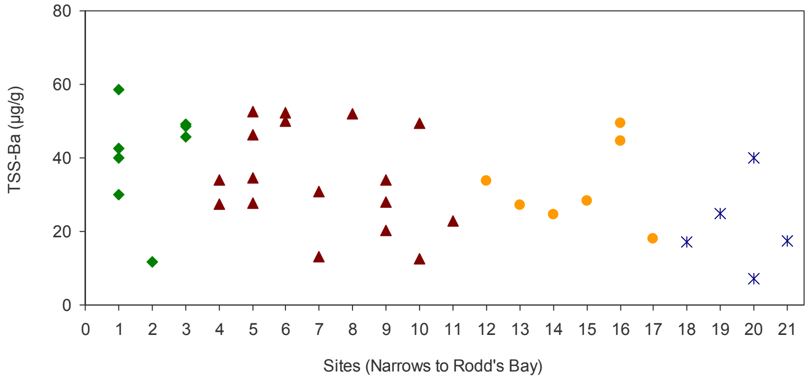

ANZECC/ARMCANZ 95% trigger value = 4.4 µg/L
Total Pb (µg/L)
0.0
0.2
0.4
0.6
0.8
1.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

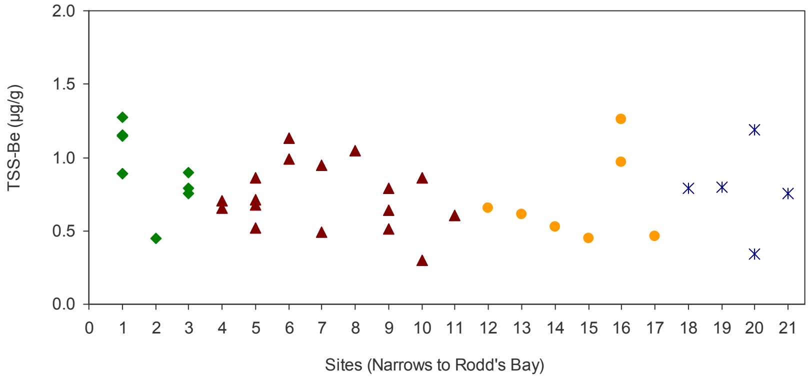

ANZECC/ARMCANZ 95% trigger value = 15 µg/L
Total Zn (µg/L)
0
1
2
3
4
5
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

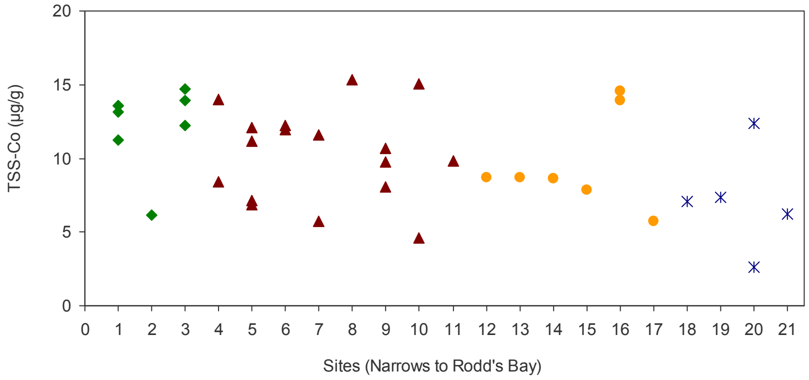
Appendix E TSS-bound metals between the Southern Narrows and Rodds Bay

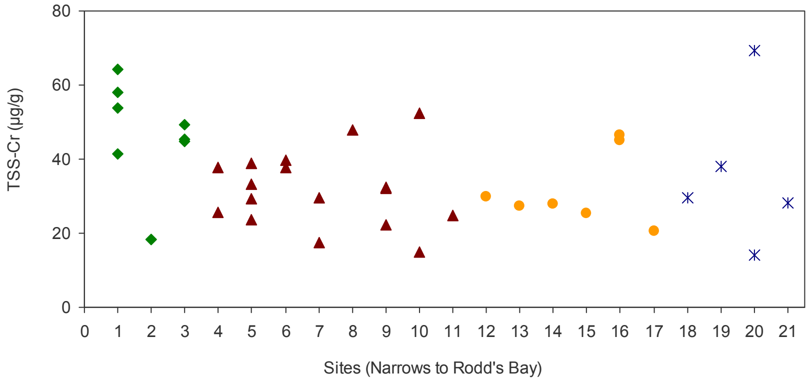


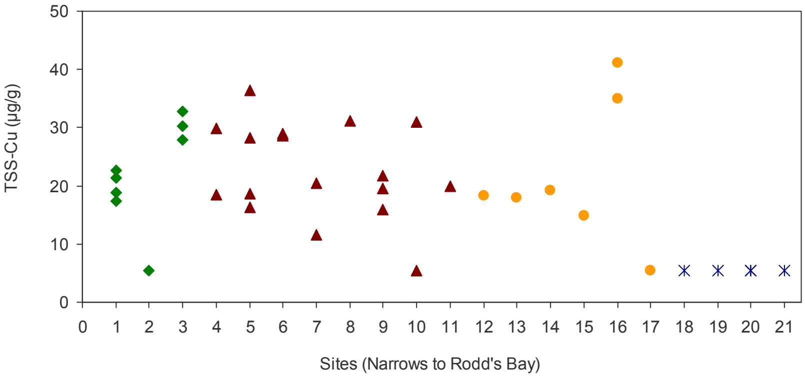


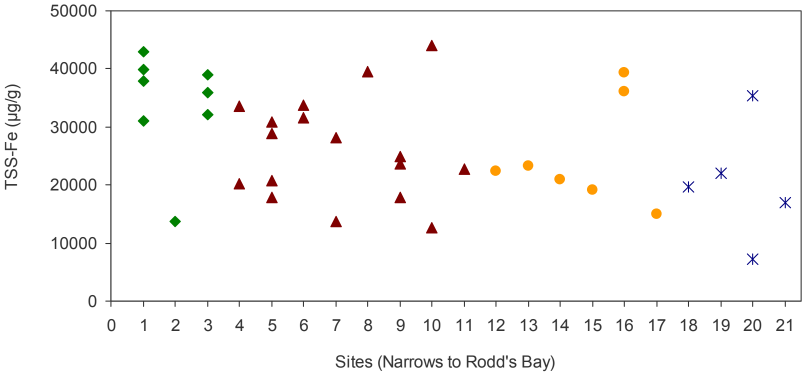


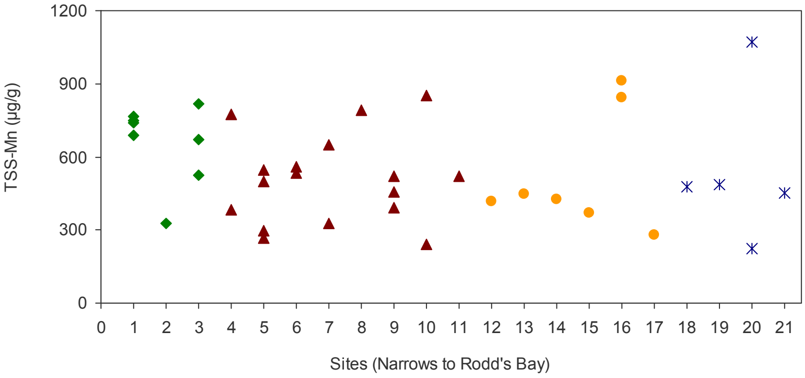

TSS-Be (µg/g)
0.0
0.5
1.0
1.5
2.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

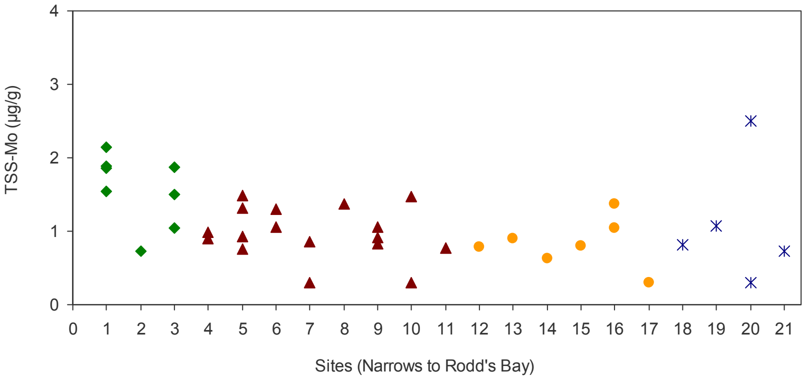

TSS-Co (µg/g)
0
5
10
15
20
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

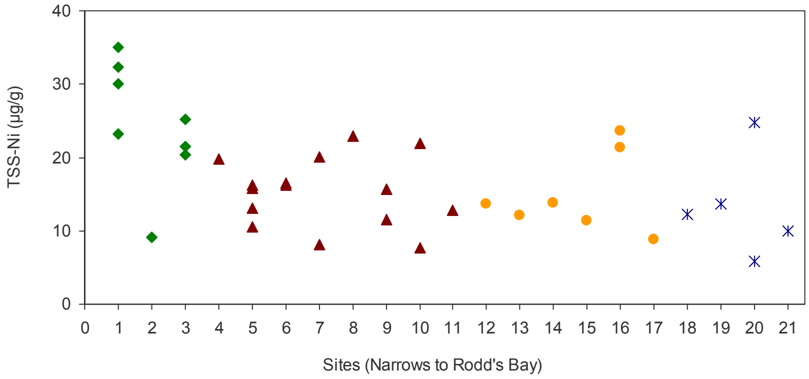

TSS-Cr (µg/g)
0
20
40
60
80
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

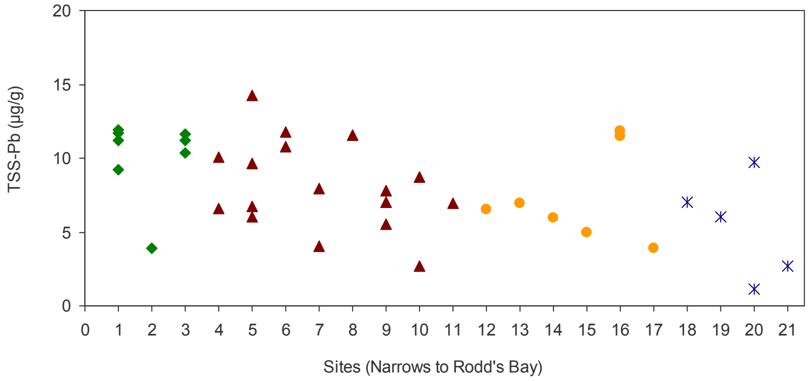

TSS-Cu (µg/g)
0
10
20
30
40
50
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

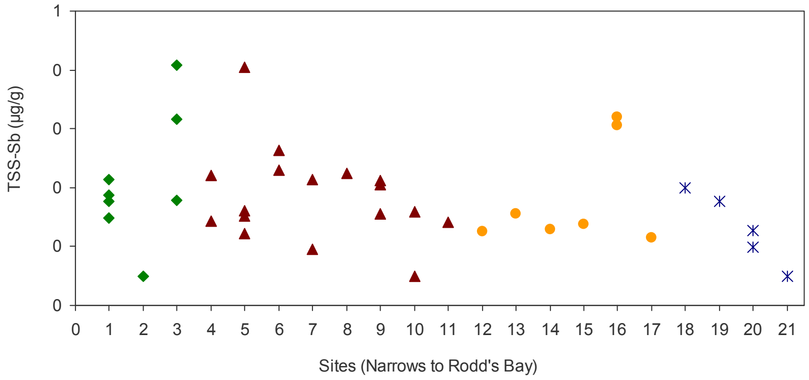

TSS-Fe (µg/g)
0
10000
20000
30000
40000
50000
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

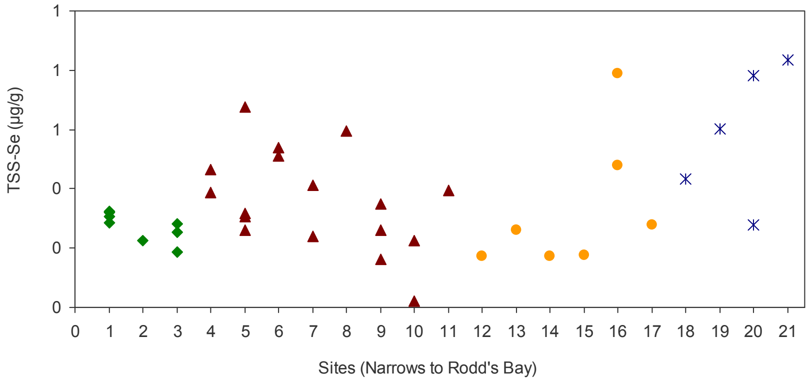

TSS-Mn (µg/g)
0
300
600
900
1200
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

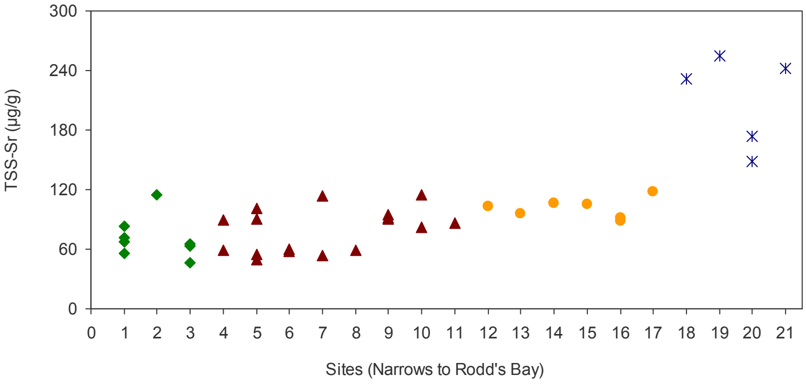

TSS-Mo (µg/g)
0
1
2
3
4
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

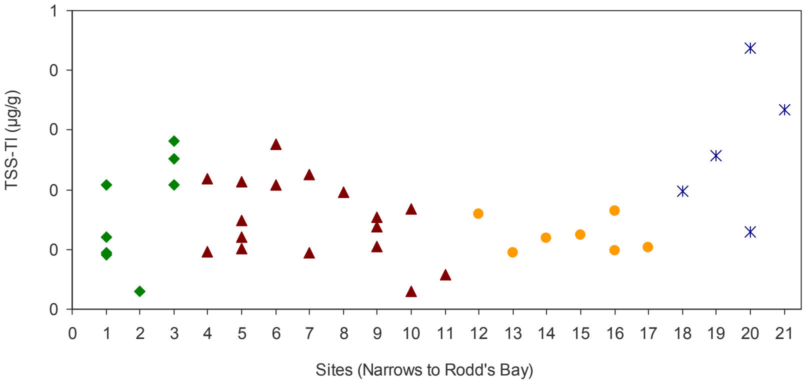

TSS-Ni (µg/g)
0
10
20
30
40
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

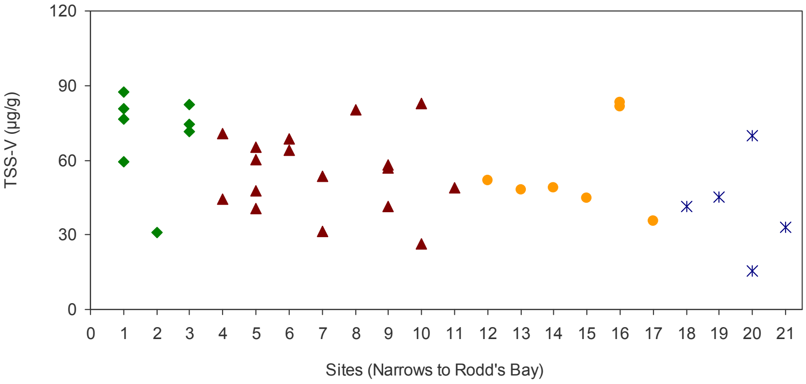

TSS-Pb (µg/g)
0
5
10
15
20
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

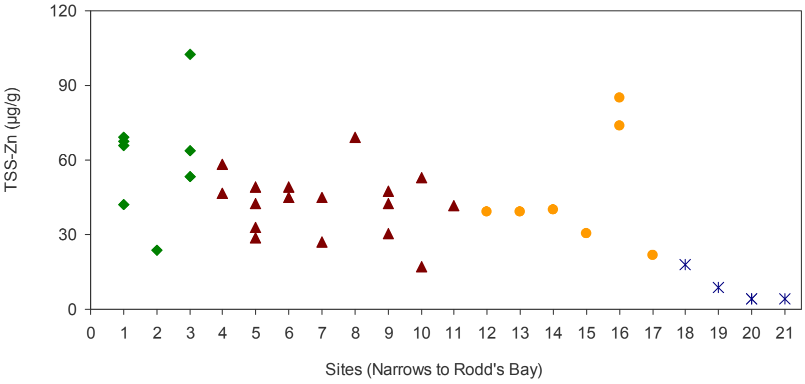

TSS-Sb (µg/g)
0
0
0
0
0
1
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)


TSS-Se (µg/g)
0
0
0
1
1
1
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

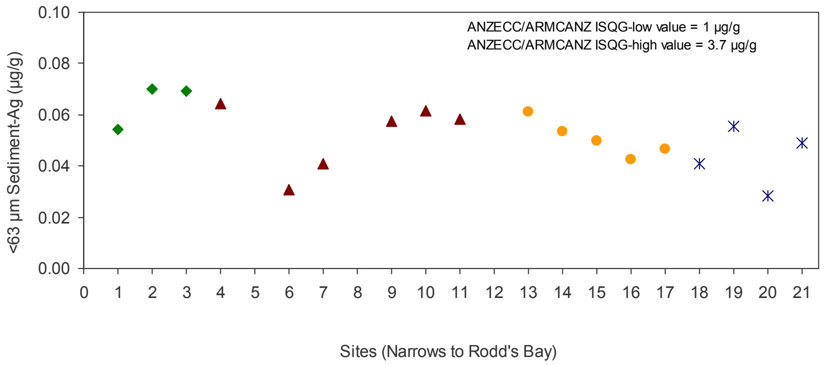

TSS-Sr (µg/g)
300
240
180
120
60
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

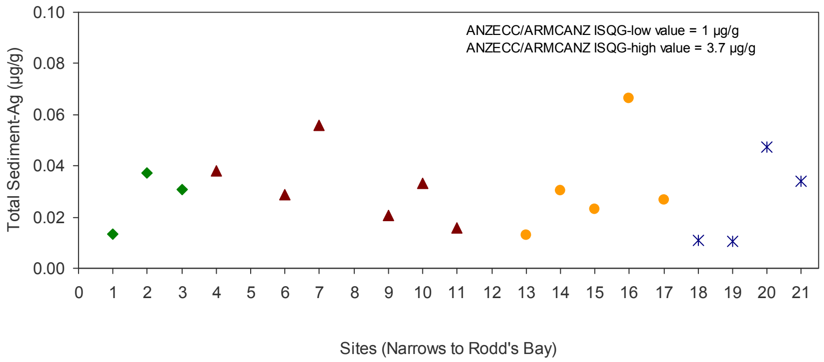

TSS-Tl (µg/g)
1
0
0
0
0
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

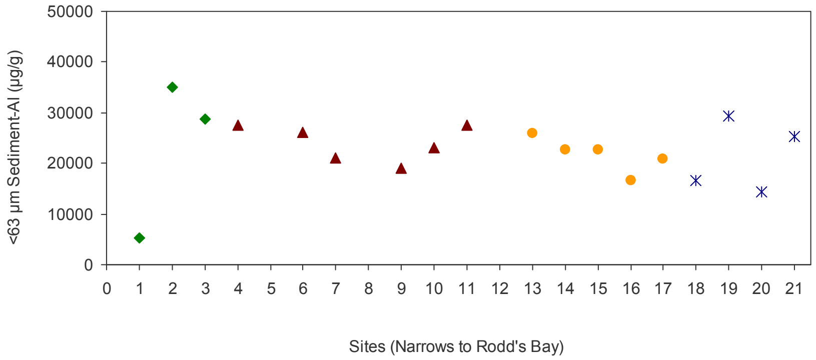

TSS-V (µg/g)
120
90
60
30
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

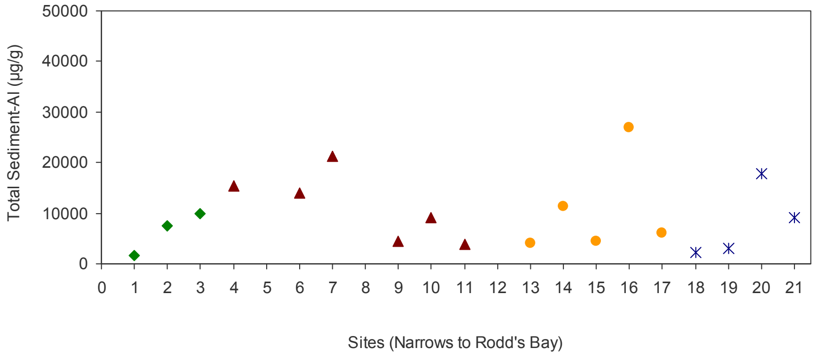

TSS-Zn (µg/g)
120
90
60
30
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

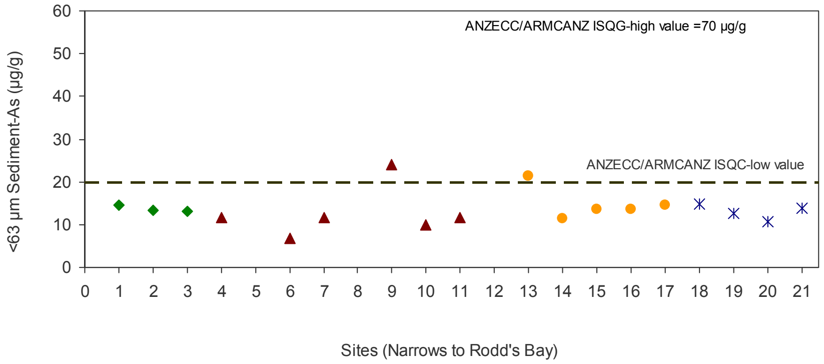
Appendix F Particulate metal concentrations measured in the total and <63 µm benthic sediment fractions between the Southern Narrows and Rodds Bay



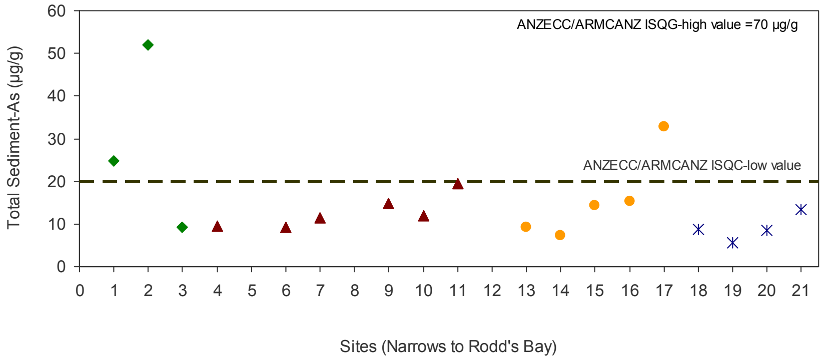




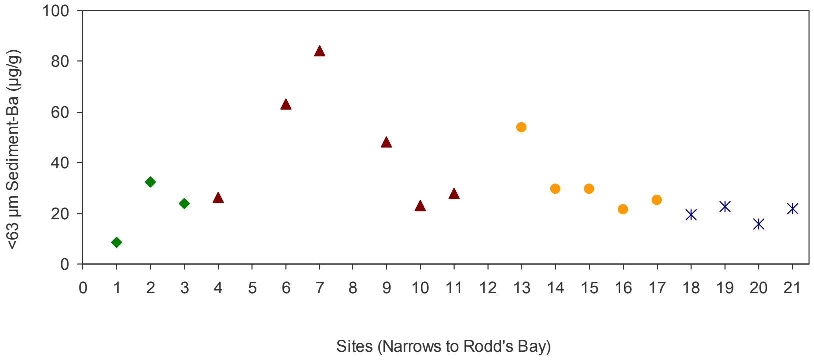




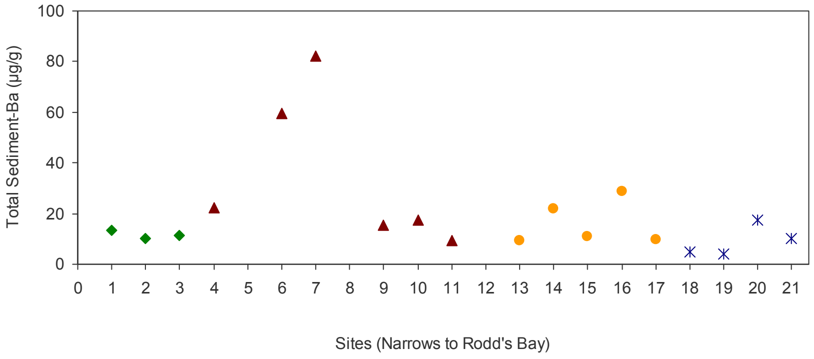
<63 µm Sediment-As (µg/g)
ANZECC/ARMCANZ ISQG-high value =70 µg/g
ANZECC/ARMCANZ ISQC-low value
0
10
20
30
40
50
60
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)



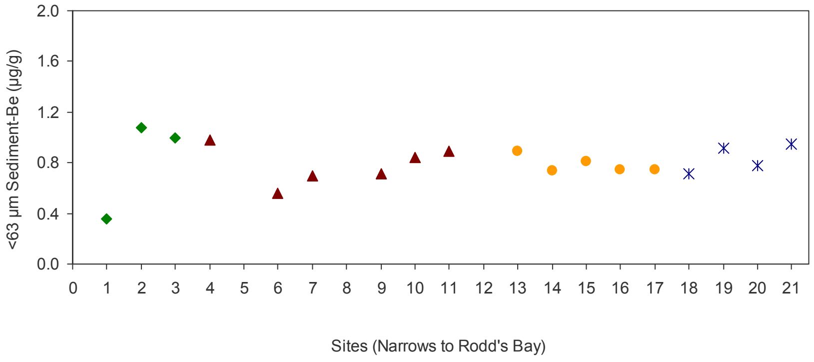
Total Sediment-As (µg/g)
ANZECC/ARMCANZ ISQG-high value =70 µg/g
ANZECC/ARMCANZ ISQC-low value
0
10
20
30
40
50
60
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)



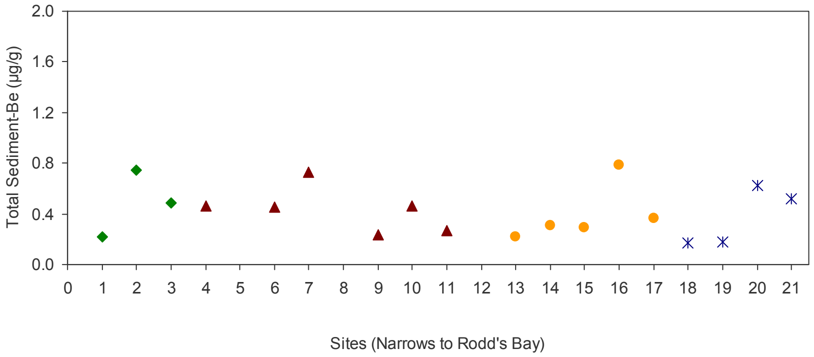
<63 µm Sediment-Ba (µg/g)
0
20
40
60
80
100
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

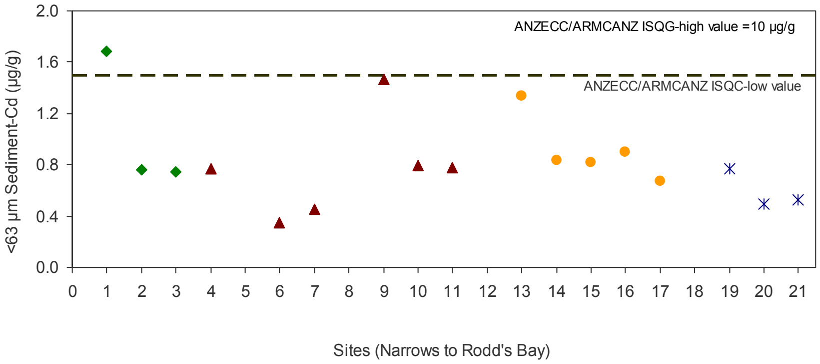


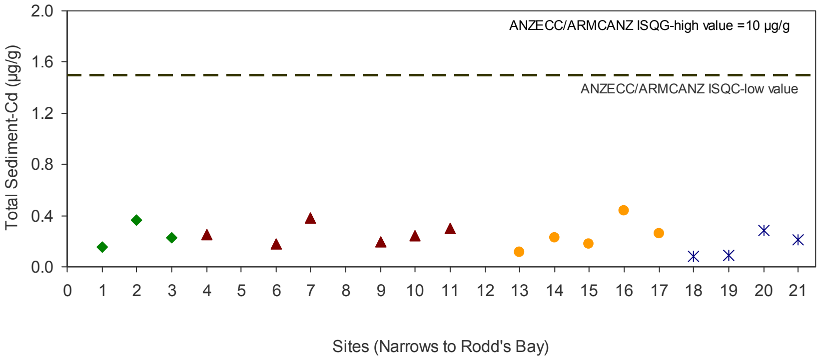
Total Sediment-Ba (µg/g)
0
20
40
60
80
100
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

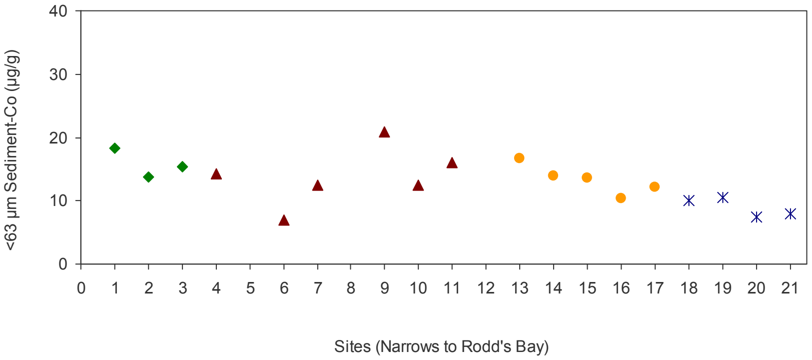


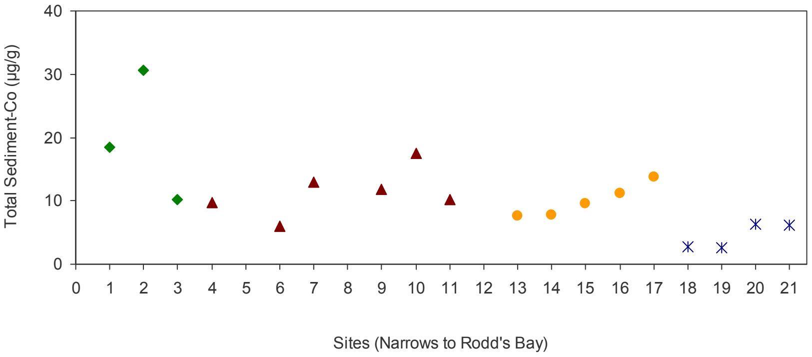
<63 µm Sediment-Be (µg/g)
0.0
0.4
0.8
1.2
1.6
2.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

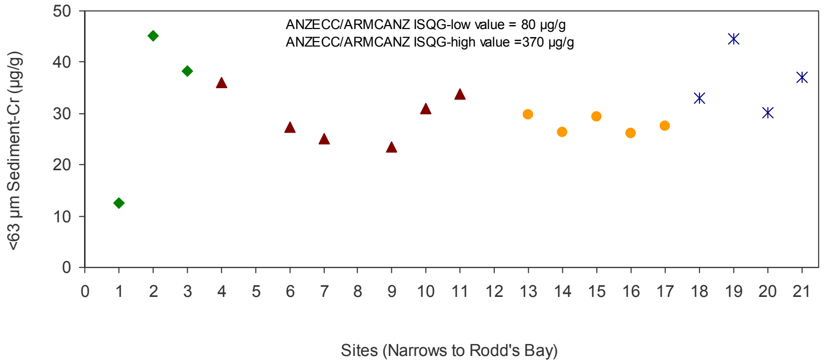

Total Sediment-Be (µg/g)
2.0
1.6
1.2
0.8
0.4
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

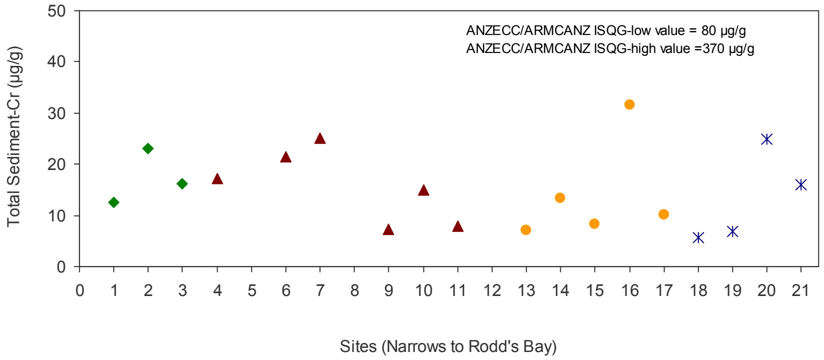

ANZECC/ARMCANZ ISQG-high value =10 µg/g
ANZECC/ARMCANZ ISQC-low value
<63 µm Sediment-Cd (µg/g)
2.0
1.6
1.2
0.8
0.4
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

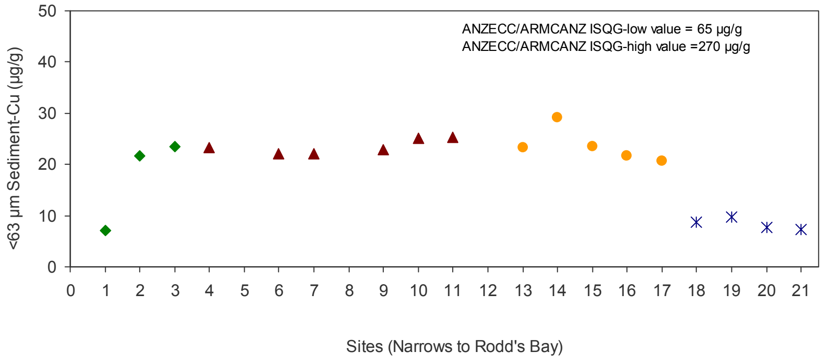

ANZECC/ARMCANZ ISQG-high value =10 µg/g
ANZECC/ARMCANZ ISQC-low value
Total Sediment-Cd (µg/g)
2.0
1.6
1.2
0.8
0.4
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

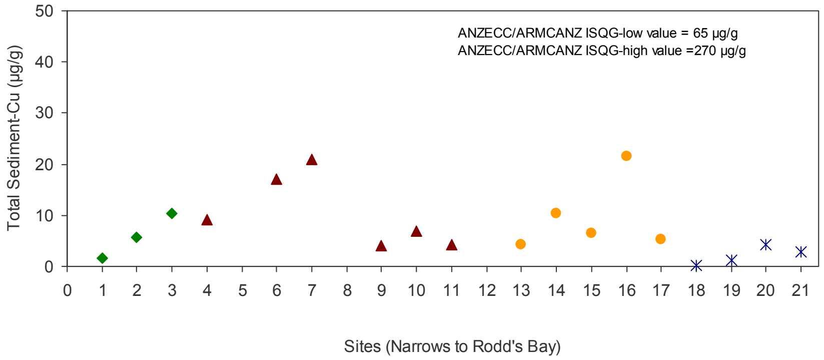

<63 µm Sediment-Co (µg/g)
40
30
20
10
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

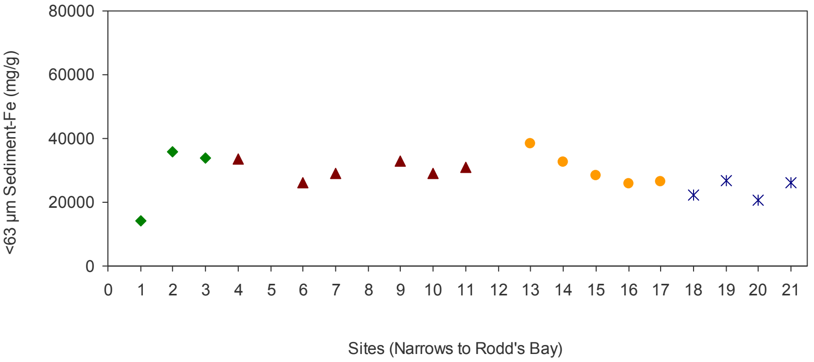

Total Sediment-Co (µg/g)
40
30
20
10
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

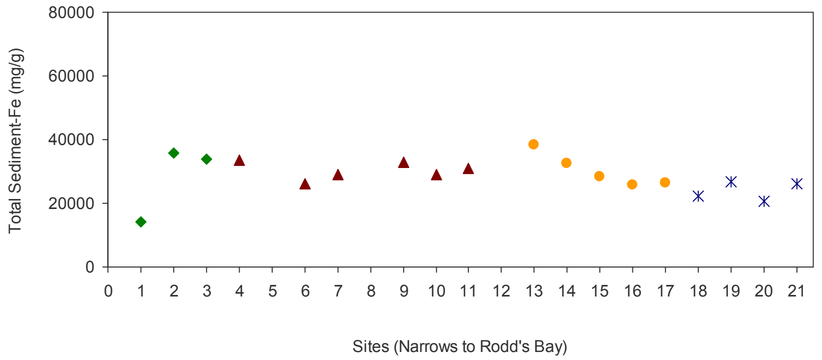

ANZECC/ARMCANZ ISQG-low value = 80 µg/g
ANZECC/ARMCANZ ISQG-high value =370 µg/g
<63 µm Sediment-Cr (µg/g)
0
10
20
30
40
50
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

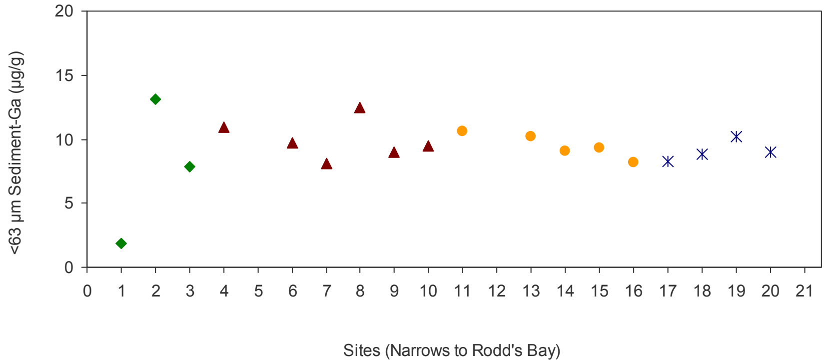

ANZECC/ARMCANZ ISQG-low value = 80 µg/g
ANZECC/ARMCANZ ISQG-high value =370 µg/g
Total Sediment-Cr (µg/g)
0
10
20
30
40
50
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

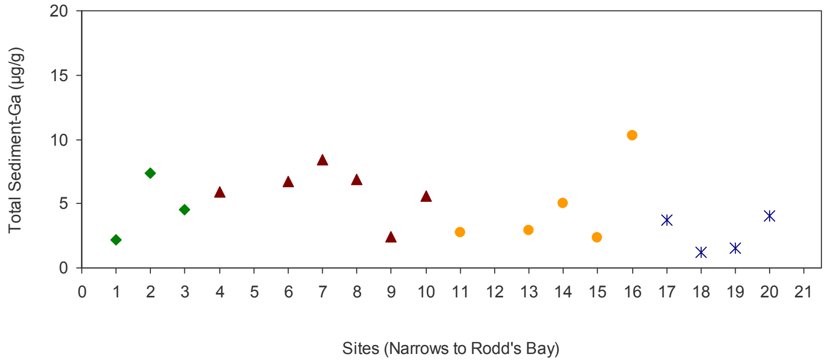

ANZECC/ARMCANZ ISQG-low value = 65 µg/g
ANZECC/ARMCANZ ISQG-high value =270 µg/g
<63 µm Sediment-Cu (µg/g)
0
10
20
30
40
50
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

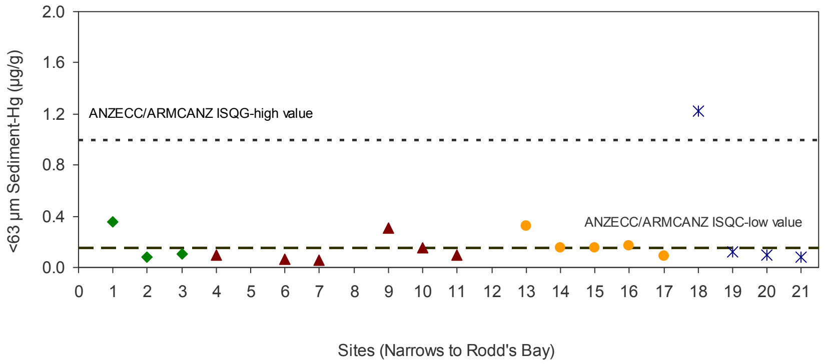

ANZECC/ARMCANZ ISQG-low value = 65 µg/g
ANZECC/ARMCANZ ISQG-high value =270 µg/g
Total Sediment-Cu (µg/g)
0
10
20
30
40
50
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

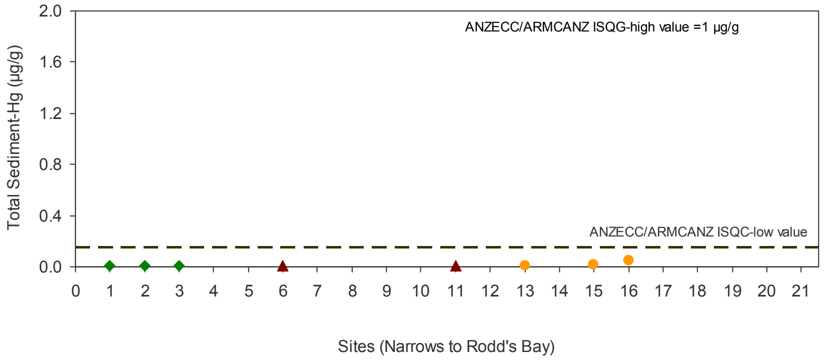

<63 µm Sediment-Fe (mg/g)
0
20000
40000
60000
80000
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

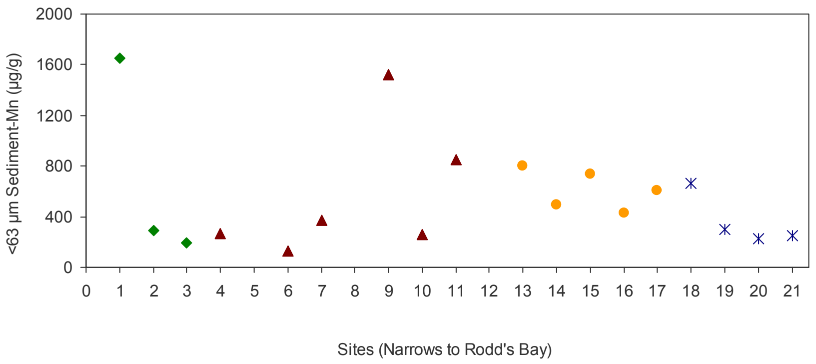

Total Sediment-Fe (mg/g)
80000
60000
40000
20000
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

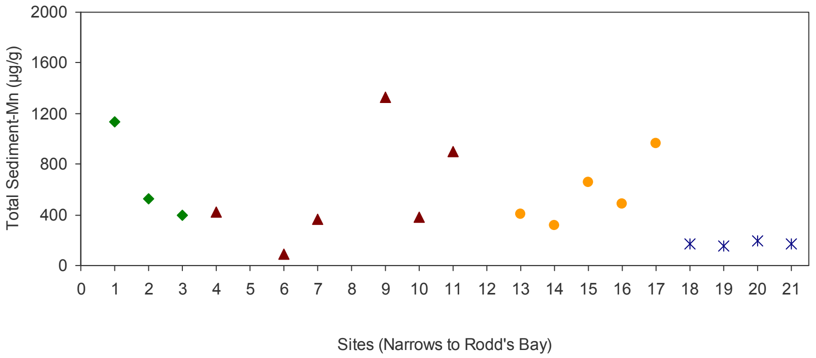

<63 µm Sediment-Ga (µg/g)
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

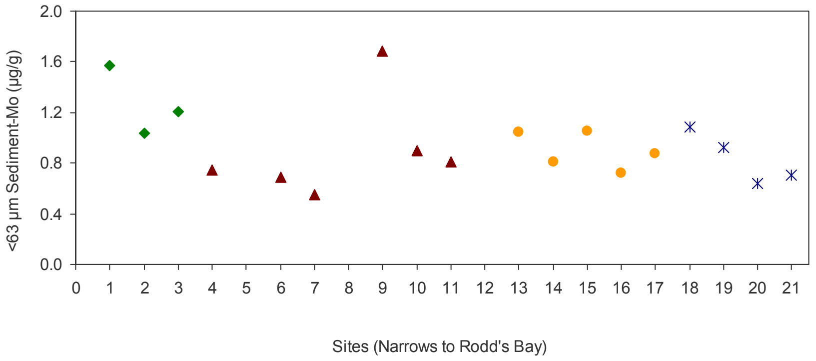

Total Sediment-Ga (µg/g)
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

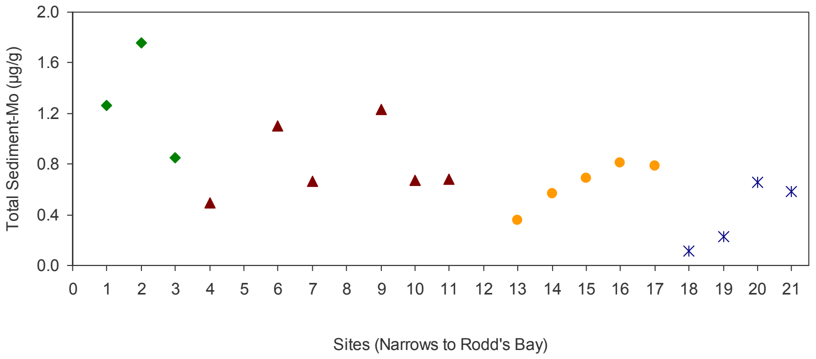

<63 µm Sediment-Hg (µg/g)
2.0
1.6
1.2
0.8
0.4
0.0
ANZECC/ARMCANZ ISQG-high value
ANZECC/ARMCANZ ISQC-low value
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

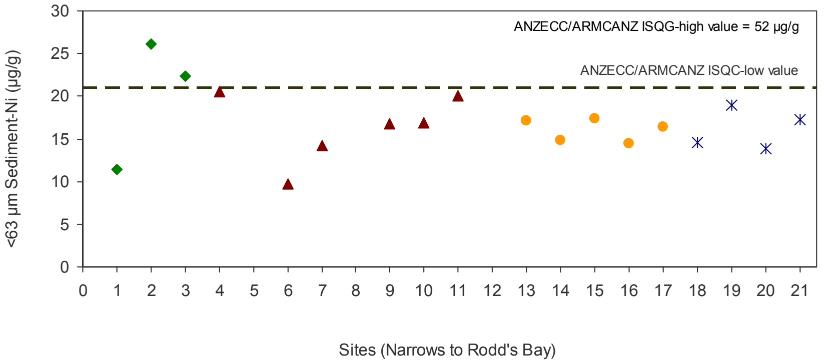

Total Sediment-Hg (µg/g)
2.0
1.6
1.2
0.8
0.4
0.0
ANZECC/ARMCANZ ISQG-high value =1 µg/g
ANZECC/ARMCANZ ISQC-low value
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

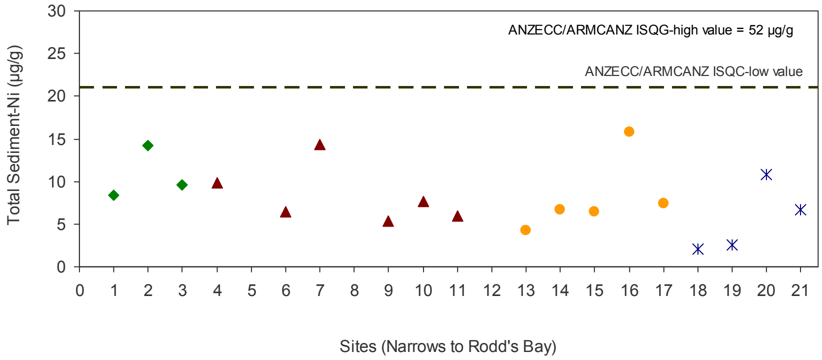

<63 µm Sediment-Mn (µg/g)
2000
1600
1200
800
400
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

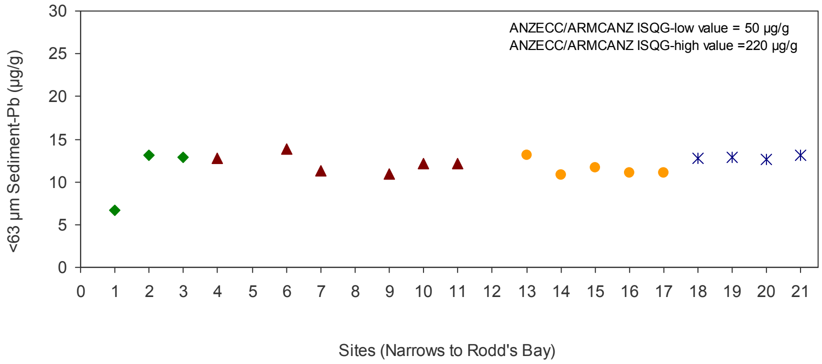

Total Sediment-Mn (µg/g)
2000
1600
1200
800
400
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

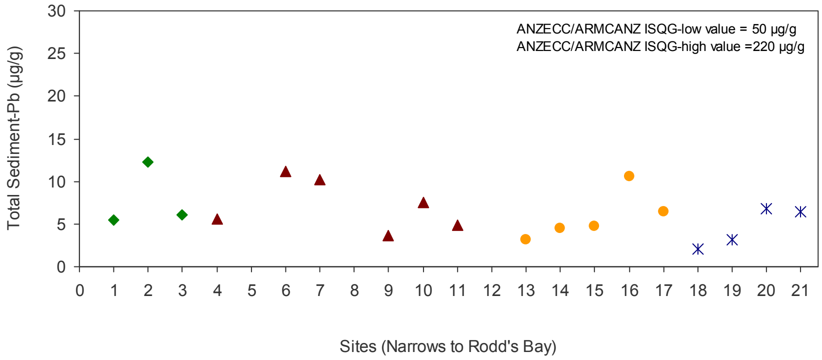

<63 µm Sediment-Mo (µg/g)
2.0
1.6
1.2
0.8
0.4
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

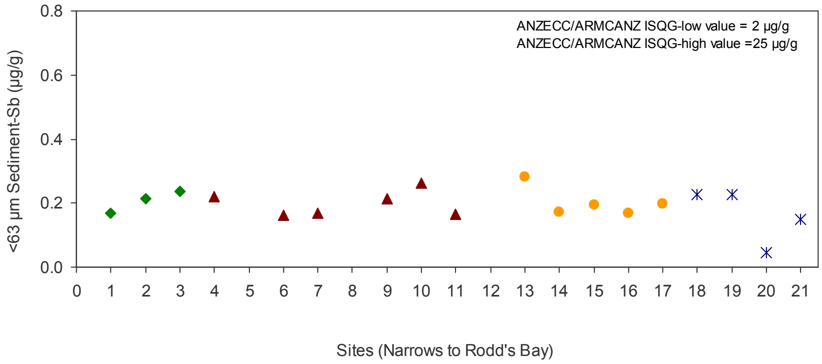

Total Sediment-Mo (µg/g)
2.0
1.6
1.2
0.8
0.4
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

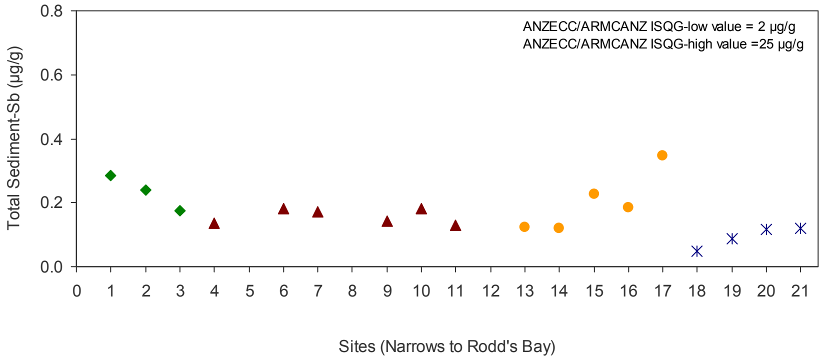

ANZECC/ARMCANZ ISQG-high value = 52 µg/g
ANZECC/ARMCANZ ISQC-low value
<63 µm Sediment-Ni (µg/g)
30
25
20
15
10
5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

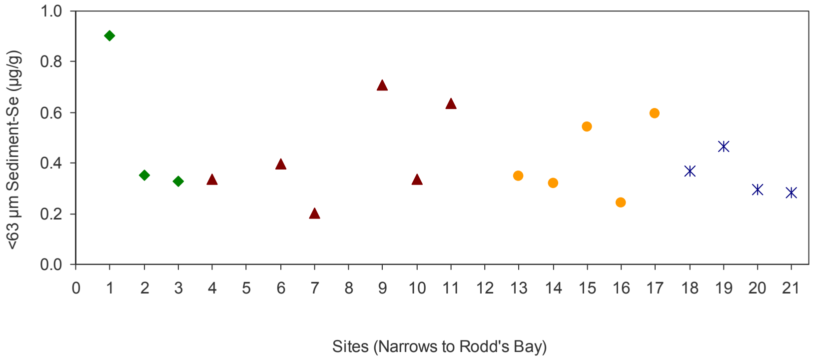

Total Sediment-Ni (µg/g)
30
25
20
15
10
5
0
ANZECC/ARMCANZ ISQG-high value = 52 µg/g
ANZECC/ARMCANZ ISQC-low value
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

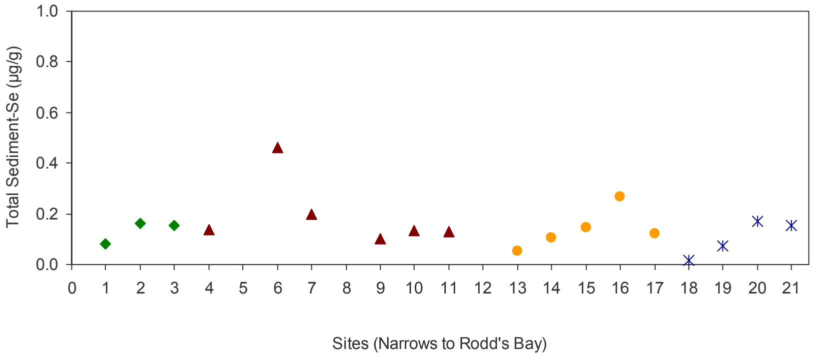

<63 µm Sediment-Pb (µg/g)
30
25
20
15
10
5
0
ANZECC/ARMCANZ ISQG-low value = 50 µg/g
ANZECC/ARMCANZ ISQG-high value =220 µg/g
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

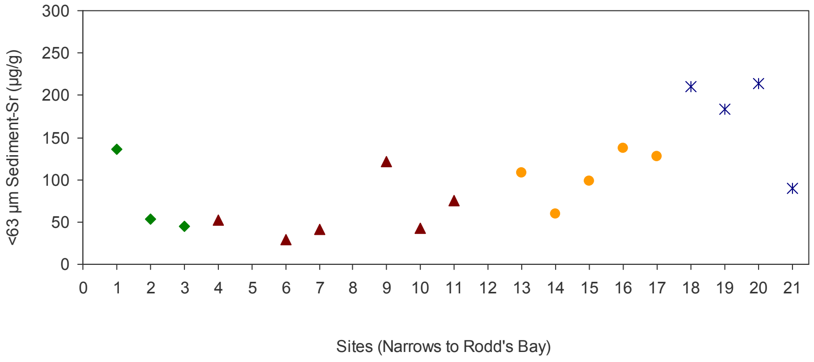

Total Sediment-Pb (µg/g)
30
25
20
15
10
5
0
ANZECC/ARMCANZ ISQG-low value = 50 µg/g
ANZECC/ARMCANZ ISQG-high value =220 µg/g
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

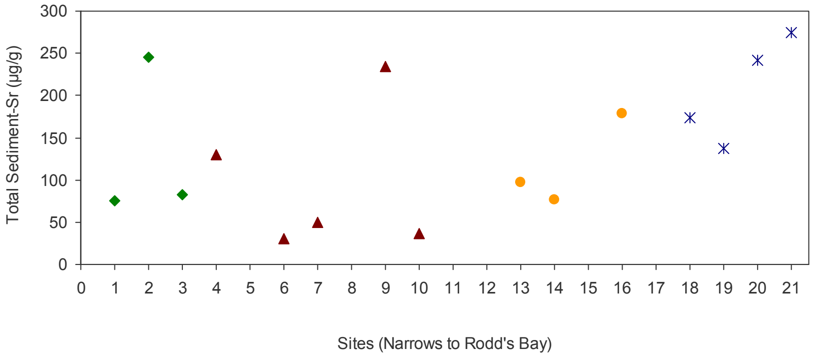

<63 µm Sediment-Sb (µg/g)
0.8
0.6
0.4
0.2
0.0
ANZECC/ARMCANZ ISQG-low value = 2 µg/g
ANZECC/ARMCANZ ISQG-high value =25 µg/g
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

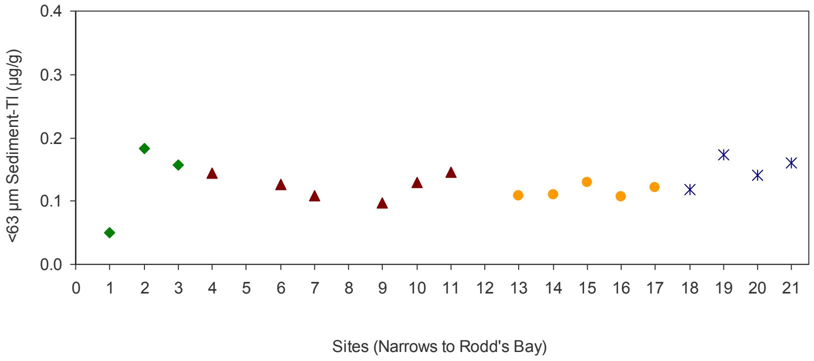

Total Sediment-Sb (µg/g)
0.8
0.6
0.4
0.2
0.0
ANZECC/ARMCANZ ISQG-low value = 2 µg/g
ANZECC/ARMCANZ ISQG-high value =25 µg/g
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

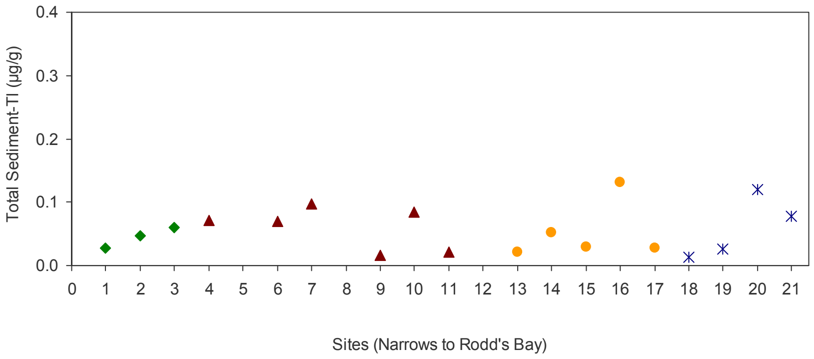

<63 µm Sediment-Se (µg/g)
1.0
0.8
0.6
0.4
0.2
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

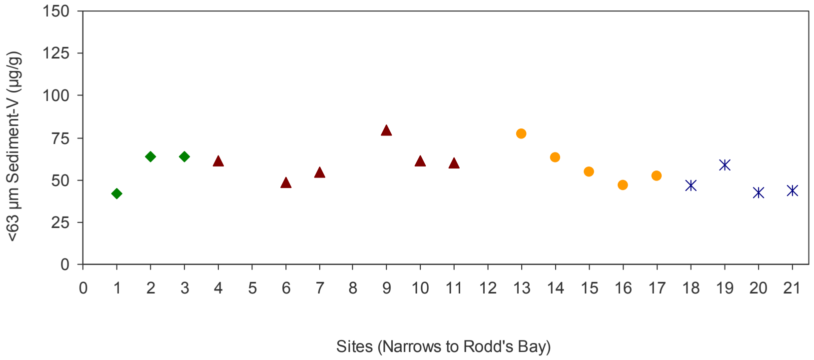

Total Sediment-Se (µg/g)
1.0
0.8
0.6
0.4
0.2
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

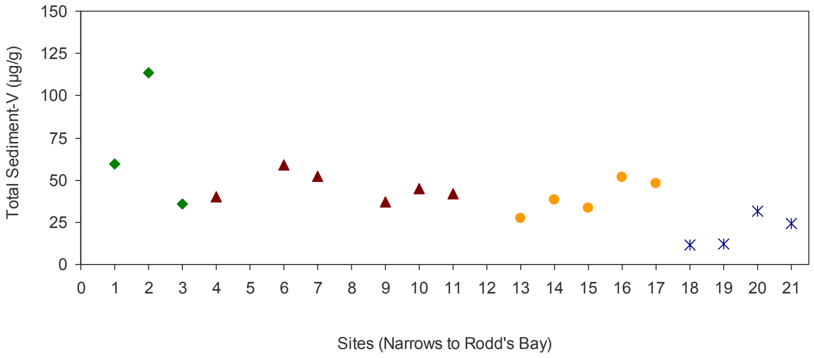

<63 µm Sediment-Sr (µg/g)
300
250
200
150
100
50
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

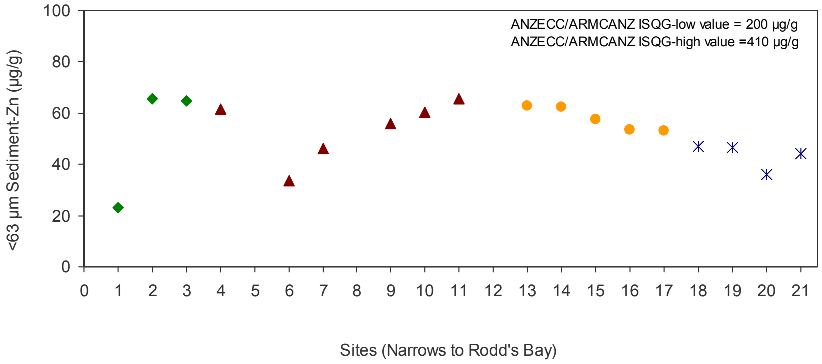

Total Sediment-Sr (µg/g)
300
250
200
150
100
50
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

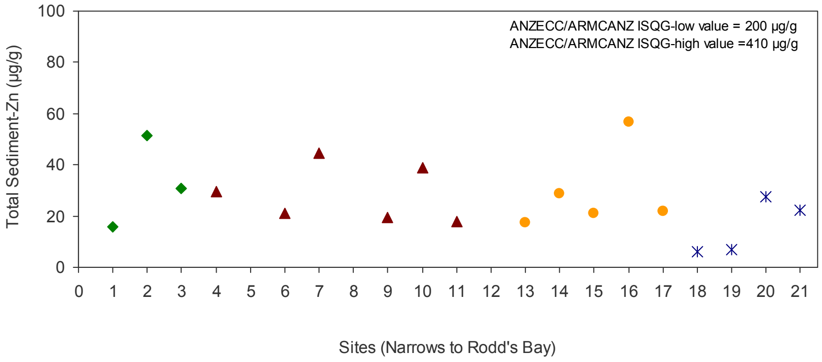

<63 µm Sediment-Tl (µg/g)
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)


Total Sediment-Tl (µg/g)
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)


<63 µm Sediment-V (µg/g)
150
125
100
75
50
25
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)


Total Sediment-V (µg/g)
150
125
100
75
50
25
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)


<63 µm Sediment-Zn (µg/g)
ANZECC/ARMCANZ ISQG-low value = 200 µg/g
ANZECC/ARMCANZ ISQG-high value =410 µg/g
100
80
60
40
20
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)


Total Sediment-Zn (µg/g)
ANZECC/ARMCANZ ISQG-low value = 200 µg/g
ANZECC/ARMCANZ ISQG-high value =410 µg/g
100
80
60
40
20
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
Sites (Narrows to Rodd's Bay)

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FOR FURTHER INFORMATION

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