

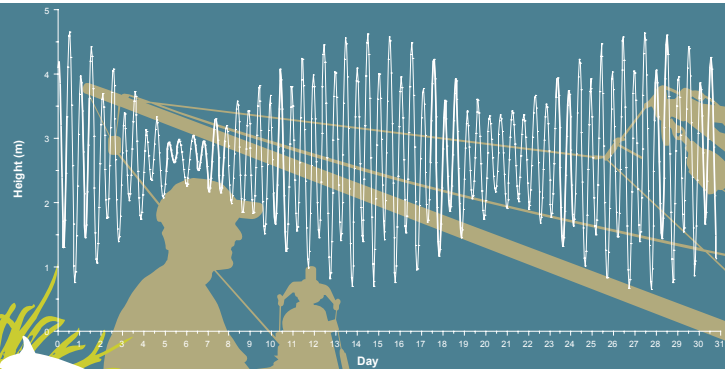


Office of the  
**Environmental Protection Authority**

**MTR 6**

# Background concentrations of selected metals and total suspended solids in the coastal waters of the Kimberley Region

Marine Technical Report Series



June 2012

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Office of the Environmental Protection Authority  
Perth, Western Australia  
Marine Technical Report Series MTR 6  
June 2012

## **Acknowledgments**

The authors acknowledge the generous assistance and advice of Dr Simon Apte, Ms Leigh Hales and Mr Chad Jarolimek of the Centre for Environmental Contaminants Research, CSIRO Land and Water, on ultra-trace metal sampling techniques and sampling equipment.

INPEX Browse Ltd and its joint venture participant Total EP Australia are thanked for allowing the authors to take water samples while on their vessels during an industry sponsored fact finding tour of the Maret Islands.

The authors of this report were employees of the Department of Environment and Conservation at the time of the field surveys. The survey team is grateful for the assistance of the DEC Broome District office and particularly for the support provided by District Manager Mr Alan Byrne.

## **Recommended reference**

McAlpine, K. W., Masini, R.J. Sim, C.V. and Daly T.W. (2005b). *Background concentrations of selected metals and Total Suspended Solids in the coastal waters of the Kimberley Region*. Marine Technical Report 6, Office of the Environmental Protection Authority, Western Australia.

**ISSN 1833-5497 (print) 1833-5500 (pdf)**

**June 2012**

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## Abstract

Several water quality surveys were undertaken in the coastal waters of the Kimberley region from September 2007 to August 2008 to measure typical TSS concentrations and determine background total and dissolved concentrations of aluminium, arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, silver and zinc. This work was undertaken to establish a baseline for the Kimberley from which to assess local and regional changes in water quality in years to come and to ascertain whether the guideline trigger values from ANZECC & ARMCANZ (2000) are relevant to the region.

The results of this study indicate that the coastal waters of the Kimberley region are generally of very high quality. The concentrations of metals across the region were relatively low and met the guideline trigger values from ANZECC and ARMCANZ (2000) for a *very high* level of ecological protection (99% species protection) at the time of sampling.

These results also highlight the need to carefully manage sampling and in-field sample processing to minimise the potential for contamination of samples when analyzing to ultra-trace levels. Direct on-site sampling using syringe filters is recommended for dissolved metal samples. However, if this is not an option then sample processing/filtering should preferably be undertaken in hygienic laboratory conditions within 48 hours of sample collection, or less preferably on the bow of the vessel facing into the breeze using procedures for minimising contamination. If sample processing under hygienic conditions can't be guaranteed then sampling for total metal analyses would be the preferable approach.

The findings of this study, along with other work undertaken on the Western Australian coast suggest that the ANZECC & ARMCANZ (2000) 99% species protection guideline trigger values for metals are appropriate for management of the marine waters in the region, except cobalt where the 95% species protection guideline trigger value is recommended.

# 1. Introduction

A highly dissected topography, including over 2,500 mapped islands, has resulted in a coastline of over 13,000 km in the Kimberley region. The Kimberley coastal zone is the most extensive area of largely un-impacted tropical marine coastline in the world (Halpern et al, 2008). Not only is there very little development along the coast, but the inland catchments of the rivers are also essentially undeveloped. As a consequence the region has very high wilderness, conservation, scientific and cultural value that could be impacted in the longer-term as pressures from natural resource exploitation and other human uses increase (Masini et al, 2009).

The climate of the area is monsoonal with the rains occurring mainly over the summer period. The area is also prone to cyclonic weather which can result in periods of very high, but localized, river flow. Average annual rainfall in the Kimberley coastal regions varies from approximately 800 mm in the west to 1500 mm in the central and east Kimberley.

The geology of the Dampier Peninsula is relatively simple and composed mainly of quaternary sands and silts, however the geology becomes very complex to the east of King Sound. Here the catchment is mainly composed of sandstones and quaternary sediments, but with significant outcrops of basaltic and granitic rock. As a result the coastal topography is very different between the two sub-regions and this is recognized in the Interim Marine Coastal Regionalisation of Australia bioregional boundaries (IMCRA Version 4.0). The coastline of the Canning and King Sound IMCRA bioregions has a relatively gentle topography with shallow sloping offshore bathymetry. On the other hand the coastline of the Kimberley bioregion east of King Sound is relatively elevated and highly dissected with deep gulfs, steep shores and island archipelagos. All three bioregions are characterised by extensive tidal flats, but the composition of the flats may vary with the location. For example, tidal flats in the mouths of rivers are generally muddy with extensive mangrove forest cover, tidal lagoons are generally silty to sandy with isolated clumps of mangroves and offshore tidal flats are generally biogenic in origin, generally formed by calcareous algae, coral reef or a combination of both.

The area experiences the largest tides in Australia, and some of the largest in the world, with spring tides ranging up to 11 m in amplitude. As a result there can be strong tidal currents in nearshore and offshore waters during spring tides and in nearshore environments these can cause significant resuspension of sediment in affected areas. During neap tides currents are significantly less and turbidity levels are relatively low.

The relative remoteness of the Kimberley coast, the harsh climate and the rugged terrain are the main reasons why the area remains largely undeveloped, but have also contributed to a lack of research and understanding of the marine environment. Recent interest by the oil and gas industry to develop nearby oil and gas fields (eg. Browse Basin), and find suitable sites along the Kimberley coast to build liquefied natural gas processing plants, has triggered broad concern at an apparent ad hoc approach to development of the Kimberley coastline. The Browse Basin alone is estimated to contain 35 trillion cubic feet of gas and 600 million barrels of condensate. As a result the State and Commonwealth Governments have agreed to jointly undertake a strategic assessment of the area to identify a suitable site for a single liquefied natural gas processing precinct.

Studies for the strategic assessment have largely been focused on broad-scale benthic habitat mapping of selected sites. However, later in the environmental impact assessment process it will be necessary to consider potential impacts from waste discharges to the marine environment and the monitoring and management strategies required to minimise any impacts. It is expected that any proposed developments will be considered within the context of the environmental quality management framework for implementing the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ, 2000) in Western Australia (SWQMS, 2004). Application of this framework requires identification of environmental values that are to be protected in the area and the environmental quality objectives that must be achieved for the values to be protected. These values and objectives represent the community's long-term desires, or goals, for the marine waters and should recognise and accommodate the range of uses to which the waters are subject. Environmental quality criteria are performance benchmarks used to determine whether the environmental quality objectives have been achieved and development of these is based on the guidelines and approaches recommended in ANZECC & ARMCANZ (2000) and requires an understanding of natural background water quality.

Metals occur naturally in seawater at very low concentrations, but actual concentrations can be influenced by surrounding geology and anthropogenic sources. Elevated concentrations are generally caused by waste discharges or deposits and if levels are sufficiently high they can be toxic, or bioaccumulate/bioconcentrate through the food chain. Concentrations of metals in sediments and water can therefore be an indicator of the health of the surrounding environment. Environmental water quality criteria that represent the limit of acceptable change in metal concentrations are useful tools for maintaining healthy water quality. Metal concentrations in seawater can be made up of both dissolved and particulate fractions, with the dissolved fraction considered to be better correlated to bioavailability of the metal. The particulate or mineralised fractions are generally considered to include metals that are unavailable for biological uptake and are therefore unlikely to affect the health of marine organisms.

Given the lack of information on natural background concentrations of most constituents in Kimberley seawater, staff from the Department of Environment and Conservation collected seawater samples on an opportunistic basis during benthic habitat field surveys so they could be analysed for ultra-trace concentrations of selected metals and give some understanding of baseline conditions. To reliably sample and analyse metal concentrations in seawater at actual background concentrations is a very difficult, time consuming and expensive exercise that most proponents and environmental consultants will not undertake. The CSIRO Centre for Environmental Contaminants Research laboratory at Lucas Heights, New South Wales, is the only laboratory with this demonstrated analytical capability in Australia and undertook the analyses reported here. Analyses were undertaken for both total (includes particulate and mineralised fractions) and total dissolved concentrations.

Seawater samples were also collected during these field trips for the measurement of total suspended solids (TSS) concentrations to better understand typical background conditions across the Kimberley. TSS is a measure of the amount of suspended particles in the water column and could influence the concentration of some metals if the mineral component of the suspended sediment was high. TSS concentration is also a key determinant of water clarity and is largely influenced by riverine discharges, current strength and wave height.

The two key objectives of the baseline water quality survey were:

- to determine whether the national water quality guidelines (ANZECC & ARMCANZ, 2000) for the selected metals are suitable for application to the coastal waters of the Kimberley region; and
- to establish natural baseline concentrations of the selected metals from which human induced changes or trends in water quality can be assessed.

A secondary objective of the project was to describe the range of TSS concentrations typically found under normal conditions in Kimberley offshore marine waters.

Similar baseline water quality surveys have been undertaken to establish natural background concentrations of a range of metals in the coastal waters of the Pilbara (Wenziker *et al.*, 2006), the waters of Jurien Bay Marine Park on the mid-west coast (McAlpine *et al.*, 2005b) and Perth metropolitan coastal waters (McAlpine *et al.*, 2005a).

## **2. Methods**

### **2.1 Field sampling**

Seawater samples for metal analyses were collected over three different field trips. The first set of samples were collected 14 – 16 September 2007 from around the Maret Islands and Berthier Island in the mid Kimberley region. The samples were collected from an aluminium punt and with the assistance of INPEX during a visit to a site being contemplated for an LNG processing facility. The second set of samples were collected 3 – 6 November 2007 during an initial benthic habitat survey of a number of potential LNG processing facility sites in the West Kimberley. Sampling was undertaken from the Fisheries patrol vessel *PV Walcott* or from the plastic tender to the *PV Walcott*. Sampling for the third set of samples from the North Kimberley was undertaken 28 August – 2 September 2008 from the Sentosa charter vessel *Equalizer* or its 4.2 m aluminium tender. All samples were taken from approximately 0.5 m below the surface of the water from the bow of the vessel while it was slowly moving forward into the wind to avoid contamination from the boat itself.

Samples for total suspended solids (TSS) concentrations were taken over the same three field trips plus an additional field trip on 1 – 3 April 2008 on the western side of the Dampier Peninsula in the south west Kimberley. Sampling during the additional field trip was undertaken on the Sentosa charter vessel *Equalizer* or its 4.2 metre aluminium tender. Surface samples were taken at all sites surveyed for TSS, while bottom waters were only sampled during the West Kimberley survey, and not at all sites. Surface water samples were collected using a bucket and bottom waters were collected using a Niskin bottle. A recorded volume was sub-sampled from each surface and bottom sample and passed through a 47 mm diameter, 1.2 µm, GFC glass fibre filter paper using a filter tower and hand vacuum pump. The filter papers were pre-weighed by the analytical laboratory before the trip. After filtering, distilled water was drawn through the pre-weighed TSS filters to remove salts. The filter papers were removed from the filter tower using plastic forceps, folded into quarters then wrapped in aluminium foil before being placed into seed envelopes and then placed in the freezer for storage. The water volume, date and site name were recorded in the field log and on the seed envelopes.

The sampling sites for metals and TSS extended from south west of Broome to near Kalumburu in the north east Kimberley (Figure 1 and Table 1), providing a reasonable coverage of the Canning and Kimberley IMCRA bioregions which include



the majority of the western and northern Kimberley coastal zone. Sampling included inshore and offshore coastal waters and both spring and neap tidal cycles.

Sampling was conducted during daylight hours and full details of the water sampling procedures are given in Appendix A.

## **2.2 Sample analysis**

The focus of the program was on determining the natural concentrations of metals in Kimberley seawater, particularly those that are known to be potential toxicants and are elevated by anthropogenic activity. The suite of metals analysed included aluminium, arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, silver and zinc. Total dissolved metal concentrations were measured at every site and total metal concentrations were measured at selected sites for comparison. The exception was mercury where total mercury was measured at most sites and total dissolved mercury was only measured at a few selected sites. Analyses for total dissolved concentrations were performed on samples filtered through a 0.45 µm filter.

The measurement of both total and total dissolved metal concentrations at the ultra-trace levels found in seawater presents a challenge both with sampling and sample handling to prevent accidental contamination. To minimize the risk of contamination during sampling a length of teflon coated PVC tubing was used to hold the sample bottle well away from the boat and approximately 0.5 m under the water surface (Appendix A). The additional handling, and sample contact with the filtering equipment required for dissolved metal analyses, greatly increases the risk of contamination of these samples. Ideally, samples for dissolved metal analysis would be transported to a laboratory with a clean room within 24 hours of sampling so they can be filtered prior to any potential metal transformations occurring in the sample, using equipment that does not leach metal contaminants and that has been specially cleaned to ensure no metal contamination from the equipment. Given the remoteness of the coastal waters of the Kimberley this was not an available option. Instead, samples had to be filtered on the vessel within 24 hours of collection. This required the CSIRO Centre for Advanced Analytical Chemistry's Environmental Contaminants Research Laboratory to freight specially cleaned and packed filtering equipment with the sample bottles for use on the boat. For the first sampling program in September 2007 syringe filters were used to directly filter the sample as it was taken. Unfortunately the syringes and filters were so small that the time taken to collect one litre of sample was not practical and this method was not used again. For the November 2007 and August 2008 surveys the laboratory freighted out specially prepared filter towers. In November 2007 these were used to filter the samples on the front deck of the vessel as it faced into the wind. For the August 2008 survey the samples were filtered inside a clear plastic bag in the shelter of the vessel fly-bridge. Filtering during the surveys was often undertaken while the vessel was underway because of the distances that needed to be covered and the time constraints.

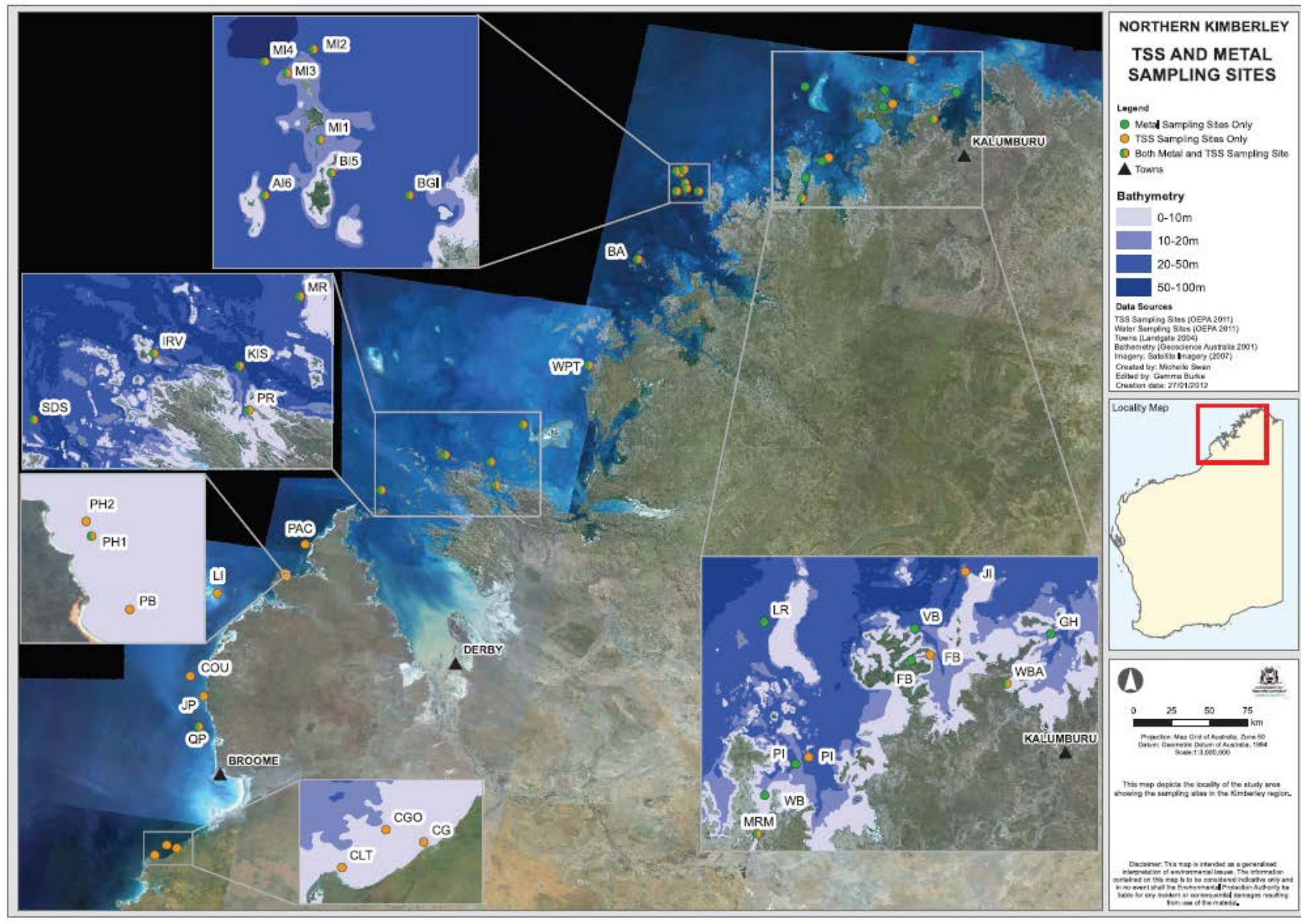


Figure 1. Locality map of the study area showing the sampling sites, Kimberly region (Site codes described in Table 1)

**Table 1: Sampling dates, locations and tide status**

| Date  | Site name                   | Site Code | Latitude     | Longitude     | Approx depth (m) | Estimated tide status |
|---|-----------------------------|-----------|--------------|---------------|------------------|-----------------------|
| <b><i>Maret Islands Survey</i></b>          |                             |           |              |               |                  |                       |
| 14 Sep 07                                   | North-east Maret Islands    | MI2       | 14° 22.71' S | 124° 59.03' E | 41               | Spring, Ebb           |
| 15 Sep 07                                   | South Maret Islands         | MI1       | 14° 27.34' S | 124° 59.38' E | 30               | Spring, Ebb           |
| 15 Sep 07                                   | East Berthier Island        | BI5       | 14° 29.30' S | 125° 00.25' E | 30               | Spring, Ebb           |
| 15 Sep 07                                   | North-east Albert Islands   | AI6       | 14° 30.71' S | 124° 56.15' E | 30               | Spring, Flood         |
| 16 Sep 07                                   | Brunei Bay, Maret Islands   | MI3       | 14° 24.26' S | 124° 57.77' E | 9.4              | Spring, Low           |
| 16 Sep 07                                   | North-west Maret Islands    | MI4       | 14° 23.45' S | 124° 56.41' E | 51               | Spring Flood          |
| <b><i>West Kimberley Survey</i></b>         |                             |           |              |               |                  |                       |
| 3 Nov 07                                    | Wilson Point                | WPT       | 15° 32.10' S | 124° 25.10' E | 20               | Neap, Ebb             |
| 3 Nov 07                                    | Mongomery Reef              | MR        | 15° 53.28' S | 124° 01.77' E | 30               | Neap, Flood           |
| 3 Nov 07                                    | Koolan Island South         | KIS       | 16° 06.70' S | 123° 50.34' E | 20               | Neap, Flood           |
| 3 Nov 07                                    | Patch Reef North            | PR        | 16° 15.22' S | 123° 52.24' E | 10               | Neap, Ebb             |
| 4 Nov 07                                    | Irvine Island East (metals) | IRV       | 16° 03.92' S | 123° 33.80' E | 30               | Neap, Flood           |
| 4 Nov 07                                    | Irvine Island East (TSS)    | IRV       | 16° 04.30' S | 123° 33.92' E | 17               | Neap, Flood           |
| 5 Nov 07                                    | Sunday Strait               | SDS       | 16° 16.90' S | 123° 11.15' E | 50               | Neap, Ebb             |
| 5 Nov 07                                    | Perpendicular Head          | PH1       | 16° 46.40' S | 122° 37.28' E | 7                | Neap, Flood           |
| 6 Nov 07                                    | Coulomb Point               | COU       | 17° 22.57' S | 122° 03.80' E | 15               | Neap, Ebb             |
| 6 Nov 07                                    | James Price Point           | JP        | 17° 29.86' S | 122° 08.30' E | 5                | Neap, Ebb             |
| 6 Nov 07                                    | Quondong Point              | QP        | 17° 40.99' S | 122° 06.70' E | 9                | Neap, Low             |
| <b><i>West Dampier Peninsula Survey</i></b> |                             |           |              |               |                  |                       |
| 1 Apr 08                                    | Cape Latouche Treville      | CLT       | 18° 26.65' S | 121° 50.98' E | 6                | Neap, Ebb             |
| 1 Apr 08                                    | Cape Gourdon Outer          | CGO       | 18° 22.79' S | 121° 55.03' E | 14.8             | Neap, Flood           |
| 1 Apr 08                                    | Cape Gourdon                | CG        | 18° 24.10' S | 121° 58.68' E | 8.7              | Neap, Flood           |
| 2 Apr 08                                    | Perpendicular Head          | PH2       | 16° 46.25' S | 122° 37.35' E | 9                | Neap, Flood           |
| 2 Apr 08                                    | Packer Island               | PAC       | 16° 36.30' S | 122° 44.32' E | 15               | Neap, Ebb             |
| 2 Apr 08                                    | Pender Bay                  | PB        | 16° 47.32' S | 122° 38.03' E | 5                | Neap, Ebb             |
| 3 Apr 08                                    | Lascepedes Island           | LI        | 16° 53.36' S | 122° 12.91' E | 7                | Neap, Flood           |

**Table 1 Sampling dates, locations and tide status (continued)**

| <b>North Kimberley Survey</b> |                         |     |              |               |     |               |
|-------------------------------|-------------------------|-----|--------------|---------------|-----|---------------|
| 28 Aug 08                     | Mitchell River Mouth    | MRM | 14° 32.95' S | 125° 40.72' E | 3.0 | Neap, Ebb     |
| 28 Aug 08                     | Walmesly Bay            | WB  | 14° 25.80' S | 125° 42.16' E | 14  | Neap, Low     |
| 28 Aug 08                     | Parry Island (metals)   | PI  | 14° 19.91' S | 125° 47.95' E | 26  | Neap, Low     |
| 28 Aug 08                     | Parry Island (TSS)      | PI  | 14° 18.86' S | 125° 50.13' E | 24  | Neap, Low     |
| 29 Aug 08                     | Jones Island            | JI  | 13° 43.81' S | 126° 19.86' E | 20  | Neap, Flood   |
| 29 Aug 08                     | West Bay (TSS)          | WBA | 14° 04.77' S | 126° 27.67' E | 6   | Neap, Flood   |
| 30 Aug 08                     | West Bay (metals)       | WBA | 14° 04.31' S | 126° 29.55' E | 6   | Spring, Flood |
| 30 Aug 08                     | Geranium Harbour        | GH  | 13° 55.47' S | 126° 35.83' E | 23  | Spring, Flood |
| 31 Aug 08                     | Freshwater Bay (TSS)    | FB  | 13° 59.30' S | 126° 12.91' E | 15  | Spring, Flood |
| 31 Aug 08                     | Freshwater Bay (metals) | FB  | 14° 00.42' S | 126° 09.68' E | 10  | Spring, High  |
| 31 Aug 08                     | Vansittart Bay          | VB  | 13° 54.49' S | 126° 10.28' E | 33  | Spring, Ebb   |
| 31 Aug 08                     | Long Reef               | LR  | 13° 53.27' S | 125° 42.09' E | 41  | Spring, Low   |
| 2 Sep 08                      | Bigge Island (metals)   | BGI | 14° 28.80' S | 125° 05.59' E | 37  | Spring, Flood |
| 2 Sep 08                      | Bigge Island (TSS)      | BGI | 14° 30.39' S | 125° 04.30' E | 37  | Spring, Flood |
| 2 Sep 08                      | Bonaparte Archipelago   | BA  | 14° 54.53' S | 124° 42.56' E | 37  | Spring, Ebb   |

\* Datum is WGS84.

All samples were kept refrigerated at or below 5°C and transported to the analytical laboratory on ice in an esky upon return to port. Sample transport to the laboratory was overnight, except for the August 2008 batch which the courier took four days to deliver. All samples were processed and acidified immediately on arrival at the CSIRO laboratory.

The CSIRO Centre for Advanced Analytical Chemistry undertook all of the metal analyses. The CSIRO laboratory is a NATA (National Association of Testing Authorities) registered laboratory, however, it is not NATA registered for the ultra-trace level metal analyses performed for this study. Strict QA/QC procedures were therefore adhered to and the results reported for all analyses. The analytical limits of reporting for the metal analyses were the lowest available in Australia. The QA/QC procedures comprised:

- Field blanks;
- Field duplicates;
- Analytical blanks;
- Spike recoveries; and
- Analysis of certified reference seawaters.

A sub-set of the sites sampled for metal analyses, plus some additional sites along the west side of the Dampier Peninsula, were also sampled to determine TSS concentrations. Samples were filtered on the deck of the vessel immediately after

collection and then the filter papers frozen for transport to the analytical laboratory. TSS concentrations for the Maret Islands survey were analysed by the CSIRO Centre for Advanced Analytical Chemistry. For the other three surveys (North and West Kimberley surveys and the West Dampier Peninsula survey) the Marine and Fresh Water Research Laboratory at Murdoch University analysed TSS concentrations and the organic component of the TSS (% loss on ignition). Unfortunately the TSS samples from the West Dampier Peninsula survey were destroyed in the laboratory during the process of measuring % loss on ignition and therefore there are no % loss on ignition data for these samples. Both analytical laboratories were NATA accredited for the TSS analyses.

Methods and procedures for preparing sample containers, collection and handling of samples, sample filtration and analysis of each selected contaminant are described more fully in Appendix A.

### **2.3 Statistical analysis**

Total metal concentration in seawater is composed of both dissolved and particulate fractions. The particulate or mineralised fractions may be related to the concentration of suspended sediments in the water column. Therefore, for each metal where there were sufficient samples with measureable total metal concentrations, correlation statistics were calculated between TSS concentrations and total metal concentrations to determine whether TSS concentration was related to any of the total metal concentrations. Both  $r$  and  $r^2$  values were calculated using Microsoft Office Excel 2007.

The *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ, 2000) recommends that the 95<sup>th</sup> percentile of concentration values at the test site should be less than the default guidelines for the toxicant. For the purposes of determining whether any of the metals measured during these surveys of the Kimberley marine waters naturally exceeded the default guidelines from ANZECC & ARMCANZ (2000), the 95<sup>th</sup> percentile of the pooled data for each metal was calculated for comparison against the guideline. When calculating the 95<sup>th</sup> percentiles, if the analytical results were reported as below the limit of reporting (LOR), these data were replaced with the LOR (e.g. <0.006 µg/L became 0.006 µg/L). Means were also calculated in the same way.

Statistics such as 95<sup>th</sup> percentiles or means can be significantly biased by any outliers in the data set that don't appear to represent typical conditions. Outliers in the concentrations data sets may result from aberrant sampling technique, contaminated samples, laboratory error or they may be real, but unusual, data points. In an attempt to minimise the influence of aberrant data on the estimated 95<sup>th</sup> percentile and mean concentrations for each metal, any extreme data outliers (representing extremely high concentrations) were removed from the data sets. Extreme outliers were identified using 2D Box Plot statistics in STATISTICA Version 9.0 (Series 0509 for Windows) and an outlier coefficient of 3.0. Outlier concentrations were not identified for those metals with a large number of results below the LOR because the identification of outliers is dependent on knowing the distribution of actual concentrations.

### **3. Results**

#### **3.1 General conditions**

The weather and sea conditions at the time of sampling were as follows:

##### ***Maret Islands***

- Sampling conducted over spring phase of tidal cycle;
- 14 September 2007: light winds from the SW, fine and sunny with a low westerly swell of ~0.3 m;
- 15 September 2007: 15 – 18 knot south-westerly wind, fine and sunny with less than 10% cloud cover, low westerly swell of <0.3 m; and
- 16 September 2007: 10 knot south-westerly wind, fine and sunny with no cloud cover, swell <0.3 m. Significant smoke haze and odour from bushfires on the adjacent Kimberley mainland.

##### ***West Kimberley survey***

- Sampling conducted over neap phase of tidal cycle;
- 3 November 2007: winds light and variable in the morning becoming light westerly late morning and freshening to 10 – 15 knot westerly by mid afternoon, fine and sunny conditions with ~10% cloud cover, no swell;
- 4 November 2007: winds light and variable, fine and sunny with ~10% cloud cover, no swell;
- 5 November 2007: winds southerly at 10 – 15 knots in the morning turning westerly at 20 knots in the afternoon, fine and sunny with ~10% cloud cover, no swell;
- 6 November 2007: winds from the south-west at 20 – 25 knots, fine and sunny with ~ 10% cloud cover, no swell.

##### ***West Dampier Peninsula survey***

- Sampling conducted between the neap and spring phases of the tidal cycle;
- 1 April 2008: winds calm early and rising to 5 – 10 knots from the north-east mid morning, fine and partly cloudy, no swell;
- 2 April 2008: 0 – 5 knot south-easterly wind in the morning rising to 5 – 8 knots from the south-south-west in the afternoon, fine and partly cloudy, no swell; and
- 3 April 2008: 5 - 8 knot south-westerly wind in the morning, fine and sunny, no swell.

##### ***North Kimberley survey***

- Sampling conducted over period bridging between neap spring phase tides. Tides were still neap on 28 August 2008, but typical of spring tides by 31 August 2009;
- 28 August 2008: light (0 – 5 knot) northerly winds in the morning increasing to a 10 knot north-westerly in the afternoon, sunny conditions, no swell;
- 29 August 2008: no wind, sunny conditions and no swell;
- 30 August 2008: light and variable winds in the morning, sunny and no swell;

- 31 August 2008: light (0 – 5 knots) north-easterly winds in the morning increasing to 10 knots from the north in late afternoon, sunny conditions, no swell;
- 2 September 2008: 5 – 10 knot southerly winds, sunny conditions, no swell.

### 3.2 Total suspended solids data

The results for the TSS and % loss on ignition analyses are presented in Table 2. TSS concentrations ranged from 0.8 to 13 mg/L, but the majority of samples were less than 2 mg/L. Most of the high TSS concentrations (9 – 12 mg/L) were from samples taken from turbid water 'boils' associated with the very strong tidal currents often experienced in the Kimberley during spring tides. The highest concentration of 13 mg/L was measured at Jones Island during neap tides, however there were strong currents in the area as the tidal flow was forced around the northern side of the island and associated reefs. The lowest concentrations were measured in samples that were collected during neap tides, although the windy conditions prevailing when sampling the PH1, COU, JP and QP sites appears to have slightly elevated the surface TSS concentrations even though the tides were neaps.

**Table 2: Total suspended solids concentrations in coastal waters of the Kimberley Region, September 2007 to August 2008** (*S* = surface; *B* = bottom)

| Site Code                           | Depth | TSS (mg/L) | % Loss (550° C) |
|-------------------------------------|-------|------------|-----------------|
| <b><i>Maret Islands Survey</i></b>  |       |            |                 |
| MI1                                 | S     | 9          |                 |
| MI2                                 | S     | 2          |                 |
| MI3                                 | S     | 3          |                 |
| MI4                                 | S     | 4          |                 |
| BI5                                 | S     | 4          |                 |
| AI6                                 | S     | 9          |                 |
| Limit of Reporting                  |       |            |                 |
| <b><i>West Kimberley Survey</i></b> |       |            |                 |
| WPT                                 | S     | 2          | 33              |
| WPT                                 | B     | 2          | 31              |
| WPT                                 | S     | 2          | 33              |
| MR                                  | S     | 2          | 28              |
| MR                                  | B     | 3          | 23              |
| KIS                                 | B     | 2          | 25              |
| KIS                                 | S     | 2          | 32              |
| PR                                  | B     | 2          | 27              |
| PR                                  | S     | 2          | 28              |
| IRV                                 | S     | 2          | 28              |
| IRV                                 | B     | 2          | 24              |
| SDS                                 | S     | 1          | 30              |
| SDS                                 | B     | 2          | 27              |
| PH1                                 | S     | 6          | 28              |
| PH1                                 | B     | <1         | 49              |
| COU                                 | S     | 5          | 33              |
| JP                                  | S     | 3          | 37              |
| QP                                  | S     | 2          | 43              |
| Limit of Reporting                  |       | <1         |                 |

**Table 2 continued**

| <b>West Dampier Peninsula Survey</b> |   |      |  |    |
|--------------------------------------|---|------|--|----|
| CLT                                  | S | 4.1  |  |    |
| CGO                                  | S | 0.9  |  |    |
| CG                                   | S | 1.2  |  |    |
| PH2                                  | S | 1.2  |  |    |
| PAC                                  | S | 0.8  |  |    |
| PB                                   | S | 1.3  |  |    |
| LI                                   | S | 2.3  |  |    |
| Limit of Reporting                   |   | <0.5 |  |    |
| <b>North Kimberley Survey</b>        |   |      |  |    |
| MRM                                  | S | 1.9  |  | 33 |
| PI                                   | S | 0.8  |  | 46 |
| JI                                   | S | 13   |  | 26 |
| WBA                                  | S | 1.7  |  | 48 |
| FB                                   | S | 7.0  |  | 29 |
| BGI                                  | S | 12   |  | 28 |
| BA                                   | S | 3.1  |  | 31 |
| Limit of Reporting                   |   | <0.5 |  |    |

Measurements of the organic component of the TSS (loss on ignition at 550° C) were only obtained for the West Kimberley and North Kimberley surveys. The organic fraction ranged from 23% to 49% of TSS concentration in the West Kimberley survey and 26% to 48% in the North Kimberley survey. The median across both surveys is 31% and the mean is 32%.

### 3.3 Trace metals data

The analytical results for the total metals and total dissolved metals analyses are presented in Table 3 and the associated quality control data are in Appendix B. Correlation statistics comparing TSS concentrations with total metal concentrations are presented in Table 4.

The analytical limit of reporting (LOR) for each metal was less than the guideline trigger level for 99% species protection (ANZECC & ARMCANZ, 2000), except cobalt. The LOR for cobalt in the West Kimberley survey was 11 ng/L compared to a trigger of 5 ng/L.

The quality control data for the Maret Islands and West Kimberley surveys are satisfactory, suggesting significant contamination of samples did not occur. However, comparison of the field blank results for total metals samples with the field blank results for total dissolved metal samples in the Maret Islands survey suggests possible low level contamination by copper, cobalt and zinc through the filtering process which may have slightly positively biased the reported total dissolved concentrations for these metals. The analysed copper concentration in the Quondong Point (QP) sample (350 ng/L) is significantly higher than any other samples from that survey and may indicate contamination of the sample. This is the only sample of the three surveys that exceeded the 99% species protection guideline for copper of 300 ng/L (ANZECC & ARMCANZ, 2000).

The quality control data for the North Kimberley survey are less satisfactory and suggest significant contamination of total dissolved metal samples may have occurred for cobalt, copper, nickel, lead and zinc and for total lead and zinc. Nevertheless, all reported concentrations for this survey are very low and, with the



exception of cobalt, do not exceed the 99% species protection guideline trigger levels (ANZECC & ARMCANZ, 2000) and are therefore consistent with a high level of ecological protection (see Table 5 for trigger values). Almost all measurable concentrations of cobalt exceeded the 99% species protection guideline of 0.005 µg/L (ANZECC & ARMCANZ, 2000) which is consistent with the findings of a similar survey conducted in the marine waters of the Perth metropolitan region (McAlpine *et al*, 2005).

The analytical LOR for these ultra-trace metal analyses is dependent on the QA/QC data generated for each batch of samples and is therefore variable between each survey. The concentrations of some metals are below the analytical limit of reporting for some surveys (eg. lead at Maret Islands, cobalt in West Kimberley survey and silver and chromium in the north Kimberley survey), but all metals were at measurable concentrations in at least one survey.

All sites sampled in all three surveys can be described as unimpacted by anthropogenic development and are effectively of 'pristine' quality. The results for each metal are discussed below.

### Aluminium (Al)

The range of total aluminium concentrations was relatively consistent across both surveys where total Al was measured, however, concentrations were variable between sites, ranging from 13,000 ng/L (Maret Island site MI2) to 140,000 ng/L (site BI at Bigge Island). Total suspended solid (TSS) values were also measured at a number of the same sites and found to be highly correlated to total Al concentration ( $r^2 = 0.87$ ,  $n = 8$ ) (Table 4). This suggests that the majority of the aluminium is likely to be mineralised in the clay and silt components of the suspended sediment.

Dissolved Al concentrations were significantly less than total Al concentrations at all sites except WBA and much less variable. The dissolved Al concentration for WBA was almost twice the total Al concentration, which suggests that the sample may have become contaminated. Dissolved Al concentration is not correlated with total Al concentration. In the Maret Islands and West Kimberley surveys dissolved Al concentrations were generally below the LOR. In the North Kimberley survey dissolved aluminium concentrations at the four sites more distant from major river mouths (LR, VB, BI and BA) were similar to the concentrations for Maret Islands and the West Kimberley survey. At the remaining sites dissolved Al concentrations significantly exceeded the LOR.

**Table 4: Correlation statistics between TSS concentration and total metal concentration**

| <b>Metal</b> | <b>n</b> | <b>r</b> | <b>r<sup>2</sup></b> |
|--------------|----------|----------|----------------------|
| Aluminium    | 8        | 0.933    | 0.870                |
| Arsenic      | 8        | 0.156    | 0.024                |
| Cadmium      | 8        | 0.707    | 0.500                |
| Cobalt       | 8        | 0.748    | 0.560                |
| Chromium     | 6        | 0.732    | 0.536                |
| Copper       | 8        | 0.467    | 0.218                |
| Mercury      | 12       | 0.143    | 0.020                |
| Nickel       | 8        | 0.878    | 0.771                |
| Zinc         | 8        | 0.893    | 0.798                |

**Table 3: Total and dissolved metal concentrations in coastal waters of the Kimberley region, September 2007 to August 2008**

| Site                          | Al    |       | As   |      | Ag   |      | Cd   |      | Co   |      | Cr   |      | Cu   |      | Hg   |      | Ni   |      | Pb   |      | Zn   |      |
|-------------------------------|-------|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
|                               | Dis.  | Tot.  | Dis. | Tot. | Dis. | Tot. | Dis. | Tot. | Dis. | Tot. | Dis. | Tot. | Dis. | Tot. | Dis. | Tot. | Dis. | Tot. | Dis. | Tot. | Dis. | Tot. |
|                               | ng/L  | ng/L  | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L | ng/L |
| <b>Maret Islands Survey</b>   |       |       |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| MI1                           |       | 78000 |      | 1540 |      | 1.1  |      | 6.7  |      | 68   |      | 490  |      | 123  |      | 0.1  |      | 249  |      | 20   |      | 170  |
| MI2                           |       | 13000 |      | 1510 |      | 2.8  |      | 6.6  |      | 36   |      | 190  |      | 98   |      | 0.1  |      | 185  |      | <20  |      | 48   |
| MI3                           | <1000 | 33000 | 1510 | 1520 | 2.6  | 0.7  | 5.6  | 6.6  | 17   | 44   | 180  | 310  | 86   | 97   | 0.1  | 0.1  | 161  | 190  | <20  | <20  | 106  | 75   |
| MI4                           | <1000 | 56000 | 1510 | 1550 | 1.2  | 0.6  | 5.9  | 7.7  | 12   | 70   | 150  | 420  | 83   | 131  | ≤0.1 | 0.2  | 160  | 234  | <20  | <20  | 123  | 126  |
| BI5                           |       | 51000 |      | 1520 |      | <0.4 |      | 6.8  |      | 54   |      | 330  |      | 123  |      | 0.2  |      | 233  |      | <20  |      | 91   |
| AI6                           | <1000 | 67000 | 1480 | 1510 | 1.8  | 1.8  | 6.4  | 6.8  | 36   | 77   | 380  | 370  | 100  | 151  | 0.2  | 0.1  | 175  | 229  | <20  | 28   | 98   | 234  |
| Limit of reporting            | 1000  | 1000  | 20   | 20   | 0.4  | 0.4  | 0.4  | 0.4  | 5    | 5    | 70   | 70   | 1    | 1    | 0.1  | 0.1  | 9    | 9    | 20   | 20   | 9    | 9    |
| <b>West Kimberley Survey</b>  |       |       |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| WPT                           | <2000 |       | 1500 |      | 1.1  |      | 4.9  |      | <11  |      | <90  |      | 156  |      |      | 0.1  | 208  |      | 27   |      | 199  |      |
| MR                            | <2000 |       | 1610 |      | 2.4  |      | 5.3  |      | <11  |      | <90  |      | 193  |      |      | 0.1  | 217  |      | 16   |      | 513  |      |
| KIS                           | 5000  |       | 1580 |      | 0.8  |      | 6.7  |      | <11  |      | <90  |      | 146  |      |      | <0.1 | 210  |      | <14  |      | 193  |      |
| PR                            | <2000 |       | 1520 |      | 1.9  |      | 5.9  |      | <11  |      | 150  |      | 123  |      |      | <0.1 | 193  |      | <14  |      | 210  |      |
| IRV                           | <2000 |       | 1560 |      | 0.3  |      | 5.2  |      | <11  |      | 180  |      | 121  |      |      | <0.1 | 186  |      | 16   |      | 234  |      |
| SDS                           | <2000 |       | 1540 |      | 5.1  |      | 5.2  |      | <11  |      | <90  |      | 95   |      |      | 0.1  | 168  |      | <14  |      | 431  |      |
| PH1                           | <2000 |       | 1480 |      | 2.3  |      | 2.5  |      | <11  |      | <90  |      | 96   |      |      | 0.1  | 160  |      | <14  |      | 638  |      |
| QP                            | <2000 |       | 1100 |      | 2.9  |      | 2.6  |      | <11  |      | <90  |      | 350  |      |      | 0.1  | 171  |      | <14  |      | 342  |      |
| Limit of reporting            | 2000  |       | 30   |      | 0.4  |      | 0.6  |      | 11   |      | 90   |      | 8    |      |      | 0.1  | 6    |      | 14   |      | 36   |      |
| <b>North Kimberley Survey</b> |       |       |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| MRM                           | 13000 |       | 1000 |      | <2   |      | 8    |      | 24   |      | <500 |      | 170  |      |      | 0.4  | 265  |      | 141  |      | 3440 |      |
| WB                            | 3000  | 17000 | 1100 | 1100 | <2   | <2   | 7    | 9    | <3   | 24   | <500 | <500 | 52   | 136  |      | 0.2  | 23   | 212  | 251  | 196  | 102  | 52   |
| PI                            | 3000  |       | 1300 |      | <2   |      | 6    |      | 9    |      | <500 |      | 208  |      |      | 0.1  | 182  |      | 160  |      | 730  |      |
| WBA                           | 30000 | 18000 | 1400 | 1200 | <2   | <2   | 6    | 5    | 27   | 14   | <500 | <500 | 159  | 151  |      | 0.1  | 218  | 158  | 264  | 244  | 75   | 116  |
| GH                            | 5000  | 30000 | 1100 | 1300 | <2   | <2   | 8    | 6    | 25   | 25   | <500 | <500 | 245  | 161  |      | 0.1  | 219  | 210  | 370  | 171  | 753  | 66   |
| FB                            | 9000  |       | 1400 |      | <2   |      | 6    |      | 5    |      | <500 |      | 103  |      |      | 0.7  | 179  |      | 261  |      | 90   |      |
| VB                            | 1000  |       | 1500 |      | <2   |      | 12   |      | 4    |      | <500 |      | 125  |      |      | 0.1  | 154  |      | 119  |      | 480  |      |
| LR                            | 1000  | 28000 | 1500 | 1500 | <2   | <2   | 14   | 7    | 36   | 18   | <500 | <500 | 258  | 100  |      | 0.5  | 219  | 194  | 202  | 211  | 122  | 62   |
| BGI                           | 2000  | 14000 | 1400 | 1400 | <2   | <2   | 5    | 10   | 6    | 67   | <500 | <500 | 109  | 145  |      | 0.2  | 189  | 304  | 191  | 119  | 783  | 219  |
| BA                            | 2000  | 0     | 1400 |      | <2   |      | 7    |      | 7    |      | <500 |      | 129  |      |      | 0.1  | 195  |      | 125  |      | 4220 |      |
| Limit of reporting            | 1000  | 1000  | 100  | 100  | 2    | 2    | 1    | 1    | 3    | 3    | 500  | 500  | 3    | 3    |      | 0.1  | 15   | 15   | 4    | 4    | 16   | 16   |

### **Arsenic (As)**

Total and dissolved arsenic concentrations were remarkably similar throughout all three surveys suggesting that almost all As in seawater is dissolved and well mixed. Total As concentration was poorly correlated with TSS concentration ( $r^2$  of 0.024) where both were measured at the same site ( $n = 8$ ) (Table 4). Concentrations were generally 1400 ng/L to 1600 ng/L, but with concentrations as low as 1100 ng/L at a few sites and even 1000 ng/L at the mouth of the Mitchell River.

### **Silver (Ag)**

Silver concentrations were very low and relatively consistent across all three surveys, generally between 1 and 3 ng/L where it could be measured. In the North Kimberley survey all Ag concentrations were below the LOR of 2 ng/L. The results appear to suggest that dissolved Ag concentration may be similar to total Ag concentrations, but more data would be required to support this hypothesis.

### **Cadmium (Cd)**

Cadmium concentrations were measureable, but consistently low across all sites. Total concentrations were similar to dissolved concentrations suggesting that the majority of cadmium in Kimberley seawater is dissolved. Total Cd concentration was relatively poorly correlated with TSS concentration ( $r^2 = 0.50$ ) where both were measured at the same site ( $n = 8$ ). The more extensive set of data for dissolved Cd suggest a possible gradation in concentrations from 12 – 14 ng/L in north Kimberley waters (sites LR and VB) to 2.5 – 2.6 ng/L on the west coast of the Dampier Peninsula (sites PH1 and QP).

### **Cobalt (Co)**

Dissolved cobalt concentrations were below the limit of reporting at all sites in the West Kimberley survey, but measurable in the other two surveys. Dissolved concentrations ranged from <3 – 36 ng/L and total Co concentrations ranged from 14 – 77 ng/L. Dissolved Co concentration was significantly lower than the total Co concentration at five of the eight sites where both total and dissolved Co were measured, the same at site GH and about double the total concentration at sites LR and WBA. These last two results confirm the contamination concerns raised earlier in this section from the results of the North Kimberley field blanks. The results for the field blanks suggest that dissolved concentrations may be contaminated and that the contamination is likely to have occurred through the filtering process. The analytical results for the Maret Islands field blanks also suggest that some contamination of the dissolved Co samples may have occurred. Correlation of total Co concentrations with TSS concentrations was relatively poor ( $r^2 = 0.56$ ,  $n = 8$ ).

### **Chromium (Cr)**

Sample analysis for chromium only measured concentrations of total and total dissolved Cr and did not consider the different valence states of Cr. Dissolved and total Cr concentrations were relatively consistent across all three surveys. All analytical results for Cr in the North Kimberley survey were below the LOR (<500 ng/L) and six of the eight sites analysed for dissolved Cr in the West Kimberley survey were below the LOR (<90 ng/L). Measurable concentrations of Cr were found at the remaining sites with dissolved concentrations ranging from 150 – 380 ng/L and total concentrations at the Maret Islands ranging from 190 – 490 ng/L. Dissolved concentration was significantly lower than total concentration in two of the three Maret Island sites where both analyses were performed. Comparison of the dissolved and total Cr analyses for the Maret Island field blanks suggest that up to half of the measured dissolved Cr concentrations could be contamination and that this contamination probably occurred during the filtering process. Correlation of total Cr concentration with TSS concentration was relatively poor ( $r^2 = 0.536$ ,  $n = 8$ ).

### **Copper (Cu)**

Copper concentrations were above the LOR at all sites. Dissolved concentrations ranged from 52 – 350 ng/L. Total Cu concentrations were relatively consistent across both surveys where they were measured and ranged from 98 – 161 ng/L. However, the majority of total and dissolved concentrations are in the range of approximately 100 – 150 ng/L. Dissolved Cu concentration was lower than total Cu concentration where measured for the Maret Islands survey, but often exceeded total Cu concentration at sites in the North Kimberley survey where both were measured. This discrepancy in the results for dissolved Cu at some North Kimberley sites can be explained by the field blank results which suggest that samples may have become contaminated with Cu during the filtering process (as discussed earlier in this section). The analytical results for the Maret Islands field blanks also suggest that some contamination of the dissolved Cu samples may have occurred. Total Cu concentration was poorly correlated with TSS concentration ( $r^2$  of 0.218) where both were measured at the same site ( $n = 8$ ).

### **Mercury (Hg)**

Measured concentrations of mercury were very low across all three surveys with the majority of concentrations either below, equal to, or just above the LOR ( $<0.1$  ng/L). Both total and dissolved concentrations were measured in the Maret Island samples, but the concentrations are too low to determine whether there is any significant difference. Total Hg concentration was poorly correlated with TSS concentration ( $r^2$  of 0.02) where both were measured at the same site ( $n = 12$ ).

### **Nickel (Ni)**

Nickel concentrations were above the LOR at all sites. Ni concentrations were relatively consistent across all three surveys. Dissolved concentrations ranged from 23 – 265 ng/L and total Ni concentrations ranged from 158 – 304 ng/L. In the North Kimberley survey dissolved Ni concentration exceeded the total concentration at a number of sites and this is likely to indicate that some contamination has occurred during the filtering process. However, the majority of the uncontaminated dissolved Ni concentrations are in the range of approximately 160 – 200 ng/L and the majority of total Ni concentrations range from 180 – 230 ng/L. Dissolved Ni concentration was lower than total Ni concentration at sites where both forms were measured in the Maret Islands survey. Total Ni concentration was relatively highly correlated with TSS concentration ( $r^2$  of 0.771) where both were measured at the same site ( $n = 8$ ). However, the data do not suggest that the nickel is bound up in the mineral matrix of the suspended sediment because the results for the dissolved nickel fraction in uncontaminated samples indicate that the majority of the nickel is in dissolved form.

### **Lead (Pb)**

Total and dissolved lead concentrations were below the LOR at most sites in the Maret Islands and West Kimberley surveys (LOR of  $<20$  ng/L and  $<14$  ng/L respectively) and where levels were measureable they were only slightly above the LORs. Pb concentrations in the North Kimberley survey were much higher than measured in the other two surveys at all sites. Dissolved Pb concentrations in the latter survey were also higher than the total Pb concentrations, suggesting contamination occurred during the filtering process. This was confirmed by the high levels of lead measured in the field blank for the filtered samples. Four of the eight sites where total Pb and TSS concentrations were measured had Pb concentrations below the LOR so  $r^2$  values could not be reliably calculated.

## Zinc (Zn)

Zinc concentrations were above the LOR at all sites. Dissolved concentrations ranged from 98 – 4220 ng/L with the lowest concentrations measured in the Maret Islands samples and the highest concentrations in the North Kimberley samples. Total Zn concentrations were consistent across the Maret Islands and North Kimberley surveys where they were measured and ranged from 48 – 234 ng/L. In the North Kimberley survey dissolved Zn concentration exceeded the total concentration at most sites where both analyses were undertaken. This is considered to be a result of significant contamination of the filtered samples by Zn during the filtering process and is confirmed by the field blank results which show a very high zinc concentration in the dissolved metal blank compared to the total metal blank. The majority of the dissolved Zn concentrations are in the range of approximately 100 – 700 ng/L, still significantly higher than the range of total Zn concentrations. Dissolved Zn concentration was lower than total Zn concentration at two of the three sites where both forms were measured in the Maret Islands survey. Total Zn concentration was highly correlated with TSS concentration ( $r^2$  of 0.798) where both were measured at the same site ( $n = 8$ ). However, the data do not suggest that the zinc is bound up in the mineral matrix of the suspended sediment because the results for the dissolved zinc fraction in uncontaminated samples indicate that the majority of the zinc is in dissolved form.

Estimated natural background metal concentrations for State marine waters in the Kimberley region are provided in Table 5 and were calculated from the 95<sup>th</sup> percentile of the metals' data for all sites across all four surveys (see Methods section 2.3 and Appendix C). In an attempt to minimise the influence of severely contaminated samples on the estimated background concentrations for each metal, any extreme data outliers (representing extremely high concentrations) were removed from the data sets. Extreme outliers were identified using 2D Box Plot statistics in STATISTICA Version 9.0 (Series 0509 for Windows) as discussed in Section 2.3. Outliers were not identified for dissolved aluminium, dissolved and total silver, dissolved cobalt, dissolved and total chromium and dissolved and total lead since a large number of results were below the analytical limit of reporting. Two extreme outliers were identified in the dissolved zinc data (3440 and 4220 ng/L), one in the total mercury data (0.7 ng/L) and one in the dissolved cadmium data (14 ng/L) (Appendix D).

Logically, the total concentration of a metal in marine waters should be greater than, or equal to, the dissolved concentration, however, for arsenic, silver, copper, lead and zinc the estimated natural background dissolved concentrations exceed the estimated natural background total concentrations. For arsenic and silver the difference is minor and may be within analytical error. For copper, lead and zinc it is suggested that the difference may be the result of contamination of some of the dissolved metal samples during the filtering process influencing the 95<sup>th</sup> percentile values, particularly in the North Kimberley survey (see earlier discussion). Nevertheless, analyses for most metals have been to ultra-low levels and the estimated natural background levels are still below levels available through commercial laboratories.

It should also be recognised that the estimated background concentrations for chromium are artificially elevated because of the relatively high analytical limit of reporting for the North Kimberley survey analyses (500 ng/L).

**Table 5: National guideline trigger values for metals in marine waters (ANZECC & ARMCANZ, 2000) and estimated 95<sup>th</sup> percentile natural background concentrations for Kimberley marine waters (µg/L)**

| Metal                            | Estimated 95 <sup>th</sup> percentile of natural background concentration (µg/L) | n  | ANZECC/ ARMCANZ guideline trigger values for marine waters (µg/L)<br>(three levels of species protection) |      |         |       |
|----------------------------------|--|----|---|------|---------|-------|
|                                  |  |    | LRV <sup>#</sup>  | 90%  | 99/95 % | 99%   |
| Aluminium (dissolved)            | 13.0   | 21 | 0.5   | n/a  | n/a     | n/a   |
| Aluminium (total)                | 109.0  | 11 |   |      |         |       |
| Arsenic (dissolved) <sup>∞</sup> | 1.58 <sup>‡</sup>  | 21 | 4.5   | n/a  | n/a     | n/a   |
| Arsenic (total) <sup>∞</sup>     | 1.55   | 11 |   |      |         |       |
| Cadmium (dissolved)              | 0.0082   | 20 |   | 14   | 0.7     | 0.7   |
| Cadmium (total)                  | 0.0095   | 11 |   |      |         |       |
| Chromium III (dissolved)*        | <0.500   | 21 |   | 48.6 | 27.4    | 7.7   |
| Chromium III (total)*            | <0.500   | 11 |   |      |         |       |
| Cobalt (dissolved)               | 0.0360   | 21 |   | 14   | 1       | 0.005 |
| Cobalt (total)                   | 0.0735   | 11 |   |      |         |       |
| Copper (dissolved)               | 0.258 <sup>‡</sup>   | 21 |   | 3    | 1.3     | 0.3   |
| Copper (total)                   | 0.156  | 11 |   |      |         |       |
| Lead (dissolved)                 | 0.2640 <sup>‡</sup>  | 21 |   | 6.6  | 4.4     | 2.2   |
| Lead (total)                     | 0.2275   | 11 |   |      |         |       |
| Mercury (dissolved inorg.)       | 0.00019  | 3  |   | 0.7  | 0.1     | 0.1   |
| Mercury (total)                  | 0.00038  | 23 |   |      |         |       |
| Nickel (dissolved)               | 0.2190   | 21 |   | 200  | 70      | 7     |
| Nickel (total)                   | 0.2765   | 11 |   |      |         |       |
| Silver (dissolved)               | 0.0029 <sup>‡</sup>  | 21 |   | 1.8  | 1.4     | 0.8   |
| Silver (total)                   | 0.0024   | 11 |   |      |         |       |
| Zinc (dissolved)                 | 0.7560 <sup>‡</sup>  | 19 |   | 23   | 15      | 7     |
| Zinc (total)                     | 0.2265   | 11 |   |      |         |       |

n/a Reliable guideline trigger value not available.

# Low reliability trigger value (ANZECC & ARMCANZ, 2000).

\* The analytical results did not differentiate between Cr III and Cr VI. Cr III is generally considered to predominate under natural background conditions;

∞ The analytical results did not differentiate between As III and As V. AsV is considered to be the more common form in marine waters.

‡ Dissolved concentration affected by contamination. Actual dissolved concentration is expected to be ≤ total concentration for that metal.

## 4. General discussion

### 4.1 Total suspended solids data

TSS concentrations in surface waters were generally relatively low across the Kimberley, except during spring tides when tidal currents were sufficiently strong to resuspend bottom sediments in turbulent flows and bring them to the surface. Bottom TSS concentrations were only measured for the West Kimberley survey during neap tides and these showed little difference to surface concentrations except at site PH1 where surface TSS was relatively high and may be indicative of elevated

phytoplankton concentrations. The TSS concentrations measured in these surveys were mostly typical of TSS values measured by Daly *et al* (2012) off the west coast of the Dampier Peninsula in the West Kimberley. Similar values are also found during the dry season along the Pilbara coast (MScience, 2009 and SKM, 2009), but slightly lower values are generally found in inshore waters along the west coast of WA (Burt *et al.*, 1995; Bancroft, 2005).

These concentrations, coupled with the large tidal ranges, suggest that sufficient light would be available at reasonable depths on the seafloor to support benthic primary producers. This is supported by benthic habitat surveys undertaken by DEC in association with the Browse LNG precinct short-listing process (unpublished) where coral reefs were recorded to depths of approximately 10 – 12 m and seagrass meadows and algal communities were recorded at depths of 15 – 20 m. Fry *et al* (2008) also found benthic primary producers at depths up to 15 – 18 m in surveys undertaken off the west coast of the Dampier Peninsula in the West Kimberley.

The marine waters at all of the sites sampled in these surveys can be assumed to be essentially of pristine quality since there is almost no urban, industrial or agricultural development in the region. Therefore, in the absence of any better data, these TSS results were used to derive an interim TSS water quality guideline of 4.1 mg/L for the whole of the Kimberley region using the recommended method from ANZECC & ARMCANZ (2000) (i.e. 80<sup>th</sup> percentile of unimpacted reference site data). However, this should only be used as a guide and the authors recommend that local data be collected across the full tidal range and each season to derive site specific guidelines for TSS should there be a need to assess TSS on a more comprehensive basis.

## **4.2 Trace metals data**

The results of the QA/QC assessments for the Maret Islands survey suggest that there may have been some low level contamination of filtered samples by copper, cobalt and zinc, although the contamination was very minimal, if at all. Nevertheless, the reported dissolved metal concentrations are still very low and, with the exception of cobalt and copper, fall well below the recommended water quality guidelines for a very high level of ecological protection represented by the guideline for 99% species protection (ANZECC & ARMCANZ, 2000). It should be noted that the low reliability trigger value for aluminium is not a recommended guideline. Cobalt is discussed later and the one exception for copper is the result for Quondong Point (350 ng/L) which exceeded the 99% species protection guideline of 300 ng/L. Unfortunately the QA/QC results for the North Kimberly survey were less than satisfactory, suggesting that significant contamination of dissolved metal samples by cobalt, copper, nickel, lead and zinc and total metal samples by lead and zinc. The majority of the contamination is likely to have occurred through the filtering process and could be a result of contaminated filter papers, contaminated filter towers, poor sample handling hygiene or non-sterile surroundings during the filtering process. The latter is considered to be the most likely source of contamination since the filtering often needed to be done while the vessel was underway and was done under the partial shelter of the fly-bridge. Even though sample handling was done inside a clean plastic bag, turbulent air movement around the fly-bridge while the vessel was underway could have carried contaminants from the decks, exhausts and other parts of the vessel.

The use of syringe filters appears to be the most effective sampling procedure for minimising contamination of samples that need to be filtered in the field, particularly from copper and zinc which appear to be the worst contaminants. However, the time required to filter a sufficient volume of water through the small syringe filters meant

that this sampling procedure was impractical for any of the later field trips where the time available at each water quality sampling site was minimal. Nevertheless, it is recommended that future water quality surveys should use a syringe filter sampling procedure to collect samples for dissolved metal analyses where samples can't be filtered in a laboratory clean room. If there are time constraints preventing the use of syringe filtering, then samples should be filtered on the front deck of the vessel while the vessel is facing into the breeze, either while at anchor or underway, and there are no potential sources of contamination up-wind.

These surveys were focused more on the dissolved metal concentrations, which better represent the bioavailable fraction, rather than total concentrations which are more likely to be influenced by TSS levels and generally poorly related to bioavailability. Dissolved metal concentration is considered to be a better indicator of metal bioavailability than total metal concentration (ANZECC & ARMCANZ, 2000), but the additional sample filtration step makes it more difficult to prevent sample contamination, particularly if filtration needs to be undertaken outside a laboratory clean room. Total metal analyses include metal atoms that are normally unavailable for biological uptake because they are bound up in the mineral matrix, and hence are significantly influenced by the particulate load in the water column. Nevertheless, total metal concentration was measured at a number of the sites for comparison with dissolved metal concentrations and because filtering of some samples from the Maret Islands survey could not be undertaken within an acceptable timeframe. A correlation analysis of TSS against total metal concentrations found that only aluminium, nickel and zinc were highly correlated to TSS, indicating that these three metals were strongly influenced by the suspended sediment concentration. However, the analytical results also suggest that nickel and zinc concentrations were mainly in dissolved form and may therefore have simply been adsorbed onto the suspended particles rather than bound into the mineral matrix. The majority of the aluminium in the water samples appears to have been strongly bound to the sediment and therefore is likely to be biologically unavailable.

The very low concentrations of dissolved and total metal concentrations found in these surveys are consistent with the unimpacted, almost pristine, character of the Kimberley coastline. Apart from lead and zinc in the North Kimberley survey, where the samples appear to have become contaminated, the metal concentrations were at levels generally consistent with offshore oceanic waters (Apte *et al.*, 1998; Nakayama *et al.*, 1981; Neff, 2002; Nozaki, 1997; OZREEF, 1997) and the marine waters can therefore be considered to be of very high quality.

Similar background water quality surveys have been conducted in Western Australia for the coastal marine waters of the Perth metropolitan region (McAlpine *et al.*, 2005a), the mid west coast (McAlpine *et al.*, 2005b) and the North West Shelf (Wenziker *et al.*, 2006). Those studies also found that metal concentrations were very low (approaching oceanic levels) away from population and development centres and showed little vertical stratification in the water column. While both surface and bottom waters were not sampled in these surveys of Kimberley waters, it is likely that the metals will also be well mixed throughout the water column in the Kimberley region given the strong currents generated by the high tidal amplitudes and semi-diurnal nature of the tides.

Comparisons of the metal concentrations found in this study to those found in other parts of Australia show some similarities and some differences. Mean dissolved metal concentrations for the Kimberley surveys, coastal waters off Perth, the North West Shelf of Western Australia, the mid-west coast of Western Australia, New South Wales and the Pacific Ocean have been provided in Table 6 for comparison. To



minimise the influence of severely contaminated samples on the calculated means, any extreme data outliers representing extremely high concentrations were removed from the data set where they could be identified for each metal using 2D Box Plot statistics in STASTICA Version 9.0 (Series 0509 for Windows) as discussed in Sections 2.3 and 3.3). A mean value could not be calculated for chromium because the large number of samples reported as less than the analytical LoR and the fact that the LoR for the North Kimberley survey was well above expected background concentrations for marine waters.

**Table 6: Comparison of mean dissolved metal concentrations in the Kimberley region with other locations**

| <b>Metal</b>               | <b>Kimberley marine waters (µg/L)</b><br>(this study) | <b>NWS marine waters (µg/L)</b><br>(Wenziker <i>et al.</i> 2006) | <b>Mid West coast marine waters (µg/L)</b><br>(McAlpine <i>et al.</i> 2005b) | <b>Perth marine waters (µg/L)</b><br>(McAlpine <i>et al.</i> 2005a) | <b><sup>1</sup>Pacific Ocean (Surface waters) (µg/L)</b> | <b>NSW coastal waters (µg/L)</b><br>(Apte <i>et al.</i> , 1998) |
|----------------------------|---|--|--|---|--|---|
| Aluminium                  | 4.3   |  |  | <0.9  |  |   |
| Arsenic                    | 1.40  |  |  | 1.7   | 1.2-1.5  | 1.58  |
| Cadmium                    | 0.006   | 0.004  | 0.002  | 0.004   | 0.002-0.003  | 0.0024  |
| Chromium (total dissolved) | #   | <0.15  | 0.19   | <0.15   | 0.125  | 0.097   |
| Cobalt                     | 0.014   |  |  | 0.009   |  |   |
| Copper                     | 0.148   | 0.10   | 0.07   | 0.07  | 0.027-0.092  | 0.031   |
| Lead                       | 0.108*  | 0.008  | 0.007  | <0.02   | 0.006-0.017  | 0.009   |
| Mercury (total)            | 0.00015   | 0.0002   | 0.0003   | 0.0003  | 0.0003-0.0004  | <0.0014   |
| Nickel                     | 0.183   |  |  |   | 0.120  | 0.18  |
| Silver                     | 0.0020  |  |  | 0.0005  | 0.0001-0.0025  | <0.0005   |
| Zinc                       | 0.327*  | 0.10   | 0.04   | 0.10  | 0.004-0.006  | <0.022  |

1 data summarised in Apte *et al.* (1998)

# too few samples with measurable concentrations above the LoR to calculate a reliable mean.

\* unreliable value as lead and zinc samples appear to have become significantly contaminated in the North Kimberley survey.

Mean dissolved arsenic and nickel concentrations in the Kimberley waters were similar to those found in coastal waters off Perth (Western Australia) and New South Wales and also the surface waters of the Pacific Ocean, while cobalt concentrations were relatively similar to concentrations measured in marine waters off Perth. Total mercury concentrations were similar, but slightly lower, than reported in each of the other regions. Mean dissolved aluminium, cadmium and silver concentrations were slightly higher than the concentrations in the other regions where reported. As discussed elsewhere in this report, some samples appear to have been significantly contaminated with copper, lead and zinc and this has biased the calculated means for the Kimberley marine waters, which may explain why the means for these metals are much higher than the mean concentrations reported in the other regions. However, because of the unreliability of the data for these three metals, comparisons with background concentrations in the marine waters of the other regions is not considered to be valid.

Despite the contamination that appears to have occurred for some of the metal analyses, it is clear from Table 5 that natural background concentrations of almost all the metals measured in these surveys are less than the guideline trigger values provided in ANZECC & ARMCANZ (2000) for the highest level of ecological protection. These results suggest that the guidelines trigger values from ANZECC & ARMCANZ for most metals are appropriate for assessing the quality of the marine waters of the Kimberley region. The exceptions are cobalt and aluminium, although there is only a low reliability guideline available for aluminium because of the lack of available toxicological data. For cobalt the 99% species protection guideline of 0.005 µg/L is very low and approximates background levels reported for oceanic waters (Nozaki, 1997; OZREEF, 1997). This appears to be an artifact of the limited toxicological database available and the curve fitting method used to derive the national guidelines. McAlpine *et al.*, (2005a) also found that natural background levels of cobalt in coastal waters off the Perth metropolitan region exceeded the 99% species protection guideline. In combination, these findings suggest that the 99% species protection guideline is too low and should be revised. An interim approach for cobalt recommended by McAlpine *et al.* (2005a) is to apply the 95% species protection guideline for cobalt (1 µg/L) until the guideline is revised. Alternatively, locality specific guidelines may need to be derived for aluminium and cobalt from suitable unimpacted reference site data.

This study did not consider seasonal changes in metal concentrations or potential trends that may occur across geographical, hydrographic or oceanographic gradients in the coastal waters of the Kimberley region. The data simply represent a 'snapshot picture' of water quality at a point in time at each site. However, as the comparison of mean metal concentrations in Table 6 shows, there do not seem to be large differences in metal concentrations in coastal waters across Australia. The extent to which this generality holds in Western Australian coastal waters will be clarified as more high resolution metal concentration data are collected from different regions and during different seasons.

## **5. Conclusion**

This survey provides important information on baseline concentrations of selected trace metals and total suspended solids in the marine coastal waters of the Kimberley region. Seasonal trends, or changes in concentrations across geographical, hydrographic or oceanographic gradients were not considered in this study and further surveys would be needed to determine whether any such trends were measurable and significant. Nevertheless, the survey results show that these waters have very low concentrations of dissolved and total metals that appear to be comparable with other regions around Australia, with the exception of the results for copper, lead and zinc. Some of the samples for dissolved copper, lead and zinc appear to have been significantly contaminated, probably through the in-field filtering process, and so comparisons between these Kimberley data and data from other regions is not considered valid. Even though the results for dissolved concentrations of these three metals seem to have been influenced by contamination of the samples, the data still show that the natural background concentrations of all metals, except aluminium and cobalt, fall below the ANZECC & ARMCANZ guidelines for the highest level of ecological protection. Unfortunately there is no reliable guideline for aluminium concentration in seawater, only a very conservative low reliability value (LRV), because of a lack of available biological effects data. TSS concentrations appear to be variable, with relatively low concentrations during neap tides and significantly elevated concentrations during spring tides or in areas where tidal currents are strong.

The results for the dissolved metal concentrations also highlight the need to carefully plan in-field sample processing to minimise the potential for contamination. If sample processing under hygienic conditions can't be guaranteed then sampling for total metal analyses would be the preferable approach (total metal concentrations do not appear to be greatly elevated above dissolved metal concentrations, except for aluminium where total concentrations appear to be highly correlated to TSS concentrations). If available sampling time is not a constraint then syringe filtering of samples on-site is the recommended approach.

Based on the findings of this study, and considering other relevant data from the Western Australian coast, it is concluded that the guideline trigger values for metals for a *very high* level of protection, represented by the 99% species protection guideline trigger values (ANZECC & ARMCANZ, 2000) are relevant to the region. This holds for all metals except cobalt, where it is recommended that a new guideline is determined and that the 95% species protection guideline trigger value be adopted in the interim.

The results of this survey will assist managers and regulators with monitoring of activities that may impact marine water quality, and will guide the design and environmental impact assessment of future proposals for ocean outfalls and other point or diffuse source discharges in the Kimberley region. A fundamental baseline from which to assess local and regional changes in water quality in years to come has been established.

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## **Appendix A: Methods**

The following methods are for sample bottle preparation, sample collection, sample filtration and the specific chemical analyses.

### **A.1 PREPARATION OF SAMPLE CONTAINERS**

#### ***A.1.1 Trace metal sample bottles***

One-litre low density polyethylene (Nalgene) bottles were cleaned using a three stage process. First, the bottles and caps were submerged for two hours in 2% Extran detergent solution, followed by rinsing with copious amounts of Milli-Q (MQ) high purity water. The bottles were then soaked for a minimum of 24 hours in 10% nitric acid (analytical reagent grade) contained in a covered plastic tank. They were then rinsed with MQ water and then filled with 1% high purity nitric acid (Merck Suprapur), capped and left to stand for at least 48 hours. The bottles were then rinsed three times with MQ water and 'double-bagged' in two zip lock polyethylene bags.

#### ***A.1.2 Mercury sample bottles***

For the sampling program, 500 mL fluorinated ethylene propylene (FEP) (Nalgene) bottles equipped with Teflon-lined caps were used for sample storage. The bottles were cleaned by soaking bottle and lid for at least 2 hours in 1% v/v Extran detergent, at least one day in 0.2% v/v nitric acid (analytical reagent grade) acidified seawater, at least three days with 50% v/v nitric acid (analytical reagent grade) and then finally with 10% v/v hydrochloric acid (Merck Tracepure) for minimum of three days. After each of these steps the bottles were rinsed with copious quantities of MQ water. The bottles were then 'double-bagged' in two zip lock polyethylene bags prior to transportation to the sampling site.

### **A.2 SAMPLE COLLECTION AND HANDLING**

#### ***A.2.1 Metals***

Water samples were collected approximately 0.5 metres below the surface using a length of Teflon coated PVC tubing shaped at one end to hold a sample bottle using a fitted cable tie. Samples were taken off the bow of the vessel as it was slowly moving forward into the current. This method of sampling was designed to ensure that potential contamination from the vessel and the sampler was minimised when analysing down to the ultra-trace levels proposed.

On the vessel, care was taken to ensure that contamination was minimised at all times by ensuring that staff handling the samplers and sample bottles wore powderless disposable vinyl gloves and the workspace was covered with clean plastic sheeting. Sample bottles for metal analyses were rinsed twice with ambient seawater before collecting a sample.

Samples for total metal and dissolved metal analyses were stored in the dark on ice and couriered overnight to the CSIRO laboratory at the end of the field trip. Samples for dissolved metal analysis were removed from the cooler and filtered in the field within 24 hours of collection and then returned to the cooler.

#### ***A.2.2 Total suspended solids***

Water samples were collected just below the surface of the sea using a bucket and then a recorded volume was sub-sampled using a measuring cylinder and passed through a 47 mm diameter, 1.2 µm, GFC glass fibre filter paper using a filter tower and hand vacuum pump. The filter papers were pre-weighed by the analytical

laboratory before the trip. After filtering, distilled water was drawn through the pre-weighed TSS filters to remove salts. The filter papers were removed from the filter tower using plastic forceps, folded into quarters then wrapped in aluminium foil before being placed into seed envelopes and then in the freezer for storage. The water volume, date and site name were recorded in the field log and written on the seed envelopes.

### **A.3 SAMPLE FILTRATION PROCEDURES FOR DISSOLVED METALS**

Dissolved metal concentrations are considered to be a better estimate of the biologically available metals than total concentration. Because of the isolated nature and size of the Kimberley region it was not possible to courier the dissolved metal samples back to the analytical laboratory each day for filtering in a laboratory clean room. It was therefore necessary to filter the samples in the field, although this increases the risk of potential contamination of the samples. All dissolved metal samples were filtered through a 0.45 µm filter in the field within 24 hours of collection and prior to transportation to the analytical laboratory.

During the Maret Islands survey the CSIRO analytical laboratory provided syringe filters to directly filter the seawater samples and minimise the potential for contamination. Syringe filters were prepared in the laboratory in the same way as the sample bottles and double bagged in two zip lock polyethylene bags for transport into the field. Samples were initially taken at each site using pre-prepared polyethylene bottles held in a gloved hand extended from the bow of the vessel as it moved forward slowly into the current. The syringe filters were then used to sub-sample from the sample bottle and the filtrates were transferred to a second set of pre-prepared double bagged polyethylene bottles and stored in the dark on ice until arrival at the analytical laboratory.

Polycarbonate filter rigs (Sartorius) fitted with 0.45 µm Millipore membrane filters were used to filter the samples with a hand vacuum pump during the West Kimberley and North Kimberley surveys. One filter rig (including fitted Millipore filter) was supplied for each site to be sampled. All filtration assemblies were rigorously cleaned in the analytical laboratory by first filtering 100 mL volumes of 10% nitric acid solution followed by 2 x 150 mL of MQ water and then double bagged in two zip lock polyethylene bags for transport into the field. Each filter rig was removed from the zip lock bags as required and rinsed with approx. 50 mL of sample prior to filtering the full sample. The filtrates were transferred to a second set of pre-prepared double bagged polyethylene bottles and stored in the dark on ice until arrival at the analytical laboratory.

All samples were preserved by addition of 2 mL/L concentrated nitric acid (Merck Suprapur) upon arrival at the laboratory.

### **A.4 ANALYTICAL METHODS**

#### **A.4.1 Metals**

##### **Aluminium**

Dissolved aluminium concentrations were determined by inductively coupled argon plasma emission spectrometry (ICP-AES, CIROS, Spectro, Germany) using matrix-matched standards.

### **Arsenic**

Arsenic was determined by hydride-generation atomic absorption spectrometry (AAS). Samples were first digested by addition of potassium persulphate (1% m/v final concentration) and heating at 120°C for 30 minutes. Arsenic (V) was then pre-reduced to As (III) by addition of hydrochloric acid (32% (v/v) final volume) and potassium iodide (1.3% (m/v) final volume) and standing for at least 20 minutes at room temperature prior to analysis.

### **Cadmium, Cobalt, Copper, Lead, Nickel and Zinc**

These metals were analysed using a dithiocarbamate complexation/solvent extraction graphite furnace AAS 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. Sample aliquots (200 mL) were buffered to pH 5 by addition of the combined reagent and extracted with two 10 mL portions of double-distilled trichloroethane. The extracts were combined and the metals back-extracted into 1 mL of concentrated nitric acid (Merck Suprapur). The back extracts were diluted to a final volume of 10 mL by addition of deionised water and analysed by GFAAS (Perkin Elmer Analyst 600) using Zeeman effect background correction and operating conditions recommended by the manufacturer.

### **Chromium**

Chromium concentrations were determined directly by GFAAS (Perkin Elmer 600) using Zeeman effect background correction and operating conditions recommended by the manufacturer. Standard addition calibration was used to quantify chromium concentrations.

### **Total Mercury**

Total Hg in water samples was determined by BrCl oxidation, stannous chloride reduction and cold vapour atomic fluorescence spectrometry (Liang and Bloom, 1993).

### **Silver**

Dissolved silver concentrations were determined by microsolvent extraction GFAAS (Apte and Gunn, 1987) using dithizone as the metal complexing ligand. A stock dithizone solution (0.1% w/v) was prepared in double-distilled trichloroethane and was further diluted with double-distilled trichloroethane to give a 0.01% (v/v) working solution (prepared on a daily basis). A 30 mL sample aliquot was accurately transferred to an acid-washed fluorinated ethylene propylene (FEP) Oak Ridge centrifuge tube to which 1.3 mL of 3M sodium acetate buffer (final pH 5.0-5.5) and 1 mL of the dithizone solution was added. The centrifuge tube was tightly capped and shaken for five minutes. Following standing for 10 minutes the tubes were uncapped and 1.5 mL of the lower portion of solution (comprising the organic extract plus some of the aqueous layer) was pipetted into a dry acid washed PTFE furnace cup. The silver content of the solvent layer was determined using a GFAAS (Perkin Elmer Analyst 600) equipped with Zeeman effect background correction and a silver hollow cathode lamp. The furnace operating conditions recommended by the manufacturer were used. The autosampler arm was adjusted so that the sampling probe penetrated the upper aqueous layer and sampled from the lower organic layer only. Standards of concentration 0, 40, 80 and 120 ng/L, were prepared by spiking amounts of stock silver standard into 2 mL/L nitric acid solutions, these were extracted alongside samples in every batch.



### **Quality control**

To check analytical accuracy, aliquots of a NRC Canada Standard Reference Seawater CASS-4 and the Institute for Reference Materials and Measurements Seawater BCR0579 were analysed with each batch of samples. Suitable reference materials were not available for cobalt, chromium, or mercury. In addition, laboratory blanks, analytical duplicates and spiked samples (where appropriate) were included in every sample batch. Method detection limits (three times the standard deviation of the blank measurements) and recoveries were calculated from these data.

#### **A.4.2 Total suspended solids**

The analytical method used by the Marine and Fresh Water Research Laboratories for TSS analysis is APHA 2540D.

The filter paper sample from each site was placed on an aluminium crucible and dried in an oven at 103 – 105 °C for one hour. The filter paper sample was cooled in a desiccator to balance temperature and then weighed. (The oven drying step was repeated as necessary until a constant weight was obtained – within 4% of the previous weighing or 0.5 mg, whichever is less.) TSS is the difference between the weight of the original clean filter paper and the dried used filter paper sample divided by the volume of water passed through the filter paper.

Percent total organic carbon (TOC) content was then measured by placing the dried filter paper sample in a muffle furnace and igniting at 550°C for 15 minutes. The sample was then cooled in a desiccator and weighed. (The muffle furnace ignition step was repeated as needed until a constant weight was obtained – within 4% of the previous weighing or 0.5 mg, whichever is less.) Percent TOC is the difference in weight between the oven dried filter paper sample and the ignited residue multiplied by 100.

## Appendix B: Metals Analytical Quality Control Data

### B1. Maret Islands

#### Method Detection Limit (3σ)

| Arsenic (µg/L) | Aluminium (µg/L) | Copper (ng/L) | Cobalt (ng/L) | Cadmium (ng/L) | Chromium (µg/L) |
|----------------|------------------|---------------|---------------|----------------|-----------------|
| 0.02           | 1                | 1             | 5             | 0.4            | 0.07            |

| Silver (ng/L) | Lead (ng/L) | Mercury (ng/L) | Nickel (ng/L) | Zinc (ng/l) |
|---------------|-------------|----------------|---------------|-------------|
| 0.4           | 20          | 0.1            | 9             | 9           |

#### Replicates

| MI3        |                      |
|------------|----------------------|
| Replicate: | Total Mercury (ng/L) |
| 1          | 0.11                 |
| 2          | 0.13                 |
| Average    | 0.12                 |

| BI5        |                      |
|------------|----------------------|
| Replicate: | Total Mercury (ng/L) |
| 1          | 0.16                 |
| 2          | 0.14                 |
| Average    | 0.15                 |

| Field Blank 2 Filtered |                      |
|------------------------|----------------------|
| Replicate:             | Total Mercury (ng/L) |
| 1                      | 0.18                 |
| 2                      | 0.18                 |
| Average                | 0.18                 |

| <b>MI1</b>        |                             |                            |                            |                            |                          |                          |
|-------------------|-----------------------------|----------------------------|----------------------------|----------------------------|--------------------------|--------------------------|
| <b>Replicate:</b> | <b>Total Cadmium (ng/L)</b> | <b>Total Cobalt (ng/L)</b> | <b>Total Copper (ng/L)</b> | <b>Total Nickel (ng/L)</b> | <b>Total Lead (ng/L)</b> | <b>Total Zinc (ng/L)</b> |
| 1                 | 5.8                         | 58                         | 96                         | 255                        | <20                      | 169                      |
| 2                 | 7.8                         | 78                         | 150                        | 242                        | 22                       | 170                      |
| <b>Average</b>    | 6.7                         | 68                         | 123                        | 249                        | 20                       | 170                      |

| <b>BI5</b>        |                            |                              |
|-------------------|----------------------------|------------------------------|
| <b>Replicate:</b> | <b>Total Silver (ng/L)</b> | <b>Total Chromium (µg/L)</b> |
| 1                 | 0.4                        | 0.35                         |
| 2                 | <0.4                       | 0.32                         |
| <b>Average</b>    | 0.3                        | 0.33                         |

| <b>MA2</b>        |                               |
|-------------------|-------------------------------|
| <b>Replicate:</b> | <b>Total Aluminium (µg/L)</b> |
| 1                 | 13                            |
| 2                 | 13                            |
| <b>Average</b>    | 13                            |

**Percentage Recovery of Trace Metal Added to Samples:**

| <b>MI4</b>         |                |
|--------------------|----------------|
| <b>Trace Metal</b> | <b>Mercury</b> |
| <b>% Recovery</b>  | 98             |

| <b>MA2</b>         |                  |
|--------------------|------------------|
| <b>Trace Metal</b> | <b>Aluminium</b> |
| <b>% Recovery</b>  | 109              |

| Trace Metal | Cadmium | Cobalt | Copper | Nickel | Lead | Zinc |
|-------------|---------|--------|--------|--------|------|------|
| % Recovery  | 96      | 98     | 96     | 95     | 98   | 94   |

**Certified Reference Materials:**

| Certified Reference Material (BCR 579) |                |
|--|----------------|
| Element                                | Mercury (ng/L) |
| Certified Concentration                | 1.9±0.2        |
| Measured Concentration                 | 2.1            |
| % Recovery                             | 110            |

| Certified Reference Material (CASS-4) |                |               |               |               |             |
|---------------------------------------|----------------|---------------|---------------|---------------|-------------|
| Element                               | Cadmium (ng/L) | Cobalt (ng/L) | Copper (ng/L) | Nickel (ng/L) | Zinc (ng/L) |
| Certified Concentration               | 0.026±0.003    | 0.026±0.003   | 0.592±0.055   | 0.314±0.030   | 0.381±0.057 |
| Measured Concentration                | 0.021          | 0.026         | 0.578         | 0.309         | 0.413       |
| % Recovery                            | 82             | 99.3          | 97.6          | 99            | 108         |

**Field Blanks:**

|                      | Arsenic (µg/L) |       | Aluminium (µg/L) |       | Copper (ng/L) |       | Cobalt (ng/L) |       | Cadmium (ng/L) |       | Chromium (µg/L) |       |
|----------------------|----------------|-------|------------------|-------|---------------|-------|---------------|-------|----------------|-------|-----------------|-------|
|                      | Dissolved      | Total | Dissolved        | Total | Dissolved     | Total | Dissolved     | Total | Dissolved      | Total | Dissolved       | Total |
| Filtered metal blank | 0.02           |       | <1               |       | 37            |       | 23            |       | 0.5            |       | 0.13            |       |
| Total metal blank    |                | 0.02  |                  | <1    |               | 19    |               | 12    |                | <0.4  |                 | 0.09  |

|                      | Silver (ng/L) |       | Lead (ng/L) |       | Mercury (ng/L) |       | Nickel (ng/L) |       | Zinc (ng/l) |       |
|----------------------|---------------|-------|-------------|-------|----------------|-------|---------------|-------|-------------|-------|
|                      | Dissolved     | Total | Dissolved   | Total | Dissolved      | Total | Dissolved     | Total | Dissolved   | Total |
| Filtered metal blank | 0.5           |       | <20         |       | 0.2            |       | 18            |       | 98          |       |
| Total metal blank    |               | <0.4  |             | <20   |                | <0.1  |               | 16    |             | 37    |

## B2. West Kimberley

### Method Detection Limit (3 $\sigma$ )

| Arsenic ( $\mu\text{g/L}$ ) | Aluminium ( $\mu\text{g/L}$ ) | Copper (ng/L) | Cobalt (ng/L) | Cadmium (ng/L) |
|-----------------------------|-------------------------------|---------------|---------------|----------------|
| 0.03                        | 2                             | 8             | 11            | 0.6            |

| Chromium ( $\mu\text{g/L}$ ) | Silver (ng/L) | Lead (ng/L) | Mercury (ng/L) | Nickel (ng/L) | Zinc (ng/L) |
|------------------------------|---------------|-------------|----------------|---------------|-------------|
| 0.09                         | 0.4           | 14          | 0.1            | 6             | 36          |

### Replicates

| SDS            |                      |
|----------------|----------------------|
| Replicate:     | Total Mercury (ng/L) |
| 1              | <0.1                 |
| 2              | 0.1                  |
| <b>Average</b> | 0.1                  |

| QP             |                      |
|----------------|----------------------|
| Replicate:     | Total Mercury (ng/L) |
| 1              | 0.1                  |
| 2              | 0.1                  |
| <b>Average</b> | 0.1                  |

| MR             |                          |                         |                         |                         |                       |                   |
|----------------|--------------------------|-------------------------|-------------------------|-------------------------|-----------------------|-------------------|
| Replicate:     | Dissolved Cadmium (ng/L) | Dissolved Cobalt (ng/L) | Dissolved Copper (ng/L) | Dissolved Nickel (ng/L) | Dissolved Lead (ng/L) | Total Zinc (ng/L) |
| 1              | 5.1                      | 12                      | 199                     | 226                     | 17                    | 487               |
| 2              | 5.4                      | 2                       | 187                     | 207                     | 13                    | 540               |
| <b>Average</b> | 5.3                      | 7                       | 193                     | 217                     | 16                    | 513               |

Reported as <11 ng/L

| SDS        |                         |
|------------|-------------------------|
| Replicate: | Dissolved Silver (ng/L) |
| 1          | 5.0                     |
| 2          | 5.1                     |
| Average    | 5.1                     |

| QP         |                           |
|------------|---------------------------|
| Replicate: | Dissolved Chromium (µg/L) |
| 1          | 0.07                      |
| 2          | 0.06                      |
| Average    | 0.07                      |

Reported as <0.09 µg/L

| IRV        |                          |
|------------|--------------------------|
| Replicate: | Dissolved Arsenic (µg/L) |
| 1          | 1.57                     |
| 2          | 1.55                     |
| Average    | 1.56                     |

| KIS        |                          |
|------------|--------------------------|
| Replicate: | Dissolved Arsenic (µg/L) |
| 1          | 1.57                     |
| 2          | 1.55                     |
| Average    | 1.56                     |

**Percentage Recovery of Trace Metal Added to Samples:**

|                    |                |                  |
|--------------------|----------------|------------------|
| <b>KIS</b>         |                |                  |
| <b>Trace Metal</b> | <b>Mercury</b> | <b>Aluminium</b> |
| <b>% Recovery</b>  | 101            | 96               |

|                    |                |               |               |               |             |             |
|--------------------|----------------|---------------|---------------|---------------|-------------|-------------|
| <b>WPT</b>         |                |               |               |               |             |             |
| <b>Trace Metal</b> | <b>Cadmium</b> | <b>Cobalt</b> | <b>Copper</b> | <b>Nickel</b> | <b>Lead</b> | <b>Zinc</b> |
| <b>% Recovery</b>  | 94             | 100           | 90            | 98            | 95          | 90          |

|                    |                |
|--------------------|----------------|
| <b>IRV</b>         |                |
| <b>Trace Metal</b> | <b>Cadmium</b> |
| <b>% Recovery</b>  | 107            |

|                    |                  |
|--------------------|------------------|
| <b>SDS</b>         |                  |
| <b>Trace Metal</b> | <b>Aluminium</b> |
| <b>% Recovery</b>  | 105              |

**Certified Reference Materials:**

|  |                       |                       |                      |                      |                      |                    |
|--|-----------------------|-----------------------|----------------------|----------------------|----------------------|--------------------|
| <b>Certified Reference Material (CASS-4)</b> |                       |                       |                      |                      |                      |                    |
| <b>Element</b>                               | <b>Arsenic (µg/L)</b> | <b>Cadmium (ng/L)</b> | <b>Cobalt (ng/L)</b> | <b>Copper (ng/L)</b> | <b>Nickel (ng/L)</b> | <b>Zinc (ng/L)</b> |
| <b>Certified Concentration</b>               | 1.11±0.16             | 0.026±0.003           | 0.026±0.003          | 0.592±0.055          | 0.314±0.030          | 0.381±0.057        |
| <b>Measured Concentration</b>                | 1.18                  | 0.025                 | 0.024                | 0.549                | 0.329                | 0.394              |
| <b>% Recovery</b>                            | 106                   | 96                    | 91                   | 93                   | 105                  | 103                |

|  |                       |
|--|-----------------------|
| <b>Certified Reference Material (BCR- 579)</b> |                       |
| <b>Element</b>                                 | <b>Mercury (ng/L)</b> |
| <b>Certified Concentration</b>                 | 1.9 ±0.2              |

|                               |     |
|-------------------------------|-----|
| <b>Measured Concentration</b> | 2.0 |
| <b>% Recovery</b>             | 106 |

**Field Blanks:**

|         | <b>Arsenic (µg/L)</b> | <b>Aluminium (µg/L)</b> | <b>Copper (ng/L)</b> | <b>Cobalt (ng/L)</b> | <b>Cadmium (ng/L)</b> | <b>Chromium (µg/L)</b> |
|---------|-----------------------|-------------------------|----------------------|----------------------|-----------------------|------------------------|
| Blank   | <0.03                 | <2                      | <8                   | <11                  | <0.6                  | <0.09                  |
| Blank 2 | <0.03                 | <2                      | <8                   | <11                  | <0.6                  | <0.09                  |

|         | <b>Silver (ng/L)</b> | <b>Lead (ng/L)</b> | <b>Mercury (ng/L)</b> | <b>Nickel (ng/L)</b> | <b>Zinc (ng/l)</b> |
|---------|----------------------|--------------------|-----------------------|----------------------|--------------------|
| Blank   | 0.2                  | <14                | <0.1                  | 18                   | 50                 |
| Blank 2 | 0.8                  | <14                | <0.1                  | 23                   | <36                |



### B3. North Kimberley

#### Quality Control Data

##### Limits of Detection

|                                      | Ag (ng/L) <sup>1</sup> | Al (µg/L) <sup>2</sup> | As (µg/L) <sup>3</sup> | Cd (ng/L) <sup>4</sup> | Co (ng/L) <sup>4</sup> | Cr (µg/L) <sup>5</sup> | Cu (ng/L) <sup>4</sup> | Hg (ng/L) <sup>6</sup> | Ni (ng/L) <sup>4</sup> | Pb (ng/L) <sup>4</sup> | Zn (ng/L) <sup>4</sup> |
|--------------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| Limit of Detection (3σ method blank) | 2                      | 1                      | 0.1                    | 1                      | 3                      | 0.5                    | 3                      | 0.1                    | 15                     | 4                      | 16                     |

<sup>1</sup> Silver was analysed using a micro-solvent extraction method

<sup>2</sup> Aluminium was analysed by ICP-AES

<sup>3</sup> Arsenic was analysed using hydride AAS

<sup>4</sup> Cadmium, cobalt, copper, nickel, lead and zinc were analysed using an APDC/DDDC solvent extraction procedure

<sup>5</sup> Chromium was analysed using standard additions followed by analysis by GFAAS

<sup>6</sup> Total mercury was analysed on unfiltered samples by cold vapour AFS

##### Certified Reference Material

|  | Cd (µg/L)   | Co (µg/L)   | Cu (µg/L)   | Ni (µg/L)   | Zn (µg/L)   |
|--|-------------|-------------|-------------|-------------|-------------|
| <b>CASS-4 (NRC) - nearshore seawater</b> | 0.023       | 0.027       | 0.55        | 0.31        | 0.36        |
| Certified concentration                  | 0.026±0.003 | 0.026±0.003 | 0.592±0.055 | 0.314±0.030 | 0.381±0.057 |
| % Recovery                               | 90          | 101         | 92          | 100         | 94          |

|  | Hg (ng/L) |
|--|-----------|
| <b>BCR-579 (IRMM) - coastal seawater</b> | 2.1       |
| Certified concentration                  | 1.9 ±0.2  |
|  |           |
| % Recovery                               | 104       |

|                                | As (µg/L)  |
|--------------------------------|------------|
| <b>NASS-5 (NRC) - seawater</b> | 1.2        |
| Certified concentration        | 1.27 ±0.12 |
|                                |            |
| % Recovery                     | 97         |

|                             | As (µg/L) |
|-----------------------------|-----------|
| <b>1643E (NIST) - water</b> | 56.8      |
| Certified Concentration     | 60.4±0.7  |
|                             |           |
| % Recovery                  | 94        |

**Spike Recovery Data**

| <b>Lab No.</b> | <b>Sample Description</b> | <b>% Ag Recovery</b> | <b>% Al Recovery</b> | <b>% As Recovery</b> | <b>% Cd Recovery</b> | <b>% Co recovery</b> | <b>% Cu recovery</b> | <b>% Hg recovery</b> | <b>% Ni Recovery</b> | <b>% Pb Recovery</b> | <b>% Zn Recovery</b> |
|----------------|---------------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| CE49-1         | MRM - total               | -                    | -                    | -                    | -                    | -                    | -                    | 101                  | -                    | -                    | -                    |
| CE49-2         | WB - dissolved            | -                    | -                    | 97                   | -                    | -                    | -                    | -                    | -                    | -                    | -                    |
| CE49-5         | GH - dissolved            | -                    | 94                   | -                    | -                    | -                    | -                    | -                    | -                    | -                    | -                    |
| CE49-5         | GH - total                | -                    | 89                   | -                    | -                    | -                    | -                    | -                    | -                    | -                    | -                    |
| CE-49-7        | VB - dissolved            | 97                   | -                    | -                    | -                    | -                    | -                    | -                    | -                    | -                    | -                    |
| CE-49-9        | Blank - dissolved         | 94                   | -                    | -                    | -                    | -                    | -                    | -                    | -                    | -                    | -                    |
| CE49-10        | BI - dissolved            | -                    | -                    | 95                   | -                    | -                    | -                    | -                    | -                    | -                    | -                    |
| CE49-10        | BI - total                | -                    | -                    | -                    | 91                   | 98                   | 97                   | -                    | 91                   | 96                   | 94                   |
| CE49-11        | Blank - total             | 89                   | -                    | -                    | -                    | -                    | -                    | -                    | -                    | -                    | -                    |
| CE49-12        | BA - dissolved            | -                    | 96                   | -                    | 93                   | 99                   | 103                  | -                    | 94                   | 97                   | 109                  |

**Sample Duplicates**

| Lab No. | Sample Description | Replicates<br>ng Ag/L | Replicates<br>µg As/L | Replicates<br>ng Cd/L | Replicates<br>ng Co/L | Replicates<br>ng Cu/L | Replicates<br>ng Hg/L | Replicates<br>ng Ni/L | Replicates<br>ng Pb/L | Replicates<br>ng Zn/L |
|---------|--------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| CE49-1  | MRM - total        | -                     | -                     | -                     | -                     | -                     | 0.47                  | -                     | -                     | -                     |
| CE49-1  | MRM - total        | -                     | -                     | -                     | -                     | -                     | 0.38                  | -                     | -                     | -                     |
| CE49-2  | WB - total         | -                     | -                     | 9                     | 25                    | 135                   | -                     | 213                   | 195                   | 56                    |
| CE49-2  | WB - total         | -                     | -                     | 9                     | 22                    | 137                   | -                     | 211                   | 198                   | 48                    |
| CE49-5  | GH - total         | -                     | -                     | -                     | -                     | -                     | 0.11                  | -                     | -                     | -                     |
| CE49-5  | GH - total         | -                     | -                     | -                     | -                     | -                     | 0.09                  | -                     | -                     | -                     |
| CE49-6  | FB - total         | -                     | -                     | -                     | -                     | -                     | 0.71                  | -                     | -                     | -                     |
| CE49-6  | FB - total         | -                     | -                     | -                     | -                     | -                     | 0.71                  | -                     | -                     | -                     |
| CE49-8  | LR - total         | -                     | -                     | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-8  | LR - total         | -                     | -                     | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-1  | MRM - filtered     | -                     | 0.9                   | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-1  | MRM - filtered     | -                     | 1.0                   | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-2  | WB - filtered      | <2                    | -                     | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-2  | WB - filtered      | <2                    | -                     | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-5  | GH - filtered      | <2                    | -                     | 7                     | 25                    | 239                   | -                     | 220                   | 370                   | 754                   |
| CE49-5  | GH - filtered      | <2                    | -                     | 8                     | 25                    | 250                   | -                     | 219                   | 389                   | 751                   |
| CE49-6  | FB - filtered      | -                     | 1.3                   | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-6  | FB - filtered      | -                     | 1.4                   | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-8  | LR - filtered      | -                     | 1.5                   | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-8  | LR - filtered      | -                     | 1.5                   | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-12 | BA - filtered      | -                     | 1.4                   | -                     | -                     | -                     | -                     | -                     | -                     | -                     |
| CE49-12 | BA - filtered      | -                     | 1.4                   | -                     | -                     | -                     | -                     | -                     | -                     | -                     |

**Field Blanks:**

|                  | Arsenic (µg/L) |       | Aluminium (µg/L) |       | Copper (ng/L) |       | Cobalt (ng/L) |       | Cadmium (ng/L) |       | Chromium (µg/L) |       |
|------------------|----------------|-------|------------------|-------|---------------|-------|---------------|-------|----------------|-------|-----------------|-------|
|                  | Dissolved      | Total | Dissolved        | Total | Dissolved     | Total | Dissolved     | Total | Dissolved      | Total | Dissolved       | Total |
| Blank (filtered) | <0.1           |       | <1               |       | 123           |       | 15            |       | <1             |       | <0.5            |       |
| Blank (total)    |                | <0.1  |                  | 5     |               | 8     |               | <0.3  |                | 3     |                 | <0.5  |

|                  | Silver (ng/L) |       | Lead (ng/L) |       | Mercury (ng/L) |       | Nickel (ng/L) |       | Zinc (ng/l) |       |
|------------------|---------------|-------|-------------|-------|----------------|-------|---------------|-------|-------------|-------|
|                  | Dissolved     | Total | Dissolved   | Total | Dissolved      | Total | Dissolved     | Total | Dissolved   | Total |
| Blank (filtered) | <2            |       | 207         |       | -              |       | 204           |       | 1340        |       |
| Blank (total)    |               | <2    |             | 70    |                | <0.1  |               | 21    |             | 146   |

## Appendix C: Data used to calculate means and 95th percentiles

### Dissolved Metals ( $\mu\text{g/L}$ )

| Site | Al | As   | Ag     | Cd     | Co    | Cr    | Cu    | Hg     | Ni    | Pb    | Zn    |
|------|----|------|--------|--------|-------|-------|-------|--------|-------|-------|-------|
| MI1  |    |      |        |        |       |       |       |        |       |       |       |
| MI2  |    |      |        |        |       |       |       |        |       |       |       |
| MI3  | 1  | 1.51 | 0.0026 | 0.0056 | 0.017 | 0.180 | 0.086 | 0.0001 | 0.161 | 0.020 | 0.106 |
| MI4  | 1  | 1.51 | 0.0012 | 0.0059 | 0.012 | 0.150 | 0.083 | 0.0001 | 0.160 | 0.020 | 0.123 |
| BI5  |    |      |        |        |       |       |       |        |       |       |       |
| AI6  | 1  | 1.48 | 0.0018 | 0.0064 | 0.036 | 0.380 | 0.100 | 0.0002 | 0.175 | 0.020 | 0.098 |
| WPT  | 2  | 1.50 | 0.0011 | 0.0049 | 0.011 | 0.090 | 0.156 |        | 0.208 | 0.027 | 0.199 |
| MR   | 2  | 1.61 | 0.0024 | 0.0053 | 0.011 | 0.090 | 0.193 |        | 0.217 | 0.016 | 0.513 |
| KIS  | 5  | 1.58 | 0.0008 | 0.0067 | 0.011 | 0.090 | 0.146 |        | 0.210 | 0.014 | 0.193 |
| PR   | 2  | 1.52 | 0.0019 | 0.0059 | 0.011 | 0.150 | 0.123 |        | 0.193 | 0.014 | 0.210 |
| IRV  | 2  | 1.56 | 0.0003 | 0.0052 | 0.011 | 0.180 | 0.121 |        | 0.186 | 0.016 | 0.234 |
| SDS  | 2  | 1.54 | 0.0051 | 0.0052 | 0.011 | 0.090 | 0.095 |        | 0.168 | 0.014 | 0.431 |
| PH1  | 2  | 1.48 | 0.0023 | 0.0025 | 0.011 | 0.090 | 0.096 |        | 0.160 | 0.014 | 0.638 |
| QP   | 2  | 1.10 | 0.0029 | 0.0026 | 0.011 | 0.090 | 0.350 |        | 0.171 | 0.014 | 0.342 |
| MRM  | 13 | 1.0  | 0.002  | 0.008  | 0.024 | 0.5   | 0.170 |        | 0.265 | 0.141 |       |
| WB   | 3  | 1.1  | 0.002  | 0.007  | 0.003 | 0.5   | 0.052 |        | 0.023 | 0.251 | 0.102 |
| PI   | 3  | 1.3  | 0.002  | 0.006  | 0.009 | 0.5   | 0.208 |        | 0.182 | 0.160 | 0.730 |
| WBA  | 30 | 1.4  | 0.002  | 0.006  | 0.027 | 0.5   | 0.159 |        | 0.218 | 0.264 | 0.075 |
| GH   | 5  | 1.1  | 0.002  | 0.008  | 0.025 | 0.5   | 0.245 |        | 0.219 | 0.370 | 0.753 |
| FB   | 9  | 1.4  | 0.002  | 0.006  | 0.005 | 0.5   | 0.103 |        | 0.179 | 0.261 | 0.090 |
| VB   | 1  | 1.5  | 0.002  | 0.012  | 0.004 | 0.5   | 0.125 |        | 0.154 | 0.119 | 0.480 |
| LR   | 1  | 1.5  | 0.002  |        | 0.036 | 0.5   | 0.258 |        | 0.219 | 0.202 | 0.122 |
| BGI  | 2  | 1.4  | 0.002  | 0.005  | 0.006 | 0.5   | 0.109 |        | 0.189 | 0.191 | 0.783 |
| BA   | 2  | 1.4  | 0.002  | 0.007  | 0.007 | 0.5   | 0.129 |        | 0.195 | 0.125 |       |

|                  |      |      |        |        |       |      |       |         |       |       |       |
|------------------|------|------|--------|--------|-------|------|-------|---------|-------|-------|-------|
| <b>95th %ile</b> | 13.0 | 1.58 | 0.0029 | 0.0082 | 0.036 | <0.5 | 0.258 | 0.00019 | 0.219 | 0.264 | 0.756 |
| <b>Mean</b>      | 4.3  | 1.40 | 0.0020 | 0.0061 | 0.014 |      | 0.148 | 0.00013 | 0.183 | 0.108 | 0.327 |
| <b>n</b>         | 21   | 21   | 21     | 20     | 21    | 21   | 21    | 3       | 21    | 21    | 19    |

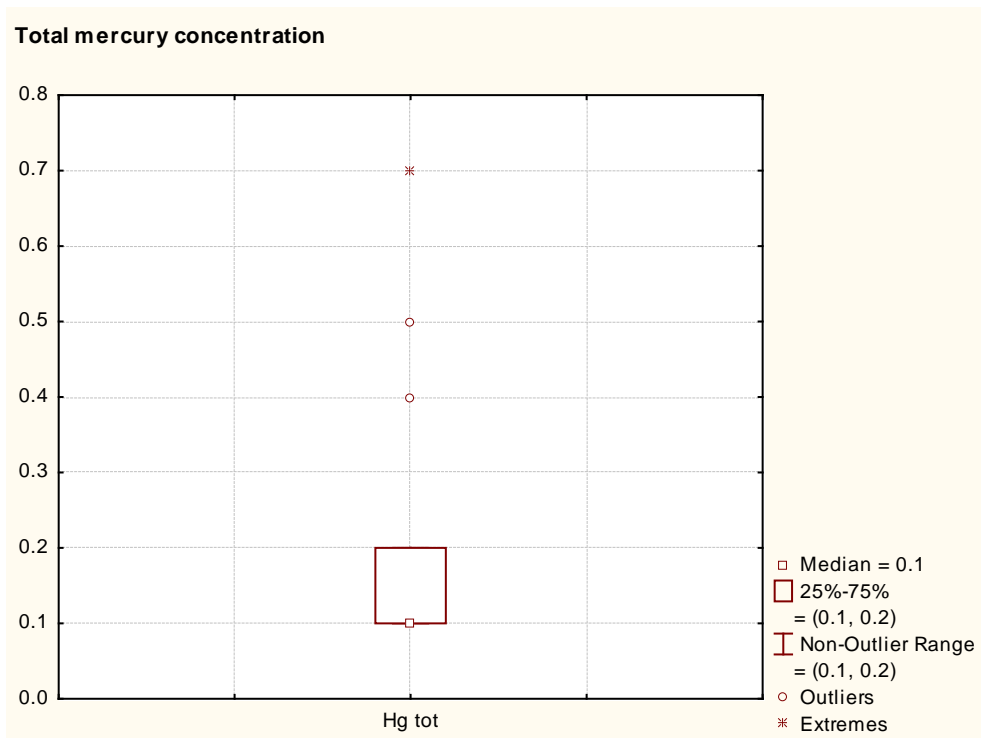
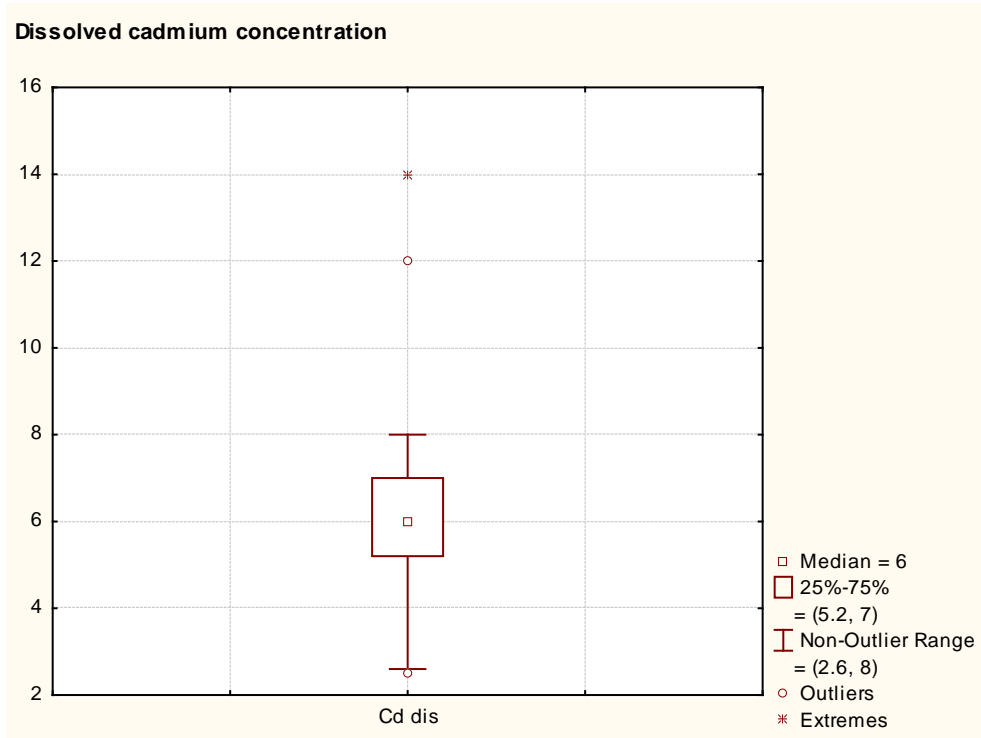
## Total Metals

| Site | Al  | As   | Ag     | Cd     | Co    | Cr    | Cu    | Hg     | Ni    | Pb    | Zn    |
|------|-----|------|--------|--------|-------|-------|-------|--------|-------|-------|-------|
| MI1  | 78  | 1.54 | 0.0011 | 0.0067 | 0.068 | 0.490 | 0.123 | 0.0001 | 0.249 | 0.020 | 0.170 |
| MI2  | 13  | 1.51 | 0.0028 | 0.0066 | 0.036 | 0.190 | 0.098 | 0.0001 | 0.185 | 0.020 | 0.048 |
| MI3  | 33  | 1.52 | 0.0007 | 0.0066 | 0.044 | 0.310 | 0.097 | 0.0001 | 0.190 | 0.020 | 0.075 |
| MI4  | 56  | 1.55 | 0.0006 | 0.0077 | 0.070 | 0.420 | 0.131 | 0.0002 | 0.234 | 0.020 | 0.126 |
| BI5  | 51  | 1.52 | 0.0004 | 0.0068 | 0.054 | 0.330 | 0.123 | 0.0002 | 0.233 | 0.020 | 0.091 |
| AI6  | 67  | 1.51 | 0.0018 | 0.0068 | 0.077 | 0.370 | 0.151 | 0.0001 | 0.229 | 0.028 | 0.234 |
| WPT  |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| MR   |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| KIS  |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| PR   |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| IRV  |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| SDS  |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| PH1  |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| QP   |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| MRM  |     |      |        |        |       |       |       | 0.0004 |       |       |       |
| WB   | 17  | 1.10 | 0.002  | 0.009  | 0.024 | 0.500 | 0.136 | 0.0002 | 0.212 | 0.196 | 0.052 |
| PI   |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| WBA  | 18  | 1.20 | 0.002  | 0.005  | 0.014 | 0.500 | 0.151 | 0.0001 | 0.158 | 0.244 | 0.116 |
| GH   | 30  | 1.30 | 0.002  | 0.006  | 0.025 | 0.500 | 0.161 | 0.0001 | 0.210 | 0.171 | 0.066 |
| FB   |     |      |        |        |       |       |       |        |       |       |       |
| VB   |     |      |        |        |       |       |       | 0.0001 |       |       |       |
| LR   | 28  | 1.50 | 0.002  | 0.007  | 0.018 | 0.500 | 0.100 | 0.0005 | 0.194 | 0.211 | 0.062 |
| BGI  | 140 | 1.40 | 0.002  | 0.010  | 0.067 | 0.500 | 0.145 | 0.0002 | 0.304 | 0.119 | 0.219 |
| BA   |     |      |        |        |       |       |       | 0.0001 |       |       |       |

|                  |      |      |        |        |        |       |       |         |        |        |        |
|------------------|------|------|--------|--------|--------|-------|-------|---------|--------|--------|--------|
| <b>95th %ile</b> | 109  | 1.55 | 0.0024 | 0.0095 | 0.0735 | 0.500 | 0.156 | 0.0008  | 0.2765 | 0.2275 | 0.2265 |
| <b>Mean</b>      | 48.3 | 1.42 | 0.0016 | 0.0071 | 0.045  | 0.419 | 0.129 | 0.00015 | 0.218  | 0.097  | 0.114  |
| <b>n</b>         | 11   | 11   | 11     | 11     | 11     | 11    | 11    | 24      | 11     | 11     | 11     |

## Appendix D: 2D Box Plots of metal data for which extreme outliers were identified

Extreme outliers identified using 2D Box Plot statistics from STATISTICA Version 9.0 (Series 0509 for Windows) and an outlier coefficient of 1.5.





### Dissolved zinc concentration

