Background concentrations of selected toxicants in the coastal waters of the Jurien Bay Marine Park

---

Department of Environment
Perth, Western Australia
Technical Series 119
December 2004

Background concentrations of selected toxicants in the coastal waters of the Jurien Bay Marine Park

K.W. M^{c}Alpine, K.J. Wenziker, S.C. Apte and R.J. Masini

ISBN: 1 920947 31 0

Department of Environment
Perth, Western Australia, 6000

Contents

Acknowledgements
Abstract

Tables

Figures

Appendices

Acknowledgments

We are most grateful to Kevin Bancroft (CALM) and Leigh Hales (CSIRO) for their comments on the penultimate draft of this report, to Leigh Hales and Rob Jung (CSIRO) who performed the metal analyses, and to Tim Daly (DoE) who assisted during the field program. This study was funded by the Commonwealth Government's Natural Heritage Trust, the Department of Environment and the Department of Conservation and Land Management.

Abstract

A water quality survey was undertaken in February 2004 to determine dissolved concentrations of cadmium, chromium, copper, lead and zinc, total mercury, polyaromatic hydrocarbons, phenols, BTEX chemicals and petroleum hydrocarbons in the coastal waters of the Jurien region. This work was undertaken to provide an estimate of background concentrations for selected metals and organic chemicals in the waters of the Jurien Bay Marine Park 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 Jurien region were generally of very high quality. The concentrations of metals were low by world standards, with localised elevations of some metals adjacent to Cervantes townsite. Concentrations of metals in seawater met the environmental quality guidelines for a *very high* level of ecological protection (99% species protection) throughout the study area at the time of sampling.

No organic chemicals were detected in any of the samples. For six of the seven organic chemicals that have guideline trigger values (ANZECC & ARMCANZ, 2000) the reporting limits were well below the values recommended for a *very high* level of ecological protection.

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 are appropriate for management of the marine waters in the region for organic chemicals and all metals, except cobalt where the 95% species protection guideline trigger value is recommended.

1. Introduction

The Jurien Bay Marine Park (JBMP) was gazetted by the Government of Western Australia on August 30, 2003. It extends over more than 90 km of coastline and out to a distance of more than 12 km offshore, incorporating a wide range of marine habitats and a number of islands. Development pressures in the region are rapidly increasing, mainly from population growth, port expansion and industrial development. The offshore area is also highly prospective for oil and gas, with several recently discovered fields being developed for production.

The Department of Conservation and Land Management (CALM) has management responsibility for the JBMP and has prepared an Indicative Management Plan (IMP) to guide future management (CALM, 2000). The management framework underpinning the IMP is based on identifying pressures on the marine environment and putting in place management objectives and strategies to manage these; they are supported by measurable targets to assess effectiveness. With respect to toxicants such as heavy metals, hydrocarbons and pesticides, the potential pressures on the environmental quality of the park as identified in the IMP include:

- Toxicant inputs from oil and chemical spills;
- Antifouling paints;
- Agricultural activities in the catchment; and,
- Urban stormwater.

The recommended short and long-term targets for toxicant-related water quality are to meet the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ, 2000).

The Jurien Bay Marine Park incorporates a large section of the mid-west coast region of Western Australia. The Western Australian Environmental Protection Authority (EPA) considers this area a priority area for establishing an environmental quality management framework (EQMF) for describing, assessing and managing activities that may impact upon the marine environment. The EPA has adopted an EQMF that is based on the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ, 2000). The management framework establishes environmental values to be protected, environmental quality objectives (broad management goals) and environmental quality criteria (EQC) to be achieved if the environmental values are to be maintained (Government of Western Australia, 2004). While the EQC are based on the numerical guidelines and approaches recommended in ANZECC & ARMCANZ (2000), there are different guidelines for different levels of protection, and furthermore it is recognised that the guidelines for the selected level of protection may need to be modified to establish site-specific criteria in regions where natural background levels exceed the guidelines.

There is a paucity of information on natural background concentrations of potentially toxic contaminants along the mid-west coast region. Most monitoring programs focus around specific developments or activities, and use commercial laboratories that are not equipped to measure at the analytical limits required to resolve *actual* background concentrations for most contaminants. It was therefore necessary, from both conservation and environmental protection perspectives, to establish baseline conditions for a range of chemical constituents of the waters of the JBMP and to confirm the relevance of the recommended guidelines in ANZECC & ARMCANZ (2000) to the region generally.

To assist with management, CALM has been allocated Natural Heritage Trust funding for a Marine Biodiversity & Conservation Program centred on the Jurien Bay Marine Park. A central component of the program is a baseline water quality monitoring program that includes a survey, systematic and on-going data collection (particularly for nutrient related water quality indicators), local stakeholder involvement and the development of an environmental quality database.

As part of this program, and with additional funding from the Department of Environment (DoE), the DoE and CALM conducted a baseline water quality survey of the JBMP for a range of selected toxicants. The objectives of the survey were firstly to determine background concentrations of selected metals and organic chemicals in 'unimpacted areas' to both confirm the relevance of the National water quality guidelines and to establish a 'natural' baseline for the region, and secondly to determine ambient concentrations to identify potential problems and establish a baseline for these chemicals in 'potentially impacted' areas.

2. Methods

2.1 Field sampling

Fieldwork for both surveys was conducted by staff from both the DoE and the CSIRO Centre for Advanced Analytical Chemistry based at Lucas Heights (NSW). Sampling was undertaken on 3 – 4 February 2004.

The 14 sampling sites selected for this study (Table 1 and Figure 1) span approximately 75 kilometers of the central west coast from near Target Rock in the south to Fisherman Islands in the north. The sampling sites were selected to represent three sub-regions:

- Nearshore (sites 1, 10, 11 and 14);
- Middle lagoon (sites 2, 5, 8 and 13); and,
- Offshore (sites 3, 7 and 12).

Potentially impacted sites (sites 4, 9 and 6) were also grouped; two of the potentially impacted sites were situated adjacent to the major towns in the area (Jurien Bay and Cervantes) while the third site was situated just north of the Hill River mouth and potentially influenced by runoff from the catchment during periods of river flow.

Surface water samples were collected at all sites for determining metal concentrations and bottom water samples were collected at five sites for mercury analysis only. Sampling for organic contaminants was undertaken at five sites, namely sites 1 and 4 (surface and bottom) and sites 6, 11 and 12 (surface only). An additional sample (called 'test') of surface water adjacent to the boat outboard motor was taken to assess the potential for sample contamination by petroleum hydrocarbons from the engine.

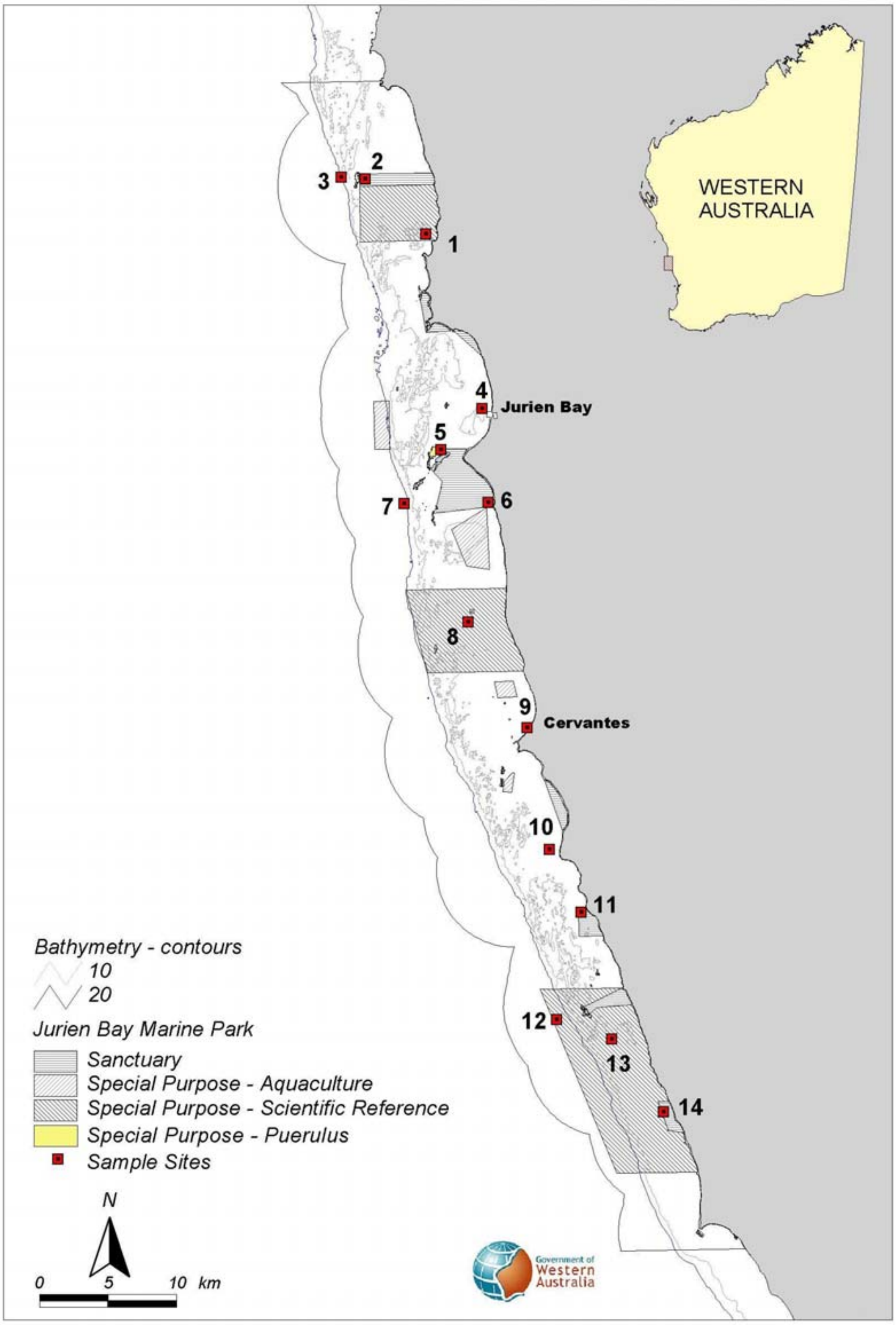

Figure 1. Locality map of the study area showing the sampling sites, Jurien region.

Table 1: Sampling locations.

Site name	Site No	Latitude	Longitude	Approx. depth (m)
Sandy Point	1	30°10.2 S	114°59.7 E	9
Fisherman Islands (east)	2	30° 08.0 S	114°57.0 E	3.4
Fisherman Islands (west)	3	30°07.9 S	114° 55.9 E	21.5
Jurien Bay	4	30° 17.1 S	115° 02.1 E	10.3
Boullanger Islands	5	30° 18.7 S	115° 00.2 E	5.2
Hill River	6	30°20.8 S	115° 02.3 E	5
Essex Rocks	7	30° 20.8 S	114° 58.5 E	23.2
Booker Rocks	8	30° 25.5 S	115° 01.3 E	6.1
Cervantes Town	9	30° 29.7 S	115° 03.9 E	3.7
Kangaroo Point	10	30° 34.5 S	115° 04.8 E	3.6
Boggy Bay	11	30° 37.0 S	115° 06.2 E	5.2
Green Islands (northwest)	12	30° 41.2 S	115° 05.0 E	25
Green Islands (southeast)	13	30° 42.0 S	115° 07.5 E	10.5
Target Rock	14	30° 44.9 S	115° 09.8 E	12.5

* Datum is WGS84.

Sampling was conducted during daylight hours on a flood tide in the spring tide cycle (Figure 2). Full details of the water sampling procedures are given in Appendix A.

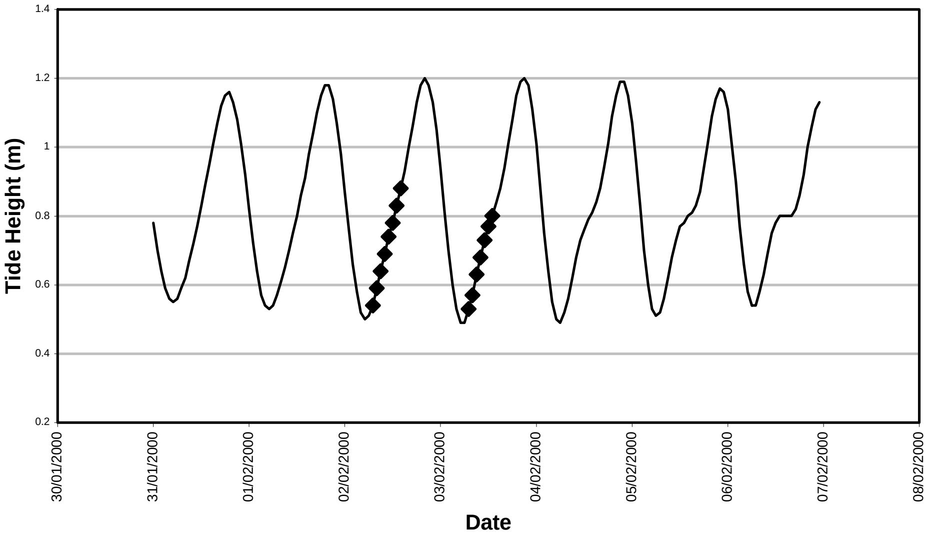

Figure 2: Predicted tide height at Jurien during the sampling period, February 2004 (diamonds represent sampling period).

2.2 Sample analysis

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

The focus of the program was on those toxic contaminants considered to be of greatest potential threat to water quality in the region over the long term. The suite of contaminants analysed included heavy metals (cadmium, chromium, copper, lead, mercury, zinc) and organic chemicals (total petroleum hydrocarbons, poly-aromatic hydrocarbons, BTEX chemicals, phenols, chlorinated phenols, organochlorine pesticides and organophosphate pesticides).

Metal analyses for total dissolved concentrations were performed on filtered samples, except for mercury where unfiltered samples (surface and bottom) were analysed and the results expressed as total mercury.

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 QA/QC procedures comprised:

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

Analysis for the organic contaminants was performed by the Australian Government Analytical Laboratories (AGAL). AGAL is NATA registered for the analyses performed in this study. The analytical limits of reporting for the organic chemical analyses were the lowest available from commercial laboratories, and for the metal analyses they were the lowest available in Australia. Organic samples were analysed within two weeks of the sampling being undertaken, and for most metals within six weeks.

2.3 Statistical analysis

It was assumed that the metals' data would not meet the assumptions that allowed parametric tests to be applied (normally distributed and equal variances). Accordingly, the non-parametric Kruskal-Wallis test was used to determine whether there were differences between sub-regions for any of the metals. Mann Whitney tests were used to determine whether there were differences in metal concentrations between sub-regions or categories. The statistics package StatView^{TM} SE + Graphics (Abacus Concepts Inc, 1998 – 1991) was used to perform all of these tests. The sampling sites were grouped into nearshore (sites 1, 10, 11 and 14), middle lagoon (sites 2, 5, 8 and 13), offshore (sites 3, 7 and 12) and potentially impacted sites (sites 4, 6 and 9).

The *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ, 2000) recommends that the 95th percentile of concentration values at the test site should be less than the default guidelines for the toxicant. For the purposes of this report the 95th percentile value was deemed to represent the natural background concentration and was used to assess whether or not the National guidelines were naturally exceeded. A 95th percentile for each metal was calculated from data from the least impacted sites (sites 4, 6 and 9 were considered to be potentially impacted sites and excluded from the analyses); means were calculated using the same data set. For calculation of percentiles and means, where analytical results were reported as ‘below detection limit’, these data were replaced with the detection limit (e.g. <0.006 μg/L became 0.006 μg/L).

3. Results

3.1 General conditions

The weather and sea conditions on the sampling days were as follows:

- 3 February 2004: 5 – 10 knot north, north-easterly wind early morning swinging to the north-west late morning and to the south-west by the afternoon, fine and sunny, swell 1 – 1.5 m; and,
- 4 February 2004: 10 - 20 knot south-westerly winds, fine and overcast, swell 1 - 1.5 m.

3.2 Trace metals data

The results for the total dissolved metals analyses are presented in Table 2 and the associated quality control data are in Appendix B. The quality control data for cadmium, chromium, lead and mercury are satisfactory, suggesting significant contamination of samples did not occur. Analysis of the field blanks for copper and zinc detected small quantities of both metals suggesting that some low level contamination of the samples occurred and may have positively biased the results. Replicate samples were collected from the surface at two sites (4 and 7) and the analysis of these samples for all six metals produced very consistent results for each pair of replicates.

Concentrations of cadmium, chromium, lead and mercury at some sites approached the limit of detection reported for these analyses, and for chromium and lead, concentrations at several sites were below the reported detection limit. However, the lead concentrations found at site 7 were an order of magnitude above the reported detection limit (0.013 μg/L).

At site 9 (located adjacent to boat moorings at the Cervantes town site) slightly elevated levels of cadmium, copper and zinc were found; the concentrations of copper and zinc were very low in absolute terms but in comparative terms were the highest found in the survey (0.099 μg/L and 0.119 μg/L respectively).

Table 2: Dissolved metal concentrations and total mercury for the coastal waters of the Jurien region, February 2004.
(s) = surface and (b) = bottom

Site	**Cd**	**Cr**	**Cu**	**Pb**	**Hg**	**Zn**
	µg/L	**µg/L**	**µg/L**	**µg/L**	**µg/L**	**µg/L**
JB1(s)	0.003	0.23	0.076	0.009	0.0004	0.041
JB1(b)					0.0002	
JB2(s)	0.001	0.26	0.064	0.007	0.0004	0.026
JB3(s)	0.001	0.24	0.061	0.004	0.0005	0.033
JB3(b)					0.0001	
JB4(s)	0.003	<0.15	0.075	0.004	0.0005	0.039
JB4(s) replicate	0.002	0.19	0.072	0.006	0.0003	0.055
JB5(s)	0.002	<0.15	0.062	0.008	0.0003	0.041
JB6(s)	0.003	0.26	0.069	0.007	0.0004	0.035
JB7(s)	0.002	0.23	0.059	0.013	0.0003	0.020
JB7(s) replicate	0.002	0.21	0.067	0.013	0.0003	0.019
JB7(b)					0.0001	
JB8(s)	0.002	0.18	0.057	0.007	0.0004	0.079
JB9(s)	0.004	0.15	0.099	<0.003	0.0004	0.119
JB10(s)	0.003	<0.15	0.066	<0.003	0.0004	0.036
JB10(b)					0.0002	
JB11(s)	0.003	<0.15	0.073	0.007	0.0003	0.047
JB12(s)	0.002	<0.15	0.064	0.007	0.0003	0.027
JB12(b)					0.0002	
JB13(s)	0.002	<0.15	0.074	0.007	0.0003	0.031
JB14(s)	0.002	<0.15	0.075	<0.003	0.0004	0.031
Limit of Detection (3 sigma)	***0.001***	***0.15***	***0.008***	***0.003***	***0.0001***	***0.006***

Concentrations of chromium were higher at some sites in the northern end of the study area than the southern end. Where most of the southern sites had values below or close to the reported limit of detection (0.15 μg/L), most of the northern sites had values above 0.2 μg/L. Sites 2 and 6 recorded chromium concentrations of 0.26 μg/L.

There was little variation in mercury concentrations across the fourteen sites; values ranged from 0.0001 μg/L to 0.0005 μg/L. Mercury concentrations were consistently lower in bottom samples compared to the surface samples for those sites where surface and bottom samples were collected.

The sampling sites were grouped into nearshore, middle lagoon, offshore and potentially impacted sites (see Methods section 2.3) and a Kruskal-Wallis test was applied to the data from the first three categories to determine whether there were differences between the sub-regions for any of the metals. The only positive result was for cadmium ($p = 0.045$). The Mann-Whitney tests showed that nearshore concentrations were significantly different from both lagoonal ($p = 0.040$) and offshore waters ($p= 0.040$), although the actual differences were only minor in absolute terms (i.e. $\leq$ 0.002 μg/L; Table 2).

Metal concentrations at the potentially impacted sites were not significantly different from concentrations at unimpacted sites or the ‘nearshore’ subset of those unimpacted sites. However, it was evident that concentrations of copper and zinc at site 9 (Cervantes town) were slightly elevated compared to the other sites.

Metals’ data were pooled into north (sites 1-7) and south (sites 8-14) categories on a fairly arbitrary basis to determine whether there were any south-north trends for concentrations of the six metals. The only trend evident was for dissolved chromium concentrations ($p = 0.008$), which were higher to the north than to the south.

Mercury data were analysed to determine whether surface and bottom concentrations were different. Total mercury concentrations were higher ($p = 0.0006$) in surface waters than in bottom waters, although actual differences were small and less than 0.0004 μg/L.

Estimated natural background metal concentrations are provided in Table 3 and were calculated from the 95th percentile of the metals’ data for all sites except the potentially impacted sites (sites 4, 6 and 9) (see Methods section 2.3, Appendix C). For mercury, the estimated background concentration has been calculated using data from both surface and bottom waters. The high 95th percentile calculated for chromium reflects the higher concentrations found in the northern section of the park. If the northern and southern sections of the park are considered separately for chromium, then the estimated background concentrations are 0.26 μg/L and 0.17 μg/L respectively.

Table 3: Estimated natural background concentrations of selected metals in coastal waters of the Jurien region (n = number of samples).

Metal	Estimated natural background[#] concentration (μg/L)	n
Cadmium	0.003	12
Chromium*	0.25	12
Copper	0.08	12
Lead	0.01	12
Mercury[‡]	0.0004	17
Zinc	0.06	12

\# Background concentration is the 95th percentile of data from all sites except those potentially impacted sites (4, 6 and 9).

* The analytical results did not differentiate between Cr species; total dissolved Cr was measured.

‡ The analytical results were for total mercury

3.3 Organic chemicals

The results of the organic analyses are presented in Table 4. Concentrations of all the organic chemicals were found to be below the analytical Limit of Reporting (LOR) in all samples, including the ‘test’ sample. National guidelines were only available for seven of the organic chemicals analysed (naphalene, phenol, pentachlorophenol, endosulphan, endrin, chlorpyifos and benzene) and the LORs for all, except chlorpyifos, were significantly below the 99% species protection guideline trigger values. For example, the LOR for phenol was 0.1 μg/L and for benzene 1.0 μg/L, which are well below their respective 99% species protection guideline trigger values of 270 μg/L and 500 μg/L. The LOR for chlorpyrifos was 0.01 μg/L, which is significantly greater than the 99% species protection guideline of 0.0005 μg/L, but below the 90% species protection guideline trigger value of 0.04 μg/L.

4. General discussion

4.1 Trace metals data

Dissolved metal concentration is considered to be a better indicator of bioavailable metal concentration than total metal concentration (ANZECC & ARMCANZ, 2000). 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. This survey therefore focused on dissolved metal concentration, which better represents the bioavailable fraction.

The low dissolved metal concentrations found in this study demonstrate that the waters of the Jurien region are effectively uncontaminated by metals or organic chemicals and can be classified as very high quality. The concentrations of the six metals in coastal waters of the Jurien region were at levels consistent with offshore

Table 4: Results of the organic chemical analyses for the Jurien region, February 2004 and the National guideline trigger values for organic chemicals in marine waters (ANZECC & ARMCANZ, 2000).

NG = No guideline value; (s) = surface and (b) = bottom

Organic Chemical	Units	Site 1(s)	Site 1(b)	Site 4(s)	Site 4(b)	Site 6(s)	Site 11(s)	Site 12(s)	Test	LOR	Guideline value		
											99%	95%	90%
Poly Aromatic Hydrocarbons													
Acenaphthene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Acenaphthylene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Anthracene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Benz(a)anthracene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Benzo(b)&(k)fluoranthene	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2	NG	NG	NG
Benzo(ghi)perylene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Benzo(a)pyrene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Chrysene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Dibenz(ah)anthracene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Fluoranthene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Fluorene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Indeno(1,2,3-cd)pyrene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Naphthalene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	**50**	**70**	**90**
Phenanthrene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Pyrene	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Phenols													
Phenol	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	**270**	**400**	520
Chlorinated Phenols													
2,4-Dichlorophenol	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
2,6-Dichlorophenol	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
2,4,6-Trichlorophenol	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2	NG	NG	NG
2,4,5-Trichlorophenol	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2	NG	NG	NG
2,3,4,6-Tetrachlorophenol	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2	NG	NG	NG
Pentachlorophenol	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2	**11**	**22**	**33**

Organic chemical	**Units**	**Site 1(s)**	**Site 1(b)**	**Site 4(s)**	**Site 4(b)**	**Site 6(s)**	**Site 11(s**	**Site 12(s)**	**Test**	**LOR**	**Guideline value**		
											99%	**95%**	**90%**
Organochlorine (OC) pesticides													
Aldrin	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Chlordane	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
DDD	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
DDE	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
DDT	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Dieldrin	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Endosulfan alpha	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Endosulfan beta	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Endosulfan sulphate	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	**0.005**	**0.01**	**0.02**
Endrin	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	**0.004**	**0.008**	**0.01**
HCB	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
HCH(BHC) Tot alpha,beta,delta	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Heptachlor	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Heptachlor epoxide	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Lindane (gamma-BHC)	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Methoxychlor	µg/L	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-	0.001	NG	NG	NG
Total OCs	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.001	NG	NG	NG
Organophosphate (OP) pesticides													
Bromophos-ethyl	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Chlorpyrifos	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	**0.0005**	**0.009**	**0.04**
Chlorpyrifos-methyl	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Chlorfenvinphos	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Diazinon	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Ethion	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Fenchlorfos	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Fenitrothion	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Malathion	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Mevinphos	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Parathion	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Parathion-methyl	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Pirimiphos-Methyl	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG

Organic chemical	**Units**	**Site 1(s)**	**Site 1(b)**	**Site 4(s)**	**Site 4(b)**	**Site 6(s)**	**Site 11(s**	**Site 12(s)**	**Test**	**LOR**	**Guideline value**		
											99%	**95%**	**90%**
Tetrachlorvinphos	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	0.01	NG	NG	NG
Total OP's	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	-	0.1	NG	NG	NG
BTEX													
Benzene	µg/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1	**500**	**700**	**900**
Toluene	µg/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1	NG	NG	NG
Ethylbenzene	µg/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1	NG	NG	NG
Xylene	µg/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1	NG	NG	NG
Total Petroleum Hydrocarbons													
TPH C6 - C9	µg/L	<25	<25	<25	<25	<25	<25	<25	<25	25	NG	NG	NG
TPH C10 - C14	µg/L	<25	<25	<25	<25	<25	<25	<25	<25	25	NG	NG	NG
TPH C15 - C28	µg/L	<100	<100	<100	<100	<100	<100	<100	<100	100	NG	NG	NG
TPH C29 - C36	µg/L	<100	<100	<100	<100	<100	<100	<100	<100	100	NG	NG	NG
Other													
o-Cresol	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	NG	NG	NG
m+p-Cresols	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2	NG	NG	NG

oceanic waters (Apte *et al*., 1998; Nakayama *et al*., 1981; Neff, 2002; Nozaki, 1997; OZREEF, 1997).

Similar background water quality surveys have been conducted for the coastal marine waters of the Perth metropolitan region (McAlpine *et al*., *in press*) and the North West Shelf (Wenziker *et al.*, *in prep*). Those studies found that, away from population and development centres metal concentrations were also very low (approaching oceanic levels) and showed little vertical stratification in the water column. Total mercury was the only exception, occasionally showing small differences between surface and bottom concentrations. Where these differences were found, they were generally higher in samples of bottom waters than surface waters.

Comparisons of metal concentrations found in this study to those found in coastal waters off Perth, the North West Shelf, New South Wales and the Pacific Ocean show similarities (Table 5). However, some interesting differences were found. Mean dissolved copper and zinc concentrations for the Jurien region were lower in comparison to those found for the coastal waters off Perth and the North West Shelf, but slightly higher than those found in coastal waters off NSW. The mean dissolved chromium concentration for the Jurien region was slightly higher compared to all the other locations. The increasing trend in dissolved chromium concentrations from south to north found for the Jurien region can not be satisfactorily explained through sample contamination or from known natural or anthropogenic influences. There are no major anthropogenic discharges in the region and the Hill River (the only river in the region) is relatively small and had not flowed for several months prior to sampling. The wind direction was from the south-west (toward land) whenever any of the high chromium samples were collected so the high values are unlikely to be a result of airborne particles.

Table 5: Comparison of mean trace metal concentrations at the Jurien region with other locations.

Metal	**Jurien Bay marine waters (µg/L)**	**NWS marine waters (µg/L)**	**Perth marine waters (µg/L)**	**[1]Pacific Ocean (Surface waters) (µg/L)**	**NSW coastal waters (Apte *et al.*, 1998) (µg/L)**
Cadmium	0.002	0.004	0.004	0.002-0.003	0.0024
Chromium (total dissolved)	0.19	<0.15	<0.15	0.125	0.097
Copper	0.07	0.10	0.07	0.027-0.092	0.031
Lead	0.007	0.008	<0.02	0.006-0.017	0.009
Mercury (total)	0.0003	0.0002	0.0003	0.0003-0.0004	<0.0014
Zinc	0.04	0.10	0.10	0.004-0.006	<0.022

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

The main sources of contaminants in the region are likely to be from agricultural runoff, stormwater drainage, and harbours and marinas. In the future, industry including oil and gas production may increase threats to the environmental values of the marine environment. Although the statistical tests found that metal concentrations for the potentially impacted sites as a whole were not significantly different from the unimpacted sites, the copper and zinc concentrations at site 9 were anomalously high and were most likely a result of human activity (antifouling paints and corrosion inhibition from moored boats). To put these results in perspective, the copper concentration measured at Jurien site 9 was higher than those found at Warnbro Sound but lower than those found in Cockburn Sound during the survey of Perth's coastal waters (McAlpine *et al.*, *in press*).

It is difficult to explain the lower concentrations of total mercury found in the bottom waters when compared to the surface waters. This trend was opposite to that found in surveys conducted in the coastal marine waters of Perth, but similar to North West Shelf waters.

To determine whether the National guideline trigger values were appropriate for the Jurien region, they were compared to the estimated natural background concentrations (Table 6). The guidelines from ANZECC & ARMCANZ (2000) for a range of ecosystem protection levels (99%, 99/95% and 90% species protection) have been included to determine whether or not local concentrations naturally exceeded the guidelines. Note that the guidelines for chromium (III) and chromium (VI) have been quoted in Table 6 because there is no guideline for total dissolved chromium.

Table 6: National guideline trigger values for metals in marine waters (ANZECC & ARMCANZ, 2000) and estimated natural background concentrations for the Jurien region.

METAL	ANZECC/ ARMCANZ trigger values for marine waters (μg/L)			ESTIMATED NATURAL BACKGROUND[#] CONCENTRATION
	Recommended guidelines for different levels of species protection			
	90%	99/95 %	99%	(μg/L)
Cadmium	14	0.7	0.7	0.003
Chromium (III)	48.6	27.4	7.7	0.25*
Chromium (VI)	20	4.4	0.14	
Copper	3	1.3	0.3	0.08
Lead	6.6	4.4	2.2	0.01
Mercury (inorganic)	0.7	0.1	0.1	0.0004[‡]
Zinc	23	15	7	0.06

\# Background concentration is the 95th percentile of data from all sites except 4, 6 and 9.

* The analytical results did not differentiate between Cr species; total dissolved Cr was measured.

‡ The analytical results were for total mercury.

The estimated natural background concentrations for all six metals were found to be below the recommended guidelines for all levels of ecological protection, including the *very high* level of protection represented by the 99% species protection guidelines. For chromium, this holds assuming that a significant proportion of the total dissolved chromium is in the chromium (III) form (Nakayama *et al.*, 1981). For all other metals, the natural background concentrations were between four and 259 times less than the most conservative guideline.

The results of this study indicate that the water quality guidelines recommended in ANZECC & ARMCANZ (2000) for all six metals are suitable for application to the coastal waters of the Jurien region. By inference, the guidelines recommended for other metals, except cobalt, are also expected to be appropriate for the waters of the Jurien region. For cobalt, McAlpine *et al.*, (2004, *in press*) and Wenziker *et al.*, (2004, *in prep*) concluded that the 99% species protection guideline of 0.005 μg/L was excessively low, approximated background levels reported for oceanic waters (Nozaki, 1997; OZREEF, 1997), and was likely to be artifact of the limited toxicological database available and the curve fitting method used to derive the national guidelines.

Until natural levels of cobalt in Western Australian coastal waters can be measured and characterised using detection limits that are below the guideline for 99% species protection, or the guideline can be revised in light of additional ecotoxicological information, the 95% species protection guideline for cobalt of 1 μg/L is recommended for use.

This study did not consider seasonal changes in metal concentrations in coastal waters of the JBMP. It is a ‘snapshot picture’ of water quality at one point in time. However, as the comparison of mean metal concentrations shows, there do not seem to be large differences between coastal waters in three regions of Western Australia (Table 5). The extent to which this generality holds in Western Australian coastal waters will be improved as more high resolution metal concentration data are collected from different regions and during different seasons.

4.2 Organic chemicals

For the organic chemicals analysed (PAHs, phenols, pesticides and petroleum hydrocarbons) the natural background concentrations were expected to be immeasurable, ranging from zero to negligible. Most of the chemicals do not occur naturally, and those that do are only found at extremely low concentrations unless augmented by anthropogenic inputs. National guidelines were only available for some of the organic chemicals tested and for these, the guidelines were greater than the limit of reporting (except for chlorpyrifos). In this study, there were no detections of any of the organic chemicals analysed indicating that the guidelines were met and could be successfully applied to coastal waters of the Jurien region. The results of the organic chemicals analyses will provide a useful reference against which future studies can be compared.

5. Conclusion

This survey provides important information on baseline concentrations of selected trace metals and organic chemicals in the marine coastal waters of the Jurien region. Seasonal changes in these concentrations were not considered in this study and further surveys would be needed to determine whether seasonal differences are significant. Nevertheless, the survey results show that these waters have very low concentrations of metals and organic chemicals by world standards.

None of the selected organic chemicals analysed in the samples were detected at concentrations above the laboratory reporting limits. Estimates of natural background concentrations for six metals in the Jurien region have been established. Although slight elevations in some dissolved metals were detected in areas close to human activity, the concentrations in absolute terms were very low and met the 99% species protection guideline trigger values.

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 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 the 95% species protection guideline trigger value be adopted.

The results of this survey will assist managers and regulators in monitoring current 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 region, and the central west coast more generally. A fundamental baseline from which to assess local and regional changes in water quality in years to come has been established.

6. References

ANZECC & ARMCANZ (2000). *Australian and New Zealand guidelines for fresh and marine water quality*. National Water Quality Management Strategy No 4, Australian and New Zealand Environment and Conservation Council and Agricultural and Resource Management Council of Australia and New Zealand, Canberra, ACT.

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

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

CALM (2000). *Indicative Management Plan for the Proposed Jurien Bay Marine Park.* Department of Conservation and Land Management and Marine Parks and Reserves Authority.

Government of Western Australia (2004). *Implementation Framework for Western Australia for the Australian and New Zealand Guidelines for Fresh and Marine Water Quality and Water Quality Monitoring and Reporting (Guidelines No.s 4 & 7: National Water Quality Management Strategy).* State Water Quality Management Strategy, Report No. 6.

Liang, L. and Bloom, N.S. (1993). Determination of total mercury by single-stage gold amalgamation with cold vapour atomic spectrometric detection. *Journal of Analytical Atomic Spectrometry* 8, 591-4.

McAlpine, K. W., Wenziker, K.J., Apte, S.C. and Masini, R.J. (in press). *Background quality for coastal marine waters of Perth, Western Australia*. Technical Series 117, Department of Environment. Perth, Western Australia.

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

Nakayama, E., Hiroyuki, T., Tooru, K. and Taitiro, F. (1981). Dissolved state of chromium in seawater. *Nature* Vol. 290, pp 768 – 770.

Neff, J. M. (2002). *Bioaccumulation in Marine Organisms – Effect of contaminants from oil well produced water*. Elsevier Science Ltd, Oxford, UK.

Nozaki, Y. (1997). *A Fresh Look at Element Distribution in the North Pacific*. EOS Electronic Supplement, http://www.agu.org/eos_elec/97025e.html.

OZREEF. (1997). *Natural Seawater Composition*. http://ozreef.org/reference/composition.html

Wenziker K.J., McAlpine, K. W., Apte, S.C. and Masini, R.J. (in press). *Background quality for coastal marine waters of the North West Shelf, Western Australia*. North West Shelf Joint Environmental Management Study, CSIRO Marine Research, GPO Box 1538, Hobart Tasmania 7001.

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 2 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 500mL fluorinated ethylene propylene (FEP) (Nalgene) bottles equipped with Teflon-lined caps were used for sample storage. The bottles were cleaned by soaking in 10% v/ AR grade hydrochloric acid for greater than 2 days, at least 3 days with 50% v/v AR grade nitric acid and then finally with 20% v/v ultra-pure grade hydrochloric acid (Merck Tracepure) for a minimum of 5 days. After each of these steps the bottles were rinsed with copious quantities of MQ water. Finally the bottles were filled with MQ water, capped and left for a minimum of 2 days. The bottles were then emptied and 'double-bagged' in two zip lock polyethylene bags prior to transportation to the sampling site.

A.1.3 Organics

Water samples for analysis of organic chemicals were stored in bottles provided by the Australian Government Chemical Laboratories (AGAL).

A.2 SAMPLE COLLECTION AND HANDLING

Water samples were collected approximately 0.5 metres below the surface (surface), and approximately one metre above the seabed (bottom). Specialised sampling equipment was required to ensure that potential contamination was minimised when analysing down to the ultra-trace levels proposed. Two different types of samplers were used:

- The CSIRO Pole sampler was used to take surface samples for metal analysis; and,
- The five-litre Teflon-coated Niskin bottle (General Oceanics model 1010 with external Teflon-coated springs) was used to take bottom samples for metal analysis and for all organic samples.

The Pole sampler had been specifically designed and tested by CSIRO for ultra-trace level metal analyses. The Pole sampler works by holding the sample bottle in a polymethylmethacrylate (Perspex) clamp attached to a polycarbonate sampling rod (Mart, 1979, as cited in Apte *et al.*, 1998).

The Niskin bottle was cleaned prior to field work for the main program by filling with 5% v/v nitric acid and maintained in an upright position for approximately one hour. The acid was removed and the sampler refilled and rinsed with at least three portions of MQ high purity water. After cleaning, the bottle was sealed in a clean plastic bag for storage and transport.

In the field, the Niskin bottle was deployed to mid-water depth in the open position at a clean site, and left to equilibrate for 30 minutes prior to use each day. At each site the Niskin bottle was also ‘soaked’ in the open position for at least two minutes before taking samples. The DoE research vessel *Zoila* was used for the fieldwork. The Niskin bottle was attached to a boom that was in turn attached to a gantry, which allowed the bottle to be deployed approximately three metres from the port side of the vessel. Sampling was always undertaken with the sampler into the current to minimise the risk of contamination from the vessel.

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 metal analysis were stored in the dark on ice and couriered overnight to the CSIRO laboratory. Samples for dissolved metal analysis were filtered in the laboratory within 24 hours of collection.

Water samples for analysis of organic chemicals were collected from the Niskin bottle. At each site, two one litre amber glass bottles and two 44 mL zero headspace glass vials were filled for the laboratory analyses. Sample containers were filled with a positive meniscus and it was ensured that no air bubbles remained. The samples were then immediately stored in the dark on ice whilst in the field and then were transported to the laboratories within 48 hours of collection.

A.3 SAMPLE FILTRATION PROCEDURES

Dissolved metal concentrations are considered to be a better estimate of the biologically available metals than total concentration. Samples for metal analyses (excluding mercury) were filtered in a laboratory clean room to reduce the potential for contamination that can be caused by filtering in the field. All metal samples (excluding mercury samples) were filtered through a 0.45 μm filter before analysis.

Polycarbonate filter rigs (Sartorius) fitted with 0.45 μm Millipore membrane filters were used to filter the samples. All filtration assemblies were rigorously cleaned before processing each sample by first filtering 100 mL volumes of 10% nitric acid solution followed by 2 x 150 mL of MQ water and finally, a 50 mL volume of sample. The filtrates were transferred to acid-washed polyethylene bottles and preserved by addition of 2 mL/L concentrated nitric acid (Merck Suprapur).

A.4 ANALYTICAL METHODS

A.4.1 Metals

Cadmium, Copper, Lead 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 (250 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 4100ZL) using Zeeman effect background correction and operating conditions recommended by the manufacturer.

Chromium

Chromium concentrations were determined directly by GFAAS (Perkin Elmer 4100 ZL) 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 and cold vapour atomic fluorescence spectrometry (Liang and Bloom, 1993).

Quality control

To check analytical accuracy, aliquots of a NRC Canada Standard Reference Seawaters NASS-5 or CASS-4 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 Organics

The analytical methods below were provided by AGAL.

Method 11.11

PAH in water (Low level)

An aliquot of water is extracted using dichloromethane (concentration factor is greater for low level determination). The combined extract is filtered through sodium sulphate then concentrated. The prepared extract is then analysed by GC-MS in SIM mode. Quantitation is by the internal standard method (using the 8270 internal standard). PAHs determined are the standard EPA 16 analytes.

Method 11.22

Phenols in water (Low level)

An aliquot of water is extracted using dichloromethane (concentration factor is greater for low level determination). The combined extract is filtered through sodium sulphate then concentrated. The prepared extract is then analysed by GC-MS in SIM mode. Quantitation is by the internal standard method (using the 8270 internal standard).

Method WL 244
BTEX and C6-C9 Total Petroleum Hydrocarbons (TPH) in water

An inert gas (Helium) is bubbled through the water sample (5mL) at ambient temperature at a pre-determined rate. The volatile compounds are efficiently transferred from the aqueous phase to the vapour phase. The vapour is swept through a sorbent trap resulting in the trapping of the volatile compounds onto the sorbent material (OV-1, Tenax-GR and Silica Gel). After purging is complete, the sorbent trap is rapidly heated and back flushed with inert gas to desorb the compound onto a gas chromatography column. The volatile compounds are separated on the GC column and detected using a Mass Selective Detector (MSD).

Method WL 203
C10-C36 Total Petroleum Hydrocarbons (TPH) in water

Water samples are extracted with dichloromethane by separatory funnel (USEPA Method 3510). Extracts are concentrated and where necessary diluted. Prepared extracts are injected into a GC where separation of individual components is achieved with a non-polar capillary column and detection is by flame ionisation (FID).

Methods NGCMS_1111 & NGCMS_1122
Semi Volatile Organic Compounds (SVOC) in water

Water samples are extracted with dichloromethane by separatory funnel (USEPA Method 3510). Extracts are concentrated and where necessary diluted. Prepared extracts are injected into a GC where separation of individual components is achieved with a non-polar capillary column and detected using a Mass Selective Detector (MSD).

Method NR_19
Organochlorine (OC) pesticides / Organophosphate (OP) pesticides in water

Water samples are extracted with dichloromethane by separatory funnel (USEPA Method 3510). Extracts are concentrated, exchanged into hexane and where necessary diluted. Prepared extracts are injected into a GC where separation of individual components is achieved with a non-polar capillary column with detection by electron capture (ECD).

Appendix B: Metals Analytical Quality Control Data

Spike Recoveries

Site sampled	% Cd Recovery	% Cu Recovery	% Pb Recovery	% Zn Recovery
9-S	90	93	93	115
14-S	96	93	93	96

Site	% Recovery Hg	[Hg] Added ng/L
Site 2-S	98	13
Site 7-S	96	13
Site 12-S	98	13

Method Blanks

Method Blank	Sample	Sample	Sample	Sample	Sample	Sample
	µg Cd/L	µg Cr/L	µg Cu/L	µg Pb/L	µg Hg/L	µg Zn/L
Mean absolute blank (n=3)	0.000	0.000	0.005	0.003		0.002
Mean absolute blank (n=2)					0.00026	
LOD (3 sigma)	0.001	0.15	0.008	0.003	0.000	0.006

Field Blanks

Field Blank	Sample	Sample	Sample	Sample	Sample	Sample
	µg Cd/L	µg Cr/L	µg Cu/L	µg Pb/L	µg Hg/L	µg Zn/L
site 1	0.001	<0.15	<0.008	<0.003		0.015
site 4	0.001	<0.15	0.008	<0.003	<0.0001	0.023
site 7	0.002	<0.15	0.017	<0.003	<0.0001	0.024
site 9	<0.001	<0.15	0.013	<0.003	<0.0001	0.013
site 12					<0.0001	
MilliQ water					0.000	

* Field blank bottle was filled with Milli-Q water and acidified with 0.2% v/v trace pure HNO_3
S = surface, B = bottom sample

CRM

CASS-4	Sample	Sample	Sample
	µg Cd/L	µg Cu/L	µg Zn/L
Certified Value	0.026±0.003	0.592±0.055	0.381±0.057
11.03.04	0.02	0.55	0.35
% recovery	86	93	91

Analytical Replicates

Site	Sample	Lab Replicate	Sample	Lab Replicate	Sample	Lab Replicate	Sample	Lab Replicate
	µg Cd/L	µg Cd/L	µg Cu/L	µg Cu/L	µg Pb/L	µg Pb/L	µg Zn/L	µg Zn/L
site 1-S	0.004	0.002	0.073	0.080	0.010	0.007	0.043	0.039
site 13-S	0.001	0.002	0.074	0.075	0.004	0.011	0.031	0.030

Site	Sample ng Hg/L	Lab Replicate ng Hg/L
Site 4-S	0.49	0.51
Site 9-S	0.36	0.42

Sampling Replicate

Site	Sample ng Hg/L	Sampling Replicate ng Hg/L
Site 4-S	0.50	0.34
Site 7-S	0.27	0.34

Appendix C: Calculations of 95th percentiles and means.

Data from 'impacted' sites (4, 6 & 9) have been excluded.

Site	µg Cd/L	µg Cr/L	µg Cu/L	µg Pb/L	µg Zn/L	µg Hg/L
1-s	0.003	0.23	0.076	0.009	0.041	0.0004
1-b						0.0002
2-s	0.001	0.26	0.064	0.007	0.026	0.0004
3-s	0.001	0.24	0.061	0.004	0.033	0.0005
3-b						0.0001
5-s	0.002	0.15	0.062	0.008	0.041	0.0003
7-s	0.002	0.23	0.059	0.013	0.020	0.0003
7-s rep.	0.002	0.21	0.067	0.013	0.019	0.0003
7-b						0.0001
8-s	0.002	0.18	0.057	0.007	0.079	0.0004
10-s	0.003	0.150	0.066	0.003	0.036	0.0004
10-b						0.0002
11-s	0.003	0.150	0.073	0.007	0.047	0.0003
12-s	0.002	0.150	0.064	0.007	0.027	0.0003
12-b						0.0003
13-s	0.002	0.150	0.074	0.007	0.031	0.0003
14-s	0.002	0.150	0.075	0.003	0.031	0.0004

95th %ile	0.003	0.25	0.076	0.013	0.062	0.0004
Mean	0.002	0.19	0.067	0.007	0.036	0.0003
n	12	12	12	12	12	17