Background quality for coastal marine waters of Perth, Western Australia

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Abstract

Water quality surveys were undertaken in Perth's coastal waters in February and June of 2003 to determine dissolved concentrations of arsenic, aluminium, cadmium, chromium, cobalt, copper, lead, silver and zinc; total mercury concentrations; concentrations of a range of organic chemicals (polyaromatic hydrocarbons, organochlorine pesticides, organophosphate pesticides, phenols, petroleum hydrocarbons and the chemicals benzene, toluene, ethylbenzene and xylene [BTEX]) and radionuclides. This work was undertaken to gain an understanding of background concentrations for a range of contaminants in these marine waters, and to ascertain whether the guideline trigger values from ANZECC & ARMCANZ (2000) were relevant to the region.

The results of this study indicate that the coastal waters of the Perth region were generally of very high quality. The concentrations of metals were low by world standards, with localised elevations of some metals in Cockburn Sound. Concentrations at the time of sampling met the environmental quality guidelines for a *very high* level of ecological protection (99% species protection) for all metals, except cobalt, throughout the sampled area. No organic chemicals were detected in any of the samples. Guideline values were available for five of the organic chemicals and the analytical reporting limits for these chemicals were well below the guideline trigger values recommended in ANZECC & ARMCANZ (2000) for a *very high* level of ecological protection.

The findings of this study therefore suggest that the ANZECC & ARMCANZ (2000) 99% species protection guidelines are appropriate for application to the region for all the relevant contaminants except cobalt. For cobalt, the 95% species protection guideline is recommended for use.

1.   Introduction

The Environmental Protection Authority (EPA) has developed a State Government endorsed environmental quality management framework for implementing the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ 2000) in Western Australia (Government of Western Australia, 2004a). This Environmental Quality Management Framework (EQMF) is being applied to the management of activities that can affect the quality of marine ecosystems. Implementation is currently focussed on Perth metropolitan coastal waters, including Cockburn Sound. The EQMF establishes environmental values that are to be protected and maintained in the marine waters, the environmental quality objectives (broad management goals) and the environmental quality criteria (EQC) that are to be achieved so that the environmental values are maintained. The environmental values and environmental quality objectives represent the community's long-term desires, or goals, for the marine waters. The EQC are based on the numerical guidelines and approaches recommended in the National guidelines document (ANZECC & ARMCANZ, 2000). However, it is recognised in the National document that the numerical guidelines may need to be modified to establish site-specific criteria in regions where natural background levels exceed the guidelines, or where particularly sensitive species exist. The main objectives of the investigations reported in this paper were to provide a best estimate of natural background concentrations for a range of chemical constituents of local concern (heavy metals, organic chemicals and radionuclides) to confirm the relevance of the National guidelines, and secondly, to characterise ambient concentrations of these constituents in areas potentially influenced by wastewater discharges.

Few sampling programs have attempted to characterise background chemical concentrations in marine waters off Perth. Most monitoring programs have focused around specific developments or activities and have used commercial laboratories that are not equipped to measure chemicals at the analytical limits required to detect *actual* background concentrations for most contaminants (BP, 2003; Crawley *et al*., 2001; DAL Science and Engineering Pty Ltd, 2002; Kinhill, 1998). In many cases the analytical limits of reporting are also above the proposed water quality guidelines as set out by the EPA (2004). A less intensive water quality survey was completed by the Department of Environment (DoE) (formerly the Department of Environmental Protection) in April 2001 (Crawley *et al.,* 2001), however, the limits of reporting (LOR) of the analytical laboratory were too high to detect most of the contaminants analysed.

This report describes the results of water quality surveys conducted in the coastal waters off Perth to determine the current background concentrations of selected metals, organic chemicals and radionuclides using analytical techniques that provided the lowest detection limits available in Australia.

The study involved two surveys; a pilot survey followed by a larger, more extensive main survey. Specifically, the objectives of the pilot survey included:

- Testing the adequacy of both DoE's sampling equipment and sampling protocols for measuring ultra-trace metal concentrations;

- Determining whether background metal concentrations were significantly different between bottom and surface waters;

- Determining whether there were significant differences in metal concentrations between inshore shallow (< 20m) and offshore (> 20m) environments; and

- Ascertaining the likely range of actual concentrations for each metal before initiating the main survey.

The main survey was undertaken to:

- Determine background water quality concentrations for the selected contaminants in Perth metropolitan coastal waters; and,

- Ascertain whether the guideline trigger values in ANZECC & ARMCANZ (2000) were relevant to the region.

The analytes measured in this study were considered to be the key contaminants of concern after considering the *Contaminant Inputs Inventory for Cockburn Sound* (Hine, 1998), the composition of domestic treated wastewater discharged into Perth coastal waters, the long term environmental fate of the chemicals and the availability of funds for the analyses.

2.   Methods

2.1   Field sampling

Fieldwork for both surveys was conducted by staff from the DoE and the CSIRO Centre for Advanced Analytical Chemistry (Lucas Heights, NSW). Sampling for the pilot survey was undertaken on the 27 February 2003 and sampling for the main program was undertaken on 9 – 10 April 2003. Full details of the water sampling procedures are given in Appendix A.

Pilot Survey

The three sites that were selected for the pilot survey were chosen to achieve the objectives listed in the Introduction and were expected to represent the range of concentrations likely to be encountered in the coastal waters off Perth. Table 1 gives site information while Figure 1 shows the sampling locations. Cockburn Sound is a relatively enclosed embayment with industry located along its eastern shoreline. Warnbro Sound has no surrounding industry but has some urban development along its shores. The location of the offshore site was largely beyond anthropogenic influences and was considered likely to be of similar composition to ocean water.

Four replicate samples were collected from the surface at site WS4 for each of the two sampling methods; the CSIRO Pole sampler and the Niskin bottle. Four replicate bottom samples were also taken with the Niskin bottle at site WS4. For sites CS8 and OS, samples were taken at the surface with both the Niskin bottle and the Pole sampler, and at the bottom with the Niskin bottle only.
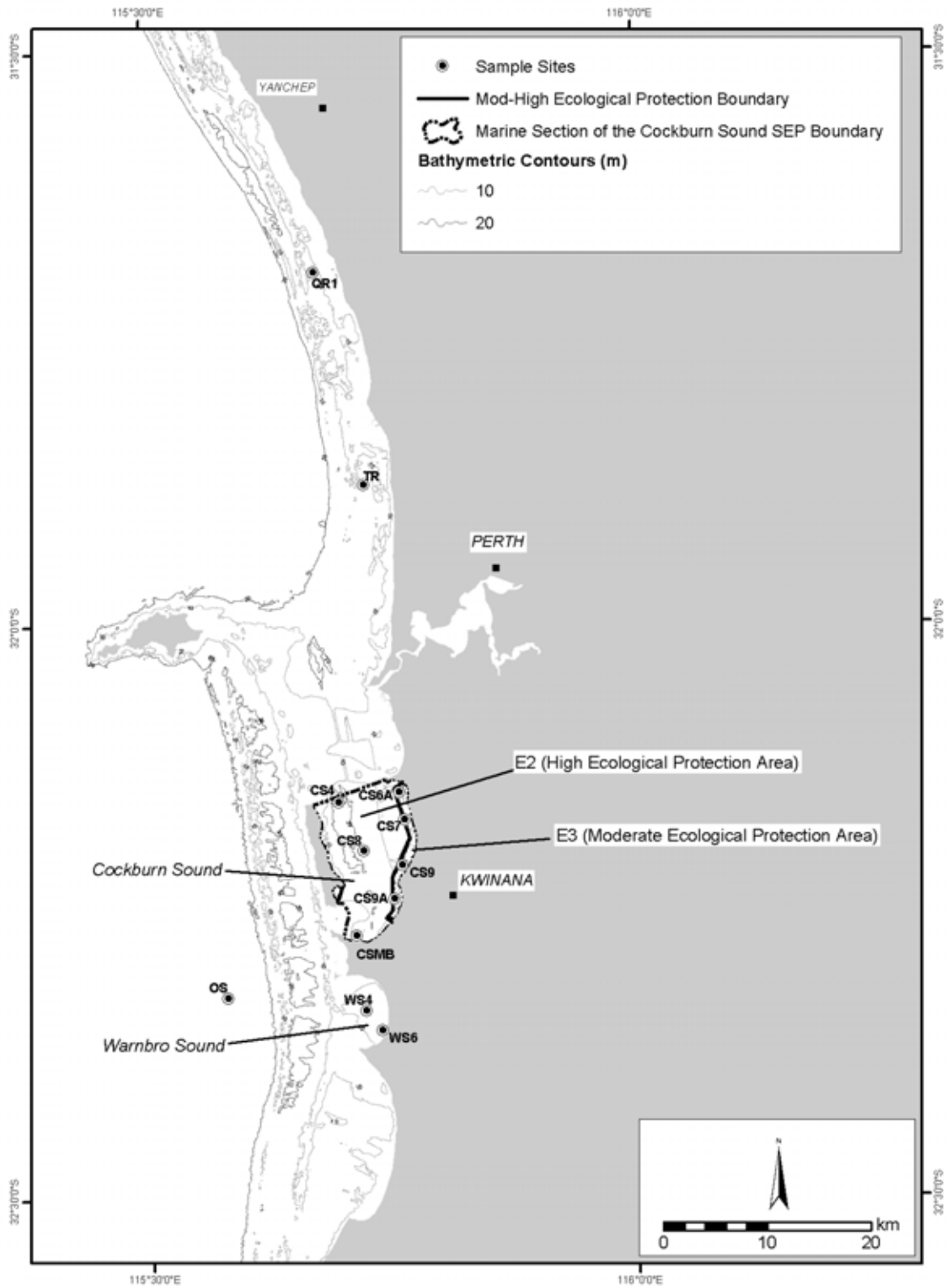
Figure 1: Locality map of the study area showing the sampling sites, Perth coastal waters.

Table 1: Sampling locations for the pilot survey.

SITE NAME	SITE CODE	LATITUDE	LONGITUDE	DEPTH (m)
Warnbro Sound 4	WS4	32.3367	115.7218	17.2
Offshore Site	OS	32.3247	115.5800	34.5
Cockburn Sound 8	CS8	32.1970	115.7207	19.7

    * Datum is WGS84.

Salinity/ temperature measurements were taken during the pilot survey to ascertain whether the water column was stratified or mixed. The predicted tidal information at Fremantle for the week during which the pilot survey was undertaken is presented in Figure 2. Samples were collected during a flood tide in the spring cycle.
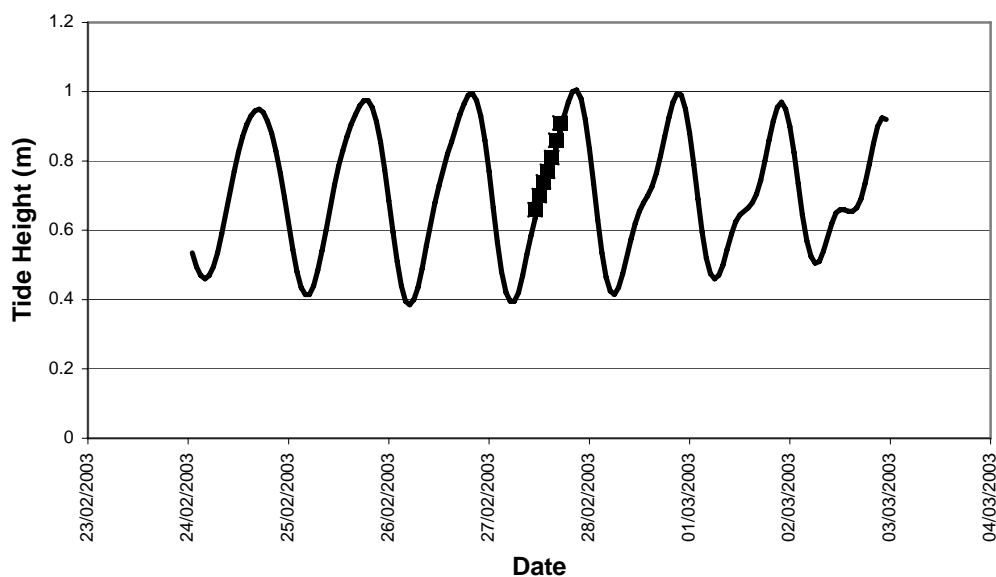
Figure 2: Predicted tides at Fremantle from 24 February to 3 March 2003 (squares represents sampling period).

Main Survey

The Perth metropolitan region has a relatively exposed coastline and a Mediterranean climate with seasonal river flow. The majority of Perth's coastal waters are therefore expected to be near oceanic in quality over the summer period. The main exception is likely to be the waters of Cockburn Sound, a relatively enclosed marine embayment with heavy industry and a naval port located along its shores. Warnbro Sound, a similar marine embayment south of Cockburn Sound, has significantly less intensive land use activity in its catchment and was considered to be a reasonable reference site for Cockburn Sound water quality. The sampling sites selected for the main survey (Figure 1 and Table 2) were distributed along the coastline of the Perth metropolitan region but with a focus on the waters of Cockburn Sound, where there is a relatively high level of management activity. As far as possible the sampling sites were selected to be consistent with sites sampled in the *Southern Metropolitan Coastal Waters*

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Study (1991 – 1994) (DEP, 1996) and the subsequent water quality monitoring programs undertaken in the Sound by the Kwinana Industries Council.

The predicted tidal information at Fremantle for the week during which the main survey was undertaken is presented in Figure 3. Samples were collected on a flood tide in a spring cycle.

Table 2: Sampling locations for the main survey.

SITE NAME	SITE CODE	LATITUDE	LONGITUDE	DEPTH (m)
Warnbro Sound 4	WS4	32.3367	115.7218	17.2
Warnbro Sound 6	WS6	32.3535	115.7378	17
Offshore Site	OS	32.3247	115.5800	34.5
Cockburn Sound 8	CS8	32.1970	115.7207	19.7
Cockburn Sound 4	CS4	32.1547	115.6950	20.9
Mangles Bay	CSMB	32.2712	115.7120	3
Cockburn Sound 9A	CS9A	32.2392	115.7518	16.2
Cockburn Sound 9	CS9	32.2097	115.7597	13
Cockburn Sound 7	CS7	32.1700	115.7625	10.8
Cockburn Sound 6A	CS6A	32.1460	115.7573	11
Trigg Island	TR	31.8783	115.7243	20
Quinns Rock	QR1	31.6928	115.6753	16.1

* Datum is WGS84.
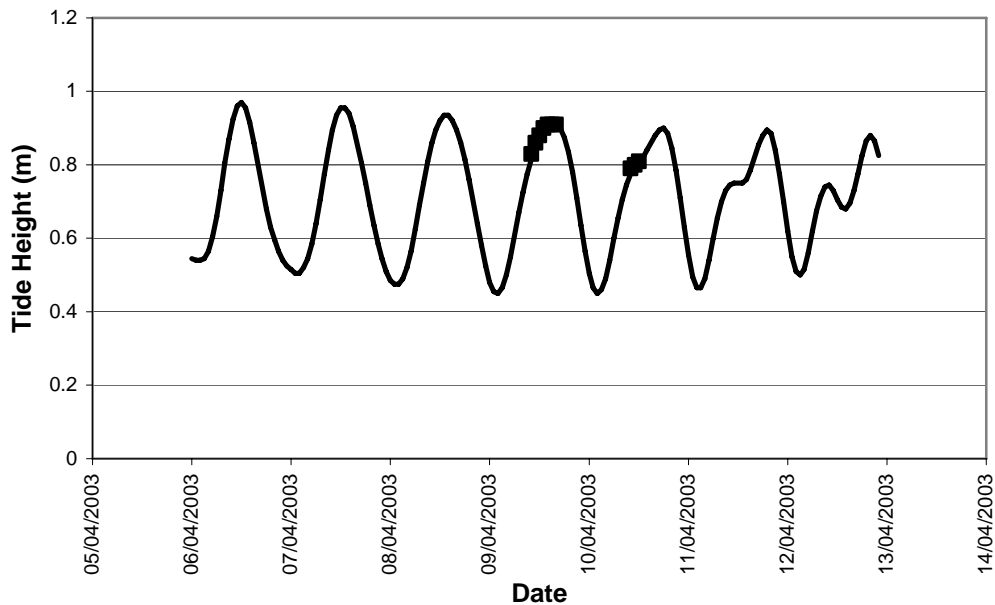
Figure 3: Predicted tide height at Fremantle from 6 April to 12 April 2003 (squares represents sampling period).

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 suite of metals chosen for analysis in the pilot survey included aluminium, cadmium, chromium, copper, mercury, silver and zinc. Samples were filtered for all analyses except mercury; unfiltered samples were analysed for total mercury. For the main survey, the suite of contaminants was extended to include arsenic, cobalt, lead, polyaromatic hydrocarbons, organochlorine pesticides, phenols, organophosphate pesticides, petroleum hydrocarbons and radionuclides (gross alpha and gross beta activity).

The CSIRO Centre for Advanced Analytical Chemistry undertook all of the metal analyses. Although the CSIRO laboratory is NATA registered for metal analyses, 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.

All samples for metal analysis (excluding mercury samples) were filtered through a 0.45 μm filter before analysis. However, three of the pilot survey samples (one from each of the sites CS8, OS and WS4) were split with half the sample filtered through a 0.2 μm filter, and half filtered through a 0.45 μm filter. This was done to determine whether the smaller filter pore size gave a significantly better estimate of the true dissolved metal concentration. Following filtration, samples were preserved by the addition of ultrapure nitric acid (2 mL/L final concentration).

Samples from the pilot survey were analysed within six weeks for most metals. Samples from the main survey were analysed within two weeks of sampling for organic chemicals and within six weeks for most metals. Ultra-trace analyses for chromium and silver required different laboratory protocols and were not completed until late August and early September 2003respectively for both the pilot and main survey.

The metals in the main survey were analysed at all sites but only ten of the 12 sites were analysed for the organic chemicals including CS7 and CS9 (surface and bottom) and WS4, WS6A, CS8, CS4, CSMB, CS9A, CS6A and TR (surface only). The Australian Government Analytical Laboratories (AGAL) performed analyses of the organic chemicals and Western Radiation Services performed the radionuclide analyses. Both of these laboratories are NATA registered.

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, non-parametric tests were applied to the data.

Mann-Whitney tests were applied to the results of the pilot study to assess whether there were significant differences between samples taken with the Pole sampler and those taken with the Niskin bottle, and also between surface and bottom samples. The tests were applied to chromium, copper, mercury and zinc data from the WS4 site. The results of these analyses were used to design and rationalise the field sampling program for the main survey.

To assess whether there were any significant differences between the broad sub-regions sampled, the metals' data from both the pilot and main studies were pooled for each sub-region (Cockburn Sound, Warnbro Sound and 'offshore' – offshore included the data from three sites OS, TR and QR1) and a Kruskal-Wallis test was applied. If a significant difference was found, then a Mann-Whitney test was applied to determine where the difference in water quality lay and which location was contributing to the difference. The analytical results for mercury in the pilot survey were excluded from the tests because of suspected contamination. Aluminium and lead were excluded because all the analytical results were below the limit of detection. Cobalt was excluded because of insufficient data.

Mann-Whitney tests were also conducted to compare metal concentrations in the High Ecological Protection Area (E2) and Moderate Ecological Protection Area (E3) of Cockburn Sound (Government of Western Australia, 2004b). Sampling sites in the High Ecological Protection Area were CS4, CS8 and CSMB, while sites in the Moderate Ecological Protection Area were CS6A, CS7, CS9 and CS9A. Arsenic was excluded from these tests because of insufficient data from the High Ecological Protection Area. The statistics package StatView[TM] SE + Graphics (Abacus Concepts Inc, 1998 – 1991) was used to perform all of these tests.

The *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ 2000) recommends that the 95th percentile of concentration values for a contaminant at a test site should be less than the default guideline. For the purposes of this report the 95th percentile of concentrations for essentially unimpacted sites (reference sites) was deemed to represent the natural background concentration and used to assess whether or not the National guidelines were exceeded.

To estimate natural background concentrations of aluminium, cadmium, chromium and copper for the Perth region, data from the pilot and main surveys were combined and a 95th percentile of data from the least impacted sites (OS, QR1, TR, WS4 and WS6) was calculated. For mercury only the main survey data from the five least impacted sites were used to estimate natural background concentrations because the pilot study results for mercury were potentially contaminated (see section 3.2). For arsenic and lead there were no pilot study data so only main study data were used. For silver and zinc, the main survey results were excluded because of potential contamination (see section 5.1) and natural background concentration was estimated by calculating the 95th percentile using the pilot study results. Cobalt was only

sampled at seven sites so all the results were used to derive a 95th percentile. Analytical results from surface and bottom samples from the pilot survey and main survey were combined to capture as much temporal and spatial variability as possible for deriving the 95th percentiles (and means). Where the pilot study data were used, all results from the replicate samples taken at WS4 were included in the calculation. Results that were reported as 'below detection limit' were counted as being at the detection limit for the calculations (e.g. <0.019 μg/L became 0.019 μg/L).

A 95th percentile was also calculated for the High Ecological Protection and Moderate Ecological Protection areas of Cockburn Sound for comparison against environmental quality guidelines already determined for the Sound (EPA, 2004). The data used to calculate natural background metal concentrations for Perth coastal waters and ambient metal concentrations in Cockburn Sound are tabulated in Appendix B.

Estimates of background concentrations and tests for significant differences between the sub-regions were not undertaken for the organic chemicals because all results were below the laboratory's analytical limits of reporting. The radionuclide data were also excluded from statistical analysis because there were insufficient data.

3.   Results: Pilot survey

3.1   General conditions

Weather conditions on 27 February 2003 were fine and sunny with fresh to moderate (15 – 18 knot) easterly winds. There was a 0.5 metre swell offshore and moderate seas.

The salinity and temperature recordings are shown in Appendix C. There was no significant stratification of the water column detected at any of the sites.

3.2   Trace metals data

Table 3 shows the metals data obtained from the pilot survey. The quality control data are provided in Appendix D. The results show that the metal concentrations in these samples were very low and approached levels recorded for oceanic waters (Neff, 2002; Apte *et al.,* 1998; Nozaki, 1997; Nakayama *et al.,* 1981; OZREEF, 1997). The concentrations of aluminium at all sites (surface and bottom) were below the reported detection limit (0.9 μg/L). The concentrations of copper reported for CS8 (0.132 μg/L to 0.145 μg/L) were higher in comparison to those reported for OS and WS4 (0.046 μg/L to 0.085 μg/L). Similarly, the concentrations of zinc were slightly higher in CS8 compared to OS and WS4. There were no obvious patterns or differences in the concentrations of cadmium, chromium and silver between the three sites.

The mercury concentrations were quite variable with some comparatively high values obtained. For example, values of 0.0082 μg/L and 0.0057 μg/L were obtained for WS4 (Niskin bottle bottom samples) and a value of 0.0074 μg/L was obtained for the surface Niskin bottle sample at CS8. The mercury samples were not filtered and measured total mercury, it is therefore possible that particulate bound mercury could have contributed to the observed variability in the data. However, the majority of the

Table 3: Results from the Perth coastal waters trace metals pilot survey, February 2003.

Site	Sampler, Depth	Ag µg/L	Al µg/L	Cd µg/L	Cr µg/L	Cu µg/L	Hg µg/L	Zn µg/L
CS8	C, S	0.0009	< 0.9	0.004	0.16	0.145	0.0012	0.122
CS8	N, S	0.0006	< 0.9	0.004	0.15	0.142	0.0074	0.202
CS8	N, B	0.0005	< 0.9	0.004	0.15	0.132	0.0013	0.182
OS	C, S	<0.0004	< 0.9	<0.004	0.18	0.046	0.0020	<0.038
OS	N, S	<0.0004	< 0.9	<0.004	<0.15	0.052	0.0002	0.147
OS	N, B	<0.0004	< 0.9	<0.004	0.17	0.056	0.0007	0.108
WS4	C, S	<0.0004	< 0.9	0.004	0.20	0.081	0.0023	0.150
WS4	C, S	<0.0004	< 0.9	0.004	<0.15	0.085	0.0008	0.114
WS4	C, S	<0.0004	< 0.9	0.004	<0.15	0.067	0.0004	<0.038
WS4	C, S	<0.0004	< 0.9	<0.004	<0.15	0.080	0.0002	0.116
WS4	N, S	0.0004	< 0.9	<0.004	<0.15	0.085	0.0013	0.109
WS4	N, S	<0.0004	< 0.9	0.004	<0.15	0.078	0.0017	0.133
WS4	N, S	0.0005	< 0.9	0.005	<0.15	0.082	0.0007	0.111
WS4	N, S	0.0006	< 0.9	0.004	<0.15	0.075	0.0020	0.074
WS4	N, B	<0.0004	< 0.9	<0.004	<0.15	0.076	0.0057	0.075
WS4	N, B	<0.0004	< 0.9	<0.004	<0.15	0.078	0.0015	0.085
WS4	N, B	0.0005	< 0.9	<0.004	<0.15	0.083	0.0082	0.084
WS4	N, B	0.0007	< 0.9	<0.004	0.15	0.085	0.0009	0.130
Limit of Detection (3 sigma)		**0.0004**	**0.9**	**0.004**	**0.15**	**0.028**	**0.0002**	**0.038**

C = sample taken with CSIRO teflon Pole sampler
N = sample taken with DoE Niskin bottle
S = surface
B = bottom

variability is thought to have resulted from the laboratory sample bottle cleaning procedure (see Appendix A). The cleaning procedure was subsequently modified to minimise mercury contamination of the sample bottles. Nevertheless, it should be noted that all of the mercury results obtained were more than an order of magnitude below the 99% species protection guideline of 0.1 μg/L (ANZECC & ARMCANZ, 2000).

Results of the Mann-Whitney tests showed that for chromium, copper, mercury and zinc there was no significant difference between the samples taken with the Pole sampler and the samples taken with the Niskin bottle at WS4 (Table 4). Similarly, no significant differences were found between the surface and bottom samples at WS4 (Table 5).

Table 4: P-values for the Mann-Whitney tests comparing copper, mercury and zinc concentrations from samples collected with the Niskin bottle and Pole sampler at WS4.

Metal	p-value
Chromium	0.32
Copper	0.88
Mercury	0.39
Zinc	0.56

Table 5: P-values from the results of the Mann-Whitney tests comparing metal concentrations from surface and bottom at WS4.

Metal	p-value
Chromium	0.48
Copper	0.80
Mercury	0.13
Zinc	0.50

Negligible differences were found in the concentrations of all metals for the three samples that were split and filtered through either a 0.45 µm filter or a 0.2 µm filter (Table 6).

Table 6: Comparison of dissolved metal concentrations measured in samples filtered through a 0.2 µm filter and a 0.45 µm filter.

Site	Filter	Ag	Al	Cd	Cr	Cu	Zn
	µm	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
CS8	0.2	0.9	< 0.9	<0.004	0.15	0.134	0.129
CS8	0.45	0.9	< 0.9	0.004	0.16	0.145	0.122
OS	0.2	<0.4	< 0.9	<0.004	0.18	0.049	0.090
OS	0.45	<0.4	< 0.9	<0.004	<0.15	0.052	0.147
WS4	0.2	<0.4	< 0.9	0.004	<0.15	0.085	0.092
WS4	0.45	<0.4	< 0.9	<0.004	<0.15	0.076	0.075

3.3 Key findings of the pilot survey

Metal concentrations in Perth's coastal waters were very low and approached oceanic levels. There were negligible differences between the concentrations of metals found in samples taken with the Pole sampler and the Niskin bottle (Table 4). As a result, the Niskin bottle was considered adequate for future ultra-trace metal sampling.

The metals' data from the pilot survey showed that there was little variation between concentrations of metals at surface and depth. Samples for the main survey could therefore be taken predominantly from the surface.

Differences in metal concentrations measured in samples filtered though a 0.2 μm filter versus a 0.45 μm filter were negligible. Samples in the main survey could therefore be filtered through a 0.45 μm filter to speed up sample processing.

Mercury analyses were variable and some contamination is thought to have resulted from the procedures used to wash the sample bottles prior to sampling. For future work, sample bottles used for ultra-trace mercury analysis would need to be rigorously cleaned using more stringent procedures appropriate for collecting seawater samples containing sub part per trillion concentrations of mercury.

4. Results: Main survey

4.1 General conditions

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

9 April 2003 – fine and sunny conditions with light to moderate (10 –15 knot) east-northeast winds, swinging north after midday and then southwest in the afternoon (reaching 15 knots by late afternoon).

10 April 2003 – thundery showers prior to vessel launch. Light north-easterly winds swinging north-westerly by midday. Swell 0.5 – 1 metre.

4.2 Trace metals data

The metals' data from the main survey are presented in Table 7 and the quality control data are attached in Appendix E. At all sites, aluminium and lead concentrations were below the reported detection limits (1 μg/L and 0.019 μg/L respectively). Similarly, at every site except OS and QR, the chromium concentrations were below the reported detection limit (0.15 μg/L). The silver and zinc results were generally higher than those obtained in the pilot survey and the high concentrations measured in the field blanks suggest the samples may have been contaminated (see section 5.1). As a consequence the silver and zinc results have not been used in calculations to estimate background water quality. Although the results for silver and zinc are likely to be positively biased, they are still well below recommended water quality guidelines for the highest level of protection (ANZECC & ARMCANZ, 2000).

Table 7: Results from the Perth coastal waters trace metals main survey, April 2003.

Site	Ag (µg/L)	Al (µg/L)	As (µg/L)	Cd (µg/L)	Co (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (µg/L)	Pb (µg/L)	Zn (µg/L)
CSMB (s)	0.0021	<1	1.7	0.005	-	<0.15	0.134	0.0004	<0.019	0.282
CS4 (s)	0.0034	<1	1.8	0.002	-	<0.15	0.056	0.0003	<0.019	0.638
CS6A (s)	0.0048	<1	1.7	0.003	0.009	<0.15	0.169	0.0004	<0.019	0.332
CS7 (s)	0.0035	<1	1.7	0.003	-	<0.15	0.171	0.0011	<0.019	0.388
CS7 (b)	0.0049	<1	1.7	0.005	0.014	<0.15	0.154	0.0005	<0.019	0.299
CS8 (s)	0.0038	<1	1.8	0.005	<0.008	<0.15	0.144	0.0004	<0.019	0.281
CS9A (s)	0.0035	<1	1.8	0.004	<0.008	<0.15	0.197	0.0008	<0.019	0.413
CS9A (b)								0.0007		
CS9 (s)	0.0041	<1	1.8	0.006	0.010	<0.15	0.142	0.0006	<0.019	0.252
CS9 (b)	0.0044	<1	1.7	0.005	-	<0.15	0.640	0.0015	<0.019	0.440
OS (s)	0.0026	<1	1.7	<0.002	-	0.15	0.038	0.0003	<0.019	0.183
QR1 (s)	0.0007	<1	1.8	0.004	-	0.20	0.085	0.0004	<0.019	0.141
TR (s)	0.0005	<1	1.7	0.003	-	<0.15	0.106	0.0003	<0.019	0.118
WS4 (s)	0.0021	<1	1.8	0.004	<0.008	<0.15	0.062	0.0003	<0.019	0.502
WS6 (s)	0.0037	<1	1.7	0.003		<0.15	0.054	0.0003	<0.019	0.171
WS6 (b)	0.0023	<1	1.6	0.005	<0.008	<0.15	0.064	0.0003	<0.019	0.531
Limit of Detection (3 sigma)	**0.0004**	**1**	**0.2**	**0.002**	**0.008**	**0.15**	**0.011**	**0.0002**	**0.019**	**0.018**

(s) = surface
(b) = bottom

The results of the main survey confirm the finding of the pilot survey, that metal concentrations in Perth's coastal marine waters are naturally very low and are at levels consistent with offshore oceanic waters (Neff, 2002; Apte *et al.,* 1998; Nozaki, 1997; Nakayama *et al.,* 1981; OZREEF, 1997).

Concentrations of silver, copper and mercury were slightly higher at the Cockburn Sound sites than at the Warnbro Sound sites, offshore site or northern metropolitan sites (QR1 and TR). There appeared to be little variation in concentrations of arsenic, cadmium and zinc between sub-regions (described in section 2.3). A Kruskal-Wallis test was applied to the pooled pilot and main survey data for arsenic, cadmium, chromium, copper, silver and zinc to test for significant differences between the three sub-regions. The test showed a significant difference for chromium, copper, silver and zinc (Table 8).

Table 8: P-values from the results of the Kruskal-Wallis and Mann-Whitney tests comparing metal concentrations of different water bodies, Perth coastal waters (alpha is set at 0.05 and significant values are shown in bold).

METAL	p-level CS vs WS vs Off	p-level CS vs WS	p-level CS vs OFF	p-level OFF vs WS	p-level E2 vs E3
Arsenic	0.688	-	-	-	-
Cadmium	0.2514	-	-	-	0.6775
Chromium (total filt.)	**0.0324**	0.9145	**0.0339**	**0.0356**	0.3173
Copper	**0.0001**	**0.0016**	**0.0017**	0.2259	**0.0129**
Mercury (total)	0.4521	-	-	-	0.8858
Silver	**0.0006**	**0.0003**	**0.0056**	0.8994	**0.0103**
Zinc	**0.0016**	**0.0014**	**0.0027**	0.726	0.1093

Mann-Whitney tests were then performed to determine which sub-regions were significantly different from each other. The Mann-Whitney test was also used to determine whether metal concentrations were significantly different between the High (E2) and Moderate (E3) Ecological Protection areas in Cockburn Sound. The results of these tests are provided in Table 8 and show:

- A significant difference between Cockburn Sound and Warnbro Sound for copper, silver and zinc;
- A significant difference between Cockburn Sound and offshore data for chromium, copper, silver and zinc;
- There was no difference found between offshore and Warnbro Sound for copper, silver and zinc, however, there was a significant difference for chromium; and
- A significant difference for concentrations of copper and silver between the High Ecological Protection and Moderate Ecological Protection areas of Cockburn Sound.

Given these results a decision was made to pool the Warnbro Sound and offshore data to create a reference database and to analyse the Cockburn Sound data separately. Although there were insufficient mercury data to test for significant differences between the sub-regions, when the Warnbro Sound and offshore site data are pooled and compared with Cockburn Sound data using a Mann-Whitney test, then a

significant difference was observed (p-level of 0.0005). Mercury concentrations in Warnbro Sound and offshore waters were similar and very low.

4.3 Organic chemicals

The results of the organic analyses are presented in Table 9. Concentrations of all the organic chemicals were below the Limit of Reporting (LOR) at all sites. The LORs for four of the chemicals were above the nationally recommended guideline trigger levels for 99% species protection (ANZECC & ARMCANZ, 2000), and above the 95% species protection guideline for one of the chemicals:

- Endrin - the results do not indicate whether the 99% or 95% species protection guideline trigger values of 0.004 and 0.008 μg/L respectively have been met (LOR of 0.01 μg/L), but they are less than the 90% species protection guideline value of 0.01 μg/L;
- Total Endosulfan - the results do not indicate whether the guideline trigger value of 0.005 μg/L for 99% or 95/99% species protection has been met (LOR of 0.01 μg/L), but they are less than the 95% species protection guideline value of 0.01 μg/L;
- Chlorpyrifos - the results do not indicate whether the 99% or 95% species protection guideline trigger values of 0.0005 and 0.009 μg/L respectively, have been met (LOR of 0.01 μg/L). However, all of the sites sampled were found to have levels below the 90% species protection guideline value of 0.04 μg/L; and
- Temephos - the results do not indicate whether the guideline trigger value of 0.0004 μg/L for 99% species protection has been met (LOR of 0.01 μg/L), but all of the sites sampled had levels below the 95% species protection guideline value of 0.05 μg/L.

Guideline trigger levels were only available for five of the remainder of the analysed organic chemicals (naphthalene, pentachlorophenol, phenol, benzene and 1,2,4-trichlorobenzene). The LORs for these were significantly less than the 99% species protection guideline trigger values, for example, the LOR for benzene was 1.0 μg/L, which was well below the 99% species protection guideline trigger value of 500 μg/L.

Table 9: Results of the organic chemical analyses for Perth coastal waters, April 2003, 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	WS4 (s)	WS6(s)	CS8 (s)	CS4 (s)	CSMB (s)	CS9A (s)	CS9 (s)	CS9 (b)	CS7(s)	CS7 (b)	CS6A (s)	TR (s)	LOR	Guideline value 99%	95%	90%
Polyaromatic Hydrocarbons															**99%**	**95%**	**90%**
Anthracene	µg/L	<0.1	<0.1	<0.1	<0.1	<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	<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	<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	<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	<0.1	<0.1	<0.1	0.1	NG	NG	NG
Chlorinated Phenols																	
Pentachlorophenol	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.2	**11**	**22**	**33**
Organochlorine (OC) Pesticides																	
HCB	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Lindane	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Heptachlor	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Aldrin	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
BHC Total (other than lindane)	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Heptachlor epoxNGe	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NGe
Chlordane	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
DDE	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Dieldrin	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Endrin	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	**0.004**	**0.008**	**0.01**
DDD	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
DDT	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Methoxychlor	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Endosulfan Total	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	**0.005**	**0.01**	**0.02**
Phenols																	
Phenol	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	**270**	**400**	520

Organic chemical	Units	WS4 (s)	WS6(s)	CS8 (s)	CS4 (s)	CSMB (s)	CS9A (s)	CS9 (s)	CS9 (b)	CS7(s)	CS7 (b)	CS6A (s)	TR (s)	LOR	Guideline value		
Organophosphate (OP) Pesticides															**99%**	**95%**	**90%**
Demeton-S-methyl	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<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	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Dimethoate	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<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	<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	<0.01	<0.01	<0.01	<0.01	0.01	**0.0005**	**0.009**	**0.04**
Parathion	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<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	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Fenthion	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<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	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Azinphos-methyl	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Temephos	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	**0.0004**	**0.05**	**0.4**
Fenitrothion	µg/L	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	NG	NG	NG
Surrogate																	
Surrogate 1 Rec.	%	98	103	101	102	102	103	105	103	106	105	105	105				
Surrogate 2 Rec.	%	94	93	92	93	92	91	92	92	91	90	90	90				
Surrogate OC Rec.	%	99	96	99	99	95	94	92	94	91	98	88	89				
Surrogate OP Rec.	%	86	88	90	86	83	79	86	96	82	89	78	74				
BTEX																	
Benzene	µg/L	<1.0	<1.0	<1.0	<1.0	<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	<1.0	<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	<1.0	<1.0	<1.0	<1.0	1	NG	NG	NG
Xylene	µg/L	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	2	NG	NG	NG
Total BTEX	µg/L	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	5	NG	NG	NG
Total Petroleum Hydrocarbons																	
TPH C6 - C9	µg/L	<25	<25	<25	<25	<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	<25	<25	<25	25	NG	NG	NG
TPH C15 - C28	µg/L	<100	<100	<100	<100	<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	<100	<100	<100	100	NG	NG	NG
Total TPH	µg/L	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	250	NG	NG	NG
Other																	
Cumene	µg/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1	NG	NG	NG
1,2,4-Trichlorobenzene	µg/L	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1	**20**	**80**	**140**

4.4   Radionuclides

The results of the radionuclide analyses for the six sites are presented in Table 10. Although there were too few data for a statistical analysis, the trend appears to be for lower gross alpha and gross beta values in Warnbro Sound than in Cockburn Sound and QR1, but there was a degree of variability in the data, especially in the gross beta data. The highest gross beta value obtained was 5.09 Bq/L at QR1 and the lowest gross beta value was 0.047 Bq/L at WS4. The highest gross alpha value obtained was 0.49 Bq/L at CS8 and the lowest value was 0.133 Bq/L at WS4.

Table 10: Results of radionuclide analyses, Perth coastal waters, April 2003.

Site	Alpha (Bq/L)	Beta (Bq/L) [‡]	K (mg/L)
WS4	0.133 +/- 0.003	0.047 +/- 0.006	180
WS6	0.197 +/- 0.0043	0.805 +/- 0.099	180
CS8	0.49 +/- 0.0097	2.828 +/- 0.335	180
CS9A	0.213 +/- 0.0047	3.826 +/- 0.444	180
CS9	0.304 +/- 0.0063	1.843 +/- 0.223	180
QR1	0.248 +/- 0.0053	5.091 +/- 0.582	180

[‡]The Beta results have been corrected for potassium-40 concentrations.
Method Detection Limit: Alpha - 0.005, Bq/L Beta - 0.010 Bq/L.

5.   General discussion

5.1   Trace metals data

Ultratrace sampling and analysis of dissolved metals in marine waters is extremely challenging and it is essential that rigorous QA/QC protocols are adopted to ensure accuracy of results. Field blank data were below detection limits in most cases (Appendix E), indicating satisfactory contamination control. There were however exceptions in the main survey for the zinc field blanks (0.076, 0.574, 0.812 µg/L) and silver field blanks (<0.0004, 0.0059, 0.010 µg/L) which were high and indicated potential contamination of samples. The field blank data were supported by the actual sample data where silver and zinc concentrations were markedly higher in the main survey than the pilot survey. It was suspected that zinc and silver contamination may have occurred during sample bottle preparation or sample collection. Survey results were positively biased and likely to overestimate actual background concentrations. Zinc concentrations in field blanks from the pilot survey were significantly lower but detectable. The zinc results from this survey may therefore also be positively biased (to a lesser extent) by sample contamination. As a result, the silver and zinc concentrations from this survey should be treated with caution.

A comparison of mean trace metal concentrations with data from the Pacific Ocean and New South Wales (NSW) coastal regions is shown in Table 11. For reasons outlined above, zinc and silver data from the main survey and mercury data from the pilot survey were excluded from the calculation of mean concentrations. The concentrations of most of the dissolved metals were in the parts per trillion range and were comparable with open ocean and uncontaminated coastal waters data.

Apte *et al*., (1998) concluded that the trace metal concentrations found off the NSW coast were "amongst the lowest reported in the southern hemisphere and were

consistent with data for the surface waters of the Pacific Ocean". The concentrations of metals found in Perth coastal waters in this study are generally comparable with those found in coastal waters off the NSW coast (Table 11). Slightly higher concentrations of cadmium, copper, silver and zinc were found in Perth coastal waters compared to NSW coastal waters. Further work would be required to understand the cause of these differences and resolve any temporal or seasonal variations in metal concentrations that may exist. The concentrations of dissolved cadmium and zinc may well be linked to phosphate and silicate nutrient cycling, as is the case in NSW coastal waters (Apte *et al*., 1998). A comparison of nutrient concentrations between the two regions would be appropriate. Inputs of metals from local anthropogenic sources will also affect the concentrations of these metals.

Table 11. Comparison of trace metal concentrations in Perth coastal waters with other locations.

Metal	Perth marine waters - mean concentrations (μg/L)	Pacific Ocean (Surface waters) [1] (μg/L)	NSW coastal waters (Apte *et al.,* 1998) (μg/L)
Aluminium	<0.9	-	-
Arsenic	1.7	1.2-1.5	1.53
Cadmium	0.004	0.002-0.003	0.0024
Chromium (total dissolved)	<0.15	0.125	0.097
Cobalt	0.009	-	-
Copper	0.07	0.027-0.092	0.031
Lead	<0.02	0.006-0.017	0.009
Mercury (total)	0.0003	0.0003-0.0004	<0.0014
Silver	0.0005	0.0001-0025	<0.0005
Zinc	0.10	0.004-0.006	<0.022

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

We are unaware of any other dissolved cobalt data for Australian coastal waters. The mean concentration of 0.009 μg/L for Perth marine waters compares favourably with a concentration of 0.008 μg/L measured in coastal waters off Massachussets, USA (Saito and Moffett, 2002).

The concentrations of copper, mercury and possibly zinc in samples from Cockburn Sound were slightly elevated compared to the samples from the rest of Perth's coastal waters (Table 7), possibly due to industrial inputs and/or antifouling or corrosion inhibiting products used on vessels and infrastructure on the eastern side of the Sound. The mercury results for the Cockburn Sound High Ecological Protection sites were very similar to results for the rest of Perth's coastal waters, but results for the Cockburn Sound Moderate Ecological Protection sites were higher. Hatje *et al.,* (2003) recently measured the concentrations of dissolved trace metals in Sydney Harbour, which receives inputs of trace metals from a number of urban sources. The mean concentrations of cadmium, copper and zinc were 0.04, 6.5 and 1.7 μg/L respectively. By comparison, the concentrations of these metals in Cockburn Sound Moderate Ecological Protection sites (sites CS6A, CS7, CS9 and CS9A) were significantly lower, but it should be noted that Cockburn Sound is significantly more

open and marine in nature than the Sydney Harbour sites located in the Port Jackson estuary.

The background concentrations of metals listed in Table 12 are recommended for use in Perth's coastal waters. All background concentrations have been calculated as the 95th percentile of the relevant data set (see Section 2.3). For most of the metals (except cobalt, mercury, silver and zinc) the estimated natural background concentrations for Perth marine waters have been derived using data from the 'least impacted' sites although these are likely to be a slight over-estimate of actual natural background conditions because of anthropogenic influences in the region. The ambient background concentrations for Cockburn Sound High Ecological Protection and Moderate Ecological Protection areas represent current ambient water quality in these zones and have been calculated using the 95th percentile of the respective data sets.

Table 12: Ambient concentrations for selected metals recommended for use in the High (E2) and Moderate (E3) Ecological Protection areas of Cockburn Sound, and best-estimates of natural background metal concentrations recommended for the remaining marine waters of the Perth metropolitan area.

Metal	Perth marine waters (estimated natural background) (µg/L)	Cockburn Sound (E2) (ambient) (µg/L)	Cockburn Sound (E3) (ambient) (µg/L)
Aluminium	<1	<1	<1
Arsenic	1.8	1.8	1.8
Cadmium	0.005	0.005	0.006
Chromium (total dissolved)	0.20	0.16	0.15
Cobalt	0.01	0.01	0.01
Copper	0.08	0.14	0.53
Lead	<0.02	<0.02	<0.02
Mercury (total)	0.0004	0.0004	0.0014
Silver	0.0007	0.0009*	
Zinc	0.15	0.2*	

* Estimate only based on 3 data points and is very unreliable.

The values recommended for aluminium and lead in all waters, and for chromium in Cockburn Sound, are at the limit of detection for the analytical methods used and hence are likely to be an overestimate of actual environmental concentrations. As analytical methods are refined and more data are collected these values are likely to decrease. It is worth noting the clear and statistically significant increasing trend in copper concentration from the least impacted sites to the High and then Moderate Ecological Protection areas in Cockburn Sound. Nevertheless, comparison of the estimated ambient copper concentrations for the two Cockburn Sound zones with the established environmental quality guidelines for each zone (Table 13) indicate that the guidelines were easily achieved at the time of sampling.

To determine the applicability of the National guideline trigger values (ANZECC & ARMCANZ, 2000), the estimated natural background concentrations have been compared with the National default guidelines for 99% and 99/95% species protection (Table 13). Note that the national guidelines for chromium (III) have been quoted in Table 13 rather than chromium (VI) because of the high dissolved organic content of Perth coastal waters (Cary *et al.,* 1995) and hence a significant proportion of the dissolved chromium is likely to be present in this form (Nakayama *et al.,* 1981).

Background concentrations measured for silver, cadmium, chromium, copper, mercury, lead and zinc were found to be well below the recommended guidelines for 99% and 99/95% species protection (ANZECC & ARMCANZ, 2000). These represent a 'very high' and 'high' level of ecological protection respectively. For example, the estimated 95th percentile for copper in least impacted sites was 0.08 μg/L, which is well below the guideline for 99% species protection (0.3 μg/L) or 99/95% species protection (1.3 μg/L). For these seven metals, the water quality guidelines recommended for the highest level of ecological protection in ANZECC & ARMCANZ (2000) are suitable for application in Perth's coastal waters.

Table 13: National guideline trigger values for metals in marine waters (ANZECC & ARMCANZ, 2000) and estimated natural background concentrations for Perth's coastal waters calculated as the 95th percentile of the reference site database (trigger values shown in bold are less than estimated background concentrations).

| METAL | ANZECC/ ARMCANZ trigger values for marine waters (μg/L) | | | ESTIMATED NATURAL BACKGROUND CONCENTRATION |
| | Recommended guidelines for different levels of species protection | | | |
	90% (E3[#])	99/95 % (E2[#])	99%	(μg/L)
Aluminium	-	-	-	<1
Arsenic	-	-	-	1.8
Cadmium	14	0.7	0.7	0.005
Chromium (III)*	48.6	27.4	7.7	0.20
Cobalt	14	1	**0.005**	0.01
Copper	3	1.3	0.3	0.08
Lead	6.6	4.4	2.2	<0.02
Mercury (total)	0.7	0.1	0.1	0.0004[‡]
Silver	1.8	1.4	0.8	0.0007
Zinc	23	15	7	0.15

*   The analytical results did not differentiate between Cr species; total dissolved Cr was measured.
‡   The analytical results were for total mercury.
\#   The national guidelines for 99/ 95% and 90% species protection have been adopted for High and Moderate levels of Ecological Protection respectively in Cockburn Sound.

For aluminium and arsenic there were no high or moderate reliability guideline trigger values recommended in the National guidelines, however, low reliability values (LRV) of 0.5 μg/L for aluminium and 4.5 μg/L for arsenic (V) are provided. In our study, no aluminium was detected in any of the samples, but the limit of detection was 1 μg/L and therefore above the LRV. The LOD for arsenic was 0.2 μg/L and measured concentrations ranged from between 1.6 μg/L and 1.8 μg/L, well below the LRV for

arsenic (V) of 4.5 μg/L. A LRV of 2.3 μg/L was provided for arsenic (III), but this form of arsenic is less common in seawater (ANZECC & ARMCANZ, 2000).

For cobalt, all of the available data (which included those located in the Moderate Ecological Protection Area of Cockburn Sound) were used to estimate natural background concentration, and hence may be an overestimate because of the higher concentrations measured in the Moderate Ecological Protection Area. The estimated 95th percentile for cobalt is 0.01 μg/L, which is higher than the 99% species protection guideline trigger value (0.005 μg/L). This guideline trigger value is extremely low and approximates concentrations reported in oceanic waters (Nozaki, 1997; OZREEF, 1997). The low value is likely to be an artefact of the curve fitting method used to calculate the guideline trigger values because only eight toxicity data points were available. The shape of the curve fitting these eight values was such that to derive a 99% species protection guideline trigger value the curve was extrapolated by more than three orders of magnitude below the lowest recorded chronic toxicity data point. The ratio of the lowest chronic No Observed Effect Concentration (NOEC), or Lowest Observed Effect Concentration (LOEC), for cobalt and the actual guideline derived for 99% species protection is 1800, compared to a ratio of between 1 and 10 for the other metals. ANZECC & ARMCANZ (2000) recommend the use of caution when selecting a curve to fit less than eight data points to derive guideline trigger values because of the errors involved in extrapolating the tails of the curves.

The 99% species protection guideline trigger value for cobalt therefore appears to be excessively low and at natural background levels. It will be difficult to achieve in areas with anthropogenic inputs, and perhaps also in areas that remain largely pristine. It should also be noted that cobalt, like nickel, complexes strongly with organic molecules and is likely to be largely unavailable for biological uptake around outfalls with high organic content, such as domestic treated wastewater outfalls. Use of the guideline trigger value for 95% species protection for cobalt is therefore recommended instead of the 99% guideline in areas that might be designated a very high level of ecological protection until there is sufficient information to derive a new set of guideline trigger values.

5.2   Organic chemicals

Most of the organic chemicals surveyed in this study do not occur naturally, and those that do are only found at extremely low concentrations unless augmented by anthropogenic inputs. Therefore, the natural background concentrations of the analysed organic chemicals were expected to be below analytical detection, ranging from zero to negligible. National guidelines were only available for some of the organic chemicals tested and of these, four were below the analytical limit of reporting. For chemicals where the guideline is less than the limit of reporting, any detection would be cause for concern and should trigger further backup monitoring and investigation.

In this study, there were no detections of any of the organic chemicals analysed, however, the limit of reporting for endrin, endosulfan, chlorpyrifos and temephos was too high to determine whether background concentrations in Perth coastal waters exceeded the 99% species protection trigger guideline values. The limits of reporting for these four chemicals were only sufficient to determine that the 95% species

protection guidelines were not exceeded for temephos or endosulfan, and the 90% species protection guidelines were not exceeded for endrin and chlorpyrifos. The limits of reporting for naphthalene, pentachlorophenol, phenol, benzene and 1,2,4-trichlorobenzene were well below all the National guideline trigger values indicating minimal contamination for these chemicals. The results of the organic chemical analyses will provide a useful reference against which future studies can be compared.

5.3 Radionuclides

There are no internationally accepted radiological water quality guidelines for recreational waters (WA Department of Health, pers com), however, there are guideline values for drinking water (NH&MRC, 1996) and the approach agreed by the Western Australian Department of Health is to multiply the drinking water guidelines by a factor of 20. This assumes swimmers will ingest no more than 100 mL of water per day compared to the 2 L daily intake on which the drinking water guidelines are based. The Australian Drinking Water Guidelines (1996) recommend measurement of gross radioactivity for initial screening when assessing drinking water quality. According to the Drinking Water Guidelines (1996), both gross alpha radioactivity and gross beta radioactivity should not exceed 0.5 Bq/L, with the contribution of potassium-40 extracted from the gross beta results. Multiplying these guidelines by a factor of 20 gives a recreational water quality guideline of 10 Bq/L for both gross alpha radioactivity and gross beta radioactivity (minus the potassium-40 contribution).

The highest gross alpha value found from the sampled sites was 0.49 Bq/L at Cockburn Sound and the highest gross beta value obtained was 5 Bq/L at Quinns Rock. Both values were below their respective guidelines of 10 Bq/L. Advice from the Department of Health (Radiation Branch) is that these results are considered acceptable, and do not warrant further analysis for specific radionuclide species. This outcome is consistent with a previous study into [226]Radium activity in sediments and blue mussels from Cockburn Sound (Toussaint, 1996) in which it was concluded that 'the amount of [226]Radium does not appear to be excessive'. The relatively large variation in the data could not be explained, although the Health Department suggested that variation in results close to shorelines could be due to contributions from naturally occurring radionuclides present in local soil types. High variability was also noted in the measurement of [226]Radium activity in Cockburn Sound sediments by Toussaint (1996).

6. Conclusion

The objective of the main survey was to characterise background water quality conditions for a range of contaminants in Perth metropolitan coastal waters and to determine whether the guideline trigger values from ANZECC & ARMCANZ (2000) were relevant to the region. Perth is a rapidly expanding city with extensive pressure being applied to the coastal and marine environments. As a result, the EPA has developed an Environmental Quality Management Framework for the region and the results from this study are an important input to the development and implementation of environmental quality criteria through this framework.

The results presented demonstrate that the ANZECC & ARMCANZ (2000) guidelines are relevant for application to Perth coastal waters. Best-estimates of

natural background water quality for Perth coastal waters and ambient water quality for Cockburn Sound have been determined for several selected metals (Tables 12 and 13). Although based on a relatively small number of samples, these results provide a useful baseline for interim use until a more comprehensive survey is undertaken.

Ambient water quality at the time of sampling met the environmental quality guidelines for both High and Moderate Ecological Protection areas in Cockburn Sound, indicating that water quality in both areas was very good. Estimated natural background levels for Perth coastal waters met the guidelines for the highest level of protection (99% species protection) for all contaminates that had a guideline and an analytical limit of reporting less than the guideline value (cadmium, chromium (III), copper, lead, mercury, silver, zinc, naphthalene, pentachlorophenol, phenol, benzene and 1,2,4-trichlorobenzene). The level of gross alpha and gross beta activity also fell below recreational water quality guidelines.

For the remaining chemicals analysed, either the limit of reporting was greater than the guideline (chlorpyrifos, cobalt, endosulfan, endrin and temephos), or there was no guideline trigger value, as was the case for most of the organic chemicals (see Table 9). Nevertheless, the results provide a useful reference against which future studies can be compared.

The 99% species protection guideline trigger value for cobalt appears to be excessively conservative, therefore, it is recommended that the guideline trigger value for 95% species protection be applied to Perth coastal waters until there is sufficient information to revise the guideline trigger value. This approach means that the methodology for assessing water quality against the guideline trigger value for cobalt will still be consistent with the overall approach used for the other metals.

7. 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.

BP (2003). *Environmental Monitoring Data (July – December 2002).* BP Refinery (Kwinana) Pty Ltd. Kwinana, Western Australia. February 2003.

Cary, J.L., Masini, R.J. and Simpson, C.J. (1995). *The water quality of the southern metropolitan coastal waters of Perth, Western Australia: The influence of regional*

and local scale forcings. Technical Series 64, Environmental Protection Authority, Western Australia. November 1995.

Crawley, K.R., Manning, C.R., Masini, R.J. and McAlpine, K. (2001). *Background water quality during April 2001 in the southern and northern metropolitan coastal waters of Perth.* Data Report SMCWS WQ-1. Department of Environmental Protection, Perth.

DAL Science and Engineering Pty Ltd. (2002). *Perth Seawater Desalination Project: Seawater Quality Assessment.* Report prepared for the Occtech Engineering Pty Ltd, June 2002.

DEP (1996). *Southern Metropolitan Coastal Waters Study (1991 – 1994) Final Report.* Report 17. Perth, Western Australia. November 1996.

EPA (2004). *Revised Environmental Quality Criteria Reference Document (Cockburn Sound).* A supporting document to the Draft State Environmental (Cockburn Sound) Policy. Environmental Protection Authority, October 2004.

Government of Western Australia (2004a). *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.

Government of Western Australia. (2004b). *Draft State Environmental (Cockburn Sound) Policy – Draft for public comment.* Perth, Western Australia. October 2004.

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

Hine, P.T. (1998). *Contaminant Inputs Inventory of the Southern Metropolitan Coastal Waters of Perth: An update – June 1998.* Department of Environmental Protection, Perth.

Kinhill Pty Ltd. (1998). *Perth Long-term Ocean Outlet Monitoring (PLOOM) Program 1995 – 1998. Project WS2: Metals and pesticides survey, 1998.* Report prepared for the WA Water Corporation, May 1998.

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.

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* 290, 768–770.

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

NHMRC & ARMCANZ (1996). *Australian Drinking Water Guidelines*. National Water Quality Management Strategy Paper No. 6, National Health and Medical Research Council and Agricultural and Resource Management Council of Australia and New Zealand, Australian Government Publishing Service, Canberra.

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

Saito, M.A. and Moffett, J.W. (2002). Temporal and spatial variability of cobalt in the Atlantic Ocean. *Geochim. Cosmochim. Acta* 66, 1943-1953.

Toussaint, L. F. (1996). *Radium-226 levels in Cockburn Sound samples – A preliminary study*. Radiation Protection in Australia 14, No. 1. Conference Paper.

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 pilot survey 500mL fluorinated ethylene propylene (FEP) (Nalgene) bottles equipped with Teflon-lined caps were used for sample storage. The bottle cleaning procedure used in this phase of the project was: immerse the bottles in a bath of 10% v/v analytical reagent (AR) grade nitric acid for 2 days, then fill them with 50% v/v AR nitric acid for at least 3 days, followed by 10% v/v ultrapure grade nitric acid (Merck Tracepure) for at least 3 days. After each step, the bottles were thoroughly rinsed with milli-Q water. Prior to transportation to the sampling site the bottles were soaked for a further 2 day period in Milli-Q water, emptied and 'double bagged'.

During the course of this part of the study, it was found that this cleaning procedure, which had been used successfully in earlier projects, was not sufficient for sampling mercury at sub part per trillion concentrations in marine waters. It was found that the chloride ions were mobilising mercury so extra cleaning using hydrochloric acid was required.

For the main sampling program the FEP bottles and 500mL Pyrex borosilicate glass bottles (Schott) 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 milli-Q 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. With the final cleaning treatment, consistent results were observed between samples stored in either FEP or borosilicate glass.

A.1.3 Organics/ radionuclides
Water samples for analysis of organics and radionuclides were stored in bottles provided by the laboratories (Table A1).

Table A1: Description of container requirements for water samples.

Analyte	Container requirements
Organics	Two 1 litre amber bottles and two 44 mL zero headspace vials
Radionuclides	1 litre HDPE (hardened polypropylene) bottle

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. As for the pilot survey, 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 all samples for organic chemical and radionuclide analysis.

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 pole (Mart, 1979, as cited in Apte *et al.,* 1998).

The Niskin bottle was cleaned prior to field work 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 then 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; it is a 7.3m long vessel with an aluminium hull and no anti-fouling paint applied. 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 36 hours of collection.

Water samples for analysis of organic chemicals were taken in bottles provided by AGAL; a one litre amber glass bottle and two 44 mL zero headspace clear glass vials were collected per site. Samples were collected from the Niskin bottle. 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.

Samples for radionuclide analysis were taken from the Niskin bottle and stored in an esky. The samples were delivered to the laboratory 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 therefore filtered in a laboratory clean room to reduce the potential for contamination caused by filtering in the field. All metal samples (excluding mercury) were filtered through a 0.45-micron filter before analysis.

Polycarbonate filter rigs (Sartorius) fitted with 0.45-micron 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

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

Arsenic
Arsenic was determined by hydride-generation atomic fluoresence spectrometry (AFS). Samples were first digested by addition of potassium persulphate (1% m/v final concentration) and heating at $120^{o}C$ 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 20 min at room temperature prior to analysis.

Cadmium, Cobalt, 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 (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 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).

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 5 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 Perkin Elmer 4100ZL graphite furnace atomic absorption spectrometer equipped with Zeeman effect background correction and a silver hollow cathode lamp. The furnace operating conditions recommended by the manufacturer was 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 Seawaters NASS-5 or CASS-4 were analysed with each batch of samples. Suitable reference materials were not available for cobalt, chromium, silver 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
PAHs 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).

A.4.3   Radionuclides

Samples were analysed for radionuclides by Western Radiation Services, a NATA registered laboratory. The method used was LTP6 Alpha/Beta – by evaporation and gas proportional counting. The beta results were corrected for potassium-40 concentrations.

Appendix B: Data used to estimate natural background metal concentrations for Perth coastal waters and ambient concentrations for Cockburn Sound.

Site	Ag	Al	As	Cd	Co*	Cr	Cu	Hg	Pb	Zn
	µg /L	µg /L	µg /L	µg /L	µg /L	µg /L	µg /L	µg /L	µg /L	µg /L
Natural background - Perth coastal waters										
OS (s)	<0.0004	< 0.9		<0.004		0.18	0.046			<0.038
OS (s)	<0.0004	< 0.9		<0.004		<0.15	0.052			0.147
OS (b)	<0.0004	< 0.9		<0.004		0.17	0.056			0.108
WS (s)	<0.0004	< 0.9		0.004		0.20	0.081			0.150
WS (s)	<0.0004	< 0.9		0.004		<0.15	0.085			0.114
WS (s)	<0.0004	< 0.9		0.004		<0.15	0.067			<0.038
WS (s)	<0.0004	< 0.9		<0.004		<0.15	0.080			0.116
WS (s)	0.0004	< 0.9		<0.004		<0.15	0.085			0.109
WS (s)	<0.0004	< 0.9		0.004		<0.15	0.078			0.133
WS (s)	0.0005	< 0.9		0.005		<0.15	0.082			0.111
WS (s)	0.0006	< 0.9		0.004		<0.15	0.075			0.074
WS (b)	<0.0004	< 0.9		<0.004		<0.15	0.076			0.075
WS (b)	<0.0004	< 0.9		<0.004		<0.15	0.078			0.085
WS (b)	0.0005	< 0.9		<0.004		<0.15	0.083			0.084
WS (b)	0.0007	< 0.9		<0.004		0.15	0.085			0.130
OS (s)		<1	1.7	<0.002	-	0.15	0.038	0.0003	<0.019	
QR1 (s)		<1	1.8	0.004	-	0.20	0.085	0.0004	<0.019	
TR (s)		<1	1.7	0.003	-	<0.15	0.106	0.0003	<0.019	
WS4 (s)		<1	1.8	0.004	<0.008	<0.15	0.062	0.0003	<0.019	
WS6 (s)		<1	1.7	0.003		<0.15	0.054	0.0003	<0.019	
WS6 (b)		<1	1.6	0.005	<0.008	<0.15	0.064	0.0003	<0.019	
Ambient water quality – Cockburn Sound High Ecological Protection										
CS8 (s)	0.0009	< 0.9		0.004		0.16	0.145			0.122
CS8 (s)	0.0006	< 0.9		0.004		0.15	0.142			0.202
CS8 (b)	0.0005	< 0.9		0.004		0.15	0.132			0.182
CS8 (s)		<1	1.8	0.005	<0.008	<0.15	0.144	0.0004	<0.019	
CS4 (s)		<1	1.8	0.002	-	<0.15	0.056	0.0003	<0.019	
CSMB (b)		<1	1.7	0.005	-	<0.15	0.134	0.0004	<0.019	
Ambient water quality – Cockburn Sound Moderate Protection										
CS6A (s)		<1	1.7	0.003	0.009	<0.15	0.169	0.0004	<0.019	
CS7 (s)		<1	1.7	0.003	-	<0.15	0.171	0.0011	<0.019	
CS7 (b)		<1	1.7	0.005	0.014	<0.15	0.154	0.0005	<0.019	
CS9 (s)		<1	1.8	0.006	0.010	<0.15	0.142	0.0006	<0.019	
CS9 (b)		<1	1.7	0.005	-	<0.15	0.640	0.0015	<0.019	
CS9A (s)		<1	1.8	0.004	<0.008	<0.15	0.197	0.0008	<0.019	
CS9A (b)								0.0007		

*All the cobalt data were combined to estimate a natural background concentration.

Appendix C: Salinity/ temperature readings.

Salinity/ temperature readings for WS4

WS4	Salinity	Temperature ^{o}C
Surface	36.6	24
5 m	36.3	24.2
10 m	36.2	24.2
15 m	36.2	24.2

Salinity/ temperature readings for OS

OS	Salinity	Temperature ^{o}C
Surface	35.6	22.6
5 m	35.4	22.6
10 m	35.4	22.5
15 m	35.4	22.6
20 m	35.4	22.6
25 m	35.4	22.6

Salinity/ temperature readings for CS

CS	Salinity	Temperature ^{o}C
Surface	36.3	24.2
5 m	36.3	24.2
10 m	36.3	24.1
15 m	36.3	24.1
20 m	36.3	24.1

Appendix D: Quality control data – Pilot survey

Spike Recoveries

Site sampled	Site	% Recovery Cu	% Recovery Cd	% Recovery Zn	% Recovery Hg	% Recovery Ag
W CS 3	WS4	93	92	110		
W CS 2	WS4	87	89	89		
W NS 4	WS4	91	84	92		
W CS4 + spike	WS4				100	
OS NB1 + spike	OS				102	
W NB 3	WS4					89
OS CS 1	OS					99

Method Blanks

	Cu µg/L	Cd µg/L	Zn µg/L	Cr µg/L	Al µg/L	Hg µg/L	Ag µg/L
04.09.03 2							0.0001
04.09.03 3							0.0
04.09.03 4							-0.0002
04.09.03 5							0.0
Mean absolute blank (n=6)	0.004	0.002	0.025	0	0		0.0
Limit of Detection (3 sigma)	0.028	0.004	0.038	0.15	0.9	0.0002	0.0004

Field Blanks

Site	Cu	Cd	Zn	Cr	Al	Hg	Ag
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
WS4	0.007	0.001	0.055	<0.15	<0.13	<0.0002	<0.0004
CS8	0.015	0.001	0.041	<0.15	0.15	<0.0002	<0.0004

CRM

CASS-4	Cu	Cd	Zn
	µg/L	µg/L	µg/L
Certified Value	0.592±0.055	0.026±0.003	0.381±0.057
17.03.03	0.544	0.025	0.345
% recovery	*92*	*96*	*91*

Analytical replicates

Site	Cu	Cu Duplicate	Cd	Cd Duplicate	Zn	Zn duplicate	Ag	Ag duplicate
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
CS8 (N, S)	0.142	0.141	0.003	0.005	0.201	0.203		
WS4 (N, S)	0.083	0.086	0.003	0.002	0.113	0.105		
CS8 (N, B)							0.0007	0.0002
WS4 (N, B)							0.0001	-0.0001

N = Niskin

S = Surface

B = Bottom

Appendix E: Quality control data – Main survey

Method Blanks

	As	Al	Cd	Co	Cu	Pb	Zn	Hg	Ag
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
04.09.03 2									0.1
04.09.03 3									0.0
04.09.03 4									-0.2
04.09.03 5									0.0
Mean absolute blank (n=4)	0	0	0.0003	0.021	0.010	0	0.019		0.0
Limit of Detection (3 sigma)	0.2	1	0.002	0.008	0.011	0.019	0.018	0.0002	0.4

Field Blanks

Field Blank	Site Code for WIN Project WA-M-BGWQ	Cr	As	Al	Cd	Co	Cu	Hg	Pb	Zn	Ag
		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	ng/L	µg/L	µg/L	µg/L
CS Field Blank	CS4	<0.15	<0.2	<1	<0.002	<0.008	<0.011	<0.2	<0.019	0.812	0.0097
WS Field Blank	WS6	<0.15	<0.2	<1	<0.002	<0.008	<0.011	<0.2	<0.019	0.574	0.0059
Trigg Island Field Blank	TR1	<0.15	<0.2	<1	<0.002	<0.008	<0.011	<0.2	<0.019	0.076	<0.0004

CRM

CASS-4	Cu	Cd	Zn	NASS-5
	µg/L	µg/L	µg/L	µg As/L
Certified Value	0.592±0.055	0.026±0.003	0.381±0.057	1.27±0.12
Obtained	0.54	0.030	0.350	1.32
% recovery	*91*	*104*	*92*	*104*

Analytical Replicates

Sample	Site Code for WIN Project WA-M-BGWQ	Cu	Cu Duplicate	Cd	Cd Duplicate	Co	Co Duplicate	Pb	Pb Duplicate	Zn	Zn Duplicate
		µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
CS7 S	CS7	0.174	0.167	0.005	<0.002			<0.019	<0.019	0.378	0.398
CS9A S	CS9A	0.191	0.203	0.006	<0.002	<0.008	<0.008	<0.019	<0.019	0.404	0.422

Sample	Site Code for WIN Project WA-M-BGWQ	Ag	Ag Duplicate
		µg/L	µg/L
CS MB S	CSMB	0.0027	0.0014
WS 6B	WS6	0.0025	0.0021

Spike Recoveries

Sample	Site Code for WIN Project WA-M-BGWQ	% Recovery	% Recovery	% Recovery	% Recovery	% Recovery	% Recovery
		Cd	Co	Cu	Pb	Zn	Ag
CS7B	CS7	100	98	95	94	108	
CS6A S	CS6A	100	98	97	93	117	
CS4 S							98
WS4 S							96