NORTH WEST SHELF
JOINT ENVIRONMENTAL
MANAGEMENT STUDY

Background quality for coastal marine waters of the North West Shelf, Western Australia

NWSJEMS
TECHNICAL REPORT No. 18

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• S. Apte • R. Masini

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Final report

North West Shelf Joint Environmental Management Study Final Report.

List of technical reports

NWSJEMS Technical Report No. 1
Review of research and data relevant to marine environmental management of Australia's North West Shelf.
A. Heyward, A. Revill and C. Sherwood

NWSJEMS Technical Report No. 2
Bibliography of research and data relevant to marine environmental management of Australia's North West Shelf.
P. Jernakoff, L. Scott, A. Heyward, A. Revill and C. Sherwood

NWSJEMS Technical Report No. 3
Summary of international conventions, Commonwealth and State legislation and other instruments affecting marine resource allocation, use, conservation and environmental protection on the North West Shelf of Australia.
D. Gordon

NWSJEMS Technical Report No. 4
Information access and inquiry.
P. Brodie and M. Fuller

NWSJEMS Technical Report No. 5
Data warehouse and metadata holdings relevant to Australia's North West Shelf.
P. Brodie, M. Fuller, T. Rees and L. Wilkes

NWSJEMS Technical Report No. 6
Modelling circulation and connectivity on Australia's North West Shelf.
S. Condie, J. Andrewartha, J. Mansbridge and J. Waring

NWSJEMS Technical Report No. 7
Modelling suspended sediment transport on Australia's North West Shelf.
N. Margvelashvili, J. Andrewartha, S. Condie, M. Herzfeld, J. Parslow, P. Sakov and J. Waring

NWSJEMS Technical Report No. 8
Biogeochemical modelling on Australia's North West Shelf.
M. Herzfeld, J. Parslow, P. Sakov and J. Andrewartha

NWSJEMS Technical Report No. 9
Trophic webs and modelling of Australia's North West Shelf.
C. Bulman

NWSJEMS Technical Report No. 10
The spatial distribution of commercial fishery production on Australia's North West Shelf.
F. Althaus, K. Woolley, X. He, P. Stephenson and R. Little

NWSJEMS Technical Report No. 11
Benthic habitat dynamics and models on Australia's North West Shelf.
E. Fulton, B. Hatfield, F. Althaus and K. Sainsbury

NWSJEMS Technical Report No. 12
Ecosystem characterisation of Australia's North West Shelf.
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NWSJEMS Technical Report No. 15
Management strategy evaluation specification for Australia's North West Shelf.
E. Fulton, K. Sainsbury, D. Hayes, V. Lyne, R. Little, M. Fuller, S. Condie, R. Gray, R. Scott,
H. Webb, B. Hatfield, M. Martin, and D. McDonald

NWSJEMS Technical Report No. 16
Ecosystem model specification within an agent based framework.
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NWSJEMS Technical Report No. 17
Management strategy evaluations for multiple use management of Australia's North West Shelf
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B. Hatfield, L. Thomas and R. Scott

NWSJEMS Technical Report No. 18
Background quality for coastal marine waters of the North West Shelf, Western Australia.
K. Wenziker, K. McAlpine, S. Apte, R.Masini

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ACRONYMS

ACRONYMS

ACOM	Australian Community Ocean Model
AFMA	Australian Fisheries Management Authority
AFZ	Australian Fishing Zone
AGSO	Australian Geological Survey Organisation now Geoscience Australia
AHC	Australian Heritage Commission
AIMS	Australian Institute of Marine Science
AMSA	Australian Maritime Safety Authority
ANCA	Australian Nature Conservation Agency
ANZECC	Australian and New Zealand Environment and Conservation Council
ANZLIC	Australian and New Zealand Land Information Council
APPEA	Australian Petroleum, Production and Exploration Association
AQIA	Australian Quarantine Inspection Service
ARMCANZ	Agricultural Resources Management council of Australia and New Zealand
ASIC	Australian Seafood Industry Council
ASDD	Australian Spatial Data Directory
CAAB	Codes for Australian Aquatic Biota
CAES	Catch and Effort Statistics
CALM	Department of Conservation and Land Management (WA Government)
CAMBA	China Australia Migratory Birds Agreement
CDF	Common data format
CITIES	Convention on International Trade in Endangered Species
CTD	conductivity-temperature-depth
CMAR	CSIRO Marine and Atmospheric Research
CMR	CSIRO Marine Research
COAG	Council of Australian Governments
ConnIe	Connectivity Interface
CPUE	Catch per unit effort
CSIRO	Commonwealth Science and Industrial Research Organisation
DCA	detrended correspondence analysis
DIC	Dissolved inorganic carbon
DISR	Department of Industry, Science and Resources (Commonwealth)
DEP	Department of Environmental Protection (WA Government)
DOM	Dissolved organic matter
DPIE	Department of Primary Industries and Energy
DRD	Department of Resources Development (WA Government)
EA	Environment Australia
EEZ	Exclusive Economic Zone
EIA	Environmental Impact Assessment
EPA	Environmental Protection Agency
EPP	Environmental Protection Policy
ENSO	El Nino Southern Oscillation
EQC	Environmental Quality Criteria (Western Australia)
EQO	Environmental Quality Objective (Western Australia)
ESD	Ecologically Sustainable Development
FRDC	Fisheries Research and Development Corporation
FRMA	Fish Resources Management Act
GA	Geoscience Australia formerly AGSO
GESAMP	Joint Group of Experts on Scientific Aspects of Environmental Protection
GIS	Geographic Information System
ICESD	Intergovernmental Committee on Ecologically Sustainable Development
ICS	International Chamber of Shipping
IOC	International Oceanographic Commission
IGAE	Intergovernmental Agreement on the Environment
ICOMOS	International Council for Monuments and Sites
IMO	International Maritime Organisation

IPCC	Intergovernmental Panel on Climate Change
IUNC	International Union for Conservation of Nature and Natural Resources
IWC	International Whaling Commission
JAMBA	Japan Australian Migratory Birds Agreement
LNG	Liquified natural gas
MarLIN	Marine Laboratories Information Network
MARPOL	International Convention for the Prevention of Pollution from Ships
MECO	Model of Estuaries and Coastal Oceans
MOU	Memorandum of Understanding
MPAs	Marine Protected Areas
MEMS	Marine Environmental Management Study
MSE	Management Strategy Evaluation
NCEP - NCAR	National Centre for Environmental Prediction – National Centre for Atmospheric Research
NEPC	National Environmental Protection Council
NEPM	National Environment Protection Measures
NGOs	Non government organisations
NRSMPA	National Representative System of Marine Protected Areas
NWQMS	National Water Quality Management Strategy
NWS	North West Shelf
NWSJEMS	North West Shelf Joint Environmental Management Study
NWSMEMS	North West Shelf Marine Environmental Management Study
ICIMF	Oil Company International Marine Forum
OCS	Offshore Constitutional Settlement
PFW	Produced formation water
P(SL)A	Petroleum (Submerged Lands) Act
PSU	Practical salinity units
SeaWiFS	Sea-viewing Wide Field-of-view Sensor
SOI	Southern Oscillation Index
SMCWS	Southern Metropolitan Coastal Waters Study (Western Australia)
TBT	Tributyl Tin
UNCED	United Nations Conference on Environment and Development
UNCLOS	United Nations Convention of the Law of the Sea
UNEP	United Nations Environment Program
UNESCO	United Nations Environment, Social and Cultural Organisation
UNFCCC	United Nations Framework Convention on Climate Change
WADEP	Western Australian Department of Environmental Protection
WADME	Western Australian Department of Minerals and Energy
WAEPA	Western Australian Environmental Protection Authority
WALIS	Western Australian Land Information System
WAPC	Western Australian Planning Commission
WHC	World Heritage Commission
WOD	World Ocean Database
www	world wide web

ABSTRACT

Water quality surveys were undertaken in February and June of 2003 to determine dissolved concentrations of cadmium, chromium, copper, lead and zinc, total mercury, polyaromatic hydrocarbons, phenols, BTEX chemicals and petroleum hydrocarbons in and around the Dampier Archipelago and Port Hedland. Most sampling sites were located in areas unlikely to be contaminated from anthropogenic sources, but for comparative purposes some sites were also located in potentially contaminated areas. This work was undertaken to provide an estimate of background concentrations for selected metals and organics in the marine waters of the North West Shelf, 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 North West Shelf are generally of very high quality. The concentrations of metals were low by world standards, with localised elevations of some metals adjacent to industrial centres and ports. Metal concentrations at the time of sampling met the environmental quality guidelines for a *very high* level of ecological protection (99% species protection) throughout the sampled area, with the exception of the inner harbour at Port Hedland, where copper and zinc levels were elevated above background, but below the 95% species protection guidelines, which represent a *high* level of ecological protection. No organic chemicals were detected in any of the samples. The reporting limits were well below the guideline trigger values recommended in ANZECC & ARMCANZ (2000) for a *very high* level of ecological protection for the five organics for which guideline values were available.

The findings of this study suggest that ANZECC & ARMCANZ (2000) 99% species protection guidelines are relevant to the region for all metals analysed, except cobalt, for which the 95% species protection guideline is recommended for use. A set of Environmental Quality Criteria is proposed.

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 (SWQMS, 2004). This Environmental Quality Management Framework (EQMF) is being applied to manage activities that can affect the quality of marine ecosystems. Implementation is currently focussed on Perth metropolitan coastal waters including Cockburn Sound and the North West Shelf (NWS). The EQMF establishes environmental values for the marine waters that are to be protected, the environmental quality objectives (broad management goals) and the environmental quality criteria (EQC) to be achieved if the environmental values are to be maintained. The environmental values and environmental quality objectives represent the community's long-term desires or goals for the marine waters, and will need to recognise and accommodate the range of uses to which these waters are subjected. For example, there are a number of ports along the coast that are important export centres for extractive industries, such as the salt, oil and iron ore industries. The Department of Conservation and Land Management (CALM) has also proposed a marine reserve for the Dampier Archipelago that includes sanctuary and special purpose zones providing for a range of conservation, recreational and commercial objectives. Local communities will also expect to be able to undertake their recreational pursuits in a clean, uncontaminated environment.

The Department of Environment (DoE) is currently establishing environmental values and environmental quality objectives for the North West Shelf through a Natural Heritage Trust funded program, *Community derived marine quality objectives for the North West Shelf.* The supporting EQC will be 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 objectives of the investigations reported here were to estimate natural background concentrations for a range of chemical constituents of local concern (heavy metals and organic chemicals) and ascertain the relevance of the national guidelines and, secondly, to measure ambient concentrations of these constituents in areas potentially influenced by wastewater discharges and other anthropogenic influences.

Few sampling programs have attempted to characterise background chemical concentrations for the marine waters of the North West Shelf (Mackey, 1984; Water Corporation, 2004). 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. This report describes the results of water quality surveys conducted in the coastal waters of the North West Shelf to determine the current background concentrations of selected heavy metals and organic chemicals using analytical techniques that provide 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 the DoE's sampling equipment and protocols for measuring ultra-trace metal concentrations;
- determining whether background metal concentrations were significantly different between bottom and surface waters;
- determining whether there were differences in metal concentrations between shallow inshore (<20 m) and deeper offshore (>20 m) environments; and
- ascertaining the likely range of actual concentrations for each metal before initiating the main survey.

The main survey was undertaken to:

- estimate background concentrations for the selected contaminants in marine waters of the North West Shelf; and,
- ascertain whether the guideline trigger values from 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 undertaken for the North West Shelf Joint Environmental Management Study (DEP & CSIRO, 2002), a report of the *Fate and pathways of key contaminants of the North West Shelf* (Revill, 2002) and availability of funds for the analyses.

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. Sampling for the pilot survey was undertaken on 25 February 2003 and sampling for the main survey was undertaken from 23 to 26 June 2003. Full details of the water sampling procedures are given in Appendix A.

Pilot survey

Sampling locations are shown in figure 1 and site information is provided in table 1. For the pilot survey, at site DOC four replicate samples were collected with both the Pole sampler and the Niskin bottle from the surface, and four replicate bottom samples were taken with the Niskin bottle. For sites KBA and BRI, one sample was taken at the surface with both the Niskin bottle and the CSIRO Pole sampler, and at the bottom with the Niskin bottle only.

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 of the North West Shelf. The King Bay site is within the Port of Dampier in relatively sheltered waters at the southern end of Mermaid Sound and surrounded by heavy industry. The Dockrell Reef site is outside the Port of Dampier and located in the relatively sheltered waters of Mermaid Strait, away from industrial activity. The site north of Brigadier Island is located in deeper water (~25 metres) outside the Dampier Archipelago and is considered to be well distant from anthropogenic influences.

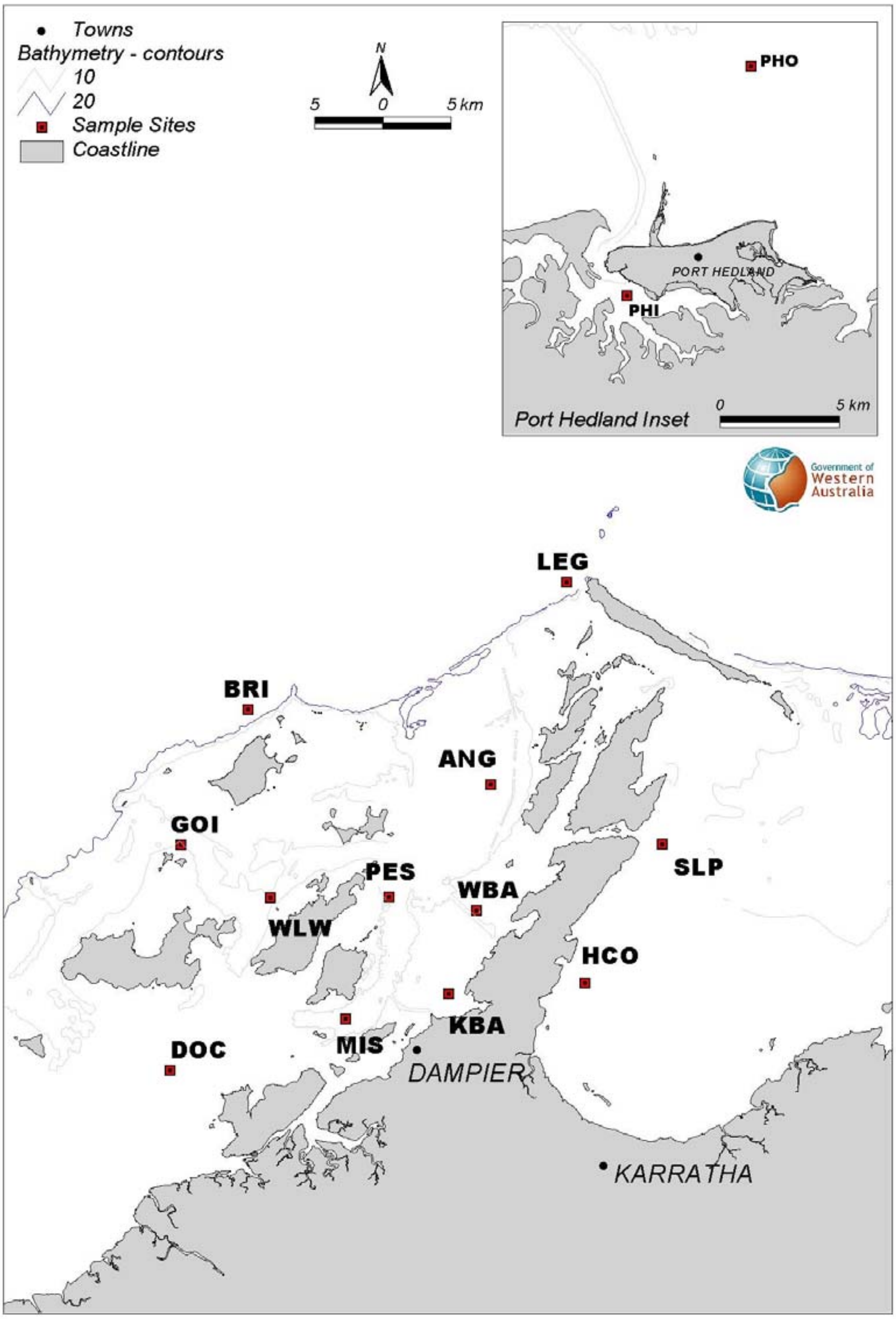


Figure 1: Locality map of the study area showing the sampling sites, North West Shelf.

Table 1: Sampling locations for the pilot survey.

SITE NAME	SITE CODE	LATITUDE	LONGITUDE	APPROXIMATE DEPTH (m)
King Bay	KBA	20°37.511 S	116°44.070 E	10
Brigadier Island	BRI	20°26.25 S	116°35.68 E	30
Dockrell Reef	DOC	20°40.50 S	116°32.29 E	10

Datum is WGS84.

Salinity/temperature measurements were taken to ascertain whether the water column was strongly stratified or relatively well mixed. The samples for the pilot survey were collected during a flood tide in the neap cycle (figure 2).

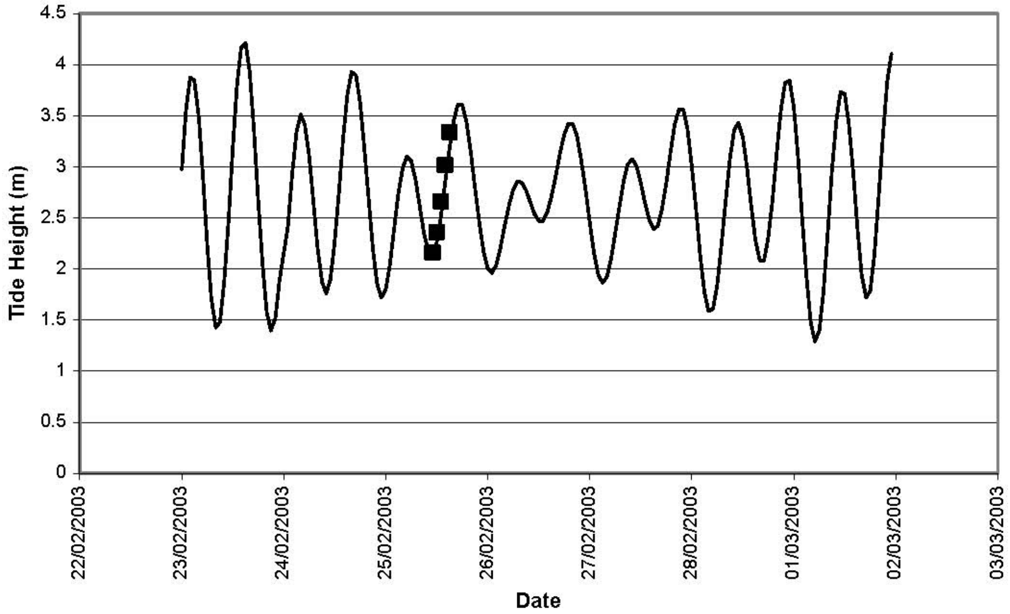


Figure 2: Predicted tides at Dampier from 22 February to 3 March 2003 (squares represents sampling period).

The North West Shelf region has a relatively dry climate, with rainfall and river flow mainly associated with cyclonic events over the summer months. Although the rivers flow infrequently, they can discharge very large volumes of runoff over relatively short periods, particularly if a tropical low pressure system moves through the area. The coastline is characterised by a combination of mangrove communities and rocky headlands, with offshore islands distributed along the coast in deeper water. The oceanography of the Dampier Archipelago has recently been reviewed; tides are semidiurnal with neap and spring tides ranging from 1 to 3.6 m, with the highest astronomical reading 5 m (Pearce et al. 2003). Heavy industry associated mainly with iron ore export, salt, and the oil and gas industry, is located at discrete points along the coastline.

Main survey

The sampling sites selected for the main survey (table 2 and figure 1) were focused mainly in the Dampier Archipelago, the location of a proposed marine reserve and the most significant heavy industrial estate on the North West Shelf. Additional samples were also collected from two sites in Nickol Bay and two sites at Port Hedland, a major iron ore exporting port. There is a relatively high level of environmental management activity at both ports and an improved understanding of background water quality will greatly assist the environmental regulators, marine reserve managers, industry and other environmental quality management agencies in the region. Sites were mainly located in unimpacted or least impacted parts of the archipelago, and wherever possible in a proposed CALM marine sanctuary zone. A site was also established adjacent to King Bay where potential impacts from surrounding industrial activity are likely to be greatest. At Port Hedland, one site was located outside the port (approximately 4 km north-east of the harbour mouth) while the second was located within the port, in shallow water just upstream of the shipping basin.

Sample analyses for total dissolved metal concentration, total mercury and the organic contaminants were undertaken at all sites, but total unfiltered metal analyses (except mercury) were only performed on samples from sites PHO, DOC and KBA (surface and bottom), and BRI, PES, and HCO (surface only).

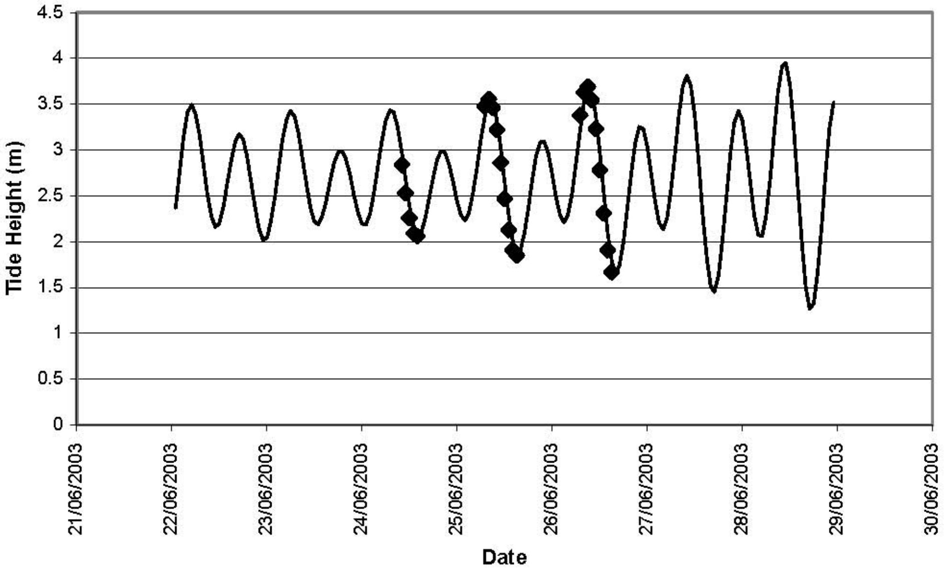
Table 2: Sampling locations for the main survey.

Site name	Site code	Latitude	Longitude	Approximate depth (m)
Port Hedland Offshore	PHO	20°14.404	118°37.836	12
Port Hedland Inshore	PHI	20°19.616	118°34.925	2.2
Legendre Island	LEG	20°21.237	116°49.031	26
Angel Island	ANG	20°29.252	116°45.861	15.2
Pueblo Shoal	PES	20°33.701	116°41.579	13
Withnell Bay	WBA	20°34.231	116°45.241	8.4
King Bay	KBA	20°37.535	116°44.114	10
Mistaken Island	MIS	20°38.494	116°39.747	14
Sloping Point	SLP	20°31.609	116°53.028	12.5
Hearson Cove	HCO	20°37.108	116°49.796	6
Brigadier Island	BRI	20°26.464	116°36.09	28.1
Goodwyn Island	GOI	20°31.605	116°32.863	12.5
West Lewis Island	WLW	20°33.700	116°36.600	13.1
Dockrell Reef	DOC	20°40.518	116°32.376	9.1

Datum is WGS84.

The predicted tidal information at the ports of Dampier and Port Hedland for the week during which sampling was undertaken for the main survey are presented in figure 3(a) and 3(b).

3(a) Dampier



3(b) Port Hedland

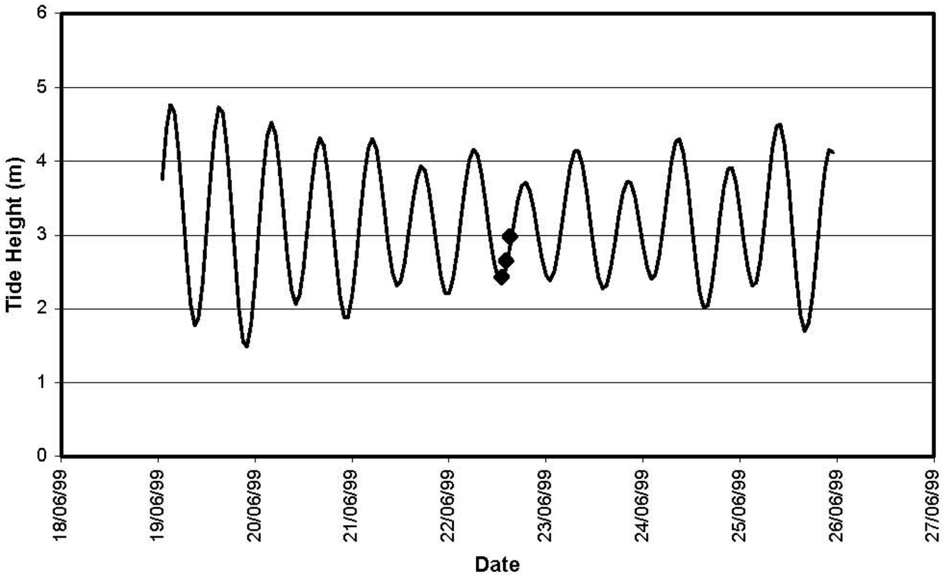


Figure 3: Predicted tide heights at (a) Dampier and (b) Port Hedland, during the sampling period, June 2004 (diamonds represent sampling period).

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 suite of contaminants analysed in the pilot survey included cadmium, chromium, copper, lead, mercury and zinc. Samples were filtered for all analyses except mercury; unfiltered samples were analysed for total mercury. The main survey was extended to include sampling for organic chemicals, including polyaromatic hydrocarbons, phenols, BTEX chemicals and petroleum hydrocarbons. Organic chemical analyses were performed on unfiltered samples.

The CSIRO Centre for Advanced Analytical Chemistry based at Lucas Heights (NSW) undertook all of the metal analyses. The CSIRO laboratory is a NATA 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.

All samples (excluding mercury samples) were filtered through a 0.45 μm filter before analysis. However, three of the samples (one from each of the sites KBA, BRI and DOC) 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 addition of ultra pure nitric acid (2 mL/L final concentration).

Samples were analysed within two weeks of collection for organics and within six weeks for most metals, however ultra-trace analyses for chromium and silver required a different laboratory protocol and were not completed until late August and early September respectively for both the pilot and main survey.

For the main survey, additional samples were collected at selected sites (BRI, DOC, PES, KBA, HCO and PHO) and analysed for total metal concentration to allow comparison with baseline water quality data being collected by the Water Corporation, prior to commissioning of an outfall adjacent to King Bay.

The Dampier Archipelago sites KBA, WBA, PES, ANG and LEG were originally sampled on 24 June 2003, however the transport of the samples to the laboratory in Sydney for processing and analysis was delayed 24 hours by the courier. An additional set of samples was therefore collected from sites KBA, WBA and PES on 26 June 2003 in case the delay affected the results.

The Australian Government Analytical Laboratories (AGAL) performed the analysis for the organic chemicals; AGAL is a NATA registered laboratory.

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 Mann-Whitney tests were applied to the data.

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

Mann-Whitney tests were applied to the results of the main survey to assess whether there were significant differences in water quality between the inner and outer regions of the Dampier Archipelago, and between King Bay and the inner archipelago. Outer archipelago sites were BRI, LEG and GOI, ANG and WLW, and inner archipelago sites were DOC, MIS, PES and WBA. Sites from Nickol Bay were not included in these tests. 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 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.

To estimate natural background metal concentrations for the Dampier Archipelago, and for the North West Shelf generally, data from the pilot and main surveys were combined and a 95th percentile of data from the least impacted sites was calculated for each metal (KBA and PHI were considered to be 'impacted' sites and excluded from the analyses). Data from 24 June (obtained during the main survey) were also excluded for all metals except mercury (analysis was for total unfiltered Hg) on the assumption that the delay in transporting the samples to the laboratory may have affected dissolved concentrations (see section 4.2). Also, to avoid bias towards the DOC site, only the pilot survey Pole sampler results were used to estimate natural background concentrations. 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).

The data set used to estimate natural background metal concentration for the North West Shelf comprised data from all of the Dampier Archipelago sites, the Nickol Bay sites and the Port Hedland offshore site. 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. The same data set used to estimate natural background concentration was used to calculate mean background water quality. The data set used to estimate natural background metal concentrations for the Dampier Archipelago comprised data from all of the Dampier Archipelago sites but excluded Nickol Bay sites and the Port Hedland sites.

For zinc, no data from samples collected with the Niskin bottle during the pilot survey were used in the calculation of 95th percentiles for either Dampier or the North West Shelf because of the contamination problems experienced with the Niskin bottle during the pilot survey. For mercury, none of the results from the pilot survey were included because of suspected contamination of samples. The data used to estimate natural background concentrations are tabulated in Appendix B.

3. RESULTS: PILOT SURVEY

3.1 General conditions

Weather conditions on 25 February 2003 were fine and partly cloudy with light to moderate (10 to 15 knots) easterly winds in the morning rising to moderate to fresh (15 to 18 knots) easterly winds in the afternoon.

The salinity and temperature recordings are in Appendix C. There was no strong vertical 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 and 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 chromium (surface and bottom) were at or below the detection limit (0.15 µg/L) in all samples. Lead concentrations were mostly below the detection limit (0.011 µg/L), only two were above. The concentrations of copper detected at KBA (0.132 µg/L to 0.164 µg/L) were slightly higher in comparison to those detected at DOC, which were in turn slightly higher than BRI (0.068 µg/L to 0.090 µg/L).

Trends in the data for cadmium, mercury and zinc were less evident. There was little range in the cadmium concentrations found over the three sites, however the highest concentration was recorded at KBA (0.008 µg/L). The mercury and zinc results were quite variable and significantly higher than expected at a number of sites. Significant variability in the zinc results was noted for samples taken with the Niskin bottle, with highest concentrations found in the first samples taken, and then concentrations progressively decreasing until the King Bay samples were taken. The high initial results are likely to be a result of contamination caused by inadequate cleaning of the bottle prior to the field sampling program. If the results from the potentially contaminated samples collected with the Niskin bottle are ignored, then the KBA site would appear to have elevated levels of zinc. The variability associated with the mercury analyses occurred in samples taken with both samplers and on investigation was found to be a result of an inappropriate cleaning procedure for sample bottles used to collect seawater for ultra-trace level analysis. Nevertheless, it should be noted that all of the mercury and zinc results were approximately an order of magnitude or more below the 99% species protection guidelines of 0.1 µg/L and 7 µg/L respectively (ANZECC & ARMCANZ, 2000).

Table 3: Results from the pilot trace metals survey, Dampier Archipelago, February 2003.

Site	Sampler, Depth	Cd µg /L	Cr µg /L	Cu µg /L	Hg µg /L	Pb µg /L	Zn µg /L
BRI	C,S	0.004	<0.15	0.068	0.0032	<0.011	0.078
BRI	N, S	0.004	<0.15	0.090	0.0035	<0.011	0.424
BRI	N, B	0.005	0.150	0.090	0.0006	<0.011	0.881
DOC	C, S	0.004	<0.15	0.110	0.0213	<0.011	0.029
DOC	C, S	0.004	<0.15	0.131	0.0013	<0.011	0.083
DOC	C, S	0.005	<0.15	0.110	0.0016	<0.011	0.082
DOC	C, S	0.005	<0.15	0.121	0.0002	<0.011	0.069
DOC	N, S	0.006	<0.15	0.100	0.0003	<0.011	0.322
DOC	N, S	0.003	<0.15	0.108	0.0007	<0.011	0.276
DOC	N, S	0.005	<0.15	0.112	0.0062	<0.011	0.084
DOC	N, S	0.006	<0.15	0.129	0.0004	0.012	0.125
DOC	N, B	0.005	<0.15	0.109	0.001	0.021	0.114
DOC	N, B	0.004	<0.15	0.102	<0.0002	<0.011	0.114
DOC	N, B	0.005	<0.15	0.105	0.0013	<0.011	0.077
DOC	N, B	0.005	<0.15	0.125	0.0004	<0.011	0.067
KBA	C, S	0.006	<0.15	0.133	0.0049	<0.011	0.446
KBA	N, S	0.006	<0.15	0.164	0.0038	<0.011	0.451
KBA	N, B	0.008	0.150	0.132	0.001	<0.011	0.405
Limit of Detection (3 sigma)		***0.002***	***0.150***	***0.015***	***0.0002***	***0.011***	***0.013***

Codes
C = sample taken with CSIRO Teflon Pole sampler
N = sample taken with DoE Niskin bottle
S = Surface
B = Bottom

Mann-Whitney tests were conducted on the results for cadmium, copper and zinc from the DOC site to determine whether there were any significant differences between the samples taken with the Pole sampler and the samples taken with the Niskin bottle, or between surface and bottom samples. Chromium and lead were excluded from the test because the results were below the analytical detection limits, while mercury was excluded because of the contamination caused by the problems outlined above. Results from the Mann-Whitney tests showed that for cadmium and copper there was no significant difference between samples taken with the different samplers (table 4), or between surface and bottom samples at the DOC site (table 5).

For zinc the Mann-Whitney test found that there was a significant difference between the samplers and between surface and bottom waters, however this is likely to be a result of zinc contamination from the Niskin bottle.

Table 4: P-values from the results of the Mann-Whitney tests comparing cadmium, copper and zinc concentrations from samples collected with the Niskin bottle and Pole sampler at DOC (alpha is set at 0.05 and significant values are shown in bold).

Metal	p-value
Cadmium	0.37
Copper	0.38
Zinc	**0.02**

Table 5: P-values from the results of the Mann-Whitney tests comparing cadmium, copper and zinc concentrations from surface and bottom samples at DOC (alpha is set at 0.05 and significant values are shown in bold).

Metal	p-value
Cadmium	0.44
Copper	0.77
Zinc	**0.02**

Table 6 presents the results for the samples that were split and filtered through either a 0.45 µm filter or a 0.2 µm filter. Negligible differences were found in the concentrations of all metals for two of the three samples. For the DOC sample the measured concentration of lead in the sub-sample filtered through the 0.2 µm filter was about half of the result for the 0.45 µm filter.

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 µm	Cd µg/L	Cr µg/L	Cu µg/L	Pb µg/L	Zn µg/L
BRI	0.2	0.005	< 0.15	0.072	<0.011	0.078
BRI	0.45	0.004	< 0.15	0.068	<0.011	0.078
DOC	0.2	0.004	< 0.15	0.107	0.012	0.091
DOC	0.45	0.005	< 0.15	<0.109	0.021	0.114
KBA	0.2	0.007	< 0.15	0.152	<0.011	0.508
KBA	0.45	0.006	< 0.15	<0.164	<0.011	0.451

3.3 Key findings of the pilot survey

Seawater metal concentrations measured in the samples were generally very low, indicating that background metal concentrations in the coastal waters of the North West Shelf approach oceanic levels.

The results of the pilot survey show that there are negligible differences between the concentrations of metals (except zinc) in samples taken with the Pole sampler and the Niskin bottle (table 4). The significant difference found for zinc is most likely to be a result of inadequate cleaning of the Niskin bottle prior to sampling, and highlights the need for rigorous cleaning and sampling procedures when analysing samples to ultra-trace levels. The Niskin bottle was considered adequate for future sampling provided it was properly cleaned prior to the sampling program.

The metals data from the pilot survey, with the exception of zinc, showed that there was little variation between concentrations of metals at surface and depth. The zinc data were affected by contamination from the Niskin bottle and could not be interpreted with any certainty. Samples for the main survey were therefore predominantly taken from the surface.

Differences in metal concentrations measured in samples filtered though a 0.2 µm filter or a 0.45 µm filter were negligible. Samples in the main survey were therefore filtered through a 0.45 µm filter to increase the sample processing rate.

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 will 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:

- 23 June 2003 (Port Hedland): 5 to 10 knot northeasterly winds and overcast, swell 0.4 m;
- 24 June 2003 (Dampier Archipelago): ~ 5 knot winds, easterly in the morning then swinging northeasterly and then northerly by mid afternoon, swell 0.5 m;
- 25 June 2003 (Dampier Archipelago): no wind in the morning and a very slight (<5 knots) northeasterly wind in the afternoon, no swell; and
- 26 June 2003 (Dampier Archipelago): ~ 5 knot northwesterly early morning increasing to 10 to 15 knots late morning and early afternoon, swell 1 m on outer archipelago.

4.2 Trace metals data

The total dissolved metals results for the main survey are presented in table 7 and the results of the total metal analyses are in table 8. The associated quality control data are attached in Appendices E and F respectively. The quality control data are satisfactory for both sets of analyses, suggesting there has not been any significant contamination of samples.

The results confirm the finding of the pilot survey that metal concentrations in coastal waters of the North West Shelf 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).

Compared to the pilot survey, the analytical levels of detection were improved slightly in the main survey, however, the dissolved concentrations measured for chromium and lead were still either below or near the limit of detection for most sites. Notable exceptions were found at King Bay and from the inner harbour of Port Hedland, with lead concentrations exceeding 0.01 μg/L. Dissolved concentrations for cadmium, copper and zinc were detectable at all sites and total mercury concentrations were detectable at almost all sites. Total concentrations for all metals were found to be below the limit of detection for the analytical method that was used.

In the Dampier Archipelago, measured levels of chromium and lead were similar to the concentrations obtained in the pilot survey, while cadmium and copper concentrations were slightly less than those measured in the pilot survey. Further work would be required to determine whether this is natural variability associated with physical oceanographic effects such as tide and wind and/or seasonal differences. It is difficult to draw conclusions from the mercury and zinc data because of the contamination that occurred in the pilot survey results, however, the zinc concentrations measured in the pilot survey samples collected with the Teflon Pole sampler are similar to concentrations measured in the main survey.

Table 7: Total mercury and total dissolved metal concentrations for the North West Shelf main survey, June 2003.
(s) = surface and (b) = bottom.

Site	Cd µg/L	Cr µg/L	Cu µg/L	Hg µg/L	Pb µg/L	Zn µg/L
ANG(s)	0.002	<0.15	0.078	≤0.0001	<0.006	0.045
BRI (s)	0.002	<0.15	0.058	0.0004	<0.006	0.155
BRI (b)				0.0002		
GOI (s)	0.002	0.15	0.060	0.0002	<0.006	0.056
GOI (b)				0.0003		
LEG (s)	0.002	0.20	0.070	≤0.0001	0.010	0.031
WLW(s)	0.003	<0.15	0.056	0.0004	<0.006	0.102
DOC(s)	0.002	<0.15	0.064	0.0003	<0.006	0.053
DOC(b)	0.003	<0.15	0.088	0.0002	<0.006	0.130
MIS (s)	0.003	0.17	0.066	0.0001	<0.006	0.031
PES (s) 26.06.03	0.002	<0.15	0.072		<0.006	0.064
PES (s) 24.06.03	0.002	0.17	0.075	0.0001	<0.006	0.019
PES (b)				0.0001		
WBA (s) 26.06.03	0.003	<0.15	0.070		<0.006	0.088
WBA (s) 24.06.03	0.002	0.16	0.074	0.0002	0.006	0.034
HCO(s)	0.010	<0.15	0.129	0.0002	<0.006	0.027
SLP(s)	0.004	<0.15	0.105	0.0002	0.009	0.031
KBA (b) 26.06.03	0.007	<0.15	0.156		0.020	0.646
KBA (b) 24.06.03	0.004	<0.15	0.141	0.0003	<0.006	0.363
KBA (s) 26.06.03	0.003	0.15	0.077		<0.006	0.251
KBA (s) 24.06.03	0.003	0.16	0.077	0.0002	0.012	0.054
PHO(s)	0.003	<0.15	0.161	0.0003	<0.006	0.063
PHO(b)	0.005	<0.15	0.193	0.0003	0.010	0.637
PHI(s)	0.007	<0.15	0.435	0.0005	0.006	5.13
PHI(b)	0.007	<0.15	0.414	0.0006	0.011	5.47
Limit of Detection (3 sigma)	***0.001***	***0.15***	***0.005***	***0.0001***	***0.006***	***0.003***

Concentrations of most metals were higher at the two Port Hedland sites (particularly the inner harbour site) than for the Dampier Archipelago sites. Zinc and copper were particularly high in the inner harbour. The two sites in Nickol Bay also had slightly different copper, zinc and cadmium concentrations than the Dampier Archipelago; the measured zinc concentrations were very low in Nickol Bay, but the copper and cadmium concentrations were slightly higher than for the archipelago sites.

There was a 24 hour delay in delivery to the laboratory of samples collected from three sites (KBA, WBA and PES). This meant that the samples were not processed for approximately 48 hours from the time they were collected. To maintain consistency with all other analyses, these sites were re-sampled two days later and the samples delivered to the laboratory within 24 hours of collection (i.e. consistent with the standard methods reported here). The analytical results from samples from the same sites that had stood for 24 and 48 hours did not vary much for cadmium, chromium, copper and lead. However, the lead concentrations at King Bay were variable and the zinc concentrations were different between the two treatments. Zinc concentrations in the samples that sat an extra 24 hours before being processed were consistently one half or less of the concentrations of samples that were processed within 24 hours. It is not possible to say whether the differences in zinc concentrations were true 'temporal' differences or an artefact of the delay before processing.

Table 8: Total (unfiltered) metal concentrations for North West Shelf waters, June 2003. (s) = surface and (b) = bottom.

Site	Cd µg /L	Cr µg /L	Cu µg /L	Pb µg /L	Zn µg /L
PHO (s)	<0.05	<0.6	<0.25	<0.25	<1
PHO (b)	<0.05	<0.6	<0.25	<0.25	<1
PES (s)	<0.05	<0.6	<0.25	<0.25	<1
KBA (s)	<0.05	<0.6	<0.25	<0.25	<1
KBA (b)	<0.05	<0.6	<0.25	<0.25	<1
HCO (s)	<0.05	<0.6	<0.25	<0.25	<1
BRI (s)	<0.05	<0.6	<0.25	<0.25	<1
DOC (s)	<0.05	<0.6	<0.25	<0.25	<1
DOC (b)	<0.05	<0.6	<0.25	<0.25	<1

Mann-Whitney tests were conducted on the data from the Dampier Archipelago sites to test for significant differences between the results of the pilot and main studies, inner and outer archipelago waters, and between the King Bay site and the rest of the archipelago. The results of the Mann-Whitney tests are presented in tables 9 and 10. Tests were only performed on the cadmium and copper results from the pilot survey data because too few samples contained detectable levels of chromium and lead, and because the mercury and zinc results were biased from contamination.

Table 9: The p-values from the results of the Mann-Whitney tests comparing metal concentrations from the pilot survey with the main survey (alpha is set at 0.05 and significant values are shown in bold).

Metal	**Pilot vs. Main** (Outer archipelago)	**Pilot vs. Main** (Inner archipelago)	**Pilot vs. Main** (Inner and Outer)
Cadmium	**0.0098**	**0.0016**	**0.0001**
Copper	0.0851	**0.0013**	**0.0001**

Table 10: The p-values from the results of the Mann-Whitney tests comparing metal concentrations of different regions of the Dampier Archipelago (alpha is set at 0.05 and significant values are shown in bold).

METAL	**Inner vs. Outer** (pilot survey)	**Inner vs. Outer** (main survey)	**Archipelago vs. King Bay** (pilot survey)	**Archipelago vs. King Bay** (main survey)
Cadmium	0.6238	0.2207	**0.0056**	**0.0471**
Copper	**0.0032**	0.2087	**0.0036**	**0.0335**
Mercury (total)	-	0.2619	-	-
Zinc	-	1.0	-	**0.0192**

The test results for copper and cadmium show a significant difference between the pilot survey and the main survey, suggesting the two data sets should be considered separately and not combined. The test results also suggest that there was no difference between the inner and outer archipelago waters, except for copper in the pilot survey. The data from all the sites sampled in the Dampier Archipelago were therefore combined into one data set. When results from the King Bay site were compared with the DOC site (pilot survey) and the rest of the Dampier Archipelago sites (main survey), King Bay was found to be significantly different from the other sites for all the metals tested.

Estimated natural background metal concentrations were calculated from the 95th percentile of the metals' data for the North West Shelf and the Dampier Archipelago sub-region (see Methods section 2.3) and are presented in table 11. The 95th percentiles for Dampier Archipelago and the North West Shelf were similar for most metals, except for copper and zinc where the 95th percentiles for the North West Shelf were slightly higher. The reason for these differences can be attributed to the elevated concentrations of these metals at the Port Hedland offshore site (table 7).

Table 11: Estimated background concentrations of selected metals in coastal waters of the Dampier Archipelago and the broader North West Shelf (calculated from the 95th percentiles of the respective databases, n = number of samples).

Metal	**Dampier Archipelago (μg/L)**	**n**	**North West Shelf (μg/L)**	**n**
Cadmium	0.005	17	0.005	21
Chromium	0.18	17	0.17	21
Copper	0.12	17	0.16	21
Lead	0.01	17	0.01	21
Mercury (total)	0.0004	13	0.0004	17
Zinc	0.14	15	0.20	19

4.3 Organic chemicals

The results of the organic chemical analyses are presented in table 12. Concentrations of all the organic chemicals were found to be below the Limit of Reporting (LOR) at all sites. National guidelines were only available for five of the organic chemicals analysed (naphalene, pentachlorophenol, phenol, benzene and 1,2,4-trichlorobenzene) and the LORs for these were significantly less than the 99% species protection guideline trigger values. For example, the LOR for benzene and 1,2,4-trichlorobenzene was 1.0 µg/L, which is well below their respective 99% species protection guideline trigger values of 500 µg/L and 20 µg/L.

Table 12: Results of the organic chemical analyses for the North West Shelf region, June 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	ANG (s)	BRI (s)	GOI (s)	LEG (s)	WLW (s)	DOC (s)	MIS (s)	PES (s)	WBA (s)	HCO (s)	SLP (s)	KBA (s)	KBA (b)	PHO (s)	PHO (b)	PHI (s)	PHI (b)
Poly Aromatic Hydrocarbons (µg/L)																	
Anthracene	<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	0.1	<0.1	<0.1	<0.1
Benzo(a)pyrene	<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	0.1	<0.1	<0.1	<0.1
Fluoranthene	<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	0.1	<0.1	<0.1	<0.1
Naphthalene *	<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	0.1	<0.1	<0.1	<0.1
Phenanthrene	<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	0.1	<0.1	<0.1	<0.1
Phenols																	
Phenol *	<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	<0.1	<0.1	<0.1	<0.1
Pentachlorophenol *	<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	<0.2	<0.2	<0.2	<0.2
BTEX																	
Benzene *	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Toluene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Ethylbenzene	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Xylene	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Total BTEX	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Total Petroleum Hydrocarbons (µg/L)																	
TPH C6 - C9	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
TPH C10 - C14	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25	<25
TPH C15 - C28	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
TPH C29 - C36	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Total TPH	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250	<250
Other (µg/L)																	
1,2,4-Trichlorobenzene *	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0

* = Guideline trigger values available for this chemical (ANZECC & ARMCANZ, 2000) (Note: all available guidelines at least 20x the limit of reporting or more)

5. GENERAL DISCUSSION

5.1 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 measure metal atoms that are normally unavailable for biological uptake because they are bound up in the mineral matrix, and hence they are significantly influenced by the particulate load in the water column. This survey has therefore focused on dissolved metal concentration.

The dissolved metal concentrations found in seawater in this study are very similar to concentrations measured in an equivalent study on the coastal waters off Perth, Western Australia (McAlpine et al. in press), and generally comparable with those found in coastal waters off the New South Wales coast (Apte et al. 1998), but with a few exceptions (table 13). Trace metal concentrations found off the NSW coast by Apte et al (1998) were reported as being among the lowest measured in the southern hemisphere and were consistent with data for the surface waters of the Pacific Ocean.

Table 13: Comparison of mean trace metal concentrations in North West Shelf coastal waters with other locations.

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

[1] data summarised in Apte et al. 1998.

A direct comparison of chromium and mercury concentrations between the west and east coast studies cannot be made because the limits of detection were different. The concentration of chromium in samples from the North West Shelf were mostly below the detection limit of 0.15 µg/L, which was above the measured chromium levels in the east coast study. The concentrations of mercury in the east coast study were mostly below the detection limit of 0.0014 µg/L, which was up to an order of magnitude greater than the concentrations measured on the North West Shelf in this study. The concentrations of cadmium and lead found on the North West Shelf are similar to concentrations found on the east coast of NSW. Copper and zinc concentrations, although similar to concentrations measured off Perth, were higher than those found in the east coast study (Cu - mean of 0.10 µg/L verses mean of ~0.031 µg/L; Zn - mean of

0.10 µg/L verses mean <0.022 µg/L). However, if the zinc result from the bottom sample collected at the Port Hedland offshore site (0.637 µg/L) is excluded, then the mean zinc concentration decreases significantly from
0.10 µg/L to 0.07 µg/L.

Unfortunately there are insufficient sampling sites to determine whether there are spatial differences in natural background water quality across the NWS. Although the samples from Nickol Bay (HCO and SLP) and offshore from Port Hedland (PHO) suggest some small differences might exist, the similarity of the North West Shelf data with the concentrations measured in the coastal waters off Perth (Western Australia) and New South Wales suggest that dissolved metal concentrations in seawater may not vary greatly around the coastline, at least during non-river flow periods. The lack of a significant difference in background dissolved metal concentrations between the outer and inner (more turbid) waters of the Dampier Archipelago during the main study provides further support for this suggestion.

This study did not consider seasonal changes in the contaminants measured. The main survey was conducted in winter (June 2003) and provides a ‘snapshot picture’ of North West Shelf water quality at one point in time. For cadmium, chromium, copper and lead, the pilot survey provides some additional information on concentrations in the Dampier Archipelago during the summer, and although the concentrations of cadmium and copper were statistically different between the pilot and main surveys (table 9), the actual differences were only minor in absolute terms (i.e. < 0.05 µg/L; table 14). Seasonal variation of dissolved metal concentrations in seawater is likely to be most noticeable when high river flows discharge contaminants from terrestrial sources. Total metal concentrations are likely to be even more affected by the discharge of flood waters, but will also be significantly influenced by other factors that affect the quantity of particulate matter suspended in the water column (e.g. tidal currents, wind and swell conditions).

Table 14: The 95th percentile of measured concentrations of cadmium and copper calculated for the pilot and main surveys, Dampier Archipelago.

METAL	Pilot survey* g/L	Main survey µg/L
Cadmium	0.006	0.003
Copper	0.129	0.084

* Pilot study data included all replicate samples for site DOC.

The limit of detection for the total metal analyses was not as low as achieved for the dissolved metal analyses and none of the six metals were detected at any of the sites sampled. The results are consistent with the Water Corporation of WA monitoring data for cadmium, chromium, lead and mercury collected quarterly from King Bay in 2003 and where there were also no detections (Water Corporation, 2004). However, the Water Corporation measured total copper above 0.25 µg/L and total zinc above 1 µg/L quite frequently. Mackey (1984) also measured total copper levels between 0.076 and 0.36 µg/L in marine waters from the eastern edge of the North West Shelf to the western

Kimberley coast. The range of copper concentrations recorded by Mackey are similar, but slightly less, than the concentrations measured by the Water Corporation.

The results of the Mann-Whitney tests show that concentrations of dissolved cadmium, copper and zinc measured at the King Bay site are slightly elevated compared to the concentrations measured for the rest of the Dampier Archipelago (table 10). This elevation may be a result of industrial effluent discharges and/or antifouling or corrosion inhibiting products used on vessels and infrastructure in the vicinity, however, the concentrations are well below the recommended guidelines that protect environmental values for the area, including ecological health. Although the Mann-Whitney tests could not be performed on the chromium, mercury and lead results, the concentrations for King Bay appear to be consistent with the concentrations measured in the rest of the archipelago. An assessment of metal concentrations in the sediments of the King Bay area would help to determine whether cadmium, copper and zinc are accumulating in the sediments.

Estimates of natural background concentrations for the metals measured in this study were made by calculating the 95th percentile of the measured concentrations from ‘unimpacted’ sites (see section 2.3). Background values have been calculated for the Dampier Archipelago as well as the broader region of the North West Shelf and are recommended for use as ‘default’ background values until there are sufficient additional ultra-trace level analytical data collected to revise them. To determine whether the National guideline trigger values are appropriate for application to the North West Shelf they have been compared with the estimated natural background concentrations (table 15). 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 15 because there is no guideline for total chromium.

Table 15: National guideline trigger values for metals in marine waters (ANZECC & ARMCANZ, 2000) and estimated natural background concentrations for the Dampier Archipelago and North West Shelf waters.

Metal	ANZECC/ARMACANZ trigger values for marine waters (µg/L)			Estimated natural background[#] concentration (µg/L)	
	Recommended guidelines for different levels of species protection				
	90%	99/95%	99%	Dampier Archipelago	North West Shelf
Cadmium	14	0.7	0.7	0.005	0.005
Chromium (III)	48.6	27.4	7.7	0.18*	0.17*
Chromium (VI)	20	4.4	0.14		
Copper	3	1.3	0.3	0.12	0.165
Lead	6.6	4.4	2.2	0.01	0.01
Mercury (inorganic)	0.7	0.1	0.1	0.0004‡	0.0004‡
Zinc	23	15	7	0.14	0.20

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

‡ The analytical results were for total mercury.

[#] Background concentration is the 95th percentile of data from ‘unimpacted’ sites; see section 2.3.

Background concentrations for all the measured 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, except copper, the background concentrations were at least 1.5 orders of magnitude below the most conservative guideline; background concentrations for copper were approximately half the guideline for 99% species protection. It is also worth noting that all metals measured at the potentially affected King Bay site easily achieved the National guidelines for 99% species protection, even though some metal concentrations were 'elevated'. However, copper and zinc concentrations were relatively high at the inner harbour site in Port Hedland and although zinc just met the 99% species protection guideline value, copper did not.

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 North West Shelf waters. By inference the guidelines recommended for other metals, except cobalt, are also expected to be appropriate for North West Shelf waters. For cobalt, McAlpine et al. (in press) found that the 99% species protection guideline of 0.005 µg/L was below the level of detection achievable for the analytical method used by CSIRO for ultra-trace metal analyses, and approximated background levels reported for oceanic waters (Nozaki, 1997; OZREEF, 1997). The guideline was considered to be excessively low and an artefact of the limited toxicological database available and the curve fitting method used to derive the national guidelines. The shape of the curve fitting the eight available data points 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 all 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. 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.

Until natural levels of cobalt in North West Shelf 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 is recommended for use.

5.2 Organic chemicals

For the organic chemicals analysed 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. 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 North West Shelf waters. The results of the organic chemical analyses will provide a useful reference against which future studies can be compared.

6. CONCLUSION

The objective of the main survey was to provide estimates of natural background concentrations for a range of contaminants in the waters of the North West Shelf and to determine whether the guideline trigger values from ANZECC & ARMCANZ (2000) were relevant to the region. The focus of the program was on the Dampier Archipelago where there is ongoing and rapid expansion of heavy industrial activity, which in turn has the potential to put significant pressure on the local coastal and marine environments. The Department of Environment is establishing the environmental values and environmental quality objectives that will apply to the North West Shelf region through the NHT funded program *Community derived marine quality objectives for the North West Shelf*. These will form the basis of an environmental quality management framework for the region and will require specific measurable environmental quality criteria for assessing the performance of management programs in achieving the values and objectives. The outcomes of this study will greatly assist in the development and implementation of the environmental quality criteria.

Estimates of the natural background dissolved concentrations of six selected metals are provided in tables 11 and 15. Analyses of the samples for the selected organic chemicals did not detect any of the chemicals above the laboratory reporting limits. The main survey was conducted in June and provides a snapshot of water quality at that time. Seasonal variation in the dissolved concentration of the selected contaminants has not been measured, but is not expected to be great. Further surveys are recommended to determine the significance of seasonal differences.

The results of this study indicate that water quality on the North West Shelf is generally very good, with only localised elevations of some contaminants near industrial centres. Water quality at the time of sampling met the environmental quality guidelines for a *very high* level of ecological protection (99% species protection) throughout the sampled area, with the exception of the inner harbour at Port Hedland, where copper and zinc levels were elevated above background. However, the 95% species protection guidelines representing a *high level* of protection were easily met in the inner harbour. Although no organic chemicals were detected in the sample analyses, the reporting limits were well below the available guideline trigger values recommended in ANZECC & ARMCANZ (2000) for a very high level of ecological protection (99% species protection). Unfortunately there were no guideline values for 13 of the organic chemicals, nevertheless the results provide a useful reference against which future studies can be compared.

This study concludes that the recommended guideline trigger values from ANZECC & ARMCANZ (2000) are suitable for use in the North West Shelf coastal waters, with the exception of cobalt. This is not because of naturally elevated levels of cobalt, rather the 99% species protection guideline trigger value for cobalt appears to be excessively conservative and well below the level of detection for currently available analytical techniques. The guideline trigger value for 95% species protection should therefore be applied to the North West Shelf waters where a very high level of ecological protection is sought. This approach is recommended until the guideline can be revised in light of additional ecotoxicological information, or analytical detection limits can be sufficiently reduced to characterise natural levels of cobalt in North West Shelf waters.

A set of environmental quality criteria modified from the *Revised Environmental Quality Criteria Reference Document (Cockburn Sound)* (EPA, 2004) is included in Appendix G for use on the North West Shelf. These criteria are based on the recommended guidelines and approaches in ANZECC & ARMCANZ (2000). They consist of environmental quality guidelines (EQG) for initial assessment of water quality, and environmental quality standards (EQS) for a more comprehensive assessment of water quality where exceedence of an EQG indicates a potential problem. For selected contaminants that do not have an EQG, a set of Low Reliability Values (LRV) are provided in Appendix H. The framework for applying the EQG, EQS and LRVs is discussed in detail in EPA (2004).

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APPENDIX A: METHODS

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

A.1 Preparation of sample containers

A.1.1 Trace metal sample bottles

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

A.1.2 Mercury sample bottles

For the pilot survey 500 mL 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 two days, then fill them with 50% v/v AR nitric acid for at least three days, followed by 10% v/v ultrapure grade nitric acid (Merck Tracepure) for at least three 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 two day period in Milli-Q water, emptied and 'double bagged'.

During the course of this part of the survey, 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 500 mL 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 two days, at least three 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 five 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 two 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

Water samples for analysis of organic chemicals were stored in bottles provided by the Australian Government Chemical Laboratories (AGAL). At each site, two 1 litre amber bottles and two 44 ml zero headspace vials were filled for the laboratory analyses.

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 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. Cleaning prior to the pilot survey was less rigorous and involved rinsing with dilute nitric acid solution followed by rinsing with distilled water.

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 CALM research vessel *Bidthangarra* 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 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 while 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 therefore filtered in a laboratory clean room to reduce the potential for contamination 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).

Total metals

Two mL of ultrapure nitric acid and 6 mL of ultrapure hydrochloric acid were added to a twenty gram aliquot of unfiltered water sample. The resulting mixture was heated to 121ºC and digested for one hour. Following cooling, total chromium was determined directly by graphite furnace AAS. The remaining digest volume was neutralised to a pH of approximately 5.5 by addition of ammonia and analysed for Cd, Cu and Zn using the same solvent extraction/GFAAS method used for dissolved metals. A method blank (deionised water), a duplicate and a spike recovery sample were included in each sample 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
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 (5 mL) 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: DATA USED TO ESTIMATE NATURAL BACKGROUND METAL CONCENTRATIONS FOR THE DAMPIER ARCHIPELAGO AND NORTH WEST SHELF

Site	Cd µg /L	Cr µg /L	Cu µg /L	Hg µg /L	Pb µg /L	Zn µg /L
Pilot program						
BRI (s)	0.004	<0.15	0.068		<0.011	0.078
BRI(s)	0.004	<0.15	0.090		<0.011	
BRI(b)	0.005	0.150	0.090		<0.011	
DOC (s)	0.004	<0.15	0.110		<0.011	0.029
DOC (s)	0.004	<0.15	0.131		<0.011	0.083
DOC (s)	0.005	<0.15	0.110		<0.011	0.082
DOC (s)	0.005	<0.15	0.121		<0.011	0.069
Main program						
ANG (s)	0.002	<0.15	0.078	≤ 0.0001	<0.006	0.045
BRI (s)	0.002	<0.15	0.058	0.0004	<0.006	0.155
BRI (b)				0.0002		
GOI(s)	0.002	0.15	0.060	0.0002	<0.006	0.056
GOI (b)				0.0003		
LEG(s)	0.002	0.20	0.070	≤ 0.0001	0.010	0.031
WLW (s)	0.003	<0.15	0.056	0.0004	<0.006	0.102
DOC (s)	0.002	<0.15	0.064	0.0003	<0.006	0.053
DOC (b)	0.003	<0.15	0.088	0.0002	<0.006	0.130
MIS(s)	0.003	0.17	0.066	0.0001	<0.006	0.031
PES (s)	0.002	<0.15	0.072	0.0001	<0.006	0.064
PES (b)				0.0001		
WBA (s)	0.003	<0.15	0.070	0.0002	<0.006	0.088
Sites outside Dampier Archipelago						
HCO (s)	0.010	<0.15	0.129	0.0002	<0.006	0.027
SLP (s)	0.004	<0.15	0.105	0.0002	0.009	0.031
PHO (s)	0.003	<0.15	0.161	0.0003	<0.006	0.063
PHO (b)	0.005	<0.15	0.193	0.0003	0.010	0.637

APPENDIX C: SALINITY/TEMPERATURE READINGS

Salinity/temperature readings for BRI

BRI	Salinity	Temperature ºC
5 m	34.5	28.9
10 m	34.4	28.6
15 m	34.7	28.5
20m	34.9	28.5
25m	35.1	28.5
>30m	35.1	28.6

Salinity/temperature readings for DOC

DOC	Salinity	Temperature ºC
5 m	35.4	29.3
10 m	36.1	29.0
>10 m	36.3	29.0

Salinity/temperature readings for KBA

KBA	Salinity	Temperature ºC
5 m	34.9	30.4
10 m	35.4	29.9
>10 m	35.7	27.7

APPENDIX D: QUALITY CONTROL DATA – PILOT SURVEY

Spike recoveries

Site sampled	**% Recovery Cd**	**% Recovery Cu**	**% Recovery Hg**	**% Recovery Pb**	**% Recovery Zn**
DOC (N, B) 2	97	93		88	111
BRI (N, S) 1	104	93		89	104
KBA (N, B) 1 + spike			98		
DOC (C, S) 4 + spike			98		

Method blanks

	Cd µg Cd/L	**Cr µg Cr/L**	**Cu µg Cu/L**	**Pb µg Pb/L**	**Zn µg Zn/L**
Mean absolute blank (n=6	0.000	0.00	0.006	0.006	0.013
Limit of Detection (3 sigma)	0.002	0.15	0.015	0.011	0.013

Field blanks

Field Blank	**Cd µg Cd/L**	**Cr µg Cr/L**	**Cu µg Cu/L**	**Hg µg Hg/L**	**Pb µg Pb/L**	**Zn µg Zn/L**
FB 1	0.002	<0.15	0.001	<0.0002	0.010	0.038
FB2	0.002	<0.15	0.002	<0.0002	0.012	0.060

CRM

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

Analytical replicates

Site sampled	Sample µg Cd/L	Lab Replicate µg Cd/L	Sample µg Cu/L	Lab Replicate µg Cu/L	Sample µg Pb/L	Lab Replicate µg Pb/L	Sample µg Zn/L	Lab Replicate µg Zn/L
DOC (N, S) 3	0.005	0.005	0.111	0.112	0.009	0.002	0.087	0.081
KBA (N, B) 1	0.007	0.008	0.130	0.133	0.009	0.005	0.408	0.401

Code: C = CSIRO Teflon Pole Sampler
N = Niskin Bottle
S = Surface sample
B = Bottom sample

APPENDIX E: QUALITY CONTROL DATA – MAIN SURVEY

Spike recoveries

Site	% Recovery Cd	% Recovery Cu	% Recovery Pb	% Recovery Zn	% Recovery Hg
SLP-dup.	85	91	87	96	99
DOC (s) dup. 26.06.03	93	93	89	103	
LEG (s)					99
KBA (s)					98

Method Blanks

Method Blank	Sample µg Cd/L	Sample µg Cu/L	Sample µg Pb/L	Sample µg Zn/L
Mean absolute blank (n=4)	0.001	0.006	0.000	0.005
Limit of Detection (3 sigma)	0.001	0.005	0.006	0.003

Method Blank	Hg ng/kg
Mean absolute blank (n=7)	0.3
Limit of Detection (3 sigma)	0.1

Field blanks

Field Blank	Sample µg Cr/L	Sample µg Cd/L	Sample µg Cu/L	Sample µg Pb/L	Sample µg Zn/L	Sample ng Hg/L
SLP blk	<0.15	0.001	<0.005	0.006	0.005	<0.1
KBA blk 24.06.03	<0.15	0.002	<0.005	0.008	<0.003	<0.1
LEG blk 24.06.03	<0.15	0.001	0.008	<0.006	0.005	<0.1
PHO blk	<0.15	0.001	0.007	0.007	0.034	<0.1
BRI Blk						<0.1

CRM

CASS-4	Sample µg Cu/L	Sample µg Cd/L	Sample µg Zn/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	Sample µg Cd/L	Lab Replicate µg Cd/L	Sample µg Cu/L	Lab Replicate µg Cu/L	Sample µg Pb/L	Lab Replicate µg Pb/L	Sample µg Zn/L	Lab Replicate µg Zn/L	Sample ng Hg/L	Lab Replicate ng Hg/L
PES (s)	0.002	0.002	0.074	0.076	0.002	0.007	0.015	0.023		
WBA-S 26.06.03	0.003	0.002	0.070	0.069	0.002	0.004	0.089	0.087		
PHO (s)									0.35	0.29
PHI (s)									0.46	0.47
WBA (s) 24.06.03									0.20	0.17
KBA (s)									0.19	0.24
MIS (s)									0.11	0.12
BRI (s)									0.42	0.40
GOI (s)									0.18	0.12
WLW (s)									0.44	0.39

Sampling replicates

Sample	Cd µg Cd/L	Cd duplicate µg Cd/L	Cr µg Cr/L	Cr duplicate µg Cr/L	Cu µg Cu/L	Cu duplicate µg Cu/L	Hg ng/kg	Hg duplicate ng/kg	Pb µg Pb/L	Pb duplicate µg Pb/L	Zn µg Zn/L	Zn duplicate µg Zn/L
SLP (s)	0.004	0.005	<0.15	<0.15	0.105	0.099	0.18	0.26	0.009	<0.006	0.031	0.021
MIS (s)							0.11	0.10				
KBA (s) 24-June & 26-June							0.27	0.22				
DOC (s)	0.002	0.002	<0.15	<0.15	0.064	0.086			<0.006	0.008	0.053	0.053

APPENDIX F: QUALITY CONTROL DATA – TOTAL METAL ANALYSES

Method blanks

Sample	Cd ug/L	Cr µg/L	Cu µug/L	Pb µg/L	Zn µg/L
Blank	<0.05	<0.6	<0.25	<0.25	<1

Method duplicates

Method Blank	Cd ug/L	Cr ug/L	Cu ug/L	Pb ug/L	Zn ug/L
DOC (s)	<0.05	<0.6	<0.25	<0.25	<1
Duplicate	<0.05	<0.6	<0.25	<0.25	<1

Spike recovery

Method Blank	Cd % Recovery	Cr % Recovery	Cu % Recovery	Pb % Recovery	Zn % Recovery
KBA (s) + spike	102	115	96	102	99

APPENDIX G: RECOMMENDED ENVIRONMENTAL QUALITY CRITERIA FOR PROTECTING NWS MARINE ECOSYSTEMS FROM THE EFFECTS OF TOXICANTS IN MARINE WATERS

<table>
<tr><th colspan="4">Environmental Quality Guidelines*</th><th colspan="2">Environmental Quality Standard*</th></tr>
<tr><td colspan="4">A. The 95%ile of the sample concentrations from the area of concern (either from one sampling run or all samples over an agreed period of time, or from a single site over an agreed period of time) should not exceed the environmental quality guideline value.
B. Where there are mixtures of toxicants, TTM should not exceed 1 for the area of concern using the total toxicity of mixtures formula[G].</td><th>High protection
Narrative</th><th>Moderate protection
Narrative</th></tr>
<tr><th>Chemical</th><th>High protection (µg/L)</th><th>Moderate protection (µg/L)</th><th>Low protection (µg/L)</th><td rowspan="16">**Bioavailable measures**
A. The 95%ile of the bioavailable contaminant concentration in the test samples should not exceed the environmental quality guideline value
and
B. TTM should not exceed 1 for chemical mixtures using median bioavailable contaminant concentrations from the area of concern (either from one sampling run or all samples over an agreed period of time, or from a single site over an agreed period of time) and environmental quality guidelines in the total toxicity of mixtures formula[G].
Indirect biological measures
C. Using direct toxicity assessment (DTA) procedures on ambient waters there should not be a statistically significant effect ($P < 0.05$) on lethal or sublethal chronic endpoints for any species, compared to the reference/control water.
D. Using direct toxicity assessment (DTA) procedures on an effluent discharge:
- the dilution of effluent at the boundary of a high protection zone should be protective of at least 95% of species calculated using the statistical distribution methodology on the results</td><td rowspan="16">**Bioavailable measures**
A. The 95%ile of the bioavailable contaminate concentration in the test samples should not exceed the environmental quality guideline value;
and
B. TTM should not exceed 1 for chemical mixtures using median bioavailable contaminant concentrations from the area of concern (either from one sampling run or all samples over an agreed period of time, or from a single site over an agreed period of time) and environmental quality guidelines in the total toxicity of mixtures formula[G].
Indirect biological measures
C. Using direct toxicity assessment (DTA) procedures on ambient waters should not be a statistically significant effects ($P<0.05$) on lethal acute endpoints, or of greater than 50% on sublethal chronic endpoints, for any species, compared to the reference/control water.
D. Using direct toxicity assessment (DTA) procedures on an effluent discharge: discharge:
- the dilution of effluent at the boundary of a moderate protection zone should be protective of at least 90% of species</td></tr>
<tr><td>METALS and METALLOIDS</td><td></td><td></td><td></td></tr>
<tr><td>Cadmium [B]</td><td>0.7</td><td>14 [C]</td><td>36 [A]</td></tr>
<tr><td>Chromium III</td><td>27.4</td><td>49</td><td></td></tr>
<tr><td>Chromium VI</td><td>4.4</td><td>20 [C]</td><td></td></tr>
<tr><td>Cobalt</td><td>1</td><td>14</td><td></td></tr>
<tr><td>Copper</td><td>1.3</td><td>3 [C]</td><td></td></tr>
<tr><td>Lead</td><td>4.4</td><td>6.6 [C]</td><td></td></tr>
<tr><td>Mercury (inorganic) [B]</td><td>0.1</td><td>0.7 [C]</td><td>1.4 [C]</td></tr>
<tr><td>Nickel</td><td>7</td><td>200 [A]</td><td></td></tr>
<tr><td>Silver</td><td>1.4</td><td>1.8</td><td></td></tr>
<tr><td>Tributyltin (as µg/L Sn)</td><td>0.0006 [C]</td><td>0.02 [C]</td><td></td></tr>
<tr><td>Vanadium</td><td>100</td><td>160</td><td></td></tr>
<tr><td>Zinc</td><td>15 [C]</td><td>23 [C]</td><td></td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
<tr><td>NON-METALLIC INORGANICS</td><td></td><td></td><td></td></tr>
</table>

Ammonia[D, E]	910	1200		of DTA using sublethal chronic endpoints on 5 species (minimum 4 taxonomic groups); *or* - if only 3 species (from 3 taxonomic groups) are tested, the dilution of effluent (as % effluent) at the boundary of a high protection zone should be greater than that represented by the lowest chronic NOEC (i.e. the NOEC for the most sensitive species) divided by a safety factor of 10.	calculated using the statistical distribution methodology on the results of DTA using sublethal chronic endpoints on 5 species (minimum 4 taxonomic groups); *or* - if only 3 species (from 3 taxonomic groups) are available, the dilution of effluent (as % effluent) at the inner boundary of a moderate protection zone should be greater than that represented by the lowest chronic NOEC (i.e. the NOEC for the most sensitive species) divided by a safety factor of 2.
Cyanide[F]	4	7			
ORGANICS					
Benzene	500[C]	900[C]			
Naphthalene	50[C]	90[C]			
Pentacholophenol[B]	11	33	55[A]		
Phenol	400	520			
1,2,4-tricholobenzene[B]	20	140	240		
ORGANOCHLORINE PESTICIDES				**Direct biological/ecological measures**	**Direct biological/ecological measures**
Endosulfan[B]	0.005	0.02	0.05[A]	E. No significant[H] change in any biological or ecological indicator beyond natural variation that can be demonstrably linked to a contaminant. F. F. Where TBT concentrations exceed the guideline the incidence of imposex in *Thais orbita* should be ≤ 5%. G. The median tissue concentration of chemicals that can adversely bioaccumulate or biomagnify should not exceed the 80th percentile of tissue concentrations from a suitable reference site.	E. The median of the distribution of measurements for any biological or ecological indication should be within the 10th and 90th percentile of the natural range measured at suitable reference sites; F. Where TBT concentrations exceed the guideline the incidence of imposex in *Thais orbita* should be ≤ 10%. G. No loss of species or types of ecosystem processes.
Endrin[B]	0.004	0.01	0.02		
ORGANOPHOSPHORUS PESTICIDES					
Chlorpyrifos[B]	0.009	0.04[A]	0.3[A]		
Temephos[B]	0.05	0.4	3.06[A]		
OIL SPILL DISPERSANTS					
Corexit 9527	1100	2200			
OTHER CHEMICALS	#	#	#		

* EQG and EQS may be applied to an individual site or to a broader area of concern.

Refer to Low reliability values in table 2c and the NWQMS Report No.4 (ANZECC & ARMCANZ, 2000). For chemicals not listed in tables 2a or 2c, guideline trigger values from ANZECC & ARMCANZ (2000) should be applied as follows: the recommended combination of 99% or 95% values (slightly disturbed systems) for high ecological protection EQG; 90% values for moderate ecological protection EQG; and 80% values for low ecological protection EQG. Low ecological protection EQG only provided for chemicals identified as potential bioaccumulators or bioconcentrators.

A Value may not protect key test species from acute and chronic toxicity (see ANZECC & ARMCANZ, 2000).

B Chemical for which possible bioaccumulation and biomagnification effects should be considered ($\log_{10}$ Kow values >4 and <7).

C Value may not protect key test species from chronic toxicity (see ANZECC & ARMCANZ, 2000).

D Total ammonia as [NH_3-N] at pH 8.

E See section 8.3.7 of ANZECC & ARMCANZ (2000) for a detailed discussion on how different environmental factors will affect toxicity of the chemical.

F Cyanide as un-ionised HCN measured as [CN].

G TTM (total toxicity of the mixture) = $\Sigma(Ci / EQGi)$ where Ci is the concentration of the ‘i’th component in the mixture and EQGi is the guideline for that component. If TTM exceeds 1, the mixture has exceeded the water quality guideline. ANZECC & ARMCANZ (2000) only recommends use of this formula on mixtures with up to 5 contaminants of concern until further scientific study confirms its relevance to more complex mixtures. The TTM should be analysed for each sampling occasion, and then the median TTM of all sampling occasions compared against the guideline. The effect of different contaminants on biota can be synergistic, antagonistic as well as additive depending on a number of factors, including the species being tested. The use of DTA is recommended for toxicant mixtures of greater than 5 components or of uncertain mixture effects. Where the effect of the different contaminants on each other is unknown, and DTA is not a viable alternative, the assumption that all contaminants have additive toxicity is acceptable.

H Significant means at the level of detection determined by the effects size and statistical decision criteria agreed by the relevant stakeholders on a case-by-case basis. This provides flexibility for stakeholders to account for the wide range in natural variability between different biological indicators and to determine a level of detection that is ecologically meaningful.

APPENDIX H: LOW RELIABILITY VALUES FOR CHEMICALS THAT DO NOT HAVE A HIGH OR MODERATE RELIABILITY GUIDELINE

(These are for guidance only and not to be used as recommended guideline trigger values)

Chemical	**High protection** (µg/L)	**Moderate protection** (µg/L)	***Low protection*** (µg/L)	**Summary of available overseas guidelines**[D]	
				(µg/L)	**Comments**
METALS and METALLOIDS					
Aluminium	0.5				
Arsenic III Arsenic V	2.3 4.5			12 12.5 25 36	(total) South Africa (total) Canada (tot. dissolved) Netherlands (tot. dissolved) USA
Manganese	80				
Molybdenum	23			290	(tot. dissolved) Netherlands
Selenium IV[B] Selenium VI[B]	3 3			1 5.3 71*	(total) Canada (tot. dissolved) Netherlands (tot. dissolved) USA
NON-METALLIC INORGANICS					
Chlorine (total residual)	3			2 7.5	British Columbia, Alaska. USA
Hydrogen sulfide [C, #]	1			2	British Columbia, Quebec, USA
ORGANICS					
Toluene	110	230		92 215 730	New York State Canada Netherlands
Ethylbenzene	5			4.5 25 370	New York State Canada Netherlands
o-xylene[E]	350				
m-xylene[E]	75				

Chemical	**High protection** (µg/L)	**Moderate protection** (µg/L)	***Low protection*** (µg/L)	**Summary of available overseas guidelines**[D]	
				(µg/L)	**Comments**
p-xylene[E]	200				
Total xylene				19	(total) New York State
Cumene	20	40		380	(total) Netherlands
Anthracene[B]	0.01	1.5	7	0.08	Netherlands
Phenanthrene[B]	0.6	4	8	0.3	Netherlands
Fluoranthene[B]	1	1.7	2	0.3	Netherlands
Benzo(a)pyrene [B]	0.1	0.4	0.7	0.2	Netherlands
Capacitor 21[B]	0.002				
Aroclor 1016	0.009				
Aroclor 1221	1.0				
Aroclor 1232	0.3				
Aroclor 1242	0.3				
Aroclor 1248	0.03				
Aroclor 1254	0.01				
4,4’-dichlorobiphenyl	0.1				
2,3,4’-trichlorobiphenyl	0.07				
2,2’4,5,5’-pentachloro-1,1’-biphenyl	0.2				
2,4,6,2’,4’,6’-hexachlorobiphenyl	0.15				
Total PCBs				0.03	USA
ORGANOCHLORINE PESTICIDES					
Aldrin[B]	0.003			0.001	Netherlands
Chlordane[B]	0.0001			0.002 0.004	Netherlands USA
DDEB	0.0005			0.0004	Netherlands
DDTB	0.0004			0.0009 0.001	Netherlands USA
Dieldrin[B]	0.01			0.0019 0.039	USA Netherlands
Heptachlor[B]	0.0004			0.0005 0.0036	Netherlands USA
ORGANOPHOSPHORUS PESTICIDES					
Fenitrothion	0.001			0.009	Netherlands
Malathion	0.05			0.013 0.1	Netherlands USA

Chemical	**High protection** (µg/L)	**Moderate protection** (µg/L)	***Low protection*** (µg/L)	**Summary of available overseas guidelines**[D] (µg/L)	**Comments**
HERBICIDES AND FUNGICIDES					
2,4-D	280			10	Netherlands
2,4,5-T	36			9	Netherlands
Metsulfuron	8				
Amitrole	22				
Atrazine	13			2.9	Netherlands
Simizine	3.2			0.14	Netherlands
Glyphosate	370				
SURFACTANTS					
Linear alkylbenzene sulfonates (LAS)	0.1				
Alcohol ethoxylated sulfate (AES)	650				
Alcohol ethoxylated surfactants (AE)	140				
OILS & PETROLEUM HYDROCARBONS					
Diesel	3				
OIL SPILL DISPERSANTS					
BP 1100 X	25				
Corexit 7664	16				
Corexit 8667	1200				
Corexit 9550	14	400			

* The USEPA suggests that the status of the fish community should be monitored if selenium concentration exceeds 5.0 µg/L because the guideline does not take into account uptake via the food chain.

\# Refer to the NWQMS Report No.4 (ANZECC & ARMCANZ, 2000). See section 8.3.7 for a detailed discussion on how different environmental factors will affect toxicity of the chemical.

A Low reliability values based on low reliability trigger value calculated from limited data (from chapter 8 of ANZECC & ARMCANZ, 2000). In most cases low reliability guidelines are only provided for high ecological protection areas because of the relatively conservative assumptions in the calculation. Action is not mandatory if they are exceeded, but regulators and management agencies should be advised and consideration given to developing strategies that will ensure environmental impacts are avoided.

B Chemical for which possible bioaccumulation and biomagnification effects should be considered ($\log_{10}$ Kow values >4 and <7).

C Sulfide as un-ionised H_2S, measured as [S] (see ANZECC & ARMCANZ, 2000).

D The overseas guidelines provided in this table have been derived to protect marine ecosystems from the chronic effects of contaminants, and not for triggering further investigations to determine if chronic effects are occurring.

E Toxicity of the xylene isomers can be assumed to be additive.

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