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Background quality of the marine sediments off the Western Australian mid-west coast

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Background quality of marine sediments off the Western Australian mid-west coast

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Contents

Tables

Figures

Appendices

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Abstract

The mid-west coast of Western Australia is a highly energetic coastline with only a few small rivers draining a relatively arid catchment. The sediments are medium to coarse grained sands interspersed between limestone reefs and the adjacent terrestrial geology is composed of reworked sands of marine and aeolian origin.

The background concentrations of heavy metals and organic contaminants in marine sediments off the mid-west coast of Western Australia (WA) are not well documented. Sediment samples were taken at three unimpacted reference locations and one potentially impacted location from the shallow coastal marine environment (<12 m depth) off the mid-west coast of WA to determine concentrations of a range of selected metalloids, metals and organic chemicals under natural background conditions. The suite of chemicals measured included aluminium, arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, zinc, butyltin compounds, total petroleum hydrocarbons, BTEX chemicals, polycyclic aromatic hydrocarbons, organochlorine and organophosphate pesticides and PCBs. The work was undertaken to achieve two primary objectives. Firstly, to provide a contemporary baseline for evaluating anthropogenic changes or trends in sediment quality around regional centers of development (eg. ports). Secondly, to ascertain whether the sediment quality guidelines for the protection of ecosystem health recommended in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC & ARMCANZ, 2000) are applicable to the region.

Background sediment quality was found to be high with concentrations below the analytical limit of reporting for all of the organic chemicals measured and some of the metals. The concentrations of metals and metalloids in the sediments were found to be at similar levels or lower than the concentrations found in other studies undertaken around Australia.

No organic chemicals were detected in any of the samples. Compliance with the recommended sediment quality guidelines (ANZECC & ARMCANZ, 2000) could not be determined for eight of the analysed chemicals (acenaphthene, anthracene, dibenzo(ah)anthracene, fluorene, lindane, chlordane, dieldrin and endrin) because the laboratory analytical limit of reporting was above the recommended guideline.

The results of this study, and the guidelines and approaches recommended in ANZECC & ARMCANZ (2000), were used to develop a set of sediment quality guidelines that could be applied to four different levels of ecological protection in the marine environment of the mid-west coast. These are presented in Table 13 of the report.

1. Introduction

The Environmental Protection Authority (EPA) has developed an environmental quality management framework (EQMF) for implementing the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ 2000) in Western Australia (SWQMS, 2004). The EQMF is being applied to manage waste discharges and deposits 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. The mid-west coast region of WA (see Figure 1) is an area where establishment of the EQMF will help strategically manage the effects of urban expansion.

The mid-west coast of Western Australia is a highly energetic coastline with a moderate swell and strong sea breezes, predominantly from the south-west. Tidal fluctuations are relatively low, ranging from 0.5 to 1.0 metre in amplitude, and generally one cycle per day. During the cooler months the Leeuwin current carries warm tropical water down the west coast and then east along the south coast toward the Great Australian Bight. The adjacent terrestrial geology is composed of reworked sands of marine and aeolian origin with only a few small rivers draining a relatively arid catchment. The marine sediments are medium to coarse grained sands interspersed between limestone reefs. These reefs are remnants of ancient coastlines and generally run parallel to the shoreline, often creating inshore lagoons and sheltering sections of the coast from the full effects of swell and wind. The sandy habitats support extensive *Posidonia* and *Amphibolis* seagrass meadows and the adjacent reefs are generally dominated by brown macroalgae.

The EQMF is based on protecting a set of environmental values for the marine environment through the achievement of environmental quality objectives (broad management goals). Selected environmental quality indicators are measured and assessed against a specific set of environmental quality criteria (EQC) to determine whether the environmental quality objectives have been achieved.

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 subject. For example, the rock lobster fishery extends along the entire mid-west coast and provides employment for the people of the region and export revenue for the State. The unique and diverse characteristics of the mid-west coastal waters led to the establishment and subsequent gazettal of the Jurien Bay Marine Park on August 30 2003 by the Government of Western Australia. It includes sanctuary and special purpose zones providing for a range of conservation, recreational and commercial objectives. Mid-west communities also expect to be able to undertake their recreational pursuits in a clean, uncontaminated environment.

Development of the EQC that support the environmental values and environmental quality objectives will be based on the numerical guidelines and approaches recommended in the National guidelines document (ANZECC & ARMCANZ, 2000). This requires an understanding of natural background conditions in the region, but few programs have attempted to characterise background concentrations of contaminants. Most sediment quality monitoring programs have focused around specific developments or activities (eg. Geraldton Port), and often used commercial laboratories that are not equipped to measure at the analytical limits required to resolve *actual* background concentrations for most contaminants.

Sediment contaminants can be divided into two groups: those that occur naturally and have a background concentration (eg. metals); and xenobiotic chemicals (eg. some organic compounds such as TBT) which are produced by humans and do not occur naturally. Concentrations of contaminants from the first group are generally influenced by geology and anthropogenic sources, concentrations of the second group are only influenced by anthropogenic sources. Elevated levels of contaminants are therefore generally caused by anthropogenic waste discharges and deposits. The concentrations of contaminants in marine sediments can be an indication of the health of the surrounding environment. Therefore, an understanding of natural background sediment quality and a set of sediment quality criteria that represent the limit of acceptable change are useful tools to assess and manage the quality of the marine environment.

The two key objectives of the sediment quality program are:

- to determine whether the national sediment quality guidelines (ANZECC & ARMCANZ, 2000) for selected toxicants are suitable for application to nearshore marine sediments of the mid west coast, and to develop new sediment quality guidelines for those chemicals where the national guidelines are not applicable; and
- to determine baseline conditions from which to assess any human-induced changes or trends in sediment quality.

The Department of Environment (DoE) has already reported on background toxicant concentrations in the marine waters of the region (McAlpine et al, 2005) and now this report will characterise background sediment quality. Together, these reports will support the establishment of the EQMF for the mid-west coast by determining the relevance of the ANZECC & ARMCANZ water and sediment quality guidelines for a range of contaminants considered to be of greatest potential threat to environmental quality in the region.

2. Methods

2.1 Site selection

Reference sites were chosen at three locations (Jurien Bay Marine Park, Cliff Head and Horrocks) where anthropogenic influences on marine sediments are thought to be minimal. The sites selected for sampling in Jurien Bay were based on the location of the sites sampled for determining baseline water quality (McAlpine et al, 2005).

Sites were also chosen in Champion Bay where sediment quality is likely to have been affected by human activity. The Town of Geraldton and the Port of Geraldton are located on Champion Bay. The port is used by a large fishing fleet that works in the region and also attracts national and international shipping.

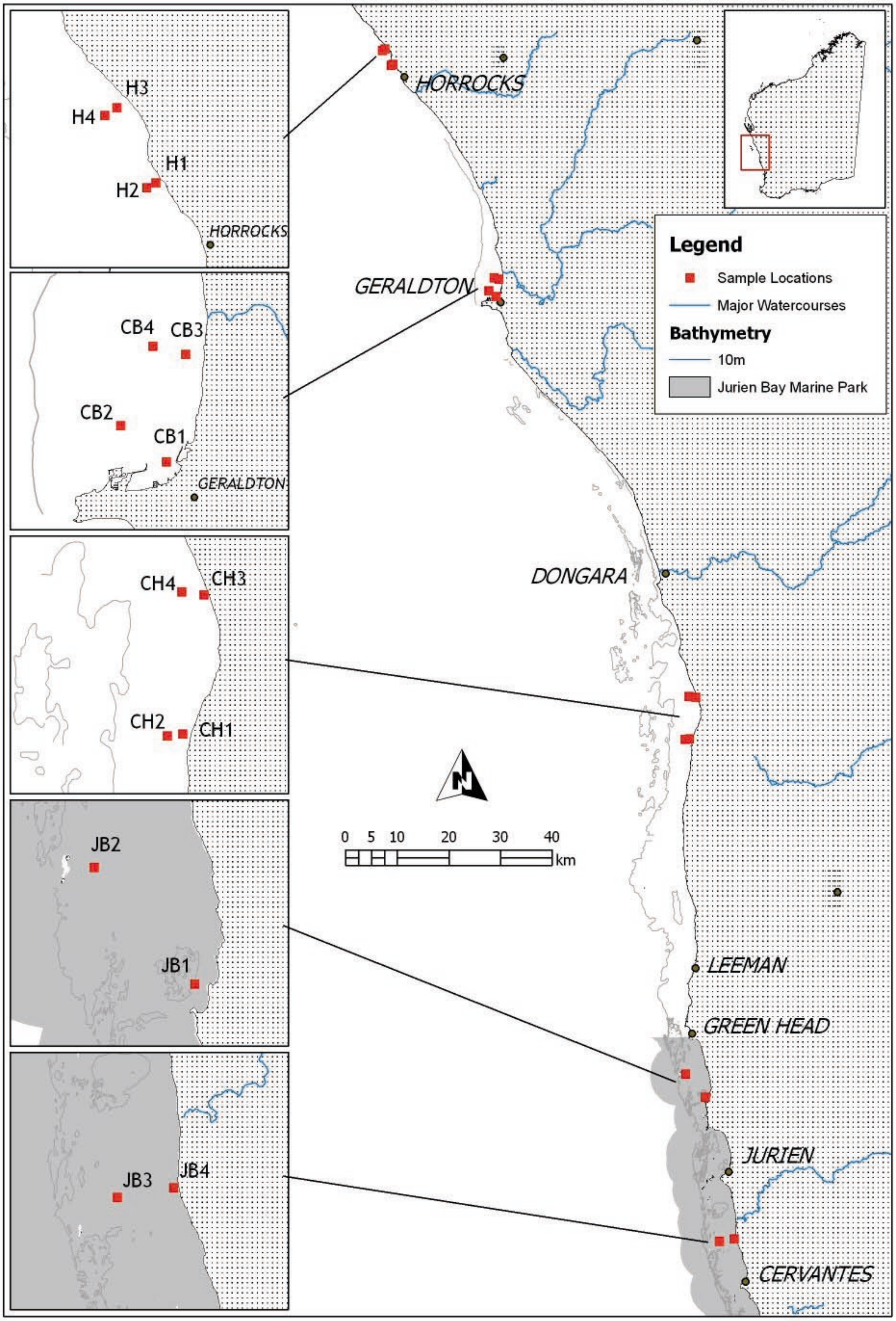

Figure 1: Locality map of the mid-west coast study area showing the sampling sites.

2.2 Field sampling

Fieldwork was conducted from the DEC (formerly DoE) research vessel *Zoila*. Sampling was undertaken in May 2005 by three DEC (formerly Department of Conservation and Land Management (CALM)) divers. Sample handling and preparation on board the *Zoila* was performed by two DEC (formerly DoE) staff.

Sixteen sampling sites were selected for this study (Figure 1 and Table 1) from four locations that span approximately 300km of the mid-west coastline. Four sites were sampled at each location at varying distances from the shore in sandy substrates.

Sampling was conducted during daylight hours over a range of tidal cycles (Figure 2) and weather and sea conditions (Table 2). The maximum tidal amplitude over the duration of this study was about 0.7m. SCUBA divers collected the sediment samples using clear polycarbonate core tubes. The intact cores were brought back to the boat and the sediment was extruded out through the top of the tube and the surface 2 centimeters cut directly into a sample container. Only the surface 2cm of sediment was sampled to ensure that the sampled sediments contained contemporary contaminant concentrations. Methods and procedures for collection and handling of samples are described in Appendix A.

Table 1: Sampling locations.

Location	Site code	Latitude*	Longitude*	Approx. depth at time of sampling (m)
Jurien Bay Marine Park	JB1	30°10.45’ S	114°59.65’ E	10.0
	JB2	30°08.00’ S	114°57.30’ E	6.2
	JB3	30°25.60’ S	115° 01.03’ E	8.0
	JB4	30°25.36’ S	115° 02.86’ E	5.0
Cliff Head	CH1	29°32.89’ S	114° 58.50’ E	3.0
	CH2	29°32.94’ S	114° 57.95’ E	7.5
	CH3	29°28.57’ S	114° 59.34’ E	6.0
	CH4	29°28.46’ S	114° 58.54’ E	6.5
Champion Bay	CB1	28° 46.13’ S	114° 36.36’ E	5.5
	CB2	28° 45.51’ S	114° 35.50’ E	11.0
	CB3	28° 44.34’ S	114° 36.76’ E	7.0
	CB4	28° 44.19’ S	114° 36.15’ E	10.0
Horrocks	H1	28° 21.59’ S	114° 24.67’ E	6.5
	H2	28° 21.68’ S	114° 24.45’ E	11.5
	H3	28° 19.97’ S	114° 23.78’ E	6.5
	H4	28° 20.12’ S	114° 23.48’ E	10.0

* Datum is WGS84.

Three replicate samples (of five cores each) were taken at each of the 16 sample sites. Each replicate was analysed separately for metal concentrations. For the organic chemical analyses, the three replicates were composited for each site, except CB2. At site CB2 the three replicates were analysed separately to assess variability among samples collected at the same site. At each site sub-samples were taken from the metal samples for sediment particle size fractionation to determine the proportion of particles <63 µm in size.

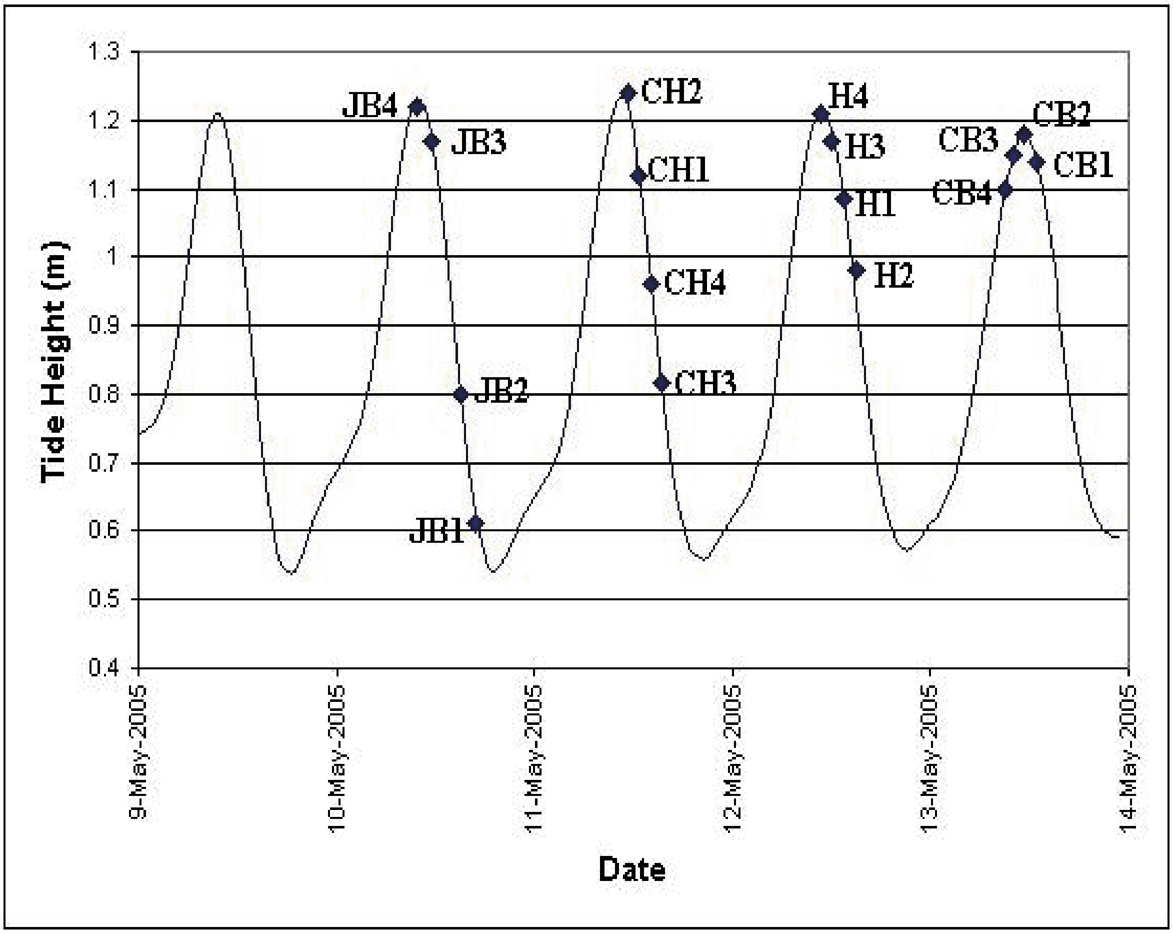

Figure 2: Predicted tide heights for the sampling period at the nearest available stations.

Table 2 : Weather and sea conditions.

Date/Location	Winds	Sun/Cloud	Swell
10 May 2005 Jurien Bay	NW at 10 knots reducing to 5 knots by mid afternoon	Fine and partly cloudy	Swell <1m
11 May 2005 Cliff Head	NW, 5-10 knots	Cloudy but fine	Swell <1m
12 May 2005 Horrocks	WNW, 5-10 knots	Fine and partly cloudy	Swell <1m
13 May 2005 Champion Bay	SE, 10–15 knots	Fine and partly cloudy	Swell <1m

All samples were kept in the dark and on ice from time of collection until delivery to the analytical laboratory. Samples were delivered to the respective analytical laboratories at the end of the field program and within 7 days of collection. Full details of the sediment sampling procedures are given in Appendix A.

2.3 Sample analysis

Methods and procedures for preparing sample containers and for analysis of each selected contaminant are described in Appendix A.

The focus of the program was on those toxic contaminants considered to be of greatest potential threat to sediment quality in the region over the long term. The suite of contaminants analysed included total metals and metalloids (aluminium, arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, zinc) and organic chemicals (TBT, total petroleum hydrocarbons, BTEX chemicals, polycyclic-aromatic hydrocarbons, organochlorine and organophosphate pesticides and PCBs).

The Marine and Freshwater Research Laboratory (MAFRL) at Murdoch University undertook the analyses for all metals except silver. MAFRL is NATA (National Association of Testing Authorities) accredited for the metal analyses performed for this study except the low level arsenic analyses. Quality assurance/quality control (QA/QC) data for the analyses were reported with the analytical results.

Particle size analysis was performed by the CSIRO Minerals Division Particle Sizing Laboratory. The particle size analysis was to determine the proportion of sediment particles in each sample that were < 63 µm in size. The proportion of sediments with particles <63 µm in size is a widely accepted characteristic for normalising metal concentrations.

Analysis for the organic contaminants and silver was performed by the National Measurement Institute (NMI). NMI is NATA accredited for the analyses performed in this study. QA/QC procedures were undertaken with the analyses and the data reported with the analytical results.

2.4 Normalisation of sediment contaminant concentrations

The physical and mineralogical characteristics of sediment can vary considerably both at large (>10s of kms) and small (<1 metre) scales and this heterogeneity significantly affects the sorptive capacity of the sediments, and hence contaminant concentrations (ANZECC & ARCANZ, 2000; Kersten and Smedes, 2002). The key factor affecting the sediment characteristics is the energy of the overlying water. In high-energy environments the fine grains and organic fractions are winnowed out leaving coarse grains with little sorptive capacity. However, in low energy environments fine sediments (eg. silts and clays) and organic particulates with high sorptive capacities can form a significant proportion of sediment composition. Normalising contaminant concentrations to some factor that accounts for these differences in sediment composition, and hence chemical adsorption capacity, helps reduce the variability in sediment contaminant data across all sampling scales, improving comparisons between different sediments and assisting in the interpretation of the data. Normalisation has been defined by Kersten and Smedes (2002) "*as a procedure to correct both background and contaminant concentrations for the influence of the natural variability in sediment granulometry and mineralogical composition mediated by the ambient energy of the aquatic system*".

Many organic chemicals are known to have a strong affinity to organic matter and hence normalisation to 1% total organic carbon content is recommended when comparing to the sediment quality guidelines (ANZECC & ARMCANZ, 2000). Metals tend to have a high affinity for the very fine particulate fraction of the sediments which are mainly made up from clay particles. The <63 µm fraction is the most widely accepted measure used for normalizing metal concentrations but normalization to geochemical normalisers such as aluminium or iron (which represent proxies for clay mineral content) are also accepted practices (ANZECC & ARMCANZ, 2000; Kersten and Smedes, 2002).

The normalisers total organic carbon, <63 µm particle size fraction and aluminium were therefore selected for analysis along with the identified contaminants.

2.5 Statistical analysis

The statistical software package *Statistica (Release 7)* by StatSoft Inc (Copyright @ statsoft inc 1984 – 2005) was used to perform statistical analyses on the data. The Shapiro-Wilk W test for normality was used to determine whether the data were normally distributed. Because the data were not normally distributed, the non-parametric Kruskal-Wallis and Mann-Whitney tests were used to determine whether there were significant differences in sediment chemistry between each of the reference locations and between the nearshore and midshore sites at each location. The Mann-Whitney test was also used to determine whether there was a significant difference between the potentially impacted sites of Champion Bay and the other sites.

The *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ, 2000) recommends that concentrations of sediment contaminants at a test site should be less than the default sediment quality guidelines provided for the toxicant, but does not specify what statistic of the test site data should be compared to the guideline. For the purposes of this report we have taken the approach accepted for assessing sediment quality in Cockburn Sound whereby the median of the test data should be less than or equal to the guideline (EPA, 2005).

To assess whether or not natural background sediment quality exceeds the national sediment quality guidelines and, where appropriate, for deriving new sediment quality guidelines for the mid-west coastal waters the ANZECC & ARMCANZ (2000) recommended approach of comparing the median of test site data with the 80th percentile value of natural reference site data has been adopted in this study. An 80th percentile for each metal was therefore calculated from reference site data; means were calculated using the same data set. For calculation of percentiles and means, where analytical results were reported as ‘below detection limit’, these data were replaced with the detection limit (e.g. <1 mg/kg became 1 mg/kg).

3. Results

3.1 Metals and metaloids

The results for the sediment metal analyses are presented in Table 3 and the associated quality control data are in Appendix B. The results of the particle size analyses are presented in Table 4.

The quality assurance and quality control (QA/QC) data for the NATA accredited analyses and the low level arsenic and selenium analyses are satisfactory given the very low concentrations of the metals measured in the sediments. The concentrations of many of the metals in the sampled sediments were very low relative to the analytical levels of detection and this has resulted in a wider range of differences in the duplicate QA/QC data than would normally be desirable. The QA/QC recovery data are satisfactory, although the recoveries for aluminium show significant variability. The analytical results for the sample replicates taken from site H2c and JB2c show consistent results for all metals analysed.

The analytical results for the low level arsenic analyses were consistent with the results from the NATA accredited method, with both methods showing arsenic concentrations to be very low. The low level arsenic results were slightly lower than NATA accredited results for most samples. The greatest difference between the two sets of results was just over 1 mg/kg for site H3c. The NATA accredited arsenic results were used in the subsequent statistical analysis of the data

Silver concentrations were analysed from the samples collected for organic chemical analyses so results are only available for samples that were composites of all three replicates. Site CB2 was the exception where each replicate was analysed separately. Silver concentrations were found to be below the analytical limit of reporting at all the sites. Mercury concentrations were

Table 3: Total concentrations of metals and metalloids in marine sediments of the Pilbara region, June 2005.

Site	Al	As (Standard)	As (Low level)	Cd	Cr	Cu	Ni	Pb	Zn	Hg	Ag
Jurien Bay											
JB1a	160	2	3.1	0.10	10	<0.2	0.5	<1	<0.5	<0.01	<0.2
JB1b	160	2	2.7	0.08	10	<0.2	1.0	<1	<0.5	<0.01	
JB1c	160	2	2.9	0.11	10	<0.2	0.5	<1	<0.5	0.01	
JB2a	140	4	3.1	0.09	8.5	0.3	0.6	<1	0.6	<0.01	<0.2
JB2b	130	3	3.2	0.09	9.1	<0.2	0.7	<1	<0.5	<0.01	
JB2c	160	4	3.0	0.08	9.0	<0.2	0.7	<1	<0.5	<0.01	
JB2d (duplicate 2c)	140	3	3.0	0.09	9.1	<0.2	0.6	<1	<0.5	<0.01	
JB3a	160	3	2.8	0.16	11	<0.2	0.6	<1	<0.5	<0.01	<0.2
JB3b	230	3	2.6	0.12	11	<0.2	0.7	<1	<0.5	<0.01	
JB3c	180	3	2.6	0.17	12	<0.2	0.7	<1	<0.5	<0.01	
JB4a	420	1	0.60	<0.06	2.2	0.2	0.5	1	1.0	<0.01	<0.2
JB4b	270	2	1.4	<0.06	7.6	<0.2	0.6	<1	0.8	<0.01	
JB4c	280	2	1.0	<0.06	8.1	<0.2	0.6	<1	0.8	<0.01	
Cliff Head											
CH1a	110	3	2.3	0.07	6.9	<0.2	0.4	<1	0.8	<0.01	<0.2
CH1b	100	4	3.0	0.07	8.7	<0.2	0.4	<1	<0.5	<0.01	
CH1c	100	3	3.1	0.06	7.0	<0.2	0.4	<1	<0.5	<0.01	
CH2a	240	2	1.2	<0.06	7.8	<0.2	0.5	<1	<0.5	<0.01	<0.2
CH2b	250	2	1.3	<0.06	7.2	<0.2	0.5	<1	<0.5	<0.01	
CH2c	240	2	1.0	<0.06	6.4	<0.2	0.4	<1	<0.5	<0.01	
CH3a	370	2	1.3	<0.06	6.8	0.2	0.6	<1	0.8	<0.01	<0.2
CH3b	2000	4	3.4	<0.06	12	0.7	1.7	<1	1.1	<0.01	
CH3c	340	2	1.2	0.06	7.5	0.3	0.6	<1	0.9	0.01	
CH4a	250	2	1.6	<0.06	7.6	<0.2	0.6	<1	<0.5	<0.01	<0.2
CH4b	270	2	1.4	<0.06	8.4	0.2	0.6	<1	0.5	<0.01	
CH4c	240	2	1.1	<0.06	7.8	<0.2	0.6	<1	<0.5	<0.01	
Horrocks											
H1a	260	1	0.55	<0.06	3.5	<0.2	<0.4	<1	0.9	<0.01	<0.2
H1b	270	1	0.50	<0.06	1.3	<0.2	<0.4	<1	0.6	<0.01	
H1c	190	2	1.3	<0.06	8.9	<0.2	0.7	<1	<0.5	<0.01	
H2a	420	2	1.8	<0.06	6.8	0.2	0.6	2	1.3	<0.01	<0.2
H2b	350	3	2.0	0.07	6.2	0.2	0.5	2	1.3	<0.01	
H2c	410	2	1.8	<0.06	6.4	0.2	0.5	1	1.3	<0.01	
H2d (duplicate 2c)	410	2	1.7	<0.06	5.7	0.4	0.6	2	1.4	0.2	
H3a	410	2	1.1	<0.06	11	0.2	0.5	1	1.3	<0.01	<0.2
H3b	450	2	1.1	<0.06	11	<0.2	0.4	1	1.3	<0.01	
H3c	370	2	0.88	<0.06	9.6	<0.2	0.4	1	1.0	<0.01	
H4a	150	1	0.49	<0.06	3.0	<0.2	<0.4	<1	0.7	<0.01	<0.2
H4b	470	1	0.92	<0.06	2.9	0.3	0.7	1	1.3	<0.01	
H4c	150	1	0.54	<0.06	3.1	<0.2	<0.4	<1	0.7	<0.01	
Champion Bay											
CB1a	780	2	1.6	0.08	9.1	1.8	0.9	2	6.8	<0.01	<0.2
CB1b	600	2	2.3	0.07	7.6	1.2	0.7	1	5.9	<0.01	
CB1c	740	2	1.4	<0.06	8.7	1.9	0.8	2	8.1	<0.01	

Table 3: continued...

Site	Al	As (Standard)	As (Low level)	Cd	Cr	Cu	Ni	Pb	Zn	Hg	Ag
CB2a	440	2	1.9	<0.06	11	0.6	0.7	1	2.3	<0.01	<0.2
CB2b	420	2	1.7	<0.06	10	0.3	0.6	1	1.5	<0.01	<0.2
CB2c	420	2	1.8	<0.06	11	0.4	0.8	<1	2.0	<0.01	<0.2
CB3a	400	1	0.62	<0.06	3.6	<0.2	<0.4	<1	1.1	<0.01	<0.2
CB3b	270	1	1.2	<0.06	5.5	0.2	0.5	<1	1.2	<0.01	
CB3c	330	2	0.81	<0.06	4.6	0.3	0.4	<1	1.2	<0.01	
CB4a	590	2	1.4	<0.06	10	0.4	0.7	2	2.6	<0.01	<0.2
CB4b	620	2	2.3	<0.06	11	0.3	0.8	1	1.4	<0.01	
CB4c	640	2	1.7	<0.06	12	0.4	1.3	1	1.4	0.01	
Reporting Limit	<20	<1	<0.05	<0.06	<0.2	<0.2	<0.4	<1	<0.5	<0.01	<0.2

Table 4: Results of particle size analyses for marine sediments of the mid-west coast region, May 2005.

Site ID	% <63µm	% >63µm	Site ID	% <63µm	% >63µm
Champion Bay			Horrocks		
CB1A	8.1	91.9	H1A	6.5	93.5
CB1B	6.4	93.6	H1B	4.4	95.6
CB1C	6.5	93.5	H1C	4.5	95.5
CB2A	1.5	98.5	H2A	2.8	97.2
CB2B	0.3	99.7	H2B	3.6	96.4
CB2C	0.7	99.3	H2C	15.0	85.0
CB3A	0.3	99.7	H3A	1.2	98.8
CB3B	0.4	99.6	H3B	0.0	100.0
CB3C	0.2	99.8	H3C	12.8	87.2
CB4A	1.7	98.3	H4A	6.3	93.7
CB4B	0.3	99.7	H4B	5.1	94.9
CB4C	0.4	99.6	H4C	1.8	98.2
Cliff Head			Jurien Bay		
CH1A	0.3	99.7	JB1A	1.5	98.5
CH1B	2.7	97.3	JB1B	2.0	98.0
CH1C	1.9	98.1	JB1C	2.4	97.6
CH2A	0.9	99.1	JB2A	2.8	97.2
CH2B	2.9	97.1	JB2B	0.8	99.2
CH2C	4.4	95.6	JB2C	0.6	99.4
CH3A	5.3	94.7	JB3A	1.2	98.8
CH3B	11.3	88.7	JB3B	1.8	98.2
CH3C	2.1	97.9	JB3C	5.4	94.6
CH4A	5.4	94.6	JB4A	0.6	99.4
CH4B	3.0	97.0	JB4B	1.0	99.0
CH4C	8.4	91.6	JB4C	1.3	98.7

also below the analytical reporting limit for all sites and cadmium concentrations were below the analytical reporting limit at most sites. Zinc, lead and copper concentrations were at or below the analytical reporting limit at all sites, except in Champion Bay. The analytical limit of reporting for all the metals were well below the recommended sediment quality guidelines for the protection of ecosystem health (ANZECC & ARMCANZ, 2000).

Copper and zinc concentrations appear to be elevated at site CB1 compared to the levels measured at all other sites along the mid-west coast. This site was located adjacent to the entrance to the Port of Geraldton and had sediments with a slightly higher proportion of fine particles (<63 µm) and aluminium concentration than the other sites sampled (Table 4).

The results of the particle size fractionation (Table 4) show that the percentage of <63 µm particles in the sampled sediments was variable, but generally low throughout all the sampled sites. For most sites the <63 µm particle size fraction was 0% – 5%, the remainder were in the 5% – 10% range.

The two normalisers (<63 µm particle size fraction and aluminium) were significantly correlated ($p < 0.05$). The correlation ($r = 0.372$) suggests that clay particles may not be dominating the composition of the fine sediment fractions (< 63 µm in size). The data for the four metals with consistently reportable concentrations from the three reference locations (arsenic, chromium, nickel and zinc) were graphed against the two normalisers to investigate which would give the best correlation (see Appendix D). Both the <63 µm particle size fraction and aluminium concentration generally correlated poorly with concentrations of the selected metal contaminants. Nickel was the only metal that correlated well with any of the normalisers ($r = 0.751$ with Al). Given the poor correlations and the consistently low concentrations of the two normalisers, metal concentrations were not normalised to either <63 µm particle size fraction or aluminium.

A Kruskal-Wallis test was applied to the data from all three reference locations to determine whether there were significant differences between the locations for the following metals and metalloids: aluminium, arsenic, chromium, copper, nickel and zinc. Concentrations for these metals that were below the reporting limit were assumed to be at the analytical reporting limit for this test. The results (Table 5) show that there were significant differences for arsenic, chromium nickel and zinc ($p < 0.05$). Cadmium, lead, mercury and silver were not included in the test because more than 60% of the results were below the analytical limit of reporting.

Table 5: P-values from the Kruskal-Wallis tests comparing the three reference sites (alpha is set at 0.05 and significant values shown in bold)

Al	As	Cr	Cu	Ni	Zn
0.0518	**0.0139**	**0.0236**	0.7923	**0.0264**	**0.0013**

Mann Whitney tests were then used to determine which locations had statistically similar concentrations of each metal. The test was applied by pairing those locations with similar concentrations of each metal to determine if there was a statistically significant difference ($p < 0.05$). The results of these tests have been used to group the locations according to their respective sediment metal concentrations (Table 6). There appears to be a slight, but discernible, north – south trend between the reference locations. Concentrations of these metals at the Horrocks and Jurien Bay sites were statistically different from each other, except for copper concentrations, which were similar across all three locations. Cliff Head, which was the central location (see Figure 1) always grouped with either the Jurien Bay or Horrocks sites. Aluminium and zinc concentrations appear to increase from south to north, while arsenic, chromium, nickel and the <63 µm particle size fraction tend to decrease from south to north.

Metal concentrations and the <63 µm particle size fraction from the two inshore sites were compared with the two offshore sites at each of the three reference locations using the Mann Whitney non-parametric test (Table 7). The only metals to show a significant difference between inshore and offshore sites were zinc at Cliff Head and arsenic at Jurien Bay and Cliff head, but the trend for arsenic was not consistent with higher concentrations offshore at Jurien Bay and inshore at Cliff Head.

Table 6: Locations with statistically similar concentration ranges for each metal contaminant (bold). (Groups ordered from highest to lowest concentration)

Parameter	<63 µm particles	Al	As	Cr	Cu	Ni	Zn
Locations	JB	H	**CH, JB**	JB	**CH, H, JB**	JB	H
	CH, H	**CH, JB**	H	**CH, H**		**CH, H**	**CH, JB**

Decreasing concentration ↓

Table 7: P-values from the Mann Whitney tests comparing inshore and offshore sediment metal concentrations (alpha is set at 0.05 and significant values shown in bold)

	<63 µm particles	Al	As	Cr	Cu	Ni	Zn
Jurien Bay	0.810	0.087	**0.002**	0.145	0.317	0.094	0.152
Cliff Head	0.423	1.00	**0.022**	0.873	0.140	0.799	**0.022**
Horrocks	0.749	0.936	0.859	0.149	0.140	0.303	0.244

Estimates of the natural background concentrations of the metals analysed in this study have been calculated for mid-west coast sediments, and for each reference site separately, using the 80th percentile of the data (Table 8). The data used to calculate natural background concentrations for all metals included those sites where concentrations were less than the analytical limit of reporting.

Table 8 shows that the estimated natural background concentrations for all metals easily met the national sediment quality guidelines (ISQG-low) recommended in ARMCANZ & ANZECC (2000).

Table 8: Estimated natural background concentrations of selected metals in sediments of the mid-west coast. (n = 12 for individual location estimates and n = 36 for mid-west coast estimates)

Metal	Jurien Bay	Cliff Head	Horrocks	Mid-West Coastal Sediments	National Guideline* (ISQG-low)
Aluminium	262	326	418	370	-
Arsenic	3.08	2.86	1.7	2.9	***20***
Cadmium	0.12	0.06	<0.06	0.09	***1.5***
Chromium	10.8	8.28	9.46	10	***80***
Copper	<0.2	0.46	0.3	0.2	***65***
Lead	<1	<1	1.8	1	***50***
Mercury	<0.01	<0.01	<0.01	<0.01	***0.15***
Nickel	0.7	0.6	0.6	0.7	***21***
Silver	<0.2	<0.2	<0.2	<0.2	***1***
Zinc	0.76	0.8	1.3	1	***200***

*** Recommended sediment quality guideline (ISQG-low) from ANZECC & ARMCANZ (2000)**

To determine whether metal concentrations in the Champion Bay sediments were statistically different from reference sites a series of Mann Whitney tests were performed (except for cadmium, mercury and silver because of the large number of results less than the analytical limit of reporting). The Champion Bay sites were compared with the combined data from Cliff Head and Horrocks to take into account the slight north – south pattern in the reference site data (Champion Bay lies between these two locations). Aluminium, copper, nickel and zinc were all found to be significantly different (Table 9). However, when compared with estimated natural background concentrations (based on the 80th percentile of reference sites) the Champion Bay data for these four metals appear to be only slightly elevated (Table 9). Concentrations of all metals in the Champion Bay samples were well below the recommended sediment quality guidelines (ANZECC & ARMCANZ, 2000). Perhaps of greater relevance is the distinctly elevated concentrations of copper and zinc at site CB1 adjacent to the Geraldton Port entrance.

Table 9: Champion Bay sediment quality compared with the adjacent reference sites, estimated natural background concentrations and national sediment quality guidelines. (significant differences are shown in bold)

	CB vs CH+H Mann Whitney test P-values (_ = 0.05)	**Champion Bay median metal concentration (mg/kg)**	**Estimated Natural Background (mg/kg)**	**National Guideline (ISQG-low) (mg/kg)**
<63 µm particle size fraction	**0.027**			
Aluminium	**<0.001**	**515**	370	-
Arsenic	0.445	2	3	20
Cadmium		<0.06	0.09	1.5
Chromium	0. 062	9.6	10.0	80
Copper	**<0.001**	**0.4**	0.2	65
Lead	0.761	1	1	50
Mercury		<0.01	<0.01	0.15
Nickel	**0.008**	**0.7**	0.7	21
Silver		<0.2	<0.2	1
Zinc	**<0.001**	**1.8**	1	200

3.2 Organic chemicals

The results of the organic analyses are presented in Table 10 and the associated quality control data are in Appendix C. Concentrations of all the organic chemicals were found to be below the analytical Limit of Reporting (LOR) in all samples. National guidelines were only available for 20 of the organic chemicals analysed and for 8 of these (acenaphthene, anthracene, dibenzo(ah)anthracene, fluorene, lindane, chlordane, dieldrin and endrin) the ISQG-low sediment quality guideline was below the limit of reporting. For example, the LOR for anthracene was 0.1 mg/kg and for Dieldrin 0.001 mg/kg, both of which are above their respective ISQG-low guideline trigger values of 0.085 mg/kg and 0.00002 mg/kg.

Total organic carbon (TOC) results are presented in Table 11. Total organic carbon concentrations were relatively consistent between most of the locations and ranged from 360 mg/kg to 2800 mg/kg. TOC was analysed so that the concentrations of organic contaminants in different sediments could be normalised to 1% organic carbon and then compared across sites and to the national sediment quality guidelines. This is the approach recommended in the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC & ARMCANZ, 2000). Since there were no measurable organic contaminants in the analysed samples normalisation is unnecessary.

Table 10: Organic chemical concentrations in marine sediments of the mid-west coast of Western Australia, May 2005, and National sediment quality guidelines (ANZECC & ARMCANZ, 2000).

NG = No guideline value;

Organic Chemical	Units	Results for all samples	LOR	Guideline value	
				ISQG low	ISQG high
Organotins					
Monobutyltin as Sn	µg/kg	<0.5	0.5	NG	NG
Dibutyltin as Sn	µg/kg	<0.5	0.5	NG	NG
Tributyltin as Sn	µg/kg	<0.5	0.5	5	70
Poly Aromatic Hydrocarbons					
Acenaphthene	mg/kg	<0.1	0.1	0.016	0.5
Acenaphthylene	mg/kg	<0.1	0.1	NG	NG
Anthracene	mg/kg	<0.1	0.1	0.085	1.1
Benz(a)anthracene	mg/kg	<0.1	0.1	0.261	1.6
Benzo(b)&(k)fluoranthene	mg/kg	<0.2	0.2	NG	NG
Benzo(ghi)perylene	mg/kg	<0.1	0.1	NG	NG
Benzo(a)pyrene	mg/kg	<0.1	0.1	0.430	1.6
Chrysene	mg/kg	<0.1	0.1	0.384	2.8
Dibenzo(ah)anthracene	mg/kg	<0.1	0.1	0.063	0.26
Fluoranthene	mg/kg	<0.1	0.1	0.600	5.1
Fluorene	mg/kg	<0.1	0.1	0.019	0.54
Indeno(1,2,3-cd)pyrene	mg/kg	<0.1	0.1	NG	NG
Naphthalene	mg/kg	<0.1	0.1	0.16	2.1
Phenanthrene	mg/kg	<0.1	0.1	0.240	1.5
Pyrene	mg/kg	<0.1	0.1	0.665	2.6
BTEX					
Benzene	mg/kg	<0.5	0.5	NG	NG
Toluene	mg/kg	<0.5	0.5	NG	NG
Ethylbenzene	mg/kg	<0.5	0.5	NG	NG
m, p - Xylene	mg/kg	<1.0	1	NG	NG
o - Xylene	mg/kg	<0.5	0.5	NG	NG
Total Petroleum Hydrocarbons					
TPH C6 - C9	mg/kg	<25	25	NG	NG
TPH C10 - C14	mg/kg	<50	50	NG	NG
TPH C15 - C28	mg/kg	<100	100	NG	NG
TPH C29 - C36	mg/kg	<100	100	NG	NG
Organophosphate (OP) pesticides					
Azinphos-ethyl	mg/kg	<0.10	0.10	NG	NG
Azinphos-methyl	mg/kg	<0.10	0.10	NG	NG
Chlorpyrifos	mg/kg	<0.10	0.10	NG	NG
Chlorpyrifos-methyl	mg/kg	<0.10	0.10	NG	NG
Chlorfenvinphos (E)	mg/kg	<0.10	0.10	NG	NG
Chlorfenvinphos (Z)	mg/kg	<0.10	0.10	NG	NG
Diazinon	mg/kg	<0.10	0.10	NG	NG
Demeton-S-Methyl	mg/kg	<0.10	0.10	NG	NG
Dichlorvos	mg/kg	<0.10	0.10	NG	NG
Dimethoate	mg/kg	<0.10	0.10	NG	NG
Ethion	mg/kg	<0.10	0.10	NG	NG
Fenitrothion	mg/kg	<0.10	0.10	NG	NG
Fenthion	mg/kg	<0.10	0.10	NG	NG

Table 10: continued …..

Malathion	mg/kg	<0.10	0.10	NG	NG
Parathion-ethyl	mg/kg	<0.10	0.10	NG	NG
Parathion-methyl	mg/kg	<0.10	0.10	NG	NG
Pirimiphos-ethyl	mg/kg	<0.10	0.10	NG	NG
Pirimiphos-methyl	mg/kg	<0.10	0.10	NG	NG
Organochlorine (OC) pesticides					
Aldrin	mg/kg	<0.001	0.001	NG	NG
BHC-alpha	mg/kg	<0.001	0.001	NG	NG
BHC-beta	mg/kg	<0.001	0.001	NG	NG
BHC-delta	mg/kg	<0.001	0.001	NG	NG
BHC-gamma (Lindane)	mg/kg	<0.001	0.001	0.00032	0.001
Chlordane-trans	mg/kg	<0.001	0.001	NG	NG
Chlordane-cis	mg/kg	<0.001	0.001	NG	NG
Oxychlordane	mg/kg	<0.001	0.001	NG	NG
Chlordane	mg/kg			0.0005	0.006
DDD	mg/kg	<0.001	0.001	0.002	0.02
DDE	mg/kg	<0.001	0.001	0.0022	0.027
DDT	mg/kg	<0.001	0.001	0.0016	0.046
Dieldrin	mg/kg	<0.001	0.001	0.00002	0.008
Endosulfan alpha	mg/kg	<0.001	0.001	NG	NG
Endosulfan beta	mg/kg	<0.001	0.001	NG	NG
Endosulfan sulphate	mg/kg	<0.001	0.001	NG	NG
Endrin	mg/kg	<0.001	0.001	0.00002	0.008
Endrin Aldehyde	mg/kg	<0.001	0.001	NG	NG
Endrin Ketone	mg/kg	<0.001	0.001	NG	NG
HCB	mg/kg	<0.001	0.001	NG	NG
Heptachlor	mg/kg	<0.001	0.001	NG	NG
Heptachlor epoxide	mg/kg	<0.001	0.001	NG	NG
Methoxychlor	mg/kg	<0.001	0.001	NG	NG
PCB Aroclors					
Arochlor 1016	mg/kg	<0.01	0.01	NG	NG
Arochlor 1221	mg/kg	<0.01	0.01	NG	NG
Arochlor 1232	mg/kg	<0.01	0.01	NG	NG
Arochlor 1242	mg/kg	<0.01	0.01	NG	NG
Arochlor 1248	mg/kg	<0.01	0.01	NG	NG
Arochlor 1254	mg/kg	<0.01	0.01	NG	NG
Arochlor 1260	mg/kg	<0.01	0.01	NG	NG
Total PCBs	mg/kg	<0.01	0.01	0.023	-

Table 11: Results of total organic carbon analyses for marine sediments of the mid-west region, May 2005.

Location and site	Total organic carbon	
	mg/kg	%
Jurien Bay		
JB1	730	0.07
JB2A	1500	0.15
JB2B	1100	0.11
JB3	1000	0.1
JB4	880	0.09
Cliff Head		
CH1	1800	0.18
CH2	370	0.04
CH3	2800	0.28
CH4	2400	0.24
Champion Bay		
CB1	650	0.07
CB2A	1500	0.15
CB2B	1100	0.11
CB2C	800	0.08
CB3	770	0.08
CB4	1100	0.11
Horrocks		
H1	730	0.07
H2	1100	0.11
H3	640	0.06
H4	360	0.04
Limit of Reporting (LOR)	**100**	0.01

4. General discussion

This work has shown that natural background concentrations of metals, metalloids and selected organic chemicals in sediments from the mid-west coast of WA are relatively low and the data indicate that the national sediment quality guidelines (ANZECC & ARMCANZ, 2000) are appropriate for use in the study area.

4.1 Metal concentrations

Sediment metal concentrations, and biological availability, are strongly influenced by sedimentary components with a high binding capacity. In most cases for metals this is represented by the clay fraction. Aluminium concentration or <63 µm particle size fraction are accepted proxies for clay mineral content in sediments and are used to normalize contaminant concentrations in sediment with different grain size distributions (Kersten and Smedes, 2002).

Metal concentrations and the concentrations of the two potential normalisers (<63 µm particle size fraction and aluminium) were found to be very low across all three reference locations and the data did not correlate well. It was therefore considered inappropriate to normalise the metal concentrations measured in this study to account for the influence of the sediment clay mineral content and so the raw analytical data have been used in this report.

Measurable metal concentrations only varied slightly between the three reference locations, but did appear to exhibit a slight north – south trend for some metals. Aluminium and zinc concentrations were slightly higher at the northern site while the <63 µm particle size fraction, arsenic, chromium, lead and nickel concentrations were slightly lower, although in absolute terms the differences were only minor. There appeared to be no significant difference between the inshore and offshore sites at each reference location.

Estimated natural background concentrations (Table 8) fell well within the interim sediment quality guidelines (ISQG-low) recommended for national use (ANZECC & ARMCANZ, 2000). The interim sediment quality guidelines are therefore considered suitable for use with the sediments of the mid-west coast of Western Australia.

Marine sediments naturally contain trace metals, but the concentrations are variable between regions and in nearshore sediments the concentration of these metals are often related to catchment geology and mineralogy (Cox and Preda, 2003; Moss and Costanzo, 1998). Estimated natural background concentrations calculated in this study (Table 8) were low, probably reflecting local geology. The mid-west coast of Western Australia is a highly energetic coastline with only a few small rivers draining a relatively arid catchment. The sediments are medium to coarse grained sands interspersed between limestone reefs and the adjacent terrestrial geology is composed of reworked sands of marine and aeolian origin. Natural terrestrial sources of metals in this region are likely to be relatively insignificant compared to other parts of Australia.

A comparison of sediment metal concentrations from this study with relatively uncontaminated sediments from other selected regions around Australia indicates that a number of metals (aluminium copper, lead, nickel and zinc) have significantly lower concentrations in mid-west coast sediments than found elsewhere in Australia (Table 12). Concentrations of the remaining five metals are also low, but fall within the range of concentrations reported for the other regions. Metal concentrations in the marine sediments of the Northern Territory/Gulf of Carpentaria coastline, the Queensland coast and from Lake Macquarie are notably higher than the levels recorded in this study.

The results of the Mann Whitney tests comparing Champion Bay sediments with reference sites and comparisons against the interim sediment quality guidelines (ANZECC & ARMCANZ, 2000) indicate that the Champion Bay sediments, although slightly elevated over regional background levels, are still relatively uncontaminated (Table 9). Aluminium, copper, nickel and zinc, were found to be slightly elevated in Champion Bay samples compared to the reference sediments, but copper and zinc were significantly more elevated in the samples from the site CB1 adjacent to the Geraldton Port entrance. Nevertheless, all samples were well below the interim sediment quality guidelines recommended by ANZECC & ARMCANZ (2000). Concentrations of all the other metals were statistically indistinguishable from the reference site sediment quality data. The main sources of trace metals in Geraldton Port are likely to include ships, shipping facilities, boat slipways, storm water discharges and dust and spillage from the loading of metal ore for export. There has also been an extensive dredging program and a beach re-nourishment program (using terrestrially sourced sand) two years prior to sampling as part of a Port Redevelopment Plan. These two activities could also have influenced sediment composition and quality adjacent to the Port and perhaps further afield in Champion Bay given the extensive plumes observed during dredging. Evidence of this effect was observed at site CB1 where a 5 – 10 cm layer of white cohesive fine grained sediment was found overlaying slightly darker, coarser sediments and decomposing posidonia seagrass rhizome mat (Figure 3). This observation is also supported by the particle size composition data in Table 4.

Table 12: Median total sediment metal concentrations from the mid-west coast of Western Australia and median or mean concentrations for other Australian localities (mg/kg)

Metal	Mid-West coast*	Pilbara*	Perth* (SMCWS)	Perth* (KIC)	Exmouth Gulf **	Gulf of Carpentaria**	NT to Gulf of Carpentaria**	Lake Macquarie#	Central NSW coast (inner shelf)*	Queensland coast *
Aluminium	245	3150	310-3900	280	9199	28560	-	-	-	-
Arsenic	1.4	18	2 - 16	2.5	-	-	<0.04 –7.21	4.6 - 23	-	-
Cadmium	<0.06	<0.06	<0.2 - 0.2	<0.1	~0.045	-	0.03 – 0.09	<0.1 – 0.2	<0.3	1.5
Chromium	7.8	17	3.7 - 15	15	-	12	-	7 - 45	-	88
Copper	<0.2	2.2	0.8 – 1.7	3.0	4.45	5	9.2 – 27.4	6 - 17	<5	19
Lead	<1	2	3.5 – 6.0	1.1	3.73	6	12.0 – 19.3	5.5 - 17	<10	5
Mercury	<0.01	<0.01	<0.05	<0.1	-	-	-	<0.01- 0.03	-	-
Nickel	0.6	5.5	1.9 – 4.6	1.8	-	6	18.3 – 24.4	11 - 57	<5	20
Silver	<0.2	<0.2	-	0.6	-	-	-	<0.01–0.07	-	-
Zinc	0.6	5.4	1.3 – 3.5	1.7	-	20	39.8 – 54.1	12 - 68	<25	84
Reference	This study	McAlpine et al, 2005	Burt et al, 1995	KIC, 2000	Brunskill et al, 2001	Cox et al, 2003	Munksgaard et al, 2002.	Roach, 2005	Matthai and Birch, 2000	Moss and Costanzo 1998

* Median concentrations
** Mean concentrations
\# Concentration ranges (minimum to maximum)

Figure 3: Sediment cores taken from site CB1 showing the white fine grained sediment overlaying the original coarser grained grey sediments and decomposing seagrass rhizome.

The environmental quality management framework being applied to the marine environment by the EPA and DoE (refer Section 1) includes the environmental value Ecosystem Health. To protect this environmental value the framework requires levels of ecological protection to be allocated spatially across the management area so that the relevant environmental quality criteria (EQC) can be determined. The different levels of ecological protection are recognition that other societal benefits also need to be considered and that these may preclude an objective of ‘no change’ in environmental quality in some localized areas. The EQC for each level of ecological protection represent the minimum acceptable level of environmental quality to be achieved through management. Four different levels of ecological protection, each with its own set of environmental quality criteria, have been defined (EPA, 2000; DoE, 2006):

- Maximum (essentially pristine, no effects on marine life);
- High (very low levels of contaminants, no effects on marine life);
- Moderate (elevated levels of contaminants, some effects on marine life);
- Low (high levels of contaminants, significant effects on marine life).

The national interim sediment quality guidelines (ISQG) initially relate to total contaminant concentrations; if the ISQG-low is exceeded then a risk-based hierarchical decision framework is triggered for assessing the quality of the sediment. The initial step in this decision framework is to measure the concentration of the contaminant that is potentially bioavailable and compare this against the ISQG-low (eg. dilute acid extractable metals or normalization to TOC for non-metallic contaminants). If the ISQG-low is still exceeded then more intensive and more thorough investigations could be undertaken to determine whether there is a high level of ecological risk from the contaminant and hence remedial action triggered. Firstly, a more accurate estimate of bioavailability could be undertaken by considering those factors that control bioavailability of the chemical. If the ISQG-low is still exceeded then ecotoxicological testing is recommended. Alternatively *in-situ* biological or ecological indicators that can be demonstrably linked to the contaminant could be monitored and assessed. This risk-based hierarchical decision framework is recommended in ANZECC & ARMCANZ (2000) for assessing sediment quality and has been applied to Cockburn Sound through the State Environmental (Cockburn Sound) Policy 2005 (GWA, 2005).

ANZECC & ARMCANZ (2000) recommend the use of the ISQG for ecosystems where the goal is for a slightly to moderately disturbed system (equivalent to high and moderate levels of ecological protection above). For highly disturbed systems (low level of ecological protection) the ISQG could be applied, or there could be some relaxation where appropriate. High conservation/ecological value areas are equivalent to the maximum level of ecological protection described above and the recommendation for these areas is no change from background variability characterized by the reference condition. A maximum level of ecological protection may be appropriate for areas such as designated marine conservation reserves.

For the coastal waters of Western Australia's mid-west the ISQG from ANZECC & ARMCANZ (2000) are recommended for use in areas designated a high, moderate and low level of ecological protection. In low ecological protection areas only the ISQG for those chemicals that have the potential to bioaccumulate/biomagnify would apply. Sediment quality guidelines for the maximum level of ecological protection should be based on natural background concentrations of the contaminants of concern and either the estimated metal concentrations in Table 8 can be used as default guidelines or site specific guidelines can be derived for new localities or additional contaminants based on the 80th percentile of reference site data. For artificial chemicals of anthropogenic origin any detection would be the trigger for management action.

If there are no national ISQG for a particular chemical then the approach recommended in ANZECC & ARMCANZ (2000) for deriving sediment quality guidelines based on natural background concentrations is adopted here for areas of high, moderate and low ecological protection. For high and moderate protection areas a guideline based on twice natural background median concentration is recommended. Three times natural background median concentration is recommended for low ecological protection areas, but in these areas guidelines should only be applied for those chemicals with the potential to bioaccumulate or biomagnify. Aluminium was the only metal measured in this study that does not have a corresponding ISQG in ANZECC & ARMCANZ (2000). The median natural background concentration calculated from the reference sites for aluminium is 245 mg/kg.

It is recommended that natural background concentrations are calculated from data from reference sediments with similar particle size distributions for metals, and similar total organic carbon concentrations for organic chemicals, as the potential impact sites to be assessed. If reference sites with similar sediment characteristics cannot be found for estimating natural background concentrations then consideration could be given to using normalised data.

Table 13: Summary of recommended sediment quality guidelines for marine sediments of the mid-west coast, Western Australia.

Level of ecological protection	ISQG available	No ISQG available
Maximum	(All metals) Use estimated natural background (Table 8); or Derive site specific SQG from 80th percentile of reference site*. (Organic chemicals) No detectable concentration using lowest LoR available. or use 80th percentile of reference site.	(All metals) Use estimated natural background (Table 8); or Derive site specific SQG from 80th percentile of reference site*. (Organic chemicals) No detectable concentration using lowest LoR available or use 80th percentile of reference site.
High	(eg. As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, Zn) Use ISQG from ANZECC & ARMCANZ (2000) (Organic chemicals) Use ISQG from ANZECC & ARMCANZ (2000) unless below LoR then guideline should be no detectable concentration.	(eg. Al) Use median of natural background concentration multiplied by a factor of 2*. (Organic chemicals) No detectable concentration using lowest LoR available or median of natural background concentration multiplied by a factor of 2.
Moderate	(eg. As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, Zn) Use ISQG from ANZECC & ARMCANZ (2000) (Organic chemicals) Use ISQG from ANZECC & ARMCANZ (2000) unless below LoR then guideline should be no detectable concentration.	(eg. Al) Use median of natural background concentration multiplied by factor of 2*. (Organic chemicals) No detectable conce ntration using lowest LoR available or median of natural background concentration multiplied by a factor of 2.
Low	(Bioaccumulators or biomagnifiers eg. Cd, Hg) Use ISQG from ANZECC & ARMCANZ (2000) unless below LoR then guideline should be no detectable concentration.	(Bioaccumulators or biomagnifiers eg. Se) Use natural background concentration multiplied by a factor of 3* unless below LoR then guideline should be no detectable concentration.

* Assessment could be done on total contaminant concentration or on potentially bioavailable concentration.

In all cases it is the median concentration of the non-normalised metal concentration at the potential impact site that should be tested against the recommended guideline for each level of ecological protection.

The sediment quality guidelines recommended for the four different levels of ecological protection in the marine waters of the mid-west coast are summarized in Table 13.

4.2 Organic chemical concentrations

The organic chemicals analysed (organotins, PAHs, BTEX, petroleum hydrocarbons, PCBs and pesticides) are man-made and therefore the natural background concentrations at the reference sites were not expected to be measurable, ranging from zero to negligible. This is because 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 ISQG were not available for all of the organic chemicals tested, but where guidelines were available the analytical limit of reporting was always well below the guideline for all except four polycyclic aromatic hydrocarbons (acenaphthene, anthracene, dibenzo(ah)anthracene and fluorene) and four organochlorine pesticides (lindane, chlordane, dieldrin and endrin). In this study, there were no detections of any of the organic chemicals analysed, indicating that the guidelines for twelve of the chemicals were met and could be successfully applied to marine sediments of the mid-west coast. However, for the remaining eight organic chemicals with available guidelines it will be difficult to assess sediment quality until laboratories can achieve suitably lower limits of reporting.

The lack of detections in the Champion Bay sites was surprising, particularly for the organotins at site CB1 adjacent to the port entrance. This may be a result of the re-distribution and settlement of 'new' sediment across much of the area from the dredging that took place 2 years earlier. Cores taken from this site still showed a layer of fine, white cohesive sediment covering older coarser, darker sediment and old dead seagrass rhizomes (Figure 3). Nevertheless, the results of the organic chemical analyses will provide a useful reference against which future studies can be compared.

Total organic carbon (TOC) concentrations in the sediments were relatively low. TOC was measured so that the organic contaminants could be normalized to 1% organic carbon, but because no organic contaminants were detected these data were not required.

Sediment quality guidelines have been recommended in Table 13 for the four different levels of ecological protection and discussed in section 4.1. The median concentration from the potential impact site is tested against the guideline where ISQG from ANZECC & ARMCANZ (2000) are available and above the analytical LoR or where natural background concentration is measurable, otherwise any detection of the chemical above the LoR should be treated as an exceedance of the guideline.

5. Conclusion

This survey provides important information on baseline concentrations of selected trace metals and organic chemicals in the marine sediments of the mid-west coast of Western Australia. The sediment survey results show that the concentrations of metals are within or below the range of concentrations measured in sediments around Australia. Concentrations of cadmium, copper, lead, mercury, silver and the selected organic chemicals were too low to adequately quantify in most samples. Unfortunately the routine analytical procedures used by most commercial laboratories are inadequate for discriminating natural background concentrations of many toxic contaminants, and for some organic chemicals the analytical limit of reporting may even significantly exceed the recommended sediment quality guideline. Therefore detection of these chemicals at the concentrations required by the national guidelines requires the services of research and/or specialist laboratories to be sought at significantly greater cost.

The metal concentrations that could be measured across the 3 sampled reference locations showed some variability and appeared to exhibit a slight north-south trend, except for copper. Aluminium and zinc concentrations increased south to north and arsenic, chromium and nickel concentrations decreased.

Metal concentrations did not correlate well with sediment aluminium concentration or the <63 µm particle size fraction and so were not normalised to either parameter. The poor correlations are likely to be a result of the low proportion of clay/silt fractions in the sediments and hence the low aluminium concentrations. Other sediment components with high sorptive capacities for metals could therefore be strongly influencing metal distribution in these sediments along with the clay fraction.

Estimates of natural background sediment concentration for 10 metals have been provided for the mid-west coast region of Western Australia (Table 8). The estimated natural background concentrations for all the metals were well within the ISQG–low recommended for use nationally (ANZECC & ARMCANZ (2000). Copper and zinc sediment concentrations from a site adjacent to the entrance to Geraldton Port were markedly elevated above background, but still easily met the recommended interim sediment quality guidelines. Aluminium and zinc concentrations were also elevated in Champion Bay compared to the reference locations, but the differences in absolute terms were very small. Three of the four sediment sampling sites in Champion Bay were located well away from shipping facilities and may have been affected by recent dredging activity.

Based on the findings of this study, and considering other relevant data from the Western Australian coast, it is concluded that the interim sediment quality guidelines are appropriate for assessing sediment quality in high, moderate and low ecological protection areas in the region. For areas designated a maximum level of ecological protection the estimated natural background concentrations (Table 8) should be used as default SQG or alternatively site specific SQG developed from local reference site data.

The results of this survey will assist managers and regulators to assess and manage the effects of existing developments and other anthropogenic activities on the quality of the marine environment, and will guide the design and environmental impact assessment of future proposals for ocean outfalls and other point or diffuse source discharges in the region. A fundamental baseline from which to assess local and regional changes in sediment quality in years to come has been established.

6. References.

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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 containers

Sample containers used to store sediments for metal analyses were provided by the Marine and Fresh Water Research Laboratory (MAFRL). The 70 mL containers were urine jars transferred direct from the manufacturer (Sarstedt) and were made of polypropylene with a polyethylene cap and produced under class 3500 clean room conditions.

A.1.2 <63 particle size fraction sample bags

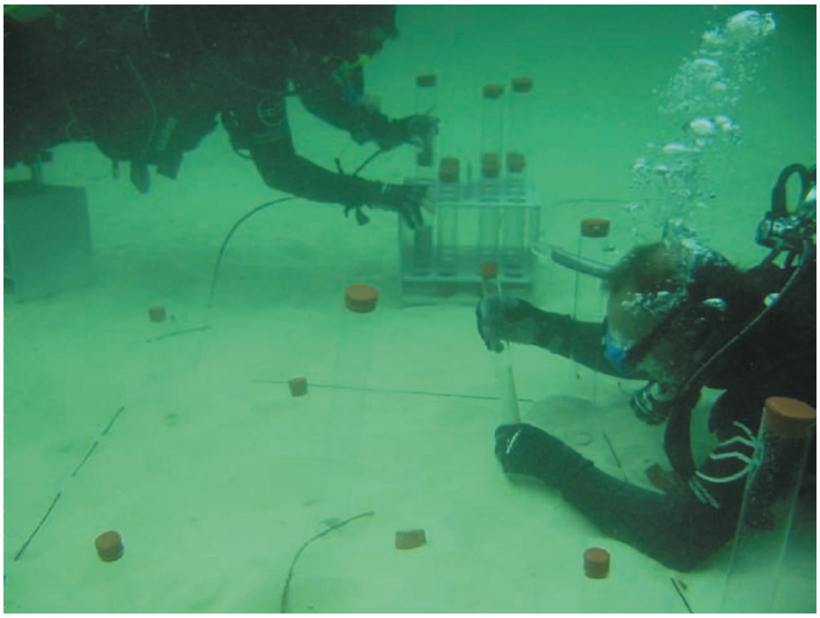
Samples for particle size fractionation were stored in plastic whirlpacs.

A.1.3 Organics and low level silver sample containers

Sediment samples for analysis of organic chemicals were stored in glass jars provided by the Australian Government Chemical Laboratories (AGAL). The bottle caps were Teflon lined. All sample bottles were transferred direct from the manufacturer (Silverlock) and free from contaminants. This was further confirmed by the analytical results.

A.2 SAMPLE COLLECTION AND HANDLING

Samples of the surface 2 cm of sediment were collected using clear polycarbonate cores pushed into the seabed and retrieved to the boat deck for sub-sampling. Prior to the field sampling program the polycarbonate cores had been acid washed, rinsed with deionised water and wrapped in plastic bags for transport to the sampling site. The DoE research vessel Zoila was used for the fieldwork.



Divers collecting sediment cores from 1 m2 quadrat.

Sediment cores were carefully pushed from the polycarbonate corer tubes using a core extruder so that the overlaying water was decanted without disturbing the surface sediment. The top 2 cm of the sediment core was then extruded above the rim of the core and sliced off into the sample collection container with a plastic knife. Where samples had to be homogenized for sub-sampling into separate sample containers (eg. metals and sediment particle size fractionation) the sediments were collected in a plastic zip-lock bag and thoroughly mixed before being sub-sampled into the respective sample storage containers.

A total of five cores made up each of the three replicate samples taken at each site for the metal analyses and the three replicates samples taken for organic analysis at site CB2. All other samples for organic chemical analyses were composed of all 15 cores taken at each site. Approximately 50 mL of sediment was sub-sampled for metal analyses and 180mL sub-sampled for the organic and low-level silver analyses. A minimum of 20 mL of sediment was collected for the particle size fractionation.

On the vessel, care was taken to ensure that contamination was minimised at all times and the workspace was covered with clean plastic sheeting. The polycarbonate core tubes were washed in clean seawater between each sampling site.

All samples were stored in the dark on ice and delivered to the respective analytical laboratories at the end of the field program (ie. within 6 days from the collection of the first samples at Jurien Bay).

A.3 ANALYTICAL METHODS

A.3.1 Metals

Sample Preparation Steps

(a) Sample Preparation follows Australian Standard 4479.1.

(b) Drying – the entire sample received shall be dried using the freeze dryer. Refer to Appendix 8 for operating instructions

(c) After drying extraneous material such as gravel, glass, roots, paper and any coarse materials must be removed.

(d) Pass the test sample through a 2 mm sieve. Lightly crush clods of soil retained by the sieve so they pass through the 2 mm sieve.

(e) Where the sample is greater than 50 g, the sample is sub-sampled by “quartering”. On greaseproof paper mix then divide the soil into four quadrants then combine the 2 diagonal quadrants. Repeat this until approximately 50 g of sample is achieved.

(f) Mill approximately 10 g of the sample until particle size is approximately 150 mm. Refer to Appendix 9 for mixer mill operating instructions.

Sample Extraction Steps

(a) Sample extraction follows Australian Standard 4479.2

(b) All glassware must be acid washed and triple rinsed with deionised water.

(c) Accurately weigh between 1.0 g and 1.1 g of the prepared sample into a digest tube. Refer to the proforma (Section 15) for the positions of the blanks, references materials, and duplicates.

(d) Wet the sample with a drop of deionised water.

(e) Carefully add 2.5 mL of HNO3 (7.2) and 7.5 mL of HCl (7.3) and cover with a glass funnel.

(f) Place tubes in aluminium digest block and steadily raise temperature to 50oC to remove any organic material. After half an hour, steadily raise the temperature to 125°C.

(g) Heat at 125°C for 2 hours.

(h) Remove the tubes from the digest block, allow to cool, make them up to the 20 mL mark with 1% nitric acid (7.4), and mix well with the vortex mixer.

(i) Allow particulate matter to settle or centrifuge.

(j) Dilute digest solutions 5 times into 10 mL auto sampler tubes using the Hamilton diluter prior to measurement.

Sample Analysis

The digested samples were analysed by AES-ICP for aluminium, standard arsenic, cadmium, cobalt, chromium, copper, iron, nickel, lead, standard selenium, silver, vanadium and zinc.

For mercury and the low-level arsenic and selenium analyses the sample passes through the hydride vapour generator before the ICP according to the following method. The vapour generation accessory (VGA) mixes the sample with acid, sodium borohydride and potassium iodide. The iodide reduces AsV to AsIII and SbV to SbIII. The borohydride reduces the AsIII, SeIV and SbIII to their volatile hydrides. The hydrides are separated from the solution by the gas/liquid separator then transferred to the plasma of the ICP-AES via the argon carrier gas. Here the extreme thermal energy of the plasma gas excites the atoms present. When these atoms return from their excited state light is emitted. The intensity of the light is characteristic of the number of these atoms present, which can be quantified by comparison with standards.

Quality control

To check analytical accuracy, laboratory duplicates and standard solutions were analysed (and recoveries calculated) for every batch of approximately 10 samples.

A.3.2 <63 µm particle size fraction

The analytical method described below was supplied by the CSIRO Minerals Division Particle Sizing Laboratory.

Moisture content:

A representative sub-sample was taken to determine the moisture content to enable a dry starting weight to be calculated.

(a) Sample and bag weighed.

(b) Contents of the bag emptied in a known weighed beaker and (sample +beaker weight recorded).

(c) Empty bag weight recorded.

(d) Beaker containing wet sample placed in a 100ºC oven for a minimum of 10 hours. Beaker removed and placed in a desiccator until it cools then the weight recorded.

(e) Moisture content and initial sample weight were determined.

Wet Sieving at 63µm

(a) Samples were wet sieved using a 63µm screen.

(b) +63µm fraction collected and dried at 100ºC and the weight recorded.

(c) -63µm percentages were calculated using the initial sample weight and the +63µm weight.

A.3.3 Organics and low-level Silver

The analytical methods below are from summaries provided by the National Measurement Institute (NMI).

Method NT 2.49
Metal analysis in sediments

Samples are digested with HNO3/HCl at 100˚C for 2 hours. After appropriate dilution the metal concentrations are determined using both ICPMS and/or ICP AES depending on concentration. All high concentrations that may be due to matrix interferences are cross-checked using both ICPMS and ICP AES.

For QA/QC purposes one blank, one matrix spike, one duplicate sample and one laboratory control sample (reference sediment) is analysed per batch or for every 20 samples if the batch is >20 samples.

Method 11.11
PAH in water (Low level)

An aliquot of sediment is taken and mixed with anhydrous sodium sulphate. The dried sample is then extracted using dichloromethane/acetone solvent (1:1) (concentration factor is greater for low level determination). A portion of the extract is then concentrated and cleaned up with silica gel. The final cleaned extract is then concentrated and analysed by GC-MS in SIM mode.

Method NR 35
Organo-tin in sediment

The sediment is extracted with acidified ethanol then derivitised by sodium tetraethylborate. The ethylated derivatives are then extracted into hexane then analysed by GC-AED where two characteristic tin emission lines are used for quantitation and identification. Quantitation is against target standards. Tripropyltin is used as a surrogate to monitor extraction/method efficiencies.

The method is in-house but has procedures based on

Attar, K.M., "Analytical Methods for the Speciation of Organotins in the Environment", Applied Organometallic Chemistry, 10, 317-337 (1996).

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Method NGCMS 1121
BTEX and C6-C9 Total Petroleum Hydrocarbons (TPH) in sediment

Sediment samples are first dispersed in methanol and an aliquot of this solution is mixed with organic free water to be analysed by the purge and trap method. In the purge and trap method a sample (normally 98% water, 2% methanol extract) is purged with nitrogen and the volatile sample components are trapped in a tube containing suitable adsorbents. After purging is complete, the sorbent tube is rapidly heated and backflushed with helium to desorb the trapped components. The analytes are transferred to the front of a narrow bore capillary column operating in the split mode. The column is then temperature and pressure programmed to separate the analytes. The volatile compounds detected by the GCMS operating in EI mode using full scan.

Method NGCMS 1112
C10-C36 Total Petroleum Hydrocarbons (TPH) in sediment

Sediments are extracted with a 50% dichloromethane/acetone solvent. 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. Concentrations are determined by comparison with alkane standards using electronic integration.

Method NR_19
Organophosphate (OP) pesticides in sediment

Sediment is mixed with anhydrous sodium sulphate and tumbled with hexane/acetone using a rotating shaker. If required, the extract is cleaned up by Gel Permeation Chromatography (GPC) and/or sulphur removal. The final extract is analysed by GC-NPD and confirmed by GCMS-NCl (for selected OP analytes). A number of specialist clean-up procedures are employed to remove non-analyte interferences where required.

Method NR_19
Organochlorine (OC) pesticides and PCB residues in sediment

Sediment matrices are mixed with anhydrous sodium sulphate and tumbled with hexane/acetone using a rotating shaker. Extracts are then cleaned up with florisil. If required, the extract is cleaned up by Gel Permeation Chromatography (GPC) and/or sulphur removal. The final extract is analysed by GC-ECD and confirmed by GCMS-NCl.

Method NWS_15
Total organic carbon in sediment

The sample is stirred and crushed to ensure all large lumps are broken up, is weighed into a small platinum boat and hydrochloric acid is added to remove inorganic carbon (carbonates and bicarbonates). The residue is heated in an oven at 100 C to dryness and the boat with the dried residue placed in the boat accessory of a Dohrmann 190 TOC analyser. The boat is heated in a furnace at 680 C to convert all organic carbon to carbon dioxide and the gas so produced is swept into the main body of the TOC analyser where its concentration is determined by an infrared detector. The instrument is fitted with software enabling it to give a read out of per cent organic carbon in the sample.

Appendix B: Metals Analytical Quality Control Data

Marine and Fresh Water Research Laboratory
Sediment Data

Date of issue: 14/9/05
Reference: DOE05-6
COC#: 24622, 24625, 24626, 24627

METHOD		ICP002	ICP002	ICP002	ICP002	ICP002	ICP002	ICP002	ICP007	ICP002	ICP004
SAMPLE		Al	Cd	Cr	Cu	Ni	Pb	Zn	Hg	As	As
CODE		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Reporting		<20	<0.06	<0.2	<0.2	<0.4	<1	<0.5	<0.01	<1	<0.05
Limit (mg/kg)											
File		05060301	05060301	05060301	05060301	05060301	05060301	05060301	05060801	05060301	05060901
Batch samples: CB1a, CB1b, CB1c, CB2a, CB2b, CB2c, CB3a, CB3b, CB3c, CB4a	Duplicate	18%	-	7%	8%	2%	9%	16%	-	25%	6%
	Recovery	88%	88%	96%	94%	98%	96%	98%	100%	92%	90%
Batch samples: CB4b, CB4c, CH5c, CH1a, CH1b, CH1c, CH2a, CH2b, CH2c, CH3a, CH3b	Duplicate	3%	-	20%	2%	5%	2%	2%	-	7%	7%
	Recovery	82%	91%	91%	89%	92%	93%	95%	100%	96%	91%
Batch samples: CH3c, CH4a, CH4b, CH4c, H1a, H1b, H1c, H2a, H2b, H2c	Duplicate	3%	-	7%	9%	2%	7%	5%	-	17%	-
	Recovery	87%	93%	91%	89%	93%	90%	91%	-	106%	-
Batch samples: H2d, H3a, H3b, H3c, H4a, H4b, H4c, JB1a, JB1b, JB1c	Duplicate	2%	34%	6%	25%	17%	11%	2%	50%	1%	40%
	Recovery	99%	103%	103%	103%	103%	102%	104%	97%	106%	124%
Batch samples: JB2a, JB2b, JB2c, JB3a, JB3b, JB3c, JB4a, JB4b, JB4c	Duplicate	3%	-	6%	-	4%	2%	12%	-	3%	-
	Recovery	117%	105%	103%	100%	103%	102%	102%		100%	-
Sample replicates											
JB2c (i)		160	0.08	9.0	<0.2	0.7	<1	<0.5	<0.01	4	3.0
JB2c (ii)		140	0.09	9.1	<0.2	0.6	<1	<0.5	<0.01	3	3.0
H2c (i)		410	<0.06	6.4	0.2	0.5	1	1.3	<0.01	2	1.8
H2c (ii)		410	<0.06	5.7	0.4	0.6	2	1.4	0.2	2	1.7

Appendix C: Analytical quality control data for the organic and low-level silver analyses

Organotins

Analyte	LOR	Blank	LCS	Sample Duplicate			Matrix Spike
			Recovery	Sample	Duplicate	RPD	Recovery
	ng/g	ng/g	%	ng/g	ng/g	%	%
Organotin				**W05/008289**			**Blank Soil**
Monobutyltin	0.50	<0.50	88	<0.50	<0.50	-	84
Dibutyltin	0.50	<0.50	86	<0.50	<0.50	-	89
Tributyltin	0.50	<0.50	91	<0.50	<0.50	-	81

Acceptable Spike recovery is 20-150% (For monobutyltin)
Acceptable Spike recovery is 40 to150% (For di- and tributyltin)
Results expressed in percentage (%) or ng/g wherever appropriate.
‘ - ‘ = Not Applicable.
Method used : NMI Method NR35
RPD= Relative Percentage Difference.

Total Organic Carbon

Analyte	Method	LOR	Blank	Duplicates			Recoveries	
				1	2	RPD	Matrix spk	LCS
		mg/kg	mg/kg	mg/kg	mg/kg	%	%	%
Waters Section				**W05/008292**		**W05/008292**		
Carbon-Total organic	NWS15	100	<100	1500	1500	0	86	98

Filename = DEPE02_050517_W1

Acceptable recovery is 80-120%.
Acceptable RPDs on duplicates is 40% at >5 times LOR. Greater RPD may be expected at <5 LOR.
LOR = Limit Of Reporting
RPD = Relative Percent Difference
LCS = Laboratory Control Sample

Results greater than ten times LOR have been rounded to two significant figures.

BTEX, TPH and PAH

Analyte	LOR	Blank	LCS	Sample Duplicates			Matrix Spike
			Recovery	Sample	Duplicate	RPD	Recovery
	mg/kg	mg/kg	%	mg/kg	mg/kg	%	%
BTEX				**W05/008293**			**Blank Soil**
Benzene	0.50	<0.50	102	<0.50	<0.50	-	117
Toluene	0.50	<0.50	86	<0.50	<0.50	-	124
Ethyl Benzene	0.50	<0.50	93	<0.50	<0.50	-	118
m, p - Xylene	1.00	<1.0	98	<1.0	<1.0	-	121
o-Xylene	0.50	<0.50	98	<0.50	<0.50	-	125
TPH				**W05/008293**			**Blank Soil**
TPH C6-C9	25	<25	96	<25	<25	-	121
				W05/08292			Blank Soil
TPH C10-C14	50	<50	104	<50	<50	-	102
TPH C15-C28	100	<100	103	<100	<100	-	102
TPH C29-C36	100	<100	-	<100	<100	-	-
PAH				**W05/08292**			**Blank Soil**
Naphthalene	0.1	<0.1	105	<0.10	<0.10	-	97
Acenaphthylene	0.1	<0.1	-	<0.10	<0.10	-	-
Acenaphthene	0.1	<0.1	-	<0.10	<0.10	-	-
Fluorene	0.1	<0.1	103	<0.10	<0.10	-	98
Phenanthrene	0.1	<0.1	103	<0.10	<0.10	-	96
Anthracene	0.1	<0.1	-	<0.10	<0.10	-	-
Fluoranthene	0.1	<0.1	-	<0.10	<0.10	-	-
Pyrene	0.1	<0.1	-	<0.10	<0.10	-	-
Benz[a]anthracene	0.1	<0.1	-	<0.10	<0.10	-	-
Chrysene	0.1	<0.1	100	<0.10	<0.10	-	91
Benzo[b]&[k]fluoranthene	0.2	<0.2	-	<0.10	<0.10	-	-
Benzo[a]pyrene	0.1	<0.1	103	<0.10	<0.10	-	97
Indeno[1_2_3-cd]pyrene	0.1	<0.1	-	<0.10	<0.10	-	-
Dibenz[ah]anthracene	0.1	<0.1	103	<0.10	<0.10	-	96
Benzo[ghi]perylene	0.1	<0.1	-	<0.10	<0.10	-	-
Surrogate 1 Recovery	-	-	93	94	94	0.0	95
Surrogate 2 Recovery	-	-	83	106	101	4.8	104

Results expressed in percentage (%) or mg/kg wherever appropriate.
 ‘ - ‘ = Not Applicable.
Method used : AGAL Method NGC/MS11.11, 11.12 and 11.21
This report shall not be reproduced except in full.
Acceptable Spike recovery is 70-130% (For BTEX and TPH C6-C9)
Acceptable Spike recovery is 50-150% (For PAH and TPH C10-C36)
Acceptable RPDs on spikes and duplicates is 40%.
RPD= Relative Percentage Difference.

OC and OP pesticides and PCBs

Analyte	LOR	Blank	LCS	Sample Duplicates			Matrix Spike
			Recovery	Sample	Duplicate	RPD	Recovery
	mg/kg	mg/kg	%	mg/kg	mg/kg	%	%
OC Pesticides				**W05/008289**			**Blank Soil**
HCB	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Heptachlor	0.0010	<0.0010	76	<0.0010	<0.0010	-	66
Heptachlor epoxide	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Aldrin	0.0010	<0.0010	100	<0.0010	<0.0010	-	112
gamma-BHC (Lindane)	0.0010	<0.0010	70	<0.0010	<0.0010	-	66
alpha-BHC	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
beta-BHC	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
delta-BHC	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
trans-Chlordane	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
cis-Chlordane	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Oxychlordane	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Dieldrin	0.0010	<0.0010	96	<0.0010	<0.0010	-	86
pp-DDE	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
pp-DDD	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
pp-DDT	0.0010	<0.0010	72	<0.0010	<0.0010	-	64
Endrin	0.0010	<0.0010	86	<0.0010	<0.0010	-	76
Endrin Aldehyde	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Endrin Ketone	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
alpha-Endosulfan	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
beta-Endosulfan	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Endosulfan Sulphate	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Methoxychlor	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Surrogate OC Rec.		83	89	101	90	12	86
PCB Compounds				**W05/008289**			**Blank Soil**
PCB	0.010	<0.010	138	<0.010	<0.010	-	134
OP Pesticides				**W05/008289**			**Blank Soil**
Dichlorvos	0.010	<0.010	-	<0.010	<0.010	-	-
Demeton-S-Methyl	0.010	<0.010	-	<0.010	<0.010	-	-
Diazinon	0.010	<0.010	92	<0.010	<0.010	-	96
Dimethoate	0.010	<0.010	-	<0.010	<0.010	-	
Chlorpyrifos	0.010	<0.010	84	<0.010	<0.010	-	64
Chlorpyrifos Methyl	0.010	<0.010	-	<0.010	<0.010	-	-
Malathion (Maldison)	0.010	<0.010	-	<0.010	<0.010	-	-
Fenthion	0.010	<0.010	-	<0.010	<0.010	-	-
Ethion	0.010	<0.010	84	<0.010	<0.010	-	72
Fenitrothion	0.010	<0.010	-	<0.010	<0.010	-	-
Chlorfenvinphos (E)	0.010	<0.010	-	<0.010	<0.010	-	-
Chlorfenvinphos (Z)	0.010	<0.010	-	<0.010	<0.010	-	-
Parathion (Ethyl)	0.010	<0.010	64	<0.010	<0.010	-	64
Parathion Methyl	0.010	<0.010	-	<0.010	<0.010	-	-
Pirimiphos Ethyl	0.010	<0.010	-	<0.010	<0.010	-	-
Pirimiphos Methyl	0.010	<0.010	-	<0.010	<0.010	-	-
Azinphos Methyl	0.010	<0.010	-	<0.010	<0.010	-	-
Azinphos Ethyl	0.010	<0.010	-	<0.010	<0.010	-	
Surrogate OP Rec.		94	100	101	95	6.1	95

LCS = Laboratory Control Spike
Results expressed in percentage (%) or mg/kg wherever appropriate.
' - ' = Not Applicable.
Method used : AGAL Method NR19
Acceptable Spike recovery is 40-150% (For OC Compounds).
Acceptable Spike recovery is 40-150% (For OP Compounds).
Acceptable RPD (Relative Percentage Difference) on Spikes and Duplicates is 40%.
QA No : PESTS1010

Silver (low level)

Analyte	Method	LOR	Blank	Duplicates			Recoveries	
				1	2	RPD	Matrix spk	LCS
				W05/008283			W05/008283	AGAL10, Sediment
		mg/kg	mg/kg	mg/kg	mg/kg	%	%	%
Silver	NT2.49	0.2	<0.2	<0.2	<0.2	ND	110	100

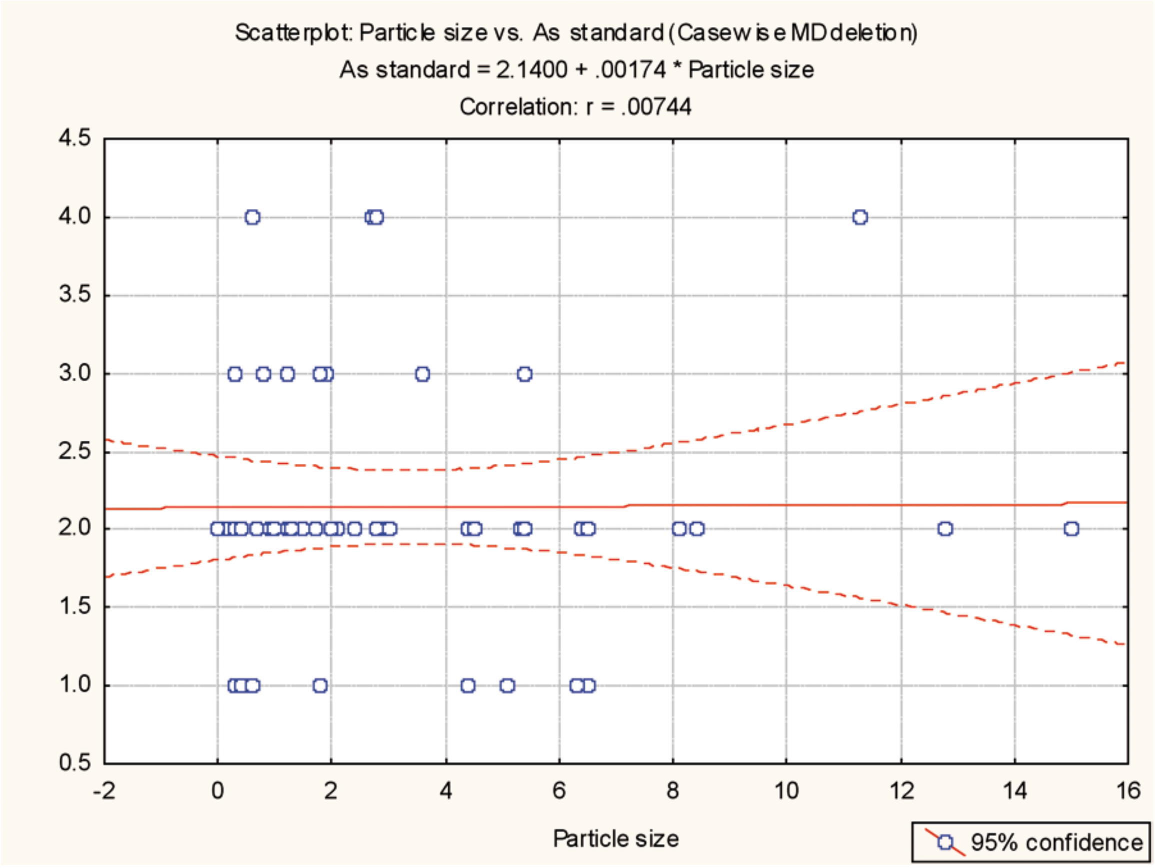
Notes:
Acceptable recovery is 75-120%.
Acceptable RPDs on duplicates is 44% at concentrations >5 times LOR. Greater RPD may be expected at <5 times LOR.
LOR: Limit Of Reporting
RPD: Relative Percent Difference
ND: Not determined
NA: Not applicable
LCS: Laboratory Control Sample
**: reference value not available

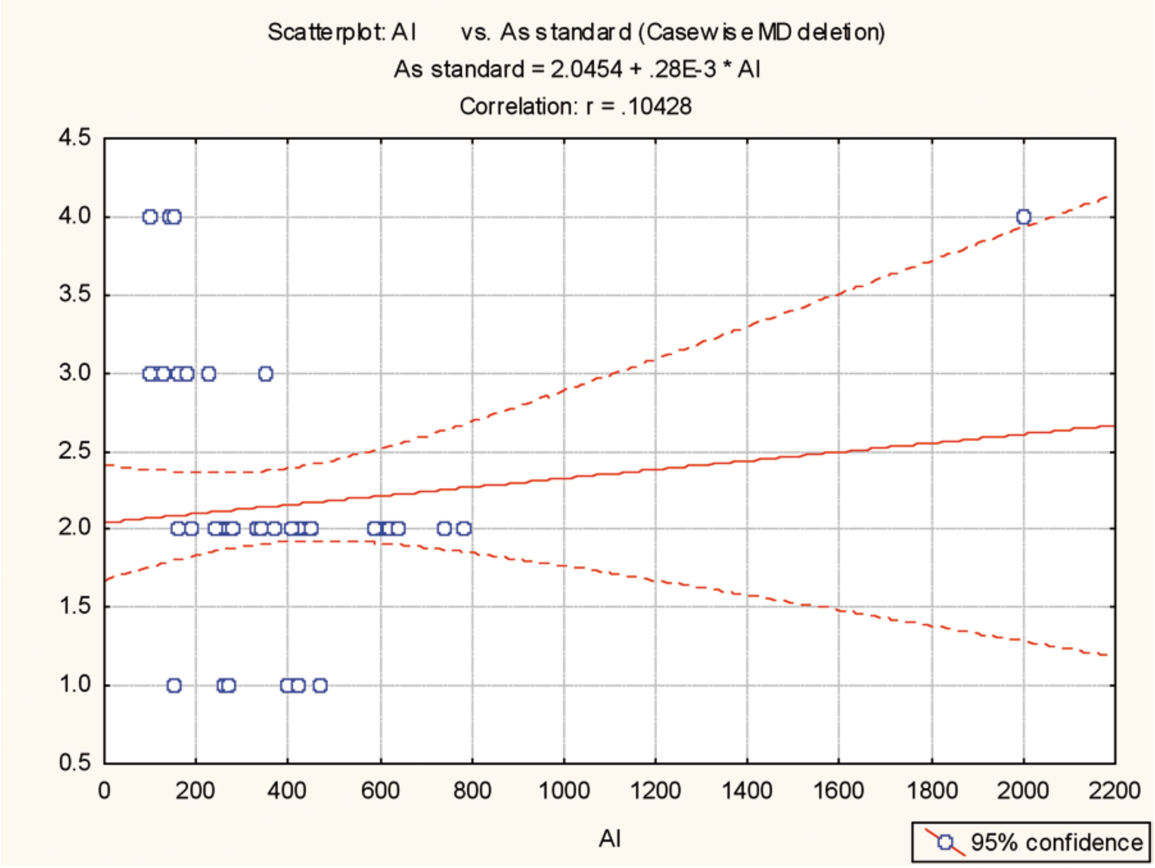
Comments:
Results greater than ten times LOR have been rounded to two significant figures.

Appendix D: Graphs of reference site metal concentrations against the three potential normalisers

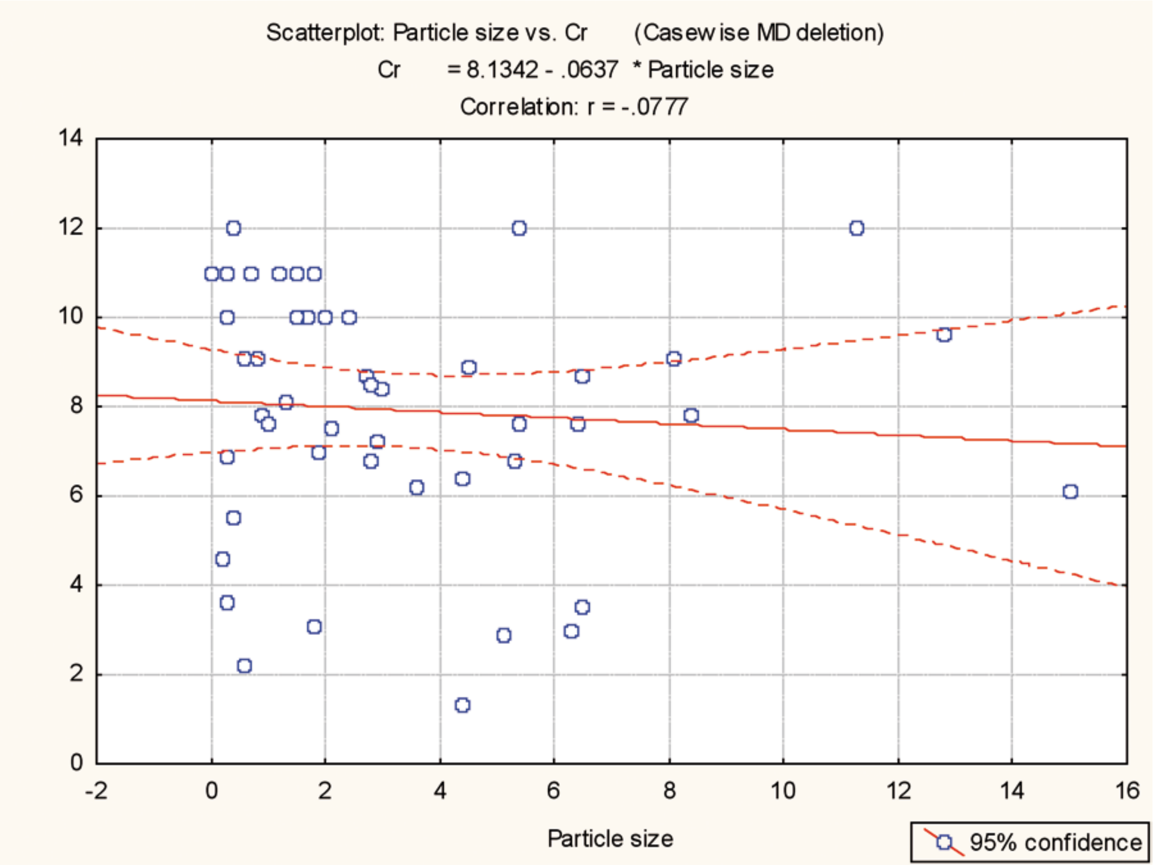
(<63 µm particle size fraction, aluminium and iron concentrations)

Arsenic

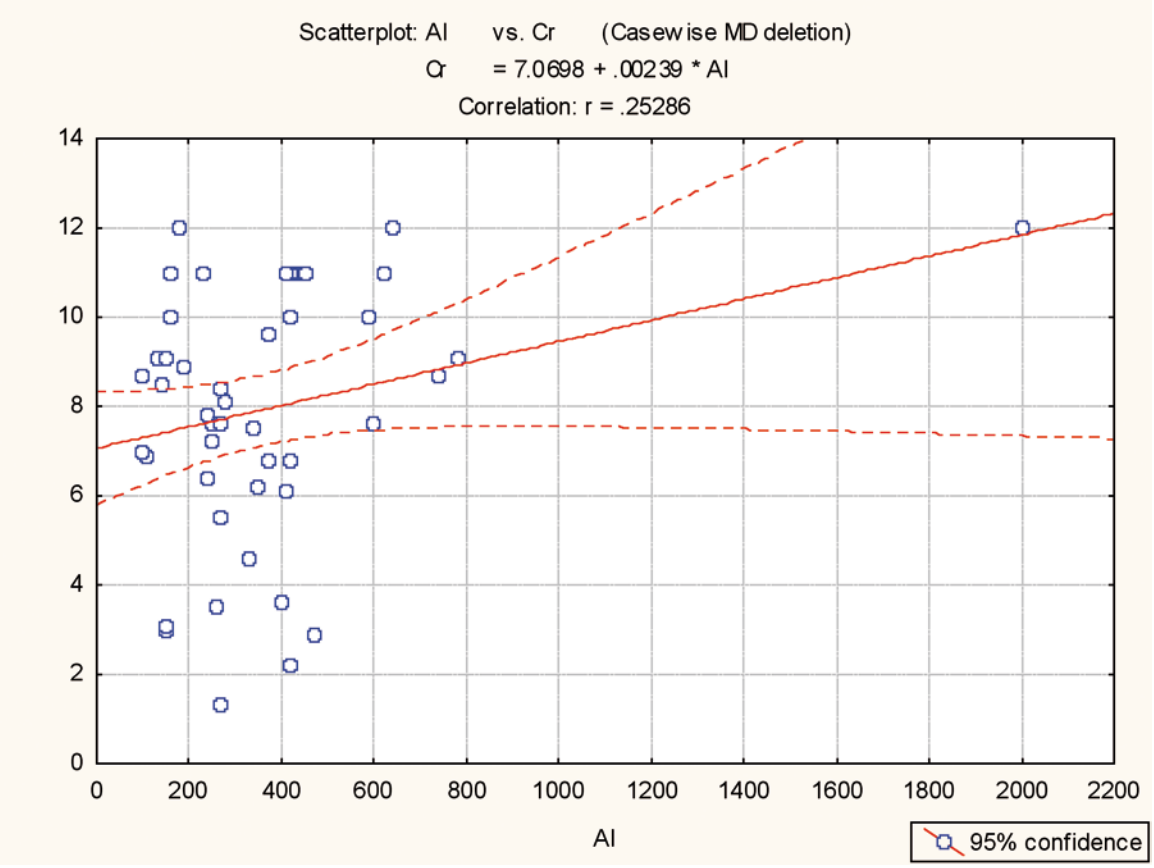

Scatterplot: Particle size vs. As standard (Casewise MD deletion)
As standard = 2.1400 + .00174 * Particle size
Correlation: r = .00744
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-2
0
2
4
6
8
10
12
14
16
Particle size
95% confidence


Scatterplot: Al vs. As standard (Casewise MD deletion)
As standard = 2.0454 + .28E-3 * Al
Correlation: r = .10428
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
Al
95% confidence

Chromium

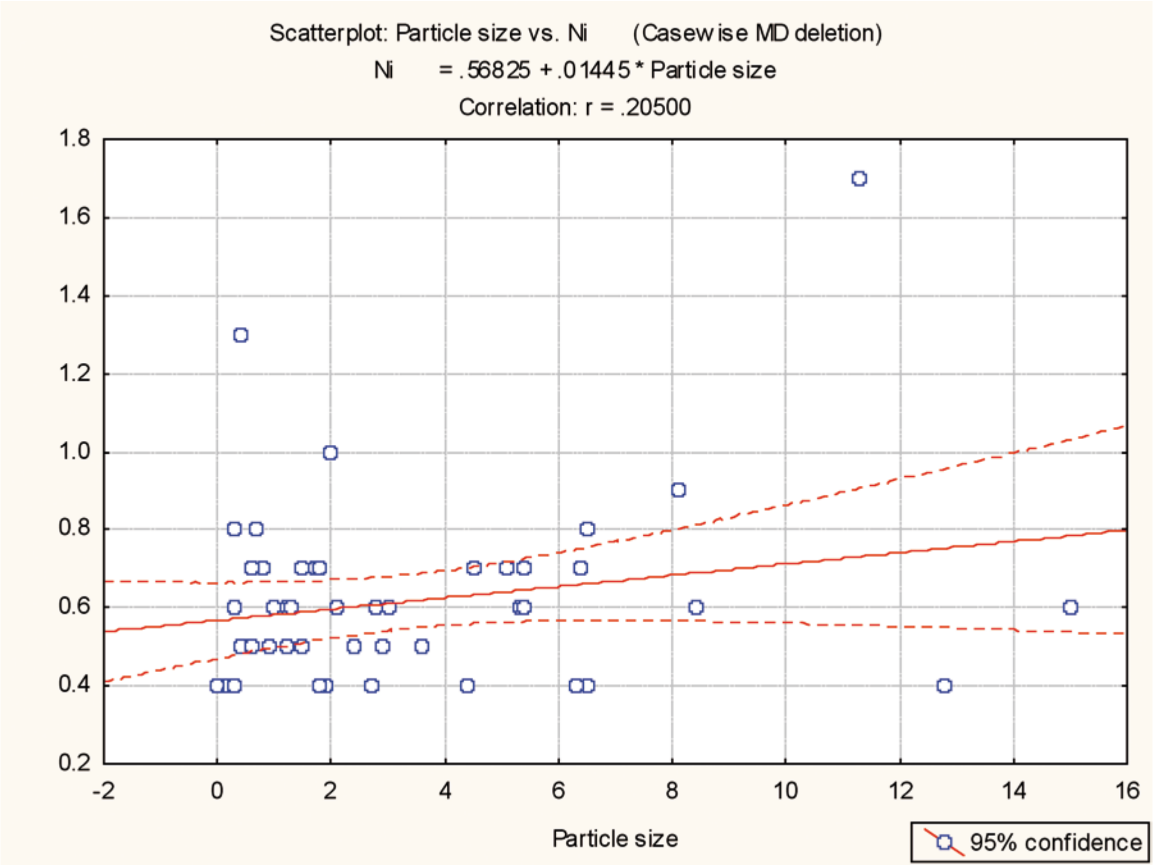


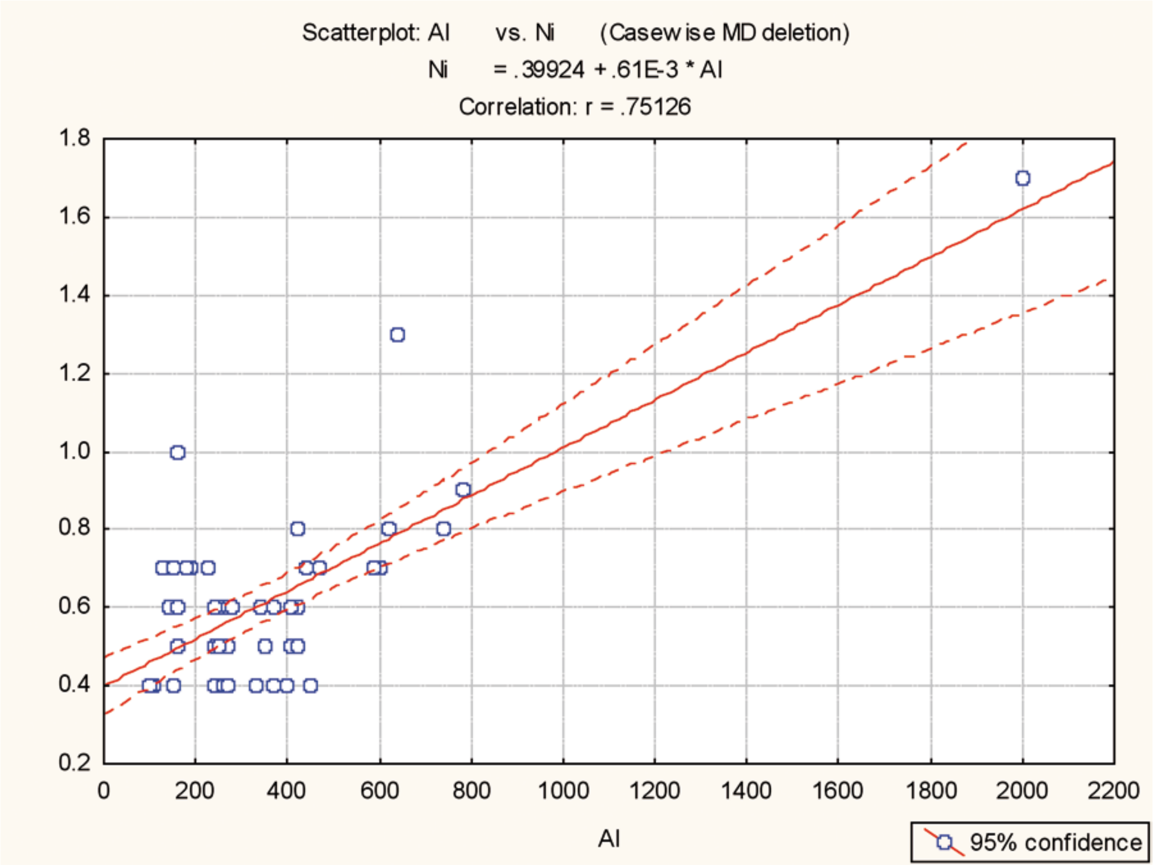
Scatterplot: Particle size vs. Cr (Casewise MD deletion)
Cr = 8.1342 - .0637 * Particle size
Correlation: r = -.0777
14
12
10
8
6
4
2
0
-2
0
2
4
6
8
10
12
14
16
Particle size
95% confidence



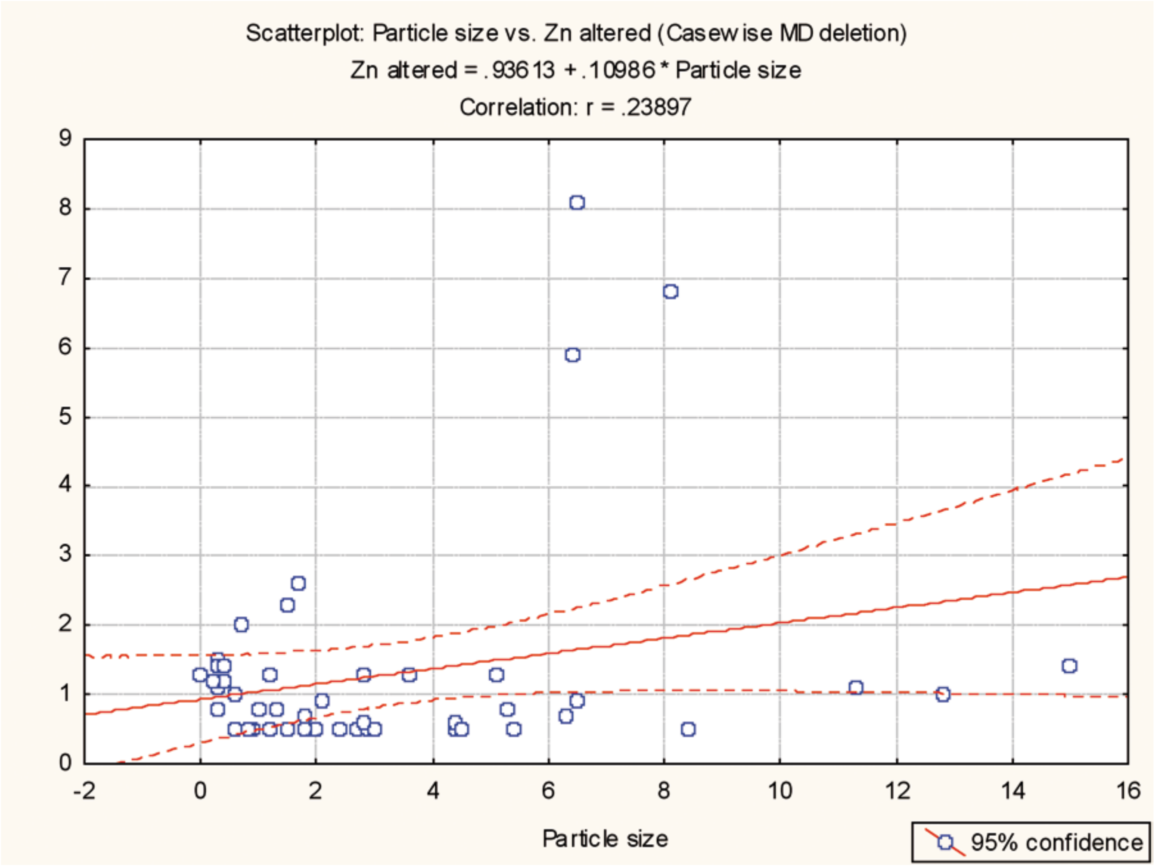
Scatterplot: Al vs. Cr (Casewise MD deletion)
Cr = 7.0698 + .00239 * Al
Correlation: r = .25286
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
Al
95% confidence

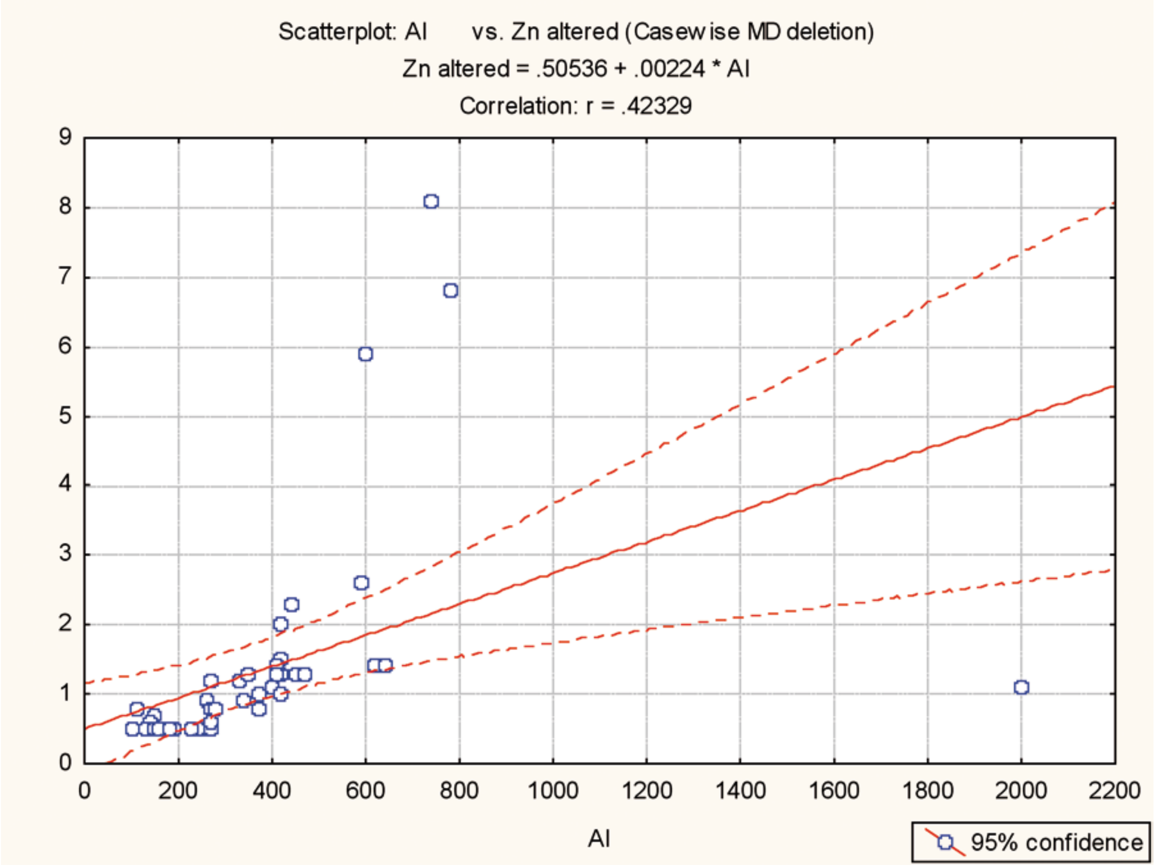
Nickel


Scatterplot: Particle size vs. Ni (Casewise MD deletion)
Ni = .56825 + .01445 * Particle size
Correlation: r = .20500
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
-2
0
2
4
6
8
10
12
14
16
Particle size
95% confidence


Scatterplot: Al vs. Ni (Casewise MD deletion)
Ni = .39924 + .61E-3 * Al
Correlation: r = .75126
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
Al
95% confidence

Zinc


Scatterplot: Particle size vs. Zn altered (Casewise MD deletion)
Zn altered = .93613 + .10986 * Particle size
Correlation: r = .23897
0
1
2
3
4
5
6
7
8
9
-2
0
2
4
6
8
10
12
14
16
Particle size
95% confidence


Scatterplot: Al vs. Zn altered (Casewise MD deletion)
Zn altered = .50536 + .00224 * Al
Correlation: r = .42329
0
1
2
3
4
5
6
7
8
9
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
Al
95% confidence

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