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Background quality of the marine sediments of the Pilbara coast

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Abstract

A sediment quality survey was undertaken at six locations in the marine waters off the Pilbara coast to determine concentrations of a range of selected metal and organic chemicals under natural background conditions. The suite of chemicals measured included arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, silver, vanadium, zinc, butyltin compounds, total petroleum hydrocarbons, BTEX chemicals, polycyclic aromatic hydrocarbons, organochlorine and organophosphate pesticides and PCBs. The work was undertaken to provide a baseline for evaluating anthropogenic changes or trends in sediment quality around regional centers of development (eg. Ports) and to ascertain the applicability the nationally recommended sediment quality guidelines from the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (ANZECC & ARMCANZ, 2000) to the region.

Background sediment quality was found to be high and concentrations of most metals and metalloids were found to be at similar levels or lower than found in other studies undertaken in northern Australia. However, total arsenic concentrations were found to be relatively high (median of 36 mg/kg for one site off Onslow) and exceeded the recommended sediment quality guideline at some of the essentially unimpacted locations sampled across the region. The elevations are considered to be natural and likely to be related to the geology of the region.

No organic chemicals were detected in any of the samples. Compliance with the recommended sediment quality guidelines could not be determined for eight of the analysed chemicals (acenaphthene, anthracene, dibenzo(ah)anthracene, fluorene, lindane, chlordane, dieldrin and endrin) because the laboratory 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 appropriate for four levels of ecological protection in the coastal marine environment of the Pilbara region. These are presented in Table 13 of the report.

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 is based on protecting a set of environmental values for the marine waters 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 Department of Environment (DoE) has recently undertaken a community consultative process to assist in establishing a set of environmental values and environmental quality objectives for the marine waters from Exmouth to Cape Keraudren. The project is supported by Natural Heritage Trust funding through the Rangelands Natural Resource Management Coordinating Group. The DoE Marine Report No. 1 *Pilbara coastal Water Quality Consultation Outcomes: Environmental Values and Environmental Quality Objectives* (DoE, 2006) summarises this study and describes the environmental values, environmental quality objectives and levels of ecological protection recommended for the Exmouth Gulf and Pilbara marine waters as a consequence of the community feedback. The EPA has endorsed the recommended management framework as interim to guide environmental impact assessment and waste discharge regulation until it is more formally established through Government policy.

The supporting EQC for water and sediment quality are being developed in parallel and are based on the numerical guidelines and approaches recommended in the National guidelines document (ANZECC & ARMCANZ, 2000). The DoE has already reported on background toxicant concentrations in the marine waters of the region (Wenziker et al, in press) and now this report will characterise background sediment quality. Together these reports establish a baseline for managing environmental quality in the region and determining the relevance of the ANZECC & ARMCANZ water and sediment quality guidelines to the area. Background sediment quality data can also be used to derive alternative locally based sediment quality guidelines for any chemical parameters found to naturally exceed the national guidelines.

Sediment contaminants can be divided into two groups: those that have a natural background concentration (eg. metals); and xenobiotic chemicals (eg. some organic compounds such as TBT) where natural background concentration is zero. Concentrations of contaminants from the first group are generally influenced by geology as well as anthropogenic discharges, concentrations of the second group are only influenced by anthropogenic discharges. Few sampling programs have attempted to characterise background chemical concentrations for the marine sediments of the North West Shelf (RPS Bowman Bishaw Gorham 2004; Water Corporation, 2004). Most sediment quality monitoring programs are focussed around specific developments or activities, and often 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 a sediment quality survey to determine current background concentrations of a range of selected heavy metals and organic chemicals in the Pilbara marine waters from Exmouth Gulf to Port Hedland.

The main objectives of this survey were to:

- Estimate background concentrations for the selected contaminants in marine sediments of the Pilbara coastal waters; and,
- Ascertain whether the guideline trigger values from ANZECC & ARMCANZ (2000) were relevant to the region.

The analytes measured in this study included key contaminants of concern identified after reviewing 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 was conducted from the DoE research vessel Zoila. Sampling was undertaken on 14 – 24 June 2005 by four DoE staff.

Twenty four sampling sites were selected for this study (Table 1 and Figure 1) from six locations that span approximately 600 kms of the Pilbara coastline from near Exmouth Gulf to Port Hedland. The sites at five of the locations were selected to represent unimpacted reference sites (Exmouth, Ashburton River Mouth, Onslow, Dampier Archipelago and Port Hedland). While the Ashburton River Mouth is remote from any potential contamination sources, it is possible that the chemical composition of these sediments could be slightly influenced by anthropogenic chemicals transported by the river from the catchment. The sampling sites in Dampier Port were located adjacent to industrial facilities and represent an area where sediment quality is most likely to have been impacted.

Four sites were sampled at each location at varying distances from the shore and where suitable substrates were found. An additional sampling site in the Exmouth Gulf (EX2) resulted from failed attempts to deploy a sediment corer from the surface to collect sediment cores in deep water. A small quantity of surface sediment was collected and analysed for metal concentrations, but there was insufficient sample for any other analyses. The results from this sample have only been included for comparative purposes and are not used in any further analyses.

Sampling was conducted during daylight hours over a range of tidal cycles (Figure 2) and weather and sea conditions (Table 2). Samples were collected using clear polycarbonate corer tubes and extruding the sediment out through the top of the tube and cutting the surface 2 centimetres directly into a sampling container. SCUBA divers had been enlisted to collect samples from deep water sites at the Exmouth and Dampier Archipelago locations, but were unable to assist on the day. The deep water sites were therefore relocated into shallower water and samples collected by free diving at the 4 Exmouth sites and at sites DA3 and DA4. At all other sites a Wildco 2401-B20 KB heavy sediment corer was deployed from the research vessel to collect the samples. Methods and procedures for collection and handling of samples are described in Appendix A.

Three replicate samples (of five cores each) were taken at each of the 24 sample sites. Each replicate was analysed separately for metal concentrations except for the Dampier Port samples. The replicates from the Dampier Port sites were composited for analysis. The replicates at all sites were also composited for organic chemical analyses, except for sites AR1 and DA3. At sites AR1 and DA3 the three organic replicates were sampled and analysed separately to assess variability of the sediment concentrations. 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.

Two of the metal samples (ONS3c and EX5a) and one of the organic samples (ONS3) were homogenised and split into two containers for separate analysis to assess variation associated with sub-sample handling.

All samples were kept in the dark and on ice from time of collection until delivery to the analytical laboratory. Samples for organic analyses were couriered to the NMI laboratory, Perth, within 4 - 7 days of collection. Samples for metal and particle size analyses were delivered to the laboratory at the end of the field program. Full details of the sediment sampling procedures are given in Appendix A.

2.2 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 environmental quality in the region over the long term. The suite of contaminants analysed included total metals and metalloids (arsenic, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, silver, vanadium, 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 all the metal analyses except the low level silver analysis. MAFRL is NATA (National Association of Testing Authorities) accredited for all the metal analyses performed for this study except the low level arsenic and selenium 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.

Analysis of the organic contaminants and low level silver was performed by the National Measurement Institute (NMI) using NATA accredited procedures. QA/QC procedures were also undertaken and the data reported with the analytical results.

Organic samples were analysed within 7 – 11 days of sampling and metal samples were analysed within four weeks of collection.

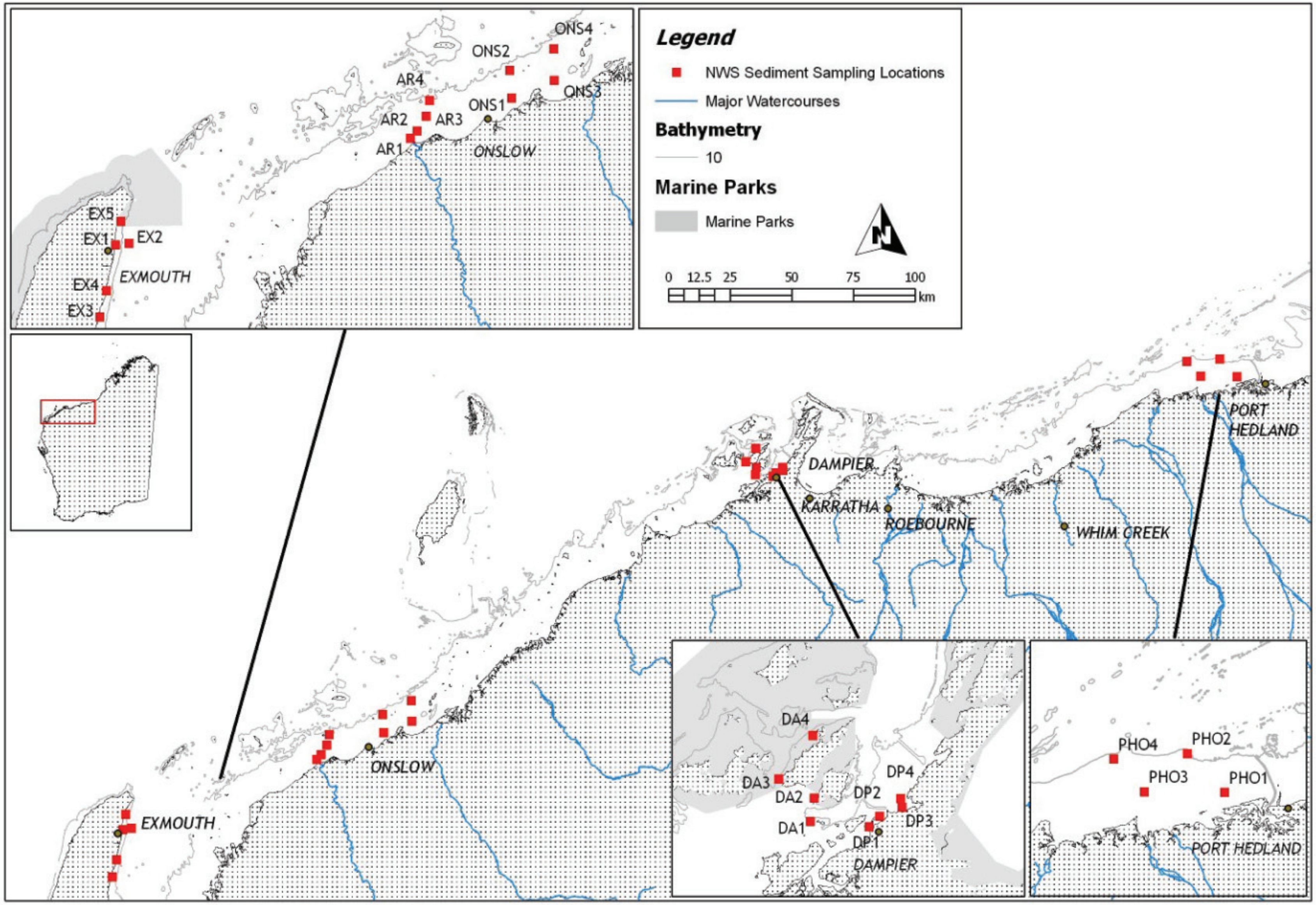

Figure 1. Locality map of the study area showing the sampling sites (Pilbara region)

Table 1: Sampling locations.

Location	Site code	Latitude*	Longitude*	Approx. depth at time of sampling (m)
Exmouth Gulf	EX1	21°55.50 S	114°08.75 E	4.5
	EX2	21° 55.30 S	114°10.80 E	17.0
	EX3	22°05.86 S	114° 06.08 E	4.5
	EX4	22° 02.10 S	114° 07.15 E	5.0
	EX5	21° 52.16 S	114° 09.56 E	7.0
Ashburton River Mouth	AR1	21°40.81 S	114° 54.56 E	4.6
	AR2	21° 39.81 S	114° 55.61 E	8.7
	AR3	21° 37.70 S	114° 57.03 E	10.3
	AR4	21° 35.42 S	114° 57.57 E	11.2
Onslow	ONS1	21° 35.18 S	115° 10.41 E	5.0
	ONS2	21° 31.20 S	115° 10.19 E	8.5
	ONS3	21° 32.71 S	115° 16.97 E	5.0
	ONS4	21° 28.20 S	115° 17.00 E	10.0
Dampier Archipelago	DA1	20° 39.06 S	116° 37.91 E	6.0
	DA2	20° 37.51 S	116° 38.20 E	5.0
	DA3	20° 36.24 S	116° 35.70 E	7.0
	DA4	20° 33.36 S	116° 38.10 E	4.0
Dampier Port	DP1	20° 39.41 S	116° 42.06 E	4.8
	DP2	20° 38.72 S	116° 42.80 E	6.8
	DP3	20° 38.12 S	116° 44.39 E	7.4
	DP4	20° 37.56 S	116° 44.31 E	7.0
Port Hedland Offshore	PHO1	20° 17.20 S	118° 30.00 E	7.6
	PHO2	20° 13.38 S	118° 26.05 E	11.6
	PHO3	20° 17.19 S	118° 21.61 E	8.0
	PHO4	20° 13.99 S	118° 18.38 E	11.8

* Datum is WGS84.

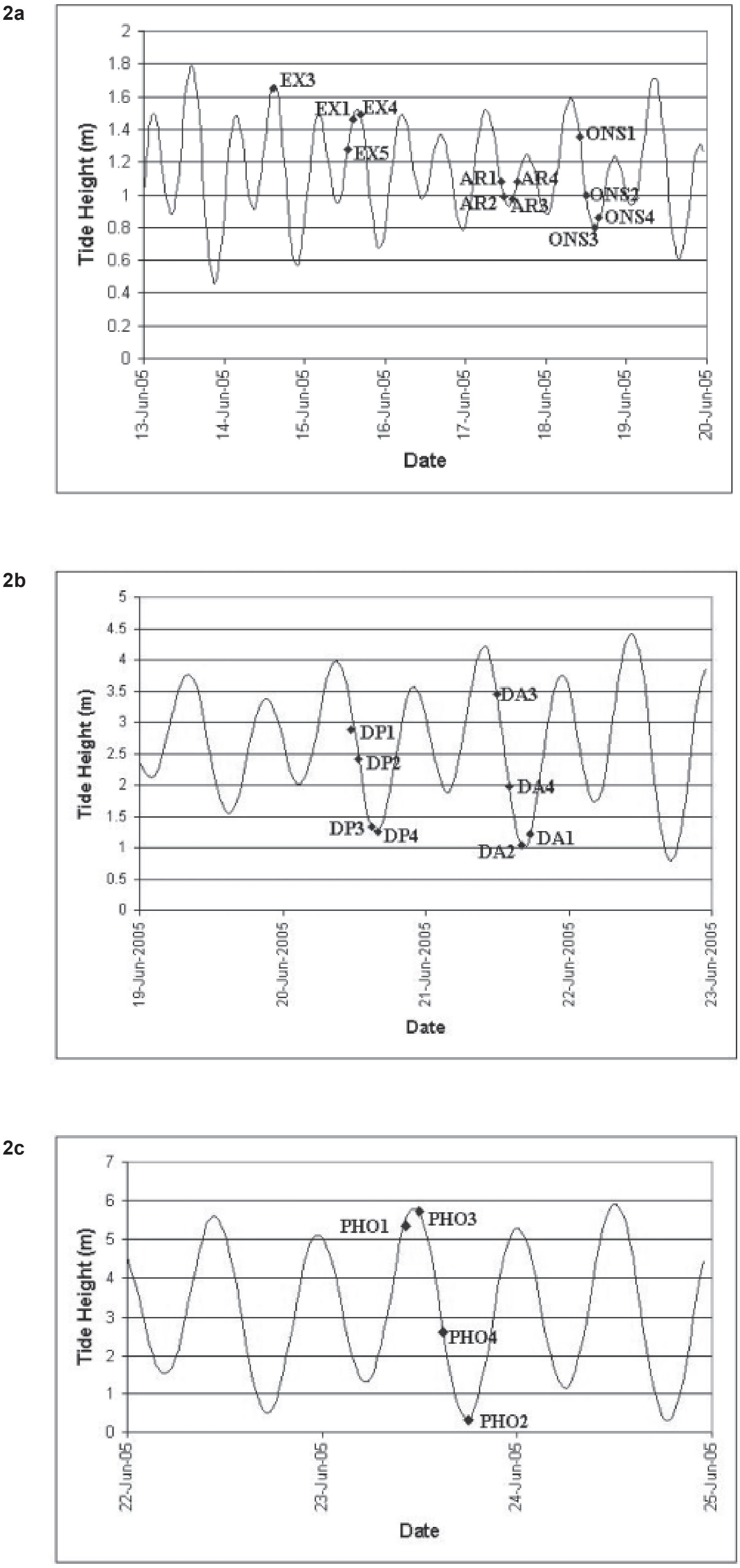

Figure 2: Predicted tide heights for the sampling period at the nearest available stations: (a) Pt Murat; (b) Dampier; and (c) Port Hedland (diamonds represent sampling period).

Table 2: Weather and sea conditions.

Date/Location	Winds	Sun/Cloud	Swell
14 June 2005 Exmouth	SSE, 10 knots	fine and sunny	no swell
15 June 2005 Exmouth	NE, 5 knots rising to 5–10 knots late afternoon	fine and sunny	no swell
17 June 2005 Ashburton R	light and variable tending northerly	fine and partly cloudy	NE swell, 0.5 m
18 June 2005 Onslow	SE, 10–15 knots	fine and sunny	NE swell, 0.5 m
20 June 2005 Dampier Arch.	E, 20–30 knots reducing to 20–25 knots in the afternoon	fine and sunny	no swell
21 June 2005 Dampier Port	E, 20–30 knots reducing to 10–20 knots late afternoon	fine and sunny	no swell
23 June 2005 Port Hedland	NE, 10–15 knots becoming calm early evening	fine and sunny	NE swell, 0.5–1.0 m

2.3 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 contaminant concentrations in sediments (ANZECC & ARMCANZ, 2000; Kersten and Smedes, 2002). The key factor affecting the physical characteristics of sediment 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 accumulate to form a significant proportion of the sediment. Normalising contaminant concentrations to some factor that accounts for these differences in sediment composition, and hence chemical adsorbtion capacity, helps reduce the variability in sediment contaminant data, 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 for comparing to the sediment quality guidelines (ANZECC & ARMCANZ, 2000). Metals tend to have a high affinity for the very fine particulate fraction of sediments which are mainly comprised of clay particles. The <63 µm fraction is the most widely accepted measure used for normalizing metal concentrations to particle size, although this fraction includes both silt (2 – 63) µm as well as clay (<2 µm) particle sizes. Normalization to geochemical normalisers such as aluminium or iron concentrations (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, aluminium and iron were therefore selected for analysis along with the identified contaminants.

2.4 Statistical analysis

The statistical software package S*tatistica (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 and hence determine whether parametric or non-parametric statistics were appropriate. 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 the reference site locations and between the nearshore and midshore sites. The Mann-Whitney test was also used to determine whether there was a significant difference between the Dampier Port sediments and the sediments of the Dampier Archipelago.

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). 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 here for assessing whether or not the natural background sediment quality naturally exceeds the national sediment quality guidelines and, where appropriate, for deriving new sediment quality guidelines for the Pilbara coastal waters. An 80th percentile for each metal was therefore calculated from reference site data; means were calculated using the same data set. To calculate percentiles and means for those metals with some analytical results reported as ‘below the detection limit’, the detection limit was used as the actual concentration (e.g. <1 mg/kg became 1 mg/kg).

3. Results

3.1 Metals

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 data for the NATA accredited analyses and the low level arsenic and selenium analyses are satisfactory. However, the analytical results for cobalt and zinc in the sample replicates taken from site EX5a show considerable variation between the two replicates, suggesting either poor homogenization of the sample prior to sub-sampling or low analytical precision. The duplicate and recovery data for these metals suggest that the error may be a result of poor sample homogenization, but none of the other metals exhibit such variability between the replicates and the error is reversed between the two metals. For this reason the error is considered to be more likely an analytical problem.

Results for the low level analyses for arsenic and selenium were consistent with the analytical results from the NATA accredited method for all samples. The low level arsenic results were consistently higher than NATA accredited results by approximately 5% - 15%. Selenium concentrations were not detectable using the NATA accredited analytical methods but reportable concentrations were detected in about half the samples using the low level analytical methods.

Silver concentrations were analysed using two different analytical methods with different reporting limits. Silver concentrations were found to be below both analytical reporting limits at all the sites. Cadmium concentrations were also below the analytical reporting limit for all sites and mercury concentrations were below the analytical reporting limit in all samples except for two sites adjacent to the Ashburton River mouth (AR1 and AR2). Selenium concentrations were generally below the limit of reporting at Exmouth and Port Hedland, but concentrations were generally measurable at the three other reference locations. Lead concentrations were at or below the analytical reporting limit at all sites. Although there is no national sediment quality guideline (ANZECC & ARMCANZ, 2000) for selenium, the analytical limit of reporting for cadmium, lead, mercury and silver were all well below the recommended sediment quality guidelines.

There appear to be no general east-west trends in the data following the alignment of the Pilbara coastline. However, concentrations of most of the analysed metals (aluminium, chromium, copper, iron, mercury, nickel, lead, vanadium and zinc) were markedly elevated at sites AR1 and AR2 compared to the levels measured at the other locations along the Pilbara coast (eg. 43 mg/kg Ni compared to 1 – 17 mg/kg at all other sites). These sites were located near the mouth of the Ashburton River and had sediments with a higher proportion of fine particles (<63 μm) than the other sites sampled (see Table 4). For these metals there was a general trend toward decreasing concentration with distance from the river mouth. Concentrations appear to have fallen to levels more typical of the Onslow sites at the two sites more distant from the river mouth (AR3 and AR4).

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

Location and site	Al	As Standard	As* low level	Ag	Ag$^{\#}$ low level	Cd	Co	Cr	Cu	Fe	Hg	Ni	Pb	Se Standard	Se* low level	V	Zn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Exmouth																	
EX1a	1200	11	10	<1	<0.2	<0.06	24	6.3	0.7	4200	<0.01	1.1	1	<2	<0.1	13	1.4
EX1b	1200	10	9.9	<1		<0.06	27	6.0	0.6	4000	<0.01	1.2	<1	<2	<0.1	12	1.4
EX1c	1500	14	15	<1		<0.06	27	7.7	0.7	5600	<0.01	1.4	1	<2	<0.1	17	1.6
EX2a	5200	18	18	<1		<0.06	24	21	2.1	24000	<0.01	4.8	3	<2	0.1	27	6.4
EX3a	1900	18	18	<1	<0.2	<0.06	22	13	0.9	8000	<0.01	1.9	2	<2	<0.1	22	2.1
EX3b	1800	19	20	<1		<0.06	22	12	0.9	7700	<0.01	1.8	2	<2	<0.1	21	1.9
EX3c	2000	19	19	<1		<0.06	9.1	13	0.8	8200	<0.01	1.8	2	<2	<0.1	23	1.8
EX4a	1800	12	11	<1	<0.2	<0.06	9.2	12	0.8	5100	<0.01	1.6	1	<2	<0.1	13	1.9
EX4b	1700	11	12	<1		<0.06	8.6	11	0.8	4900	<0.01	1.6	1	<2	<0.1	13	1.7
EX4c	1800	11	11	<1		<0.06	6.8	12	0.8	5200	<0.01	1.6	1	<2	<0.1	13	1.8
EX5a	1300	8	7.6	<1	<0.2	<0.06	0.5	6.7	0.7	3800	<0.01	1.2	1	<2	0.1	12	9.8
EX5b	1100	8	7.9	<1		<0.06	6.8	6.2	0.5	3700	<0.01	1.0	<1	<2	<0.1	11	1.2
EX5c	1300	8	7.8	<1		<0.06	6.7	6.6	0.6	3900	<0.01	1.1	<1	<2	<0.1	12	1.3
EX5d (duplicate 5a)	1300	7	7.0	<1		<0.06	11	6.7	0.6	3700	<0.01	1.0	<1	<2	<0.1	11	1.3
Ashburton River mouth																	
AR1a	31000	11	9.9	<1	<0.2	<0.06	14	85	48	78000	0.03	40	14	<2	0.2	110	77
AR1b	32000	11	11	<1	<0.2	<0.06	13	87	53	84000	0.03	42	14	<2	0.3	110	83
AR1c	34000	11	10	<1	<0.2	<0.06	8.1	90	54	86000	0.03	43	15	<2	0.3	110	87
AR2a	40000	20	20	<1	<0.2	<0.06	7.7	92	44	74000	0.02	43	15	<2	0.2	110	77
AR2b	42000	20	19	<1		<0.06	8.3	92	44	73000	0.02	42	15	<2	0.2	110	75
AR2c	41000	19	18	<1		<0.06	5.3	91	44	73000	0.02	42	14	<2	0.2	110	76
AR3a	12000	21	20	<1	<0.2	<0.06	4.9	32	9.7	30000	0.01	12	5	<2	0.1	46	20
AR3b	11000	20	21	<1		<0.06	4.8	31	9.5	29000	<0.01	12	5	<2	<0.1	46	20
AR3c	11000	21	20	<1		<0.06	5.0	31	9.4	30000	<0.01	11	5	<2	0.1	47	19
AR4a	9200	16	17	<1	<0.2	<0.06	6.0	32	6.7	29000	<0.01	10	5	<2	0.1	44	16
AR4b	8700	17	18	<1		<0.06	5.8	31	6.3	28000	0.01	9.5	5	<2	0.1	44	15
AR4c	9600	18	18	<1		<0.06	6.0	33	7.0	30000	<0.01	10	5	<2	0.1	45	16
Onslow																	
ONS1a	13000	26	29	<1	<0.2	<0.06	9.3	28	10	32000	<0.01	12	5	<2	0.2	51	21
ONS1b	17000	26	29	<1		<0.06	11	36	15	37000	<0.01	16	6	<2	0.2	59	29
ONS1c	15000	28	33	<1		<0.06	11	31	12	35000	<0.01	14	5	<2	0.2	54	24
ONS2a	10000	23	25	<1	<0.2	<0.06	6.8	32	6.5	37000	<0.01	10	5	<2	0.1	44	15
ONS2b	9400	23	25	<1		<0.06	6.4	31	6.4	38000	<0.01	10	5	<2	0.1	44	15
ONS2c	11000	23	25	<1		<0.06	6.7	32	7.4	36000	<0.01	11	5	<2	0.1	44	17
ONS3a	6000	35	38	<1	<0.2	<0.06	4.4	20	3.5	26000	<0.01	6.4	4	<2	<0.1	42	8.4
ONS3b	5300	38	44	<1		<0.06	3.8	17	2.9	24000	<0.01	5.2	3	<2	<0.1	40	7.0
ONS3c	5600	36	39	<1		<0.06	4.1	18	3.1	24000	<0.01	5.6	3	<2	<0.1	40	7.6
ONS3d (duplicate 3c)	5300	36	41	<1		<0.06	4.0	18	3.1	23000	<0.01	5.5	3	<2	<0.1	39	7.1

Table 3 continued…..

Location and site	Al	As Standard	As* low level	Ag	Ag# low level	Cd	Co	Cr	Cu	Fe	Hg	Ni	Pb	Se Standard	Se* low level	V	Zn
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
ONS4a	11000	20	22	<1	<0.2	<0.06	4.9	24	6.9	26000	<0.01	9.9	4	<2	0.2	35	14
ONS4b	9700	20	22	<1		<0.06	4.6	22	6.0	25000	<0.01	8.7	4	<2	0.1	34	12
ONS4c	11000	20	21	<1		<0.06	4.9	25	7.1	26000	<0.01	10	4	<2	0.2	35	14
Dampier Archipelago																	
DA1a	8000	12	13	<1	<0.2	<0.06	6.2	42	6.1	17000	<0.01	16	3	<2	<0.1	26	15
DA1b	8700	13	14	<1		<0.06	6.8	45	6.8	19000	<0.01	17	3	<2	0.1	26	15
DA1c	9200	11	14	<1		<0.06	6.6	45	6.9	19000	<0.01	17	3	<2	0.1	27	16
DA2a	3700	7	7.7	<1	<0.2	<0.06	1.5	17	2.1	6200	<0.01	5.2	2	<2	0.1	7.8	5.3
DA2b	4100	8	8.3	<1		<0.06	1.6	19	2.4	6800	<0.01	6.3	2	<2	0.1	8.4	6.1
DA2c	4100	8	8.7	<1		<0.06	1.6	19	2.4	6800	<0.01	6.1	2	<2	0.1	8.5	5.5
DA3a	1700	4	4.2	<1	<0.2	<0.06	0.8	6.3	1.4	3200	<0.01	2.1	<1	<2	<0.1	6.9	2.0
DA3b	1400	4	3.8	<1	<0.2	<0.06	0.8	5.1	1.4	2800	<0.01	1.7	<1	<2	0.1	6.6	1.9
DA3c	1900	4	3.8	<1	<0.2	<0.06	0.9	7.0	1.3	3300	<0.01	2.3	<1	<2	0.1	7.0	2.2
DA4a	1200	6	6.7	<1	<0.2	<0.06	0.5	5.9	0.7	3100	<0.01	1.6	<1	<2	0.2	9.5	1.3
DA4b	1300	6	6.7	<1		<0.06	0.5	6.5	0.8	3200	<0.01	1.7	<1	<2	0.1	9.4	1.2
DA4c	1100	6	7.0	<1		<0.06	0.4	5.7	0.6	3100	<0.01	1.4	1	<2	<0.1	9.6	1.1
Dampier Port																	
DP1	3400	13	14	<1	<0.2	<0.06	1.8	14	2.0	12000	<0.01	4.6	2	<2	<0.1	14	8.9
DP2	10000	12	15	<1	<0.2	<0.06	6.0	41	7.8	28000	<0.01	15	5	<2	0.1	23	26
DP3	6700	13	14	<1	<0.2	<0.06	3.4	28	4.4	18000	<0.01	9.3	4	<2	0.1	17	17
DP4	15000	12	14	<1	<0.2	<0.06	6.8	55	12	25000	<0.01	20	5	<2	0.2	31	23
Port Hedland																	
PH1a	1500	19	21	<1	<0.2	<0.06	2.1	17	1.1	6700	<0.01	4.0	2	<2	<0.1	19	3.4
PH1b	1700	20	22	<1		<0.06	2.0	17	1.2	6300	<0.01	4.3	2	<2	<0.1	19	3.0
PH1c	1600	20	22	<1		<0.06	2.2	19	1.2	6600	<0.01	4.2	2	<2	<0.1	20	3.2
PH2a	2600	26	30	<1	<0.2	<0.06	2.8	15	1.9	11000	<0.01	5.5	3	<2	<0.1	23	3.5
PH2b	2500	25	30	<1		<0.06	2.5	16	1.7	10000	<0.01	4.8	3	<2	<0.1	22	3.1
PH2c	1800	16	18	<1		<0.06	1.8	13	1.4	7400	<0.01	3.7	2	<2	<0.1	15	2.3
PH3a	2200	17	18	<1	<0.2	<0.06	3.3	15	1.7	6300	<0.01	5.5	1	<2	<0.1	17	3.4
PH3b	2000	16	17	<1		<0.06	3.0	14	1.5	5800	<0.01	4.7	1	<2	<0.1	16	3.2
PH3c	2500	18	20	<1		<0.06	3.7	16	2.3	7400	<0.01	6.5	2	<2	<0.1	18	4.2
PH4a	2100	19	22	<1	<0.2	<0.06	2.1	13	1.4	7000	<0.01	4.2	2	<2	<0.1	18	2.7
PH4b	2100	18	21	<1		<0.06	2.0	13	1.3	6400	<0.01	4.0	2	<2	<0.1	17	2.5
PH4c	2000	18	20	<1		<0.06	1.9	13	1.4	6400	<0.01	4.0	2	<2	<0.1	17	2.5
Limit of Reporting	**20**	**1**	**0.05**	**1**	**0.2**	**0.06**	**0.2**	**0.2**	**0.2**	**5**	**0.01**	**0.4**	**1**	**<2**	**0.1**	**0.1**	**0.5**

* Low level analyses for As and Se are not NATA accredited.

Sediment samples for organic analyses were also analysed for Ag by NMI. In most cases the analysed sample was a composite of the 3 replicates.

Table 4: <63 µm sediment particle size fraction analyses

Location and site	<63 %	>63 µm %
Exmouth		
EX1a EX1b EX1c	11.3 6.6 11.2	88.7 93.4 88.8
EX3a EX3b EX3c	6.6 0.5 1.4	93.4 99.5 98.6
EX4a EX4b EX4c	2.1 2.9 2.2	97.9 97.1 97.8
EX5a EX5b EX5c	3.7 3.8 5.1	96.3 96.2 94.9
Ashburton River mouth		
AR1a AR1b AR1c	57.8 76.0 60.5	42.2 24.0 39.5
AR2a AR2b AR2c	47.4 47.2 38.4	52.6 52.8 61.6
AR3a AR3b AR3c	0.4 21.7 19.7	99.6 78.3 80.3
AR4a AR4b AR4c	23.7 8.0 15.8	76.3 92.0 84.2
Onslow		
ONS1a ONS1b ONS1c	23.6 35.1 24.2	76.4 64.9 75.8
ONS2a ONS2b ONS2c	16.6 21.9 21.5	83.4 78.1 78.5
ONS3a ONS3b ONS3c	10.4 6.9 6.9	89.6 93.1 93.1
ONS4a ONS4b ONS4c	13.3 24.0 22.8	86.7 76.0 77.2

Table 4: continued

Location and site	**<63 µm %**	**>63 µm %**
Dampier Archipelago		
DA1a DA1b DA1c	29.9 25.2 21.9	70.1 74.8 78.1
DA2a DA2b DA2c	20.8 21.7 19.8	79.2 78.3 80.2
DA3a DA3b DA3c	1.9 0.1 6.0	98.1 99.9 94.0
DA4a DA4b DA4c	1.3 5.3 1.6	98.7 94.7 98.4
Dampier Port		
DP1	12.3	87.7
DP2	8.3	91.7
DP3	35.3	64.7
DP4	63.1	36.9
Port Hedland		
PH1a PH1b PH1c	0.7 0.8 0.8	99.3 99.2 99.2
PH2a PH2b PH2c	0.3 1.7 0.5	99.7 98.3 99.5
PH3a PH3b PH3c	0.2 0.1 0.9	99.8 99.9 99.1
PH4a PH4b PH4c	0.3 0.1 0.3	99.7 99.9 99.7
Limit of Reporting (LOR)	**0.1**	**0.1**

Arsenic concentrations in the sediments were relatively high at most of the sites sampled except for the Dampier Archipelago and the outer Exmouth Gulf. Concentrations of chromium, copper, nickel, lead, vanadium and zinc tended to be higher in the sediments sampled from the Ashburton river mouth and Onslow locations than the other locations. The Exmouth sediments were particularly low in copper, nickel and zinc concentrations as were the outer Dampier Archipelago sites for zinc, vanadium and cobalt. Cobalt concentrations were relatively high in the sediments from sites EX1, EX2 and EX3.

The results of the particle size fractionation show that the proportion of the sampled sediments with grain sizes <63 µm was variable and is likely to be dependent on depth, tidal current speed, exposure and proximity to riverine sediment sources. The percentage of <63 µm particle sizes in sediments ranged from 40% – 80% near the mouth of the Ashburton River, 10% - 60% in Dampier Port, 20% – 30% at 2 sites in Dampier Archipelago, 10% - 25% at Onslow and the 2 sites distant from the Ashburton River mouth, 1% - 5% at Exmouth and the remaining 2 sites in Dampier Archipelago and <1% off Port Hedland.

The three normalisers (<63 µm particle size fraction, aluminium concentration and iron concentration) correlated well with each other (Table 5) indicating that aluminium and iron concentrations were related to particle size distribution. The data for each metal contaminant (except silver, cadmium, mercury and selenium) from the five reference location sites were graphed against the normalisers <63 µm particle size fraction and aluminium and iron concentration to investigate which would give the best correlation (see Appendix D). Silver and cadmium concentrations were below detection at all sites, mercury concentrations were below detection at almost all sites and selenium concentrations were below detection at over half the sites. Concentrations of aluminium and iron correlated well with most metal contaminant concentrations, with aluminium giving slightly better correlations overall. Both aluminium and iron predicted metal concentration significantly better than the <63 µm particle size fraction. Arsenic and cobalt concentrations appeared to be independent of normaliser concentrations and did not correlate with any of the normalisers.

Table 5 Correlation coefficients between the normalisers aluminium concentration, iron concentration and <63µm particle size fraction.

(Correlations in bold are significant at p<0.05)

	<63 µm vs Al	**<63 µm vs Fe**	**Al vs Fe**
Correlation coefficient (r)	**0.874**	**0.893**	**0.960**

The metal contaminant concentrations for chromium, copper, nickel, lead, vanadium and zinc were then normalized to the median aluminium concentration and graphed against aluminium concentration as a check on the quality of the normalization (the normalized concentration should not differ significantly and show no relation with the normaliser concentration). The plots are provided in Appendix E. The relationship between the normalized concentrations and the normaliser tended to break down in the sediments with very low aluminium concentrations. The implication is that another factor is also correlated with metal concentrations and that its influence on actual concentration only becomes significant in the coarser grained sediments that contain very little of the fine clay fraction. The normalized data for these 6 metals were used for subsequent statistical comparisons of sediment concentrations between the different sites. The metal data used for these comparisons are provided in Appendix F.

A Kruskal-Wallis test was applied to the data from all five reference locations to determine whether there were significant differences between the locations for each metal contaminant (except silver, cadmium, mercury and selenium) and the normaliser aluminium concentration. The results (Table 6) show that there were significant differences for all of the metals ($p < 0.01$).

Table 6. P-values from the Kruskal-Wallis tests comparing the five reference sites

(alpha is set at 0.05 and significant values shown in bold).

As	**Co**	**Cr**	**Cu**	**Ni**	**Pb**	**Se**	**V**	**Zn**
<0.0001	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**0.0014**

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 7). There appears to be no consistent discernible trend between the reference locations. The reference locations have grouped similarly for lead and vanadium and also for zinc and copper (and perhaps aluminium).

Table 7. Locations with statistically similar concentration ranges (bold) for the normaliser aluminium concentration and for each metal contaminant

Groups ordered from highest to lowest concentration.

Al	As	Co	Cr	Cu	Ni	Pb	V	Zn
AR	ONS	Ex	PHO	AR	PHO	**Ex, PHO**	**Ex, PHO**	
ONS	**AR, PHO**	**AR, ONS**	Ex	**ONS, DA, PHO**	DA	**AR, ONS, DA**	**AR, ONS, DA**	**ONS, DA, PHO**
DA, PHO	Ex	PHO	DA	Ex	AR			Ex
Ex	DA	DA	**AR, ONS**		**Ex, ONS**			

↓ Decreasing concentration

Metal concentrations from the two inshore sites at Port Hedland, Onslow and Ashburton River were compared with the two off shore sites for each location using the Mann Whitney non-parametric test (Table 8). The normalized concentrations for Cr, Cu, Ni, Pb, V and Zn were used in the test. Concentrations of aluminium did not vary significantly between inshore and offshore sites at Onslow or Port Hedland, however, the two inner sites on the Ashburton River mouth transect were significantly different from the two outer sites on the transect. This also corresponded to the observed differences in the proportion of <63 µm particles in the sediment. Of the measurable metals, only arsenic and nickel concentrations were not significantly different between the inshore and offshore sites at Ashburton River. At Onslow there was no significant difference between the inshore and offshore sites except for arsenic, and for Port Hedland there were minor but significant differences for chromium, nickel and zinc.

Natural background metal concentrations have been calculated for each of the reference sites and for the Pilbara marine sediments as a whole using the 80th percentile of the data (Table 9). The data used to calculate natural background concentrations for silver, cadmium, mercury and selenium included those sites where concentrations were less than the limit of reporting. For chromium, copper, nickel, lead, vanadium and zinc natural background concentrations have been calculated for both raw data and normalized data.

Table 8. 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)

	Al	As	Co	Cr	Cu	Ni	Pb	V	Zn
Ashburton River	**0.004**	0.193	**0.015**	**0.010**	**0.004**	0.333	**0.016**	**0.004**	**0.006**
Onslow	1.00	**0.003**	1.00	0.749	1.00	0.519	0.748	0.199	0.149
Port Hedland	0.198	0.627	0.108	**0.030**	0.054	**0.004**	0.873	1.00	**0.004**

Table 9. Estimated natural background concentrations of selected metals in Pilbara coastal marine sediments (units = mg/kg)

(estimates that exceed the national guidelines are in bold)

Metal	**Exmouth†**	**Ashburton River Mouth†**	**Onslow†**	**Dampier Archipelago†**	**Port Hedland†**	**Pilbara Coastal Sediments∆**	**National Guideline#** (ISQG-low)
Aluminium	1800	38800	12600	7220	2440	11000	-
Arsenic	17	20	**34**	10	20	**21**	20
Cadmium	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	1.5
Chromium (normalized*)	12.0 (21.0)	**90.8** (10.4)	31.8 (10.1)	37.4 (16.1)	16.8 (29.8)	32.0 (20.4)	80
Cobalt	23.6	8.3	8.8	5.3	3.0	8.7	-
Copper (normalized*)	0.8 (1.6)	47.2 (4.6)	9.5 (2.4)	5.4 (2.5)	1.7 (2.4)	7.8 (2.6)	65
Iron	7280	77200	36800	14960	7400	30400	-
Lead (normalized*)	1.8 (3.1)	14.8 (1.6)	5.0 (1.7)	2.8 (2.4)	2.0 (3.8)	5.0 (2.9)	50
Mercury	<0.01	0.03	<0.01	<0.01	<0.01	<0.01	0.15
Nickel (normalized*)	1.8 (3.1)	**42.0** (3.9)	11.8 (3.2)	14.1 (5.6)	5.4 (8.1)	12.0 (6.1)	21
Selenium	<0.1	0.2	0.2	0.1	<0.1	0.1	-
Silver	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	1
Vanadium (normalized*)	20.2 (36.1)	110.0 (14.5)	49.6 (20.6)	22.7 (21.2)	19.8 (33.7)	45.2 (28.1)	-
Zinc (normalized*)	1.9 (3.6)	77.0 (7.5)	20.2 (5.0)	13.2 (5.3)	3.4 (5.5)	17.4 (5.5)	200

* metal concentration normalized to 3150mg/kg Al.
\# Recommended sediment quality guideline (ISQG-low) from ANZECC & ARMCANZ (2000)
† n = 12
∆ n = 60

The estimated natural background arsenic concentrations for Onslow and for the Pilbara region both exceeded the national guideline. Arsenic concentrations were equal to the national guideline at the Ashburton River Mouth and Port Hedland. The national sediment quality guidelines for chromium and nickel were also exceeded in the Ashburton River mouth sediments, but easily met the guideline when the data were normalized to aluminium concentration.

Mann Whitney tests were performed on the data to determine whether concentrations of each metal in the Dampier Port sediments were statistically different from those of the Dampier Archipelago reference sites. The data used for the comparison, including the low level selenium analyses and normalized data for chromium, copper, nickel, lead, vanadium and zinc, are from Appendix F Zinc and arsenic were the only two metals to give a significant result (Table 10), with both metals at slightly elevated concentrations in the Port sediments. Interestingly, all other metal concentrations above the analytical limit of reporting were numerically lower in the Dampier Port samples compared to the reference sites, but the differences were not significant.

3.2 Organic chemicals

The results of the organic analyses are presented in Table 11 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.

Table 10. Dampier Port sediment quality compared with the Dampier Archipelago reference sites and national sediment quality guidelines (units = mg/kg)

(significant differences are shown in bold).

	DP vs DA Mann Whitney test P values (α = 0.05)	**Dampier Port median metal concentration**	**Natural Background (Dampier Archipelago)**	**National Guideline (ISQG-low)**
Aluminium	0.069			-
Arsenic	**0.014**	**12.5**	**10**	20
Cadmium		<0.06	<0.06	1.5
Chromium	0. 089	12.9	16.1	80
Cobalt	0. 078	4.7	5.3	-
Copper	0.467	2.3	2.5	65
Lead	0.761	1.7	2.4	50
Mercury		<0.01	<0.01	0.15
Nickel	0.856	4.3	5.6	21
Selenium	0.673	0.1	0.1	-
Silver		<0.2	<0.2	1
Vanadium	0.275	7.6	21.2	-
Zinc	**0.011**	**8.1**	**5.3**	200

Total organic carbon (TOC) results are presented in Table 12. Total organic carbon concentrations were relatively consistent between most of the locations. Highest concentrations were found in the sediment from the mouth of the Ashburton River (site AR1) and lowest concentrations were found in the Port Hedland samples. This trend was consistent with the sediment particle size results. 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 11: Organic chemical concentrations in marine sediments of the Pilbara region, June 2005, and National sediment quality guidelines (ANZECC & ARMCANZ, 2000)

NG = No guideline value;

Organic Chemical	Units (dry wt.)	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**
Polycyclic Aromatic Hydrocarbons					
Acenaphthene	mg/kg	<0.1	0.1	**0.016**	**0.500**
Acenaphthylene	mg/kg	<0.1	0.1	NG	NG
Anthracene	mg/kg	<0.1	0.1	**0.085**	**1.100**
Benz(a)anthracene	mg/kg	<0.1	0.1	**0.261**	**1.600**
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**	**1.600**
Chrysene	mg/kg	<0.1	0.1	**0.384**	**2.800**
Dibenzo(ah)anthracene	mg/kg	<0.1	0.1	**0.063**	**0.260**
Fluoranthene	mg/kg	<0.1	0.1	**0.600**	**5.100**
Fluorene	mg/kg	<0.1	0.1	**0.019**	**0.540**
Indeno(1,2,3-cd)pyrene	mg/kg	<0.1	0.1	NG	NG
Naphthalene	mg/kg	<0.1	0.1	**0.160**	**2.100**
Phenanthrene	mg/kg	<0.1	0.1	**0.240**	**1.500**
Pyrene	mg/kg	<0.1	0.1	**0.665**	**2.600**
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
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

Table 11 continued….

Organic Chemical	Units	Results for all samples	LOR	Guideline value	
				ISQG low	ISQG high
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**	**0.020**
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 12: Total organic carbon content of marine sediments in the Pilbara region, June 2005

Location and site	Total organic carbon	
	mg/kg	%
Exmouth		
EX1	6900	0.69
EX3	7000	0.70
EX4	4300	0.43
EX5	3100	0.31
Ashburton River mouth		
AR1a (replicate)	7000	0.70
AR1b (replicate)	13000	1.30
AR1c (replicate)	12000	1.20
AR2	7700	0.77
AR3	5200	0.52
AR4	2700	0.27
Onslow		
ONS1	5200	0.52
ONS2	4200	0.42
ONS3 A (field duplicate)	2100	0.21
ONS3 B (field duplicate)	2400	0.24
ONS4	4400	0.44
Dampier Archipelago		
DA1	4600	0.46
DA2	4000	0.40
DA3a (replicate)	4200	0.42
DA3b (replicate)	3700	0.37
DA3c (replicate)	3000	0.30
DA4	4500	0.45
Dampier Port		
DP1	5400	0.54
DP2	3500	0.35
DP3	2500	0.25
DP4	6200	0.62
Port Hedland		
PH1	1300	0.13
PH2	2000	0.20
PH3	1300	0.13
PH4	2400	0.24
Limit of Reporting (LOR)	**100**	**0.01**

4. General discussion

Surface sediments were sampled from six regional locations within the Pilbara Coastal Waters with the objective of broadly characterising natural background sediment quality for a range of selected contaminants and to determine whether the national sediment quality guidelines (ANZECC & ARMCANZ, 2000) were appropriate for use on these sediments. Only the surface 2 cm of sediment was sampled to ensure that the sampled sediments contained contemporary contaminant concentrations.

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 concentrations of equally contaminated sediment with different grain size distributions (Kersten and Smedes, 2002). Iron is also often used because iron oxides have a high metal binding capacity and are also strongly correlated to the clay fraction (as particle surface coatings).

Metal concentrations for all reference site data (except cadmium, mercury, selenium and silver) were plotted against <63 μm particle size fraction, aluminium and iron concentration to determine which would be the better normaliser. Concentrations of chromium, copper, nickel, lead, vanadium and zinc were highly correlated to aluminium and iron concentration but only moderately correlated with the <63 μm particle size fraction. This may be a consequence of the fact that both silt and clay particles are included in the <63 μm particle size fraction, whereas metals tend to have a high affinity for the finer clay particles (<2 μm). Concentrations of these metals were therefore normalized to the median aluminium concentration for the reference site samples (3150 mg/kg). Arsenic and cobalt correlated poorly with all three potential normalisers and therefore the unmodified analytical data for these metals were used in this report.

Metal concentrations varied between the five sampled reference locations, but did not exhibit a consistent trend except at the Ashburton River mouth where measured concentrations of chromium, copper, lead, nickel, vanadium and zinc were consistently high. These high concentrations were correlated with the high proportion of fine grains (<63 μm) in these sediments and the high aluminium and iron concentrations which generally reflect a high clay content in the sediment. When normalized to median aluminium concentration the metal concentrations in the sediments of the two Ashburton River Mouth sites were similar to concentrations found at other reference sites. However, when comparing inshore sites with offshore sites at the Ashburton River Mouth (Table 8) sediment concentrations of these 6 metals were still found to be significantly different. Although significant differences were also observed between inshore and offshore sediment concentrations of some metals at Onslow and Port Hedland, in absolute terms the differences were only minor and there was no consistent trend across all three reference locations.

Marine sediments naturally contain trace metals, but the concentrations are variable between regions and in nearshore waters they are dependent on the geology and mineraolgy of the adjacent area. Background concentrations calculated in this study (using normalized concentrations where calculated) appeared to be slightly elevated in some regions, but other areas appeared to exhibit regional depressions in the concentrations of some metals (Table 9). Cobalt was at relatively low concentrations in surface sediments at Port Hedland, but at relatively high concentrations in Exmouth sediments. On the other hand zinc and copper were found in low concentrations in Exmouth sediments, whereas chromium, lead and nickel were at relatively high concentrations at Port Hedland. Nevertheless, for almost all metals the sediment concentrations were well within the interim sediment quality guidelines (ISQG-low) recommended for national use (ANZECC & ARMCANZ, 2000). The exception was arsenic which was found to be consistently high at all locations except Dampier Archipelago. At Onslow in particular the arsenic content of the relatively pristine sediments (median = 24.5 mg/kg) exceeded the interim sediment quality guideline of 20 mg/kg. The implication is that the interim sediment quality guideline for arsenic may not be suitable for use across much of the marine environment of the Pilbara region and that alternative guidelines based on local data should be derived.

Table 13 Estimated background median or mean metal concentrations from Pilbara marine sediments and marine sediments from other Australian localities (mg/kg)

(Note: Normalised data not used for this comparison)

Metal	**Pilbara***	**Perth* (SMCWS)**	**Perth* (KIC)**	**Exmouth Gulf ****	**Gulf of Carpentaria****	**NT to Gulf of Carpentaria****	**Lake Macquarie#**
Aluminium	3150	310-3900	280	9199	28560	-	
Arsenic	18	2 - 16	2.5	-	-	<0.04 – 7.21	4.6 - 23
Cadmium	<0.06	<0.2 - 0.2	<0.1	~0.045	-	0.03 – 0.09	<0.1 – 0.2
Chromium	17	3.7 - 15	15	-	12	-	7 - 45
Cobalt	5.0	-	-	-	3	10.0 – 14.4	-
Copper	2.2	0.8 – 1.7	3.0	4.45	5	9.2 – 27.4	6 - 17
Iron	8100	-	-	20106	16087	34400 - 43400	-
Lead	2	3.5 – 6.0	1.1	3.73	6	12.0 – 19.3	5.5 - 17
Mercury	<0.01	<0.05	<0.1	-	-	-	<0.01 – 0.03
Nickel	5.5	1.9 – 4.6	1.8	-	6	18.3 – 24.4	11 - 57
Selenium	<0.01	-	<0.1	-	-	-	0.28 – 1.36
Silver	<0.2	-	0.6	-	-	-	<0.01 – 0.07
Vanadium	22	-	2	-	-	-	-
Zinc	5.4	1.3 – 3.5	1.7	-	20	39.8 – 54.1	12 - 68
Reference	**This study**	**Burt et al, 1995**	**KIC, 2000**	**Brunskill et al, 2001**	**Cox et al, 2003**	**Munksgaard et al, 2002.**	**Roach, 2005**

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

A comparison of sediment metal concentrations found in this study with relatively uncontaminated sediments from other selected regions around Australia shows that most metals are within a similar range of concentrations or slightly lower (Table 13). The most notable difference is the high arsenic concentrations measured in this Pilbara study compared to the other studies. The analytical methods used to analyse for arsenic in the Perth Southern Metropolitan Coastal Waters Study (SMCWS) were apparently biased high from an interference with calcium carbonate (R Masini, pers com). The range of medians reported in the table for the SMCWS study are therefore an over estimate of the actual concentrations. The high concentrations of arsenic reported in Pilbara marine sediments in this study is consistent with anecdotal reports of high levels of arsenic found in sediments in the vicinity of Exmouth Gulf and in groundwater near Roebourne. The source of these elevated arsenic concentrations is unknown. The only other notable difference in the concentrations tabulated below is that the concentrations of most metals found in marine sediments around the Northern Territory/Gulf of Carpentaria coastline and from Lake Macquarie are comparatively higher than in Western Australian sediments.

The results of the Mann Whitney tests and comparisons against the interim sediment quality guidelines recommended by ANZECC & ARMCANZ (2000) (Table 10) indicate that the sediments in the Dampier Port are relatively uncontaminated. Only two metals, arsenic and zinc, were found to be slightly elevated in Dampier Port samples compared to the Dampier Archipelago reference sediments, but both were 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 for Dampier Archipelago. There are a number of potential sources of contaminants in the port of Dampier (eg. gas refinery, ship loading facilities for iron ore, salt and other products, power station outfall and boating facilities), but the port is relatively well flushed by the strong tidal currents experienced throughout Mermaid Sound. There have also been two extensive dredging campaigns conducted in the southern end of Mermaid Sound over the last 2 years totaling more than 7 million cubic metres and which may have significantly affected the composition of surface sediments in the area. The resettlement of fine relatively uncontaminated sediment particles dredged from the deeper sediment layers and suspended in the water column may have diluted, or blanketed, the surrounding surface sediments with relatively clean sediment. Evidence of this latter process was observed at a number of locations when sampling the Dampier Port sediments. Three of the four sampling sites had to be relocated to avoid a 0.3 to >0.6 metre layer of a yellowish, very soft clay like material that had settled out and covered extensive areas of the seabed at the southeastern end of Mermaid Sound (Figure 3).

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 a recognition that other societal benefits also need to be considered and that these may preclude an objective of ‘no change’ in environmental quality. 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 first step in this decision framework is to measure the concentration of the contaminant that is potentially bioavailable and compare this against the ISQG (eg. dilute acid extractable metals or normalization to TOC for non-metallic contaminants). If the ISQG 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 considering all those factors that control bioavailability of the chemical, if the ISQG 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 sanctuary zones in Marine Conservation Reserves.

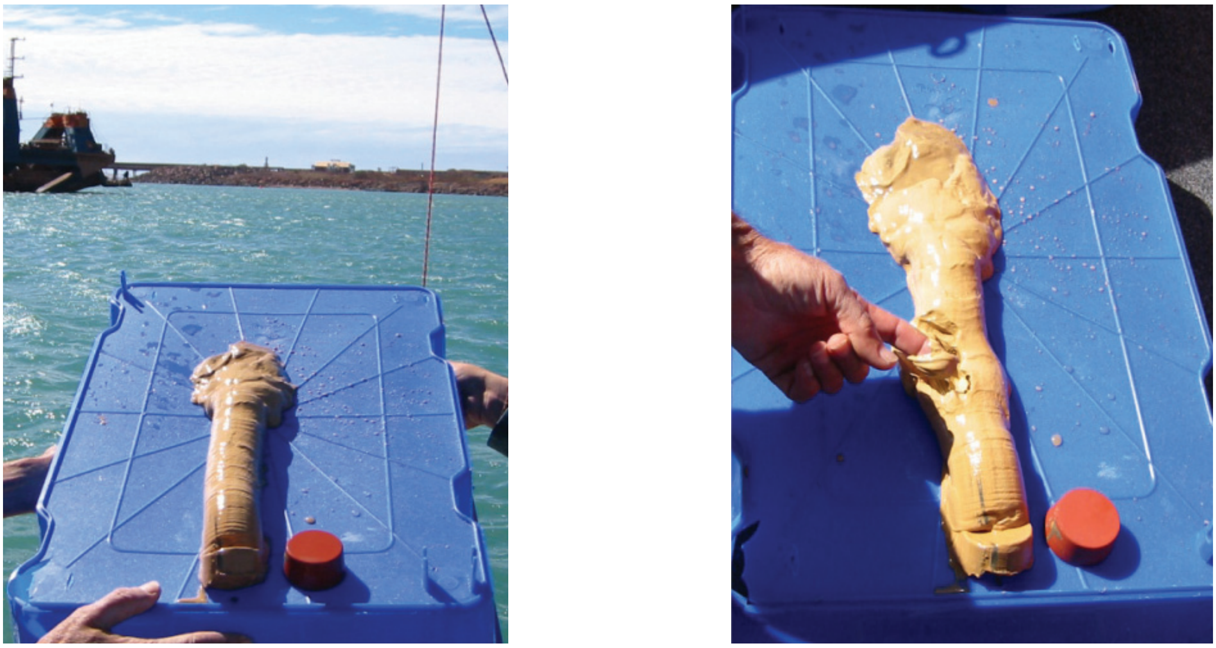

Figure 3: Sediment core taken from west of Parker Point, Dampier Port, showing the yellow clay-like material overlaying the original sediments

For the Pilbara coastal waters the ISQG from ANZECC & ARMCANZ (2000) are recommended for use in areas designated a high, moderate and low level of ecological protection with the exception of arsenic. In low ecological protection areas only the ISQG for those chemicals that have the potential to bioaccumulate/biomagnify would apply. For arsenic the estimated natural background concentrations in Table 9 that exceed 20 mg/kg should be used as the default total arsenic sediment quality guideline in those areas. Alternatively, site specific total arsenic guidelines could be derived for new areas, or dilute acid extractable concentrations could be compared against the national ISQG-low of 20mg/kg. 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 concentrations in Table 9 can be used as default guideline 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. For low ecological protection three times natural background median concentration is recommended, but only for those chemicals with the potential to bioaccumulate or biomagnify. 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.

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 Pilbara coastal waters are summarized in Table 14. Median concentrations for those metals that do not have a corresponding ISQG (see Table 8) are included in Table 15.

4.2 Organic chemicals

For the organic chemicals analysed (organotins, PAHs, BTEX, petroleum hydrocarbons, PCBs and pesticides) the natural background concentrations at the reference sites were not expected to be measurable, 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 ISQG were only available for some of the organic chemicals tested, but where guidelines were available the analytical limit of reporting was below the ISQG-low 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 across the north-west shelf. 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 Dampier Port was surprising, particularly for the organotins, given the number of ship movements through the port each year. As discussed for the metals, the reason is likely to be a result of the high degree of tidal flushing experienced in this area or the re-distribution and settlement of ‘new’ sediment across much of the southern end of Mermaid Sound. Several of the Dampier Port sampling sites had to be relocated to avoid a layer of sticky, yellow, fine clay-like sediment that was up to 50 cm deep covering the original grey sandy seabed (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 followed a similar trend to the <63 m particle size fraction with highest concentrations found at the two Ashburton River Mouth sites and lowest concentrations measured in Port Hedland samples. 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 14 for the four different levels of ecological protection proposed for the Pilbara coastal waters 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.

Table 14. Summary of recommended sediment quality guidelines for the Pilbara coastal waters

Level of ecological protection	ISQG available	ISQG exceeded by natural background	No ISQG available
Maximum	***(All metals)*** Use estimated natural background (Table 9); 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 9); 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	(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.	***(As)*** Use estimated natural background concentration (Table 9); or Compare dilute acid extractable concentration with ISQG.	***(eg. Al, Co, Fe, Se, V)*** Use median of natural background concentration multiplied by 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	***(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.	***(As)*** Use estimated natural background concentration (Table 9); or Compare dilute acid extractable concentration with ISQG.	***(eg. Al, Co, Fe, Se, V)*** Use median of natural background concentration multiplied by factor of 2*. ***(Organic chemicals)*** No detectable concentration 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.

Table 15. Median concentrations of selected metals in marine sediments of the Pilbara

(n = 12 for reference location estimates and n = 60 for Pilbara coastal sediments)

Metal	Exmouth	Ashburton River Mouth	Onslow	Dampier Archipelago	Port Hedland	Pilbara Coastal Sediments
Aluminium	1600	21500	10500	2800	2050	3150
Cobalt	9.2	6.0	5.7	1.2	2.2	5.0
Iron	5000	51500	29000	4750	6650	8100
Selenium	<0.1	0.2	0.1	0.1	<0.1	<0.1
Vanadium (normalized*)	13 (32)	79 (12)	43 (12)	9 (11)	18 (27)	22 (19)

* metal concentration normalized to 3150mg/kg Al.

5. Conclusion

This survey provides important information on baseline concentrations of selected trace metals and organic chemicals in the marine sediments of the Pilbara region. The sediment survey results show that the concentrations of metals are generally within the range of concentrations measured in sediments around Australia. Concentrations of cadmium, mercury, silver, selenium and the selected organic chemicals were too low for the chosen analytical laboratories to adequately quantify. 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.

Metal concentrations across the five sampled reference locations were variable with no specific trends except in the sediments of the Ashburton River Mouth which contained high concentrations of a number of metals in association with the fine muddy sediments. These sediments were very high in aluminium and iron concentration which suggests a high clay content.

Concentrations of chromium, copper, nickel, lead, vanadium and zinc were highly correlated to aluminium and iron content. Normalisation of these 6 metals to aluminium concentration is therefore suggested to account for the influence of variable sediment structure and composition on the metal concentrations.

Estimates of natural background sediment concentration for 14 metals have been provided for the Pilbara region (Table 9). Estimated natural background concentrations of chromium and nickel exceeded the ISQG–low (ANZECC & ARMCANZ (2000) at the Ashburton River Mouth prior to normalisation to aluminium concentration. Arsenic concentrations were generally high across all of the sampled sites, except Dampier Archipelago, and natural background concentrations were close to or above the recommended interim sediment quality guideline.

Slight elevations in arsenic and zinc were detected in the sediments of an industrialized port. However, the differences in absolute terms were very small and the concentrations were well below the ISQG recommended for use nationally. The sediment sampling sites in the port were located well away from shipping facilities and may have been affected by recent dredging activity.

Based on the findings of this study a set of sediment quality guidelines for use in Pilbara coastal waters have been recommended in Table 14. Natural background sediment concentrations for all the contaminants measured in this study, except total arsenic, were below the interim sediment quality guidelines recommended for use in Australia (ANZECC & ARMCANZ, 2000). 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. This holds for all metals except total arsenic, where it is recommended that the estimated natural background concentrations in Table 9 be adopted or dilute acid extractable arsenic concentrations be measured for comparison against the ISQG-low. For areas designated a maximum level of ecological protection the estimated natural background concentrations (Table 9) should be used as default sediment quality guidelines, or alternatively site specific guidelines developed from local reference site data. In sediments with a high concentration of <63 μm sized particles this study found it beneficial to normalise the analysed concentrations of chromium, copper, lead, nickel, vanadium and zinc to aluminium concentration.

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 or other point or diffuse source discharges in the region. A fundamental baseline from which to assess local and regional changes in water quality in years to come has been established.

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Appendices

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.

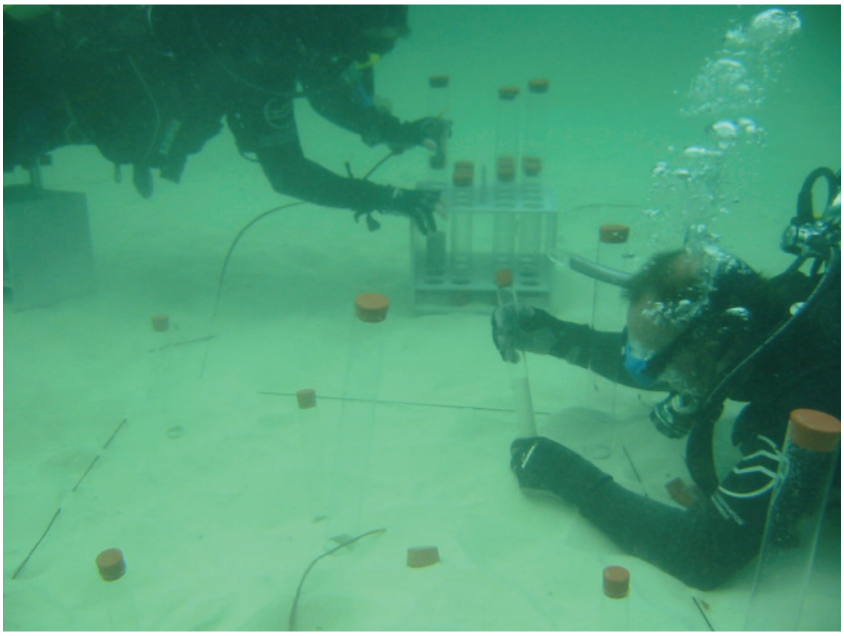


Figure 1. Divers collecting sediment cores from 1 m^2 quadrat.

Two different methods for the collection and retrieval of the cores were used:

- Free-divers deploying the cores by hand and delivering to the boat (Exmouth sites, DA3 and DA4);
- Deployment of a modified Wildco 2401-B20 KB heavy corer from the boat and retrieval by winch.

Sediment cores collected by free-divers were taken by forcing the tube into the sediment to at least a 10 cm depth, plugging the top of the core, tilting it slightly and scraping away sufficient sediment to plug the bottom of the core and then retrieving it. Three replicates of five cores each were taken at each sampling site. One core was taken from each corner and in the centre of a randomly located 1 m^2 quadrat. Quadrats were located approximately 10 metres apart.

Figure 1. Wildco 2401-B20 KB heavy corer being deployed using the gantry and winch on the Department of Environment research vessel Zoila (note the spherical stopper attached to the fishing line and threaded through the core tube).

To collect sediment cores using the Wildco corer, the corer was attached to a spectra rope that was in turn attached to the boats gantry arm which held the corer about one metre from the boat hull. It would be allowed to free fall into the sediment and a neoprene plunger would then seal the top of the corer. The corer was then pulled out of the sediment and the bottom of the corer sealed with a spherical stopper pulled into position using a separate fishing line that passed through the corer and was attached to a fishing rod. The corer was then retrieved by the gantry winch and the fishing line wound in at the same rate to keep the pressure on the stopper and prevent the sediment core from escaping. Five cores were taken in this way for the first replicate at each site, then the anchor rope was let out approximately 10 metres and another 5 cores taken. This was repeated again for the third replicate.

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 replicate sample for metal analyses and the three replicates taken for organic analysis at sites AR1 and DA3. All other samples for organic chemical analyses, and the Dampier Port metal samples, were composed of all 15 cores taken for each site. Approximately 50 mLs 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 by ensuring that staff handling the samples wore powderless disposable vinyl gloves and the workspace was covered with clean plastic sheeting. The polycarbonate core tubes were washed in clean seawater between each sampling site.

Samples for total metal analysis and particle size fractionation were stored in the dark on ice and delivered to the respective analytical laboratories at the end of the field program (13 days from the collection of the first samples at Exmouth). The samples for organic chemical and total silver analysis were also stored in the dark on ice whilst in the field and then were couriered to the laboratory and received within 7 days of collection.

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 clumps of sediment 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 sediment 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 μm. 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 HNO_3 (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 50°C 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 a laboratory standard reference material were analysed for every batch of approximately 10 samples and recoveries calculated for the laboratory standard material. The laboratory standard reference material is tested once every month against the certified reference material TH-2 (a Toronto Harbour Sediment for Trace Elements) from the National Water Research Institute of Canada (www.nwri.ca).

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) 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).

Abalos, M., Bayona,J., Compano, R., Grandos, M., Leal, C., Prat, M., “ Analytical Procedures for the determination of organotin compounds in sediment and Biota: a critical review”, *Journal of Chromatography A*, 788, 1-49 (1997).

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 back-flushed 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 sulfate and tumbled with hexane/acetone using a rotating shaker. If required, the extract is cleaned up by Gel Permeation Chromatography (GPC) and/or sulfur removal. The final extract is analysed by GC-NPD and confirmed by GCMS-NCI (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 sulfate 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 sulfur removal. The final extract is analysed by GC-ECD and confirmed by GCMS-NCI.

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 infra-red 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: 28/7/05
Reference: DOE05-12
COC#: 24261, 24642, 24643, 24644, 24645, 24646

METHOD		ICP002	ICP002	ICP002	ICP002	ICP002	ICP002	ICP002	ICP002	ICP002	ICP002	ICP002	ICP007		ICP004	ICP002	ICP004
SAMPLE CODE		Ag	Al	Cd	Co	Cr	Cu	Fe	Ni	Pb	V	Zn	Hg	As	As	Se	Se
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Reporting Limit		<1	<20	<0.06	<0.2	<0.2	<0.2	<5	<0.4	<1	<0.1	<0.5	<0.01	<1	<0.05	<2	<0.1
File		05071801	05071801	05071801	05071801	05071801	05071801	05071801	05071801	05071801	05071801	05071801	05072001-2002-2102	5071801	05072201-2701	5071801	05072201-2701
Batch samples: Ex1a, Ex1b, Ex1c, Ex2a, Ex3a, Ex3b, Ex3c, Ex4a, Ex4b, Ex4c																	
	Duplicate	-	4%	-	3%	2%	4%	4%	2%	11%	2%	4%	-	1%	1%	-	-
	Recovery	101%	96%	102%	102%	100%	104%	100%	100%	104%	101%	103%	99%	99%	85%	100%	87%
Batch samples: Ex5a, Ex5b, Ex5c, Ar1a, Ar1b, Ar1c, Ar2a, Ar2b, Ar2c																	
	Duplicate	-	3%	-	1%	1%	1%	1%	1%	2%	1%	1%	3%	6%	6%	-	5%
	Recovery	102%	98%	99%	101%	101%	103%	102%	101%	102%	101%	99%	100%	96%		102%	
Batch samples: Ar3a, Ar3b, Ar3c, Ar4a, Ar4b, Ar4c, Ons1a, Ons1b, Ons1c, Ons2a																	
	Duplicate	-	0%	-	2%	1%	3%	2%	4%	2%	2%	2%		2%	2%	-	2%
	Recovery	104%	99%	105%	105%	103%	107%	103%	103%	107%	104%	106%		101%		95%	

Batch samples: Ons2b, Ons2c, Ons3a, Ons3b, Ons3c, Ons4a, Ons4b, Ons4c, DP1																	
	Duplicate	-	1%	-	1%	0%	1%	1%	0%	4%	1%	1%	-	5%	2%	-	-
	Recovery	100%	101%	99%	100%	100%	102%	104%	100%	98%	101%	99%	98%	101%	106%	92%	102%
Batch samples: Dp2, Dp3, Dp4, Da1a, Da1b, Da1c, Da2a, Da2b, Da2c, Da3a																	
	Duplicate	-	3%	-	5%	3%	7%	2%	3%	-	8%	1%	-	6%	5%	-	-
	Recovery	102%	104%	104%	101%	102%	103%	104%	102%	102%	101%	102%	99%	102%	104%	104%	107%
Batch samples: Da3b, Da3c, Da4a, Da4b, Da4c, Pho1a, Pho1b, Pho1c, Pho2a, Pho2b																	
	Duplicate	-	1%	-	0%	1%	4%	6%	8%	0%	6%	3%		10%	5%	-	-
	Recovery	103%	112%	99%	104%	105%	105%	107%	105%	102%	104%	102%		99%	105%	100%	103%
Batch samples: Pho2c, Pho3a, Pho3b, Pho3c, Pho4a, Pho4b, Pho4c																	
	Duplicate	-	3%	-	0%	2%	2%	2%	7%	4%	1%	3%		3%	0%	-	-
	Recovery	102%	98%	101%	101%	101%	102%	103%	101%	101%	101%	100%		101%		101%	
Sample replicates																	
Ex5a (I)		<1	1300	<0.06	0.5	6.7	0.7	3800	1.2	1	12	9.8	<0.01	8	7.6	<2	0.1
Ex5a (ii)		<1	1300	<0.06	11	6.7	0.6	3700	1	<1	11	1.3	<0.01	7	7	<2	<0.1
Ons3c (I)		<1	5600	<0.06	4.1	18	3.1	24000	5.6	3	40	7.6	<0.01	36	39	<2	<0.1
Ons 3c (ii)		<1	5300	<0.06	4	18	3.1	23000	5.5	3	39	7.1	<0.01	36	41	<2	<0.1

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

Organotins

Exmouth

Analyte	LOR	Blank	LCS	Sample Duplicates			Matrix Spike
			Recovery	Sample	Duplicate	RPD	Recovery
	ng/g	ng/g	ng/g	ng/g	mg/kg	%	%
Organotin				**N05/016646**			
Monobutyltin	0.50	<0.50	84	<0.50	<0.50	-	78
Dibutyltin	0.50	<0.50	87	<0.50	<0.50	-	91
Tributyltin	0.50	<0.50	91	<0.50	<0.50	-	96

Ashburton River, Onslow, Dampier archipelago and Dampier Port

Analyte	LOR	Blank	LCS	Sample Duplicates			Matrix Spike
			Recovery	Sample	Duplicate	RPD	Recovery
	ng/g	ng/g	ng/g	ng/g	mg/kg	%	%
Organotin				**N05/016646**			
Monobutyltin	0.50	<0.50	84	<0.50	<0.50	-	78
Dibutyltin	0.50	<0.50	87	<0.50	<0.50	-	91
Tributyltin	0.50	<0.50	91	<0.50	<0.50	-	96

Port Hedland

Analyte	LOR	Blank	LCS
			Recovery
	ng/g	ng/g	ng/g
Organotin			
Monobutyltin	0.50	<0.50	84
Dibutyltin	0.50	<0.50	87
Tributyltin	0.50	<0.50	91

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 : AGAL Method NR35
RPD= Relative Percentage Difference.

BTEX, TPH and PAH

Exmouth

Analyte	LOR	Blank	LCS
			Recovery
	mg/kg	mg/kg	%
BTEX			
Benzene	0.50	<0.50	71
Toluene	0.50	<0.50	72
Ethyl Benzene	0.50	<0.50	71
m, p - Xylene	1.0	<1.0	72
o-Xylene	0.50	<0.50	71
TPH			
TPH C6-C9	25	<25	71
TPH C10-C14	50	<50	106
TPH C15-C28	100	<100	109
TPH C29-C36	100	<100	-
PAH			
Naphthalene	0.10	<0.10	103
Acenaphthylene	0.10	<0.10	-
Acenaphthene	0.10	<0.10	-
Fluorene	0.10	<0.10	102
Phenanthrene	0.10	<0.10	103
Anthracene	0.10	<0.10	-
Fluoranthene	0.10	<0.10	-
Pyrene	0.10	<0.10	-
Benz[a]anthracene	0.10	<0.10	-
Chrysene	0.10	<0.10	101
Benzo[b]&[k]fluoranthene	0.20	<0.20	-
Benzo[a]pyrene	0.10	<0.10	100
Indeno[1_2_3-cd]pyrene	0.10	<0.10	-
Dibenz[ah]anthracene	0.10	<0.10	102
Benzo[ghi]perylene	0.10	<0.10	-
Surrogate 1 Recovery	-	-	98
Surrogate 2 Recovery	-	-	100

Ashburton River, Onslow, Dampier archipelago and Dampier Port

Analyte	**LOR**	**Blank**	**LCS**	**Sample Duplicates**			**Matrix Spike**
			Recovery	**Sample**	**Duplicate**	**RPD**	**Recovery**
	mg/kg	**mg/kg**	**%**	**mg/kg**	**mg/kg**	**%**	**%**
BTEX				**W05/011646**			**Blank Soil**
Benzene	0.50	<0.50	82	<0.50	<0.50	-	106
Toluene	0.50	<0.50	89	<0.50	<0.50	-	110
Ethyl Benzene	0.50	<0.50	91	<0.50	<0.50	-	111
m, p - Xylene	1.00	<1.0	98	<1.0	<1.0	-	118
o-Xylene	0.50	<0.50	95	<0.50	<0.50	-	109
TPH				**W05/011646**			**Blank Soil**
TPH C6-C9	25	<25	78	<25	<25	-	111
				W05/011654			**Blank Soil**
TPH C10-C14	50	<50	104	<50	<50	-	106
TPH C15-C28	100	<100	106	<100	<100	-	108
TPH C29-C36	100	<100	-	<100	<100	-	-
PAH				**W05/011463**			**Blank Soil**
Naphthalene	0.1	<0.1	82	<0.1	<0.1	-	87
Acenaphthylene	0.1	<0.1	-	<0.1	<0.1	-	-
Acenaphthene	0.1	<0.1	-	<0.1	<0.1	-	-
Fluorene	0.1	<0.1	75	<0.1	<0.1	-	80
Phenanthrene	0.1	<0.1	75	<0.1	<0.1	-	80
Anthracene	0.1	<0.1	-	<0.1	<0.1	-	-
Fluoranthene	0.1	<0.1	-	<0.1	<0.1	-	-
Pyrene	0.1	<0.1	-	<0.1	<0.1	-	-
Benz[a]anthracene	0.1	<0.1	-	<0.1	<0.1	-	-
Chrysene	0.1	<0.1	74	<0.1	<0.1	-	80
Benzo[b]&[k]fluoranthene	0.2	<0.2	-	<0.2	<0.2	-	-
Benzo[a]pyrene	0.1	<0.1	70	<0.1	<0.1	-	70
Indeno[1_2_3-cd]pyrene	0.1	<0.1	-	<0.1	<0.1	-	-
Dibenz[ah]anthracene	0.1	<0.1	75	<0.1	<0.1	-	79
Benzo[ghi]perylene	0.1	<0.1	-	<0.1	<0.1	-	-
Surrogate 1 Recovery	-	-	103	99	99	-	83
Surrogate 2 Recovery	-	-	99	98	97	1.0	104

Port Hedland

Analyte	**LOR**	**Blank**	**LCS**
			Recovery
	mg/kg	**mg/kg**	**%**
BTEX			
Benzene	0.50	<0.50	70
Toluene	0.50	<0.50	72
Ethyl Benzene	0.50	<0.50	77
m, p - Xylene	1.0	<1.0	79
o-Xylene	0.50	<0.50	79
TPH			
TPH C6-C9	25	<25	75
TPH C10-C14	50	<50	98
TPH C15-C28	100	<100	96
TPH C29-C36	100	<100	-
PAH			
Naphthalene	0.1	<0.1	100
Acenaphthylene	0.1	<0.1	-
Acenaphthene	0.1	<0.1	-
Fluorene	0.1	<0.1	92
Phenanthrene	0.1	<0.1	95
Anthracene	0.1	<0.1	-
Fluoranthene	0.1	<0.1	-
Pyrene	0.1	<0.1	-
Benz[a]anthracene	0.1	<0.1	-
Chrysene	0.1	<0.1	100
Benzo[b]&[k]fluoranthene	0.2	<0.2	-
Benzo[a]pyrene	0.1	<0.1	96
Indeno[1_2_3-cd]pyrene	0.1	<0.1	-
Dibenz[ah]anthracene	0.1	<0.1	96
Benzo[ghi]perylene	0.1	<0.1	-
Surrogate 1 Recovery	-	-	84
Surrogate 2 Recovery	-	-	89

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 pesiticides and PCBs

Exmouth

Analyte	**LOR**	**Blank**	**LCS**
			Recovery
	mg/kg	**mg/kg**	**%**
OC Pesticides			
HCB	0.0010	<0.0010	-
Heptachlor	0.0010	<0.0010	96
Heptachlor epoxide	0.0010	<0.0010	-
Aldrin	0.0010	<0.0010	126
gamma-BHC (Lindane)	0.0010	<0.0010	102
alpha-BHC	0.0010	<0.0010	-
beta-BHC	0.0010	<0.0010	-
delta-BHC	0.0010	<0.0010	-
trans-Chlordane	0.0010	<0.0010	-
cis-Chlordane	0.0010	<0.0010	-
Oxychlordane	0.0010	<0.0010	-
Dieldrin	0.0010	<0.0010	86
pp-DDE	0.0010	<0.0010	-
pp-DDD	0.0010	<0.0010	-
pp-DDT	0.0010	<0.0010	64
Endrin	0.0010	<0.0010	82
Endrin Aldehyde	0.0010	<0.0010	-
Endrin Ketone	0.0010	<0.0010	-
alpha-Endosulfan	0.0010	<0.0010	-
beta-Endosulfan	0.0010	<0.0010	-
Endosulfan Sulfate	0.0010	<0.0010	-
Methoxychlor	0.0010	<0.0010	-
Surrogate OC Rec.		97	100
PCB Compounds			
PCB	0.010	<0.010	101
OP Pesticides			
Dichlorvos	0.10	<0.10	-
Demeton-S-Methyl	0.10	<0.10	-
Diazinon	0.10	<0.10	88
Dimethoate	0.10	<0.10	-
Chlorpyrifos	0.10	<0.10	84
Chlorpyrifos Methyl	0.10	<0.10	-
Malathion (Maldison)	0.10	<0.10	-
Fenthion	0.10	<0.10	-
Ethion	0.10	<0.10	88
Fenitrothion	0.10	<0.10	-
Chlorfenvinphos (E)	0.10	<0.10	-
Chlorfenvinphos (Z)	0.10	<0.10	-
Parathion (Ethyl)	0.10	<0.10	88
Parathion Methyl	0.10	<0.10	-
Pirimiphos Ethyl	0.10	<0.10	-
Pirimiphos Methyl	0.10	<0.10	-
Azinphos Methyl	0.10	<0.10	-
Azinphos Ethyl	0.10	<0.10	-
Surrogate OP Rec.		135	137

Ashburton River, Onslow, Dampier archipelago and Dampier Port

Analyte	LOR	Blank	LCS	Sample Duplicates			Matrix Spike
			Recovery	Sample	Duplicate	RPD	Recovery
	mg/kg	mg/kg	%	mg/kg	mg/kg	%	%
OC Pesticides				**W05/011664**			**Blank Soil**
HCB	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Heptachlor	0.0010	<0.0010	100	<0.0010	<0.0010	-	104
Heptachlor epoxide	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Aldrin	0.0010	<0.0010	110	<0.0010	<0.0010	-	126
gamma-BHC (Lindane)	0.0010	<0.0010	90	<0.0010	<0.0010	-	102
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	94	<0.0010	<0.0010	-	106
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	128	<0.0010	<0.0010	-	112
Endrin	0.0010	<0.0010	104	<0.0010	<0.0010	-	108
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 Sulfate	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Methoxychlor	0.0010	<0.0010	-	<0.0010	<0.0010	-	-
Surrogate OC Rec.			95	122	135	9.5	123
PCB Compounds				**W05/011664**			**Blank Soil**
PCB	0.010	<0.010	98	<0.10	<0.10	-	78
OP Pesticides				**W05/011664**			**Blank Soil**
Dichlorvos	0.10	<0.10	-	<0.10	<0.10	-	-
Demeton-S-Methyl	0.10	<0.10	-	<0.10	<0.10	-	-
Diazinon	0.10	<0.10	100	<0.10	<0.10	-	112
Dimethoate	0.10	<0.10	-	<0.10	<0.10	-	-
Chlorpyrifos	0.10	<0.10	104	<0.10	<0.10	-	132
Chlorpyrifos Methyl	0.10	<0.10	-	<0.10	<0.10	-	-
Malathion (Maldison)	0.10	<0.10	-	<0.10	<0.10	-	-
Fenthion	0.10	<0.10	-	<0.10	<0.10	-	-
Ethion	0.10	<0.10	96	<0.10	<0.10	-	128
Fenitrothion	0.10	<0.10	-	<0.10	<0.10	-	-
Chlorfenvinphos (E)	0.10	<0.10	-	<0.10	<0.10	-	-
Chlorfenvinphos (Z)	0.10	<0.10	-	<0.10	<0.10	-	-
Parathion (Ethyl)	0.10	<0.10	88	<0.10	<0.10	-	132
Parathion Methyl	0.10	<0.10	-	<0.10	<0.10	-	-
Pirimiphos Ethyl	0.10	<0.10	-	<0.10	<0.10	-	-
Pirimiphos Methyl	0.10	<0.10	-	<0.10	<0.10	-	-
Azinphos Methyl	0.10	<0.10	-	<0.10	<0.10	-	-
Azinphos Ethyl	0.10	<0.10	-	<0.10	<0.10	-	-
Surrogate OP Rec.			79	98	87	12	97

Port Hedland

Analyte	LOR	Blank	LCS
			Recovery
	mg/kg	mg/kg	%
OC Pesticides			
HCB	0.0010	<0.0010	-
Heptachlor	0.0010	<0.0010	110
Heptachlor epoxide	0.0010	<0.0010	-
Aldrin	0.0010	<0.0010	128
gamma-BHC (Lindane)	0.0010	<0.0010	106
alpha-BHC	0.0010	<0.0010	-
beta-BHC	0.0010	<0.0010	-
delta-BHC	0.0010	<0.0010	-
trans-Chlordane	0.0010	<0.0010	-
cis-Chlordane	0.0010	<0.0010	-
Oxychlordane	0.0010	<0.0010	-
Dieldrin	0.0010	<0.0010	78
pp-DDE	0.0010	<0.0010	-
pp-DDD	0.0010	<0.0010	-
pp-DDT	0.0010	<0.0010	126
Endrin	0.0010	<0.0010	104
Endrin Aldehyde	0.0010	<0.0010	-
Endrin Ketone	0.0010	<0.0010	-
alpha-Endosulfan	0.0010	<0.0010	-
beta-Endosulfan	0.0010	<0.0010	-
Endosulfan Sulfate	0.0010	<0.0010	-
Methoxychlor	0.0010	<0.0010	-
Surrogate OC Rec.			97
PCB Compounds			
PCB	0.010	<0.010	82
OP Pesticides			
Diazinon	0.10	<0.10	95
Dimethoate	0.10	<0.10	-
Chlorpyrifos	0.10	<0.10	104
Chlorpyrifos Methyl	0.10	<0.10	-
Malathion (Maldison)	0.10	<0.10	-
Fenthion	0.10	<0.10	-
Ethion	0.10	<0.10	100
Fenitrothion	0.10	<0.10	-
Chlorfenvinphos (E)	0.10	<0.10	-
Chlorfenvinphos (Z)	0.10	<0.10	-
Parathion (Ethyl)	0.10	<0.10	100
Parathion Methyl	0.10	<0.10	-
Pirimiphos Ethyl	0.10	<0.10	-
Pirimiphos Methyl	0.10	<0.10	-
Azinphos Methyl	0.10	<0.10	-
Azinphos Ethyl	0.10	<0.10	-
Surrogate OP Rec.			89

LCS = Laboratory Control Spike

Results expressed in percentage (%) or mg/kg wherever appropriate.

‘ - ‘ = Not Applicable.

Method used : NMI 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%.

Total Organic Carbon

Exmouth

Analyte	Method	LOR	Blank	Duplicates			Recoveries	
				1	2	RPD	Matrix spk	LCS
		mg/kg	mg/kg	mg/kg	mg/kg	%	%	%
Waters Section								
Carbon-Total organic	NWS15	100	<100	NA	NA	NA	NA	89

Ashburton River, Onslow, Dampier archipelago and Dampier Port

Analyte	Method	LOR	Blank	Duplicates			Recoveries	
				1	2	RPD	Matrix spk	LCS
		mg/kg	mg/kg	mg/kg	mg/kg	%	%	%
Waters Section				**W05/011648**			**W05/011648**	
Carbon-Total organic	NWS15	100	<100	11000	12000	9	94	83

Port Hedland

Analyte	Method	LOR	Blank	Duplicates			Recoveries	
				1	2	RPD	Matrix spk	LCS
		mg/kg	mg/kg	mg/kg	mg/kg	%	%	%
Waters Section				**W05/011882**			**W05/011882**	
Carbon-Total organic	NWS15	100	<100	1300	1300	0	87	83

Legend

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

Silver (low level)

Exmouth

Analyte	Method	LOR	Blank	Duplicates			Recoveries	
				1	2	RPD	Matrix spk	LCS
				W05/011145			W05/011145	AGAL10, Sediment
		mg/kg	mg/kg	mg/kg	mg/kg	%	%	%
Silver	NT2.49	0.2	<0.2	<0.2	<0.2	ND	93	111

Ashburton River, Onslow, Dampier archipelago and Dampier Port

Analyte	Method	LOR	Blank	Duplicates			Duplicates			Recoveries	
				1	2	RPD	1	2	RPD	Matrix spk	LCS
				W05/011646			W05/011659			W05/011646	AGAL10, Sediment
		mg/kg	mg/kg	mg/kg	mg/kg	%	mg/kg	mg/kg	%	%	%
Silver	NT2.49	0.2	<0.2	<0.2	<0.2	ND	<0.2	<0.2	ND	92	102

Port hedland

Analyte	Method	LOR	Blank	Duplicates			Recoveries	
				1	2	RPD	Matrix spk	LCS
				W05/011882			W05/011882	AGAL10, Sediment
		mg/kg	mg/kg	mg/kg	mg/kg	%	%	%
Silver	NT2.49	0.2	<0.2	<0.2	<0.2	ND	NA	104

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

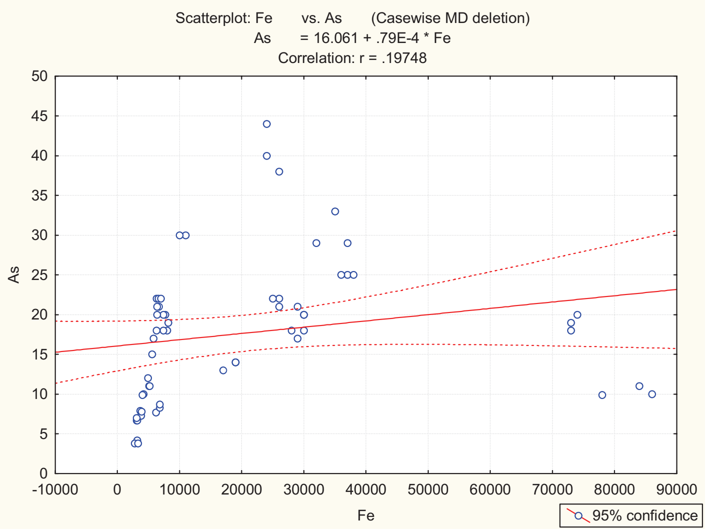
NA: Not applicable
LCS: Laboratory Control
Sample
#: Spike level is less than 50% of the sample's concentration, hence the recovery data is not reliable.

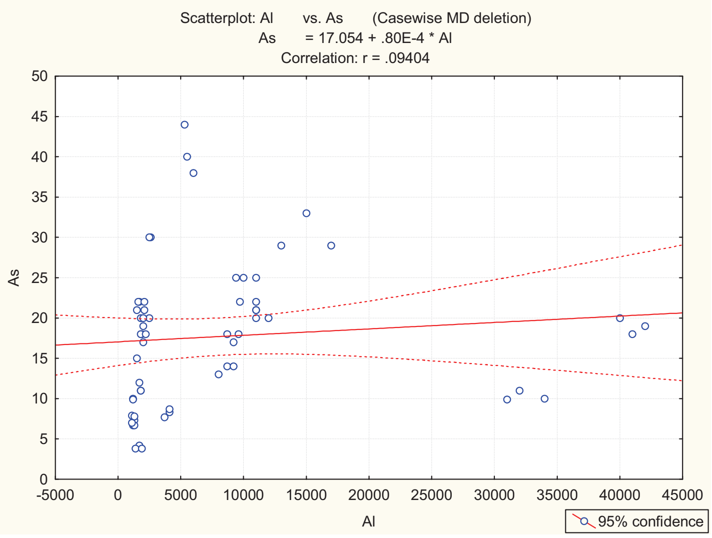
Comments:
Results greater than ten times LOR have been rounded to two significant
figures.

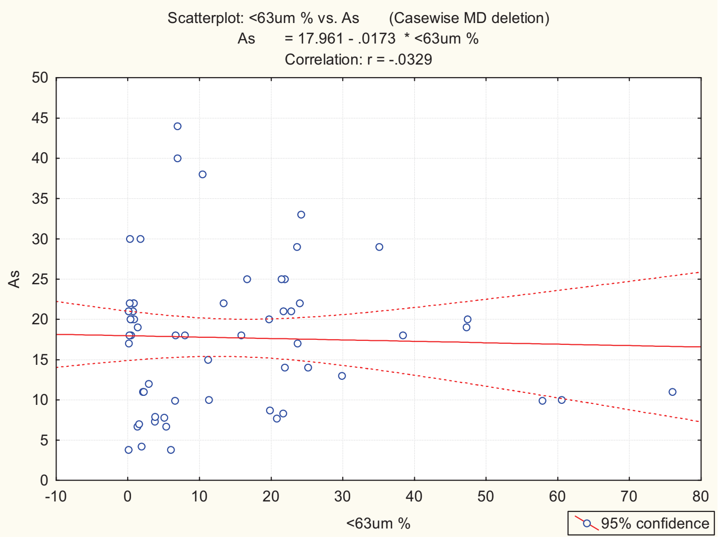
Appendix D: Graphs of reference site metal concentrations against the three potential normalisers

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

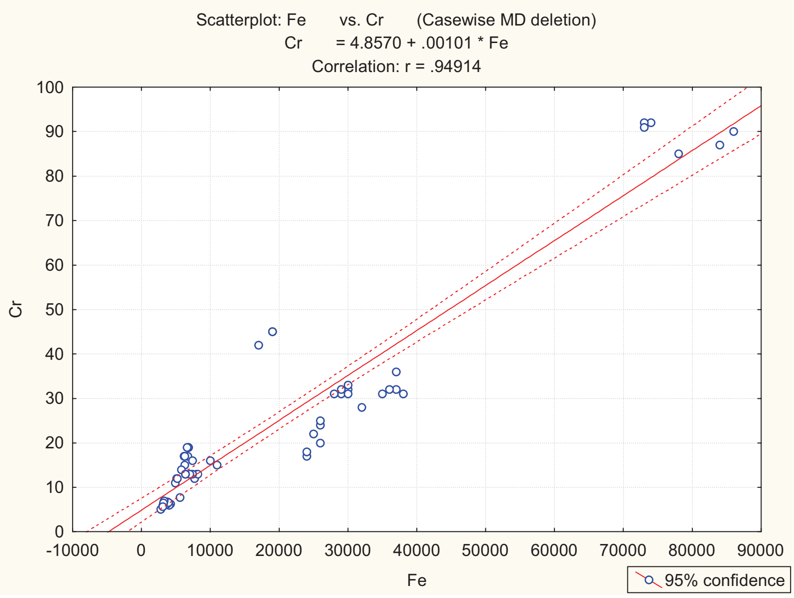
Arsenic

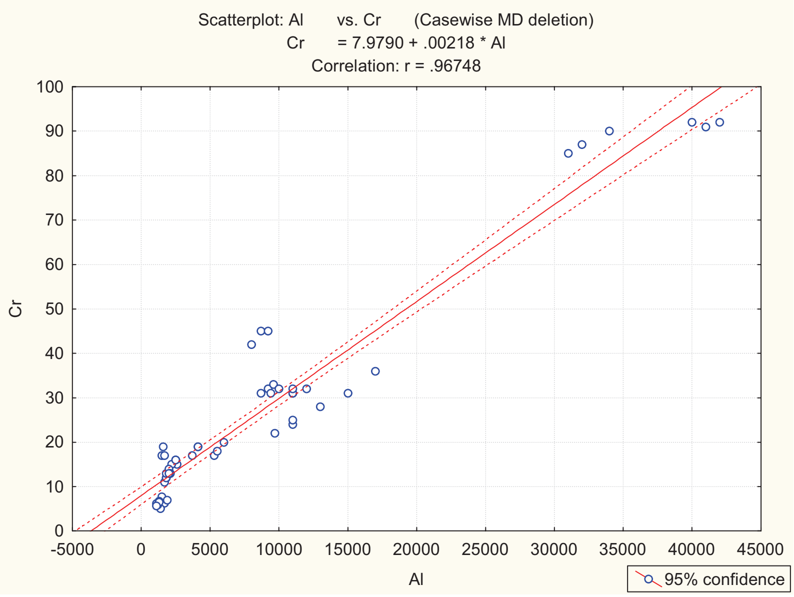


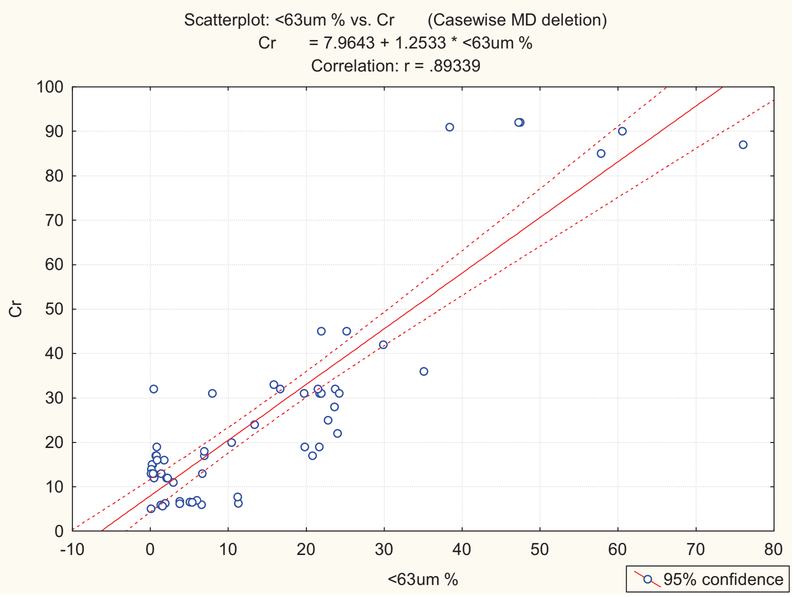




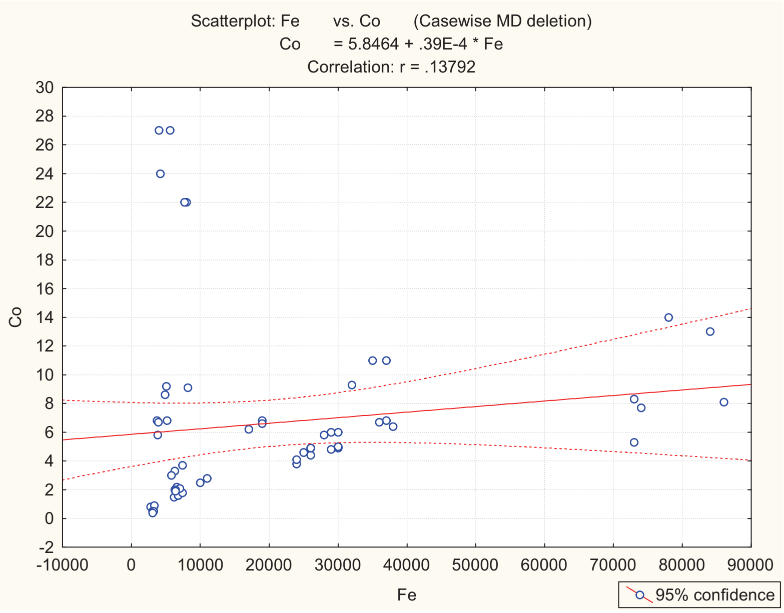
Chromium

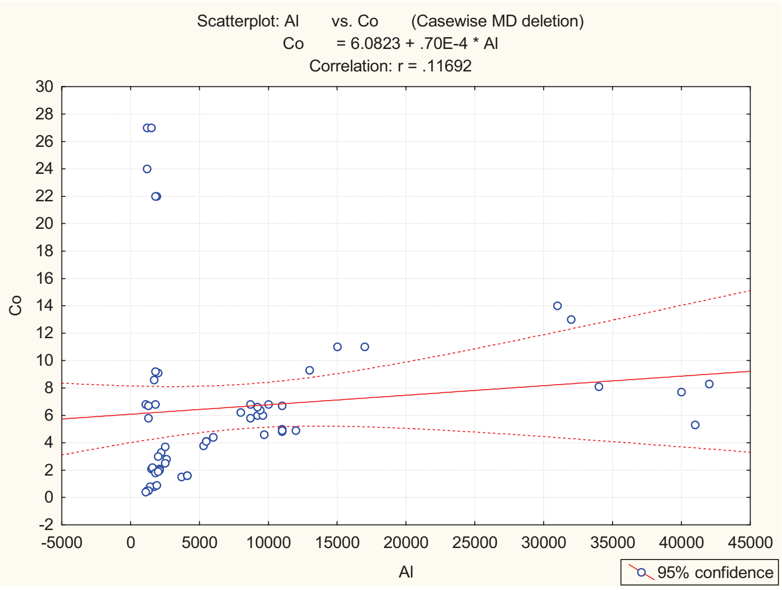

Scatterplot: Fe vs. Cr (Casewise MD deletion)
Cr = 4.8570 + .00101 * Fe
Correlation: r = .94914
Cr
100
90
80
70
60
50
40
30
20
10
0
-10000
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
Fe
95% confidence

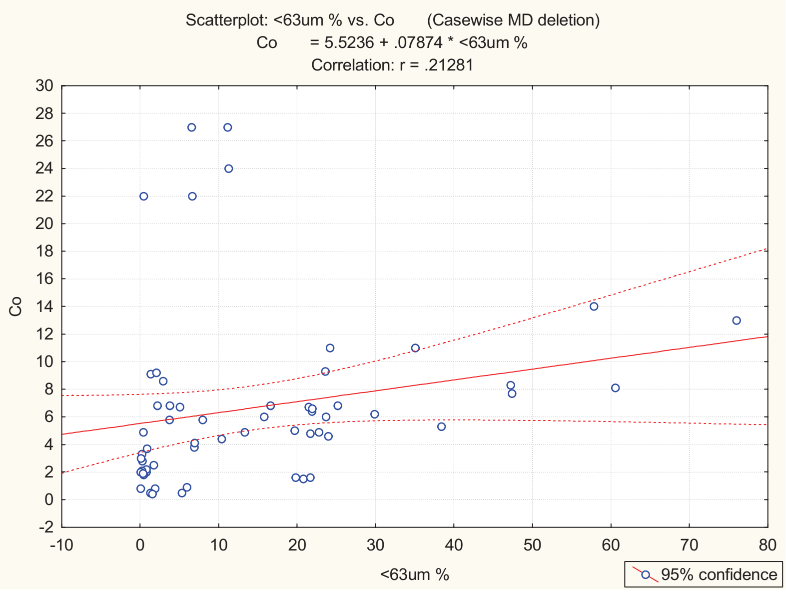

Scatterplot: Al vs. Cr (Casewise MD deletion)
Cr = 7.9790 + .00218 * Al
Correlation: r = .96748
Cr
100
90
80
70
60
50
40
30
20
10
0
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
Al
95% confidence


Scatterplot: <63um % vs. Cr (Casewise MD deletion)
Cr = 7.9643 + 1.2533 * <63um %
Correlation: r = .89339
Cr
100
90
80
70
60
50
40
30
20
10
0
-10
0
10
20
30
40
50
60
70
80
<63um %
95% confidence

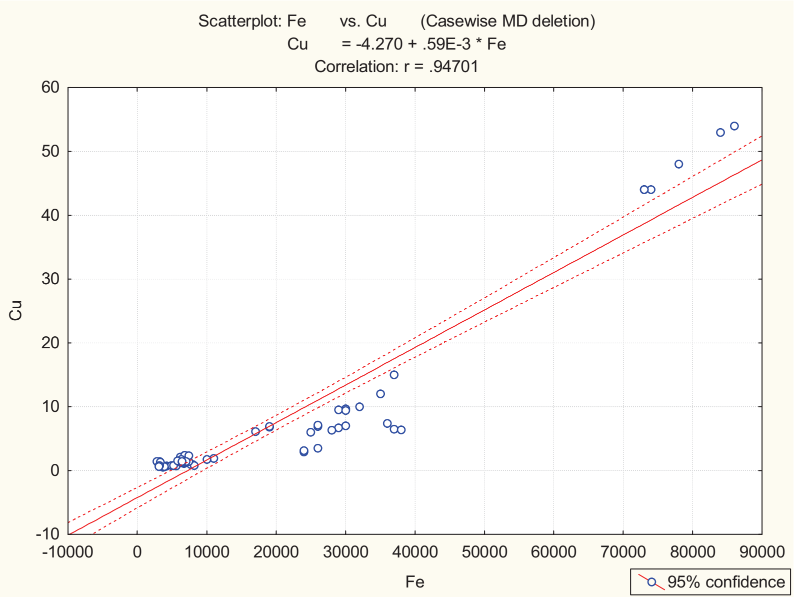
Cobalt


Scatterplot: Fe vs. Co (Casewise MD deletion)
Co = 5.8464 + .39E-4 * Fe
Correlation: r = .13792
Co
Fe
-2
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
-10000
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
95% confidence

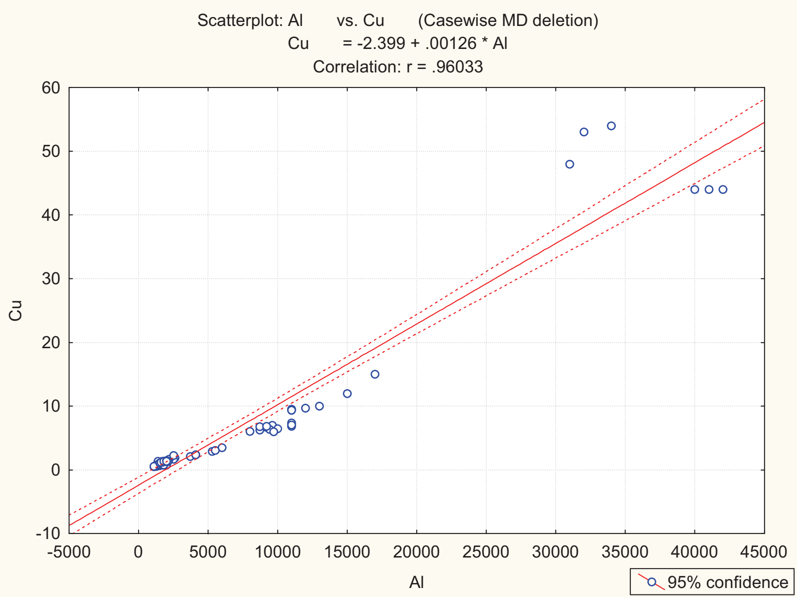

Scatterplot: Al vs. Co (Casewise MD deletion)
Co = 6.0823 + .70E-4 * Al
Correlation: r = .11692
Co
Al
-2
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
95% confidence


Scatterplot: <63um % vs. Co (Casewise MD deletion)
Co = 5.5236 + .07874 * <63um %
Correlation: r = .21281
Co
<63um %
-2
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
-10
0
10
20
30
40
50
60
70
80
95% confidence

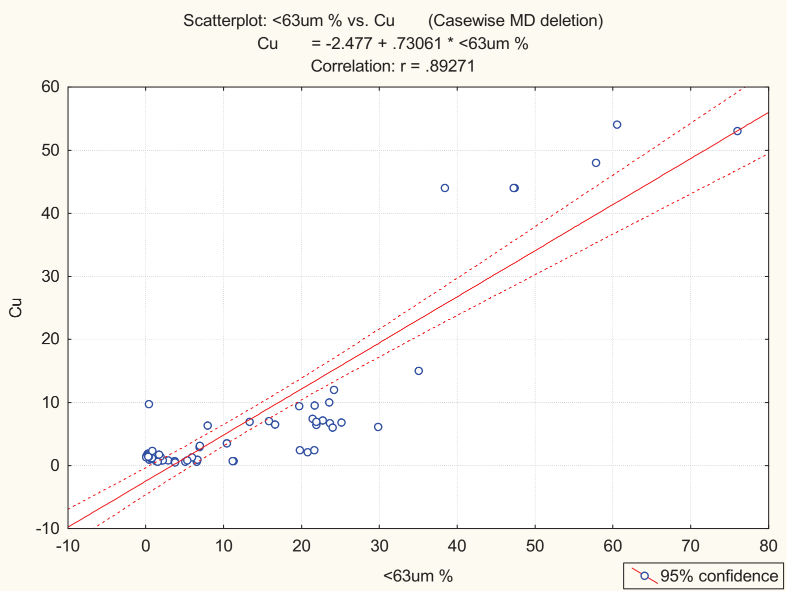
Copper



Scatterplot: Fe vs. Cu (Casewise MD deletion)
Cu = -4.270 + .59E-3 * Fe
Correlation: r = .94701
Cu
60
50
40
30
20
10
0
-10
-10000
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
Fe
95% confidence

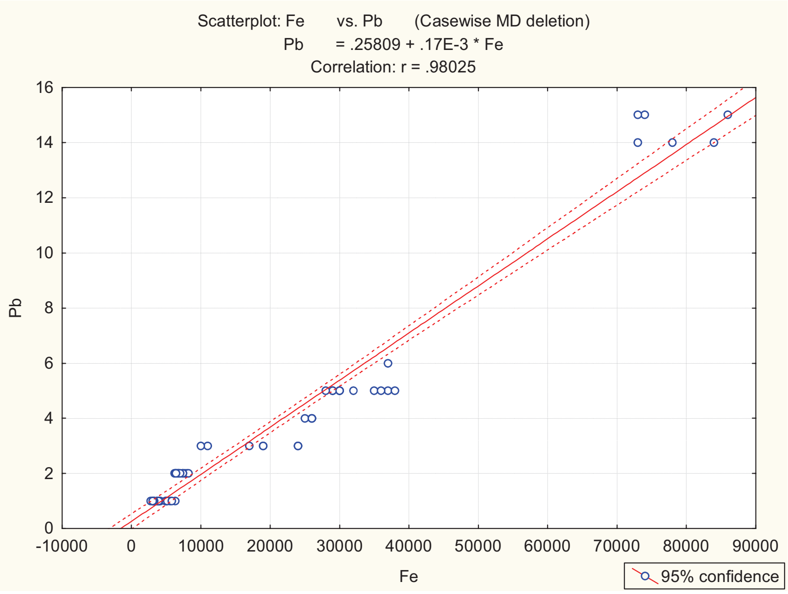


Scatterplot: Al vs. Cu (Casewise MD deletion)
Cu = -2.399 + .00126 * Al
Correlation: r = .96033
Cu
60
50
40
30
20
10
0
-10
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
Al
95% confidence

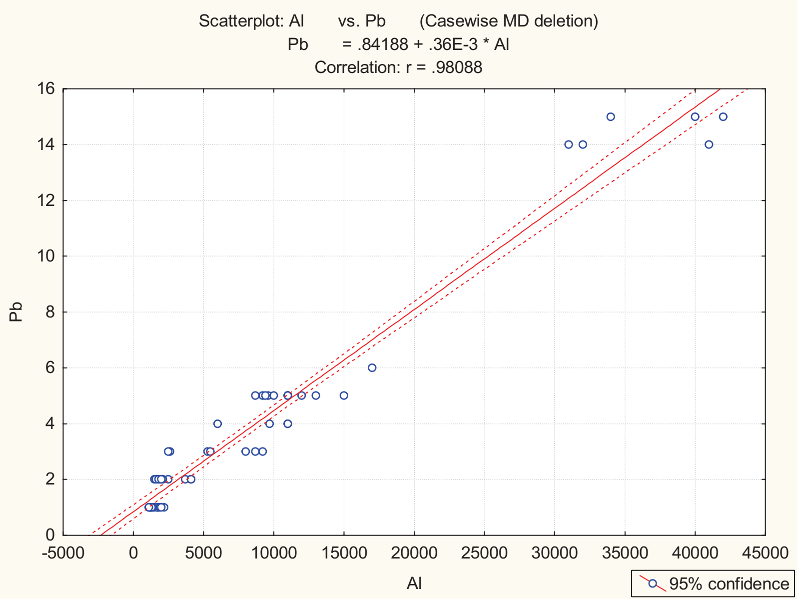


Scatterplot: <63um % vs. Cu (Casewise MD deletion)
Cu = -2.477 + .73061 * <63um %
Correlation: r = .89271
Cu
60
50
40
30
20
10
0
-10
-10
0
10
20
30
40
50
60
70
80
<63um %
95% confidence

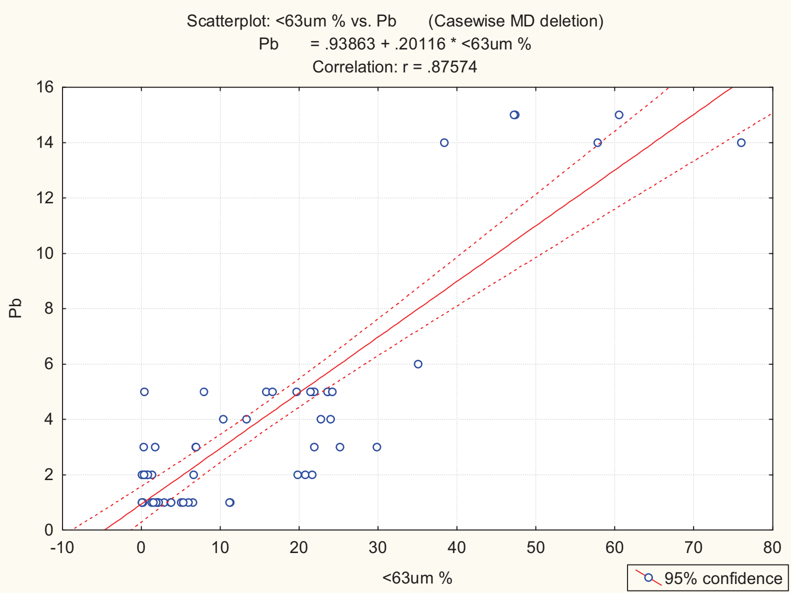
Lead



Scatterplot: Fe vs. Pb (Casewise MD deletion)
Pb = .25809 + .17E-3 * Fe
Correlation: r = .98025
Pb
0
2
4
6
8
10
12
14
16
-10000
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
Fe
95% confidence

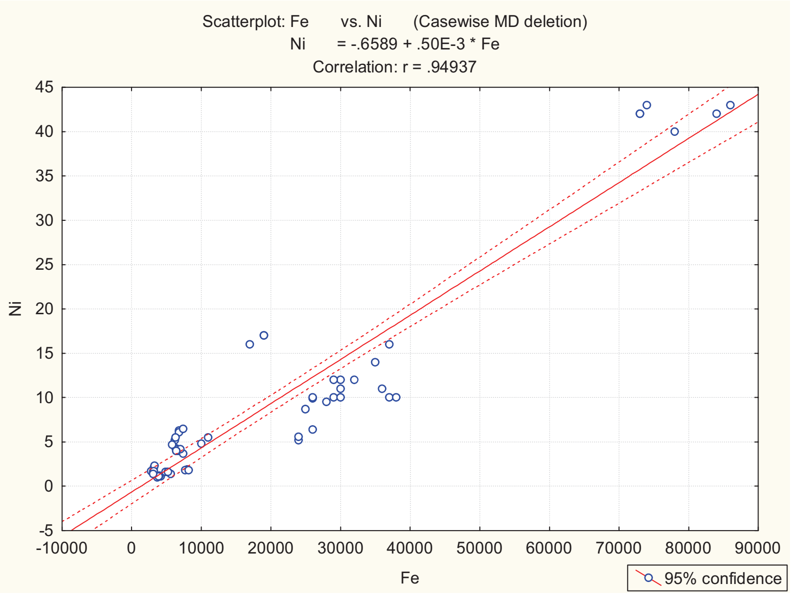


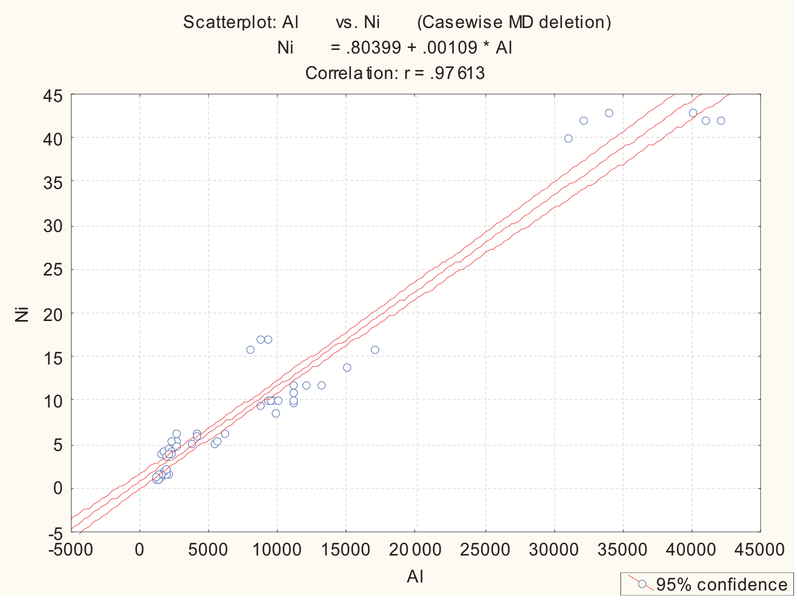
Scatterplot: Al vs. Pb (Casewise MD deletion)
Pb = .84188 + .36E-3 * Al
Correlation: r = .98088
Pb
0
2
4
6
8
10
12
14
16
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
Al
95% confidence

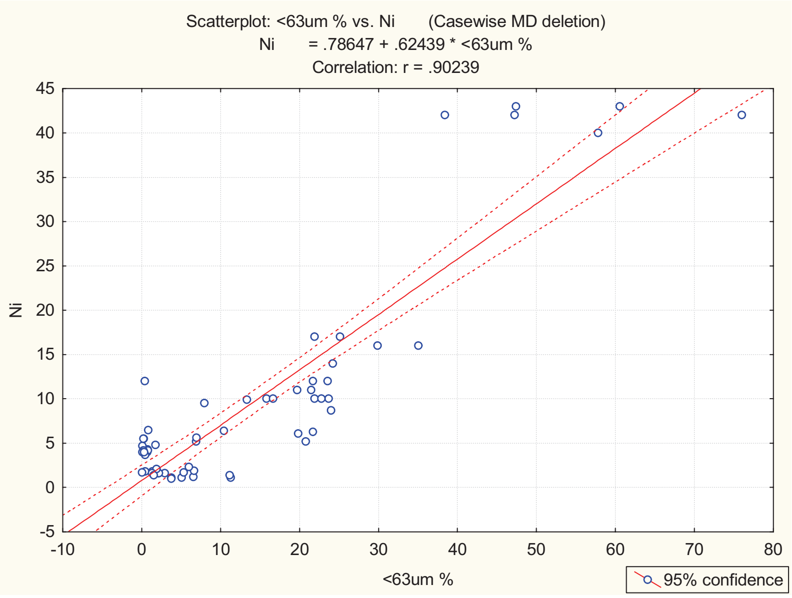


Scatterplot: <63um % vs. Pb (Casewise MD deletion)
Pb = .93863 + .20116 * <63um %
Correlation: r = .87574
Pb
0
2
4
6
8
10
12
14
16
-10
0
10
20
30
40
50
60
70
80
<63um %
95% confidence

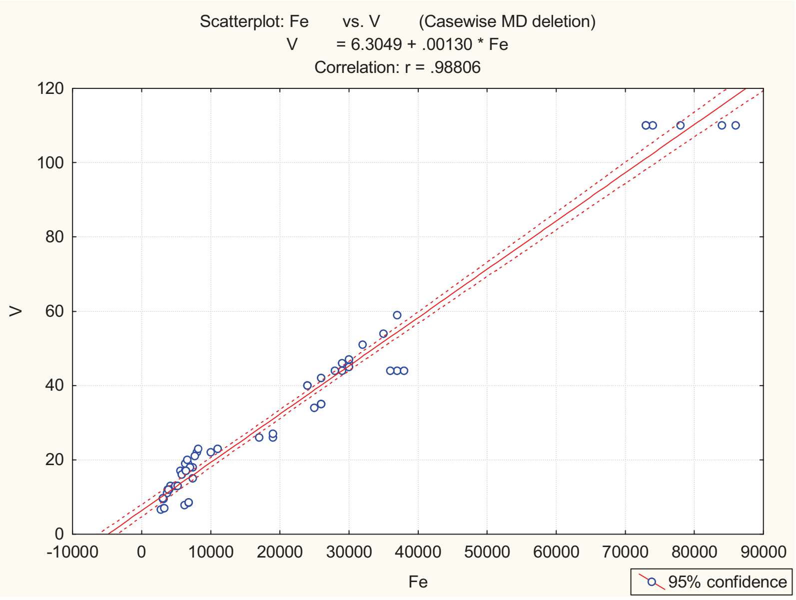
Nickel

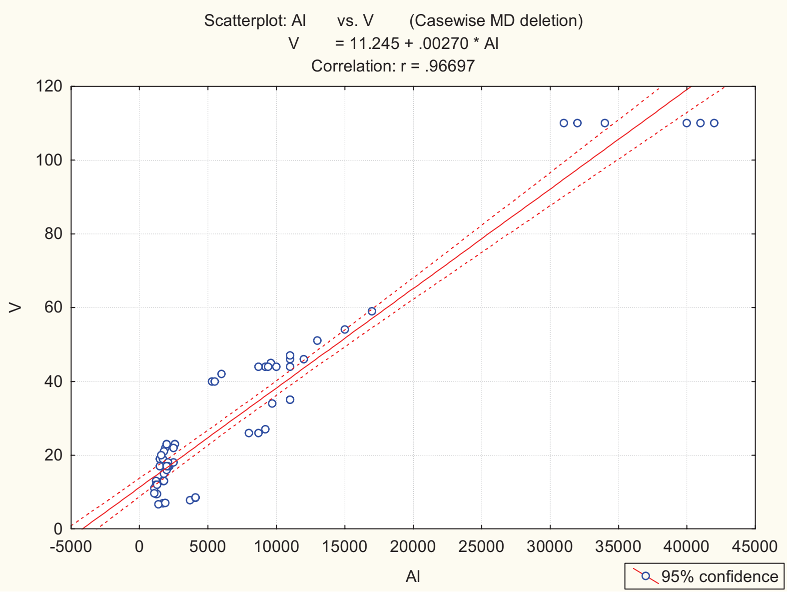

Scatterplot: Fe vs. Ni (Casewise MD deletion)
Ni = -.6589 + .50E-3 * Fe
Correlation: r = .94937
45
40
35
30
25
20
15
10
5
0
-5
Ni
-10000
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
Fe
95% confidence

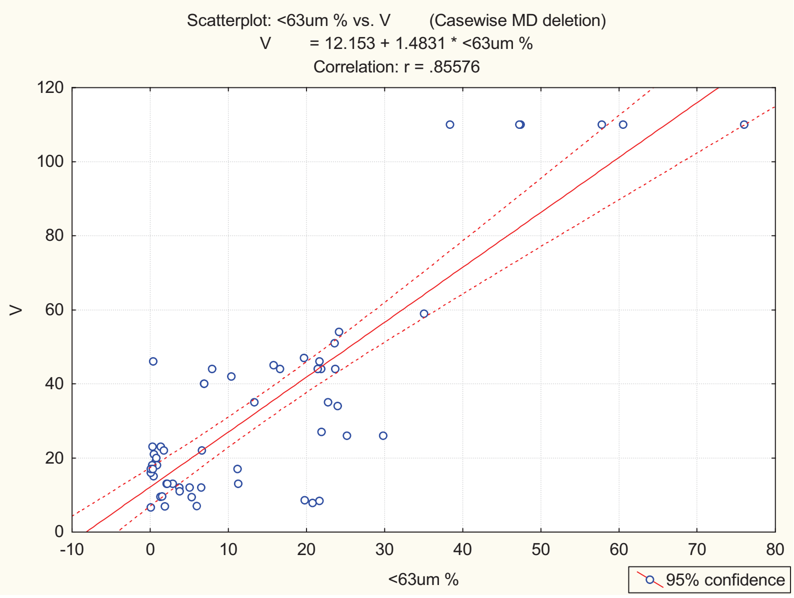

Scatterplot: Al vs. Ni (Casewise MD deletion)
Ni = .80399 + .00109 * Al
Correlation: r = .97613
45
40
35
30
25
20
15
10
5
0
-5
Ni
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
Al
95% confidence


Scatterplot: <63um % vs. Ni (Casewise MD deletion)
Ni = .78647 + .62439 * <63um %
Correlation: r = .90239
45
40
35
30
25
20
15
10
5
0
-5
Ni
-10
0
10
20
30
40
50
60
70
80
<63um %
95% confidence

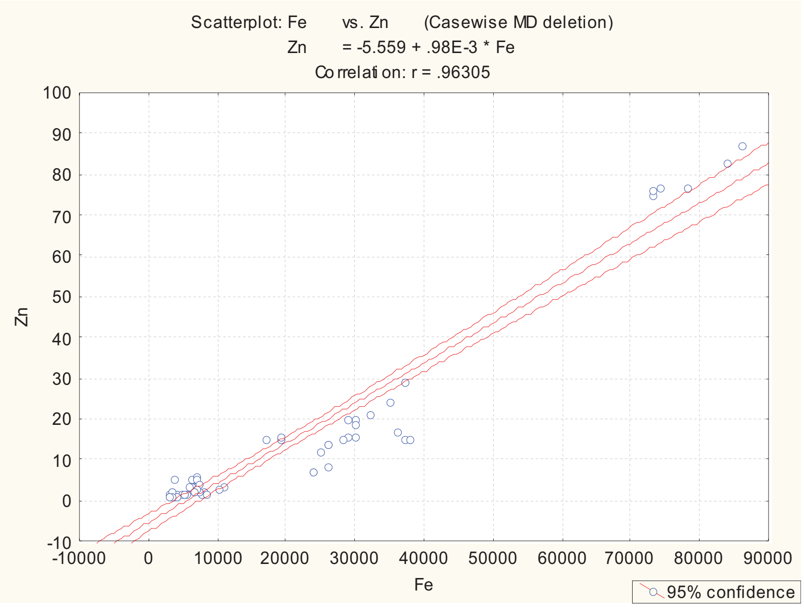
Vanadium

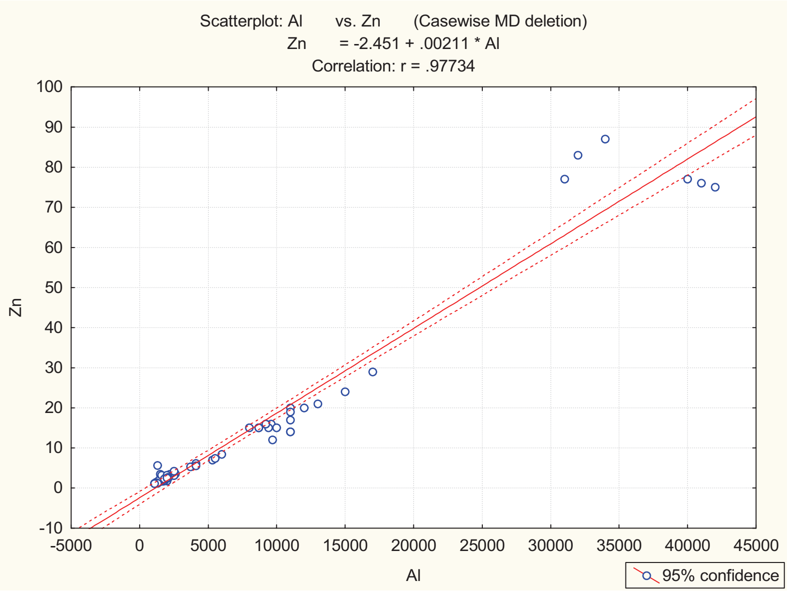

Scatterplot: Fe vs. V (Casewise MD deletion)
V = 6.3049 + .00130 * Fe
Correlation: r = .98806
V
0
20
40
60
80
100
120
-10000
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
Fe
95% confidence

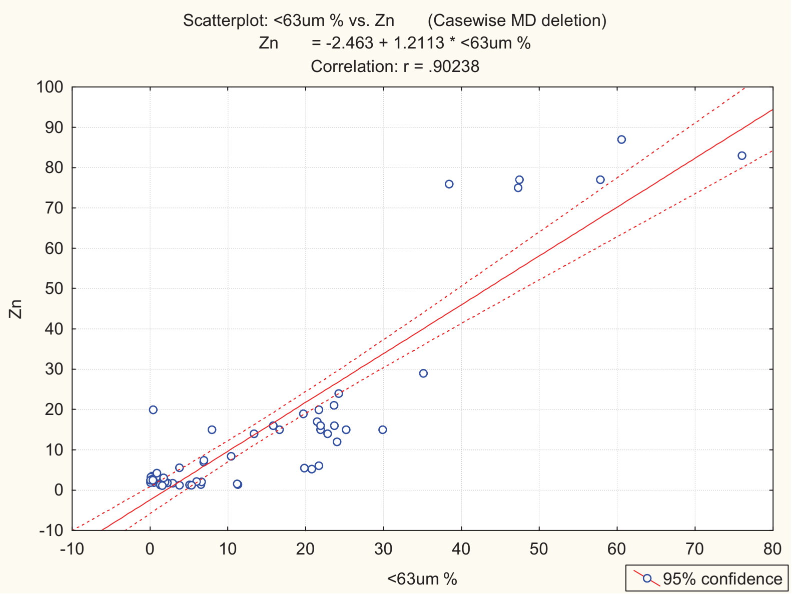

Scatterplot: Al vs. V (Casewise MD deletion)
V = 11.245 + .00270 * Al
Correlation: r = .96697
V
0
20
40
60
80
100
120
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
Al
95% confidence


Scatterplot: <63um % vs. V (Casewise MD deletion)
V = 12.153 + 1.4831 * <63um %
Correlation: r = .85576
V
0
20
40
60
80
100
120
-10
0
10
20
30
40
50
60
70
80
<63um %
95% confidence

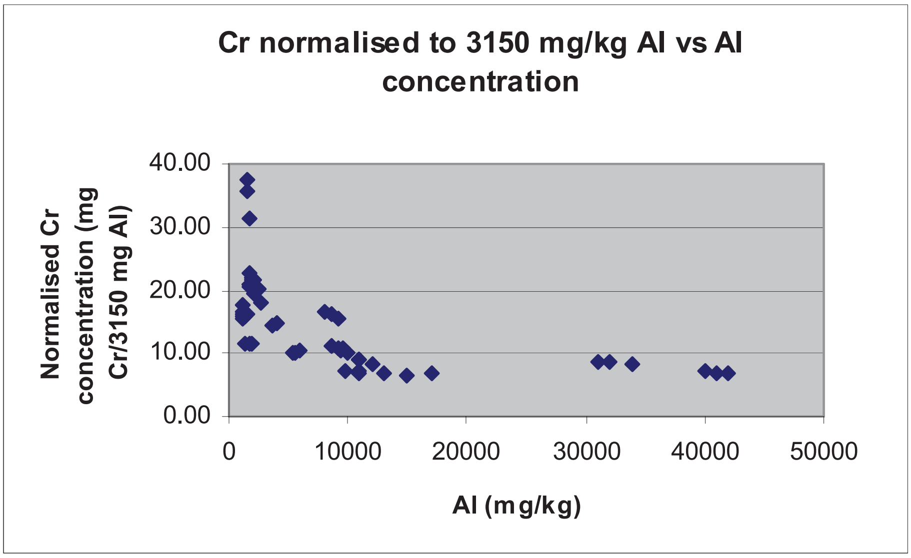
Zinc

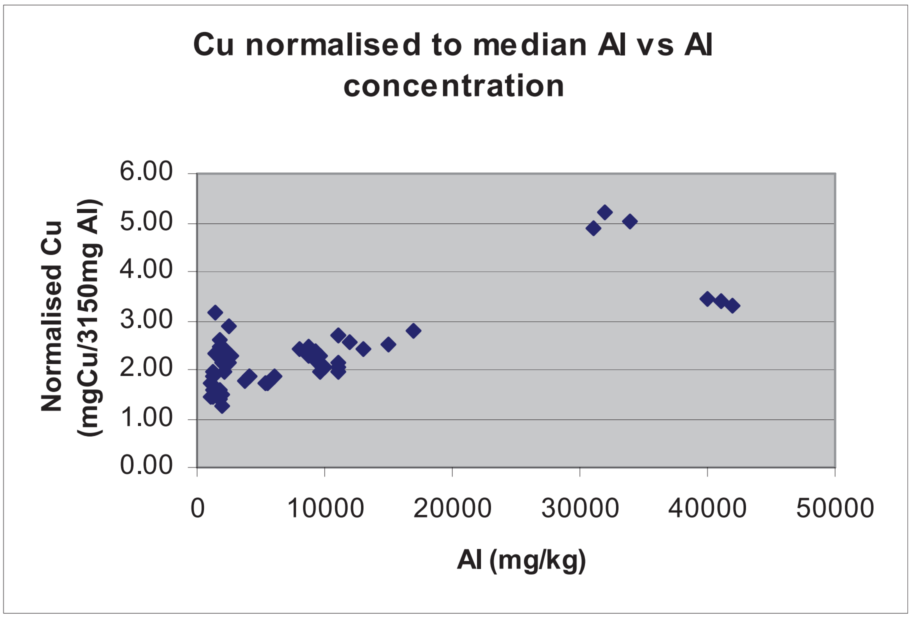

Scatterplot: Fe vs. Zn (Casewise MD deletion)
Zn = -5.559 + .98E-3 * Fe
Correlation: r = .96305
Zn
Fe
100
90
80
70
60
50
40
30
20
10
0
-10
-10000
0
10000
20000
30000
40000
50000
60000
70000
80000
90000
95% confidence

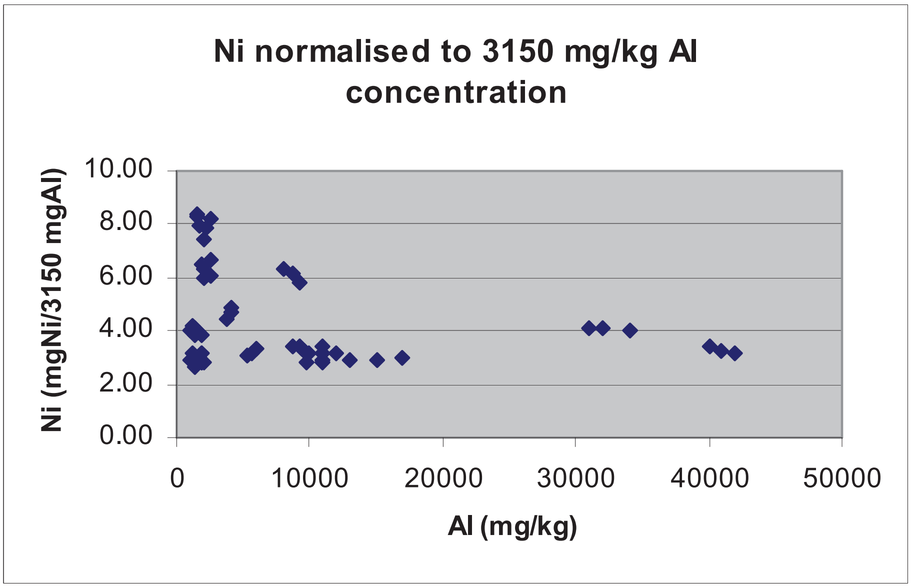

Scatterplot: Al vs. Zn (Casewise MD deletion)
Zn = -2.451 + .00211 * Al
Correlation: r = .97734
Zn
Al
100
90
80
70
60
50
40
30
20
10
0
-10
-5000
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
95% confidence

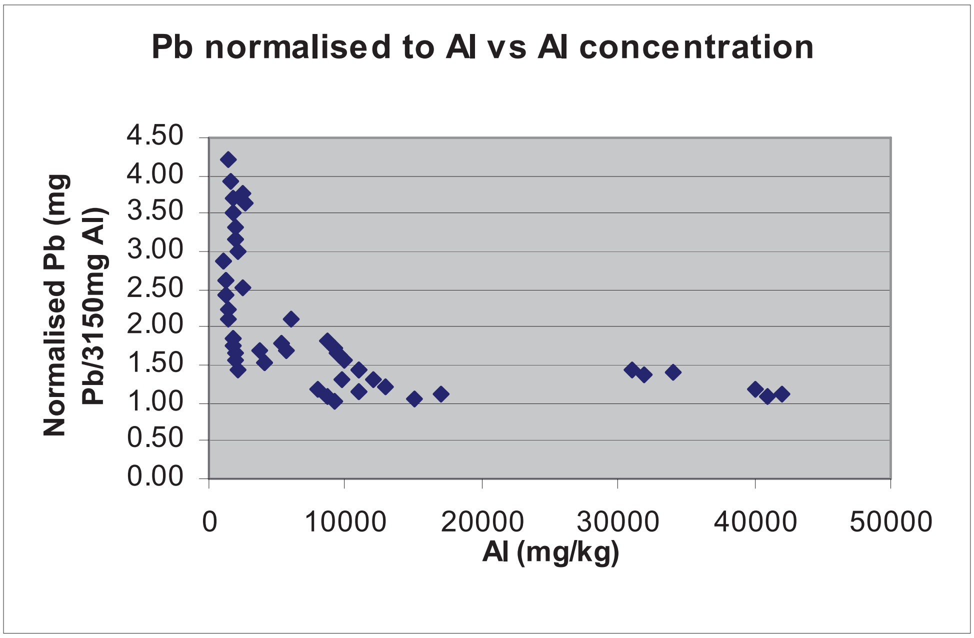

Scatterplot: <63um % vs. Zn (Casewise MD deletion)
Zn = -2.463 + 1.2113 * <63um %
Correlation: r = .90238
Zn
<63um %
100
90
80
70
60
50
40
30
20
10
0
-10
-10
0
10
20
30
40
50
60
70
80
95% confidence

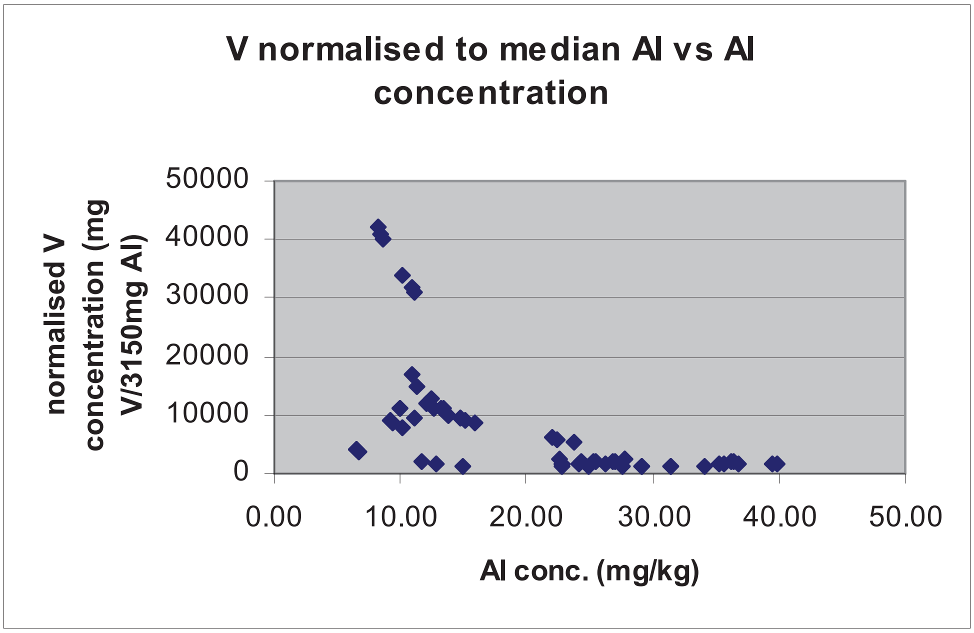
Appendix E: Normalised metal concentrations graphed against normaliser (aluminium) concentration

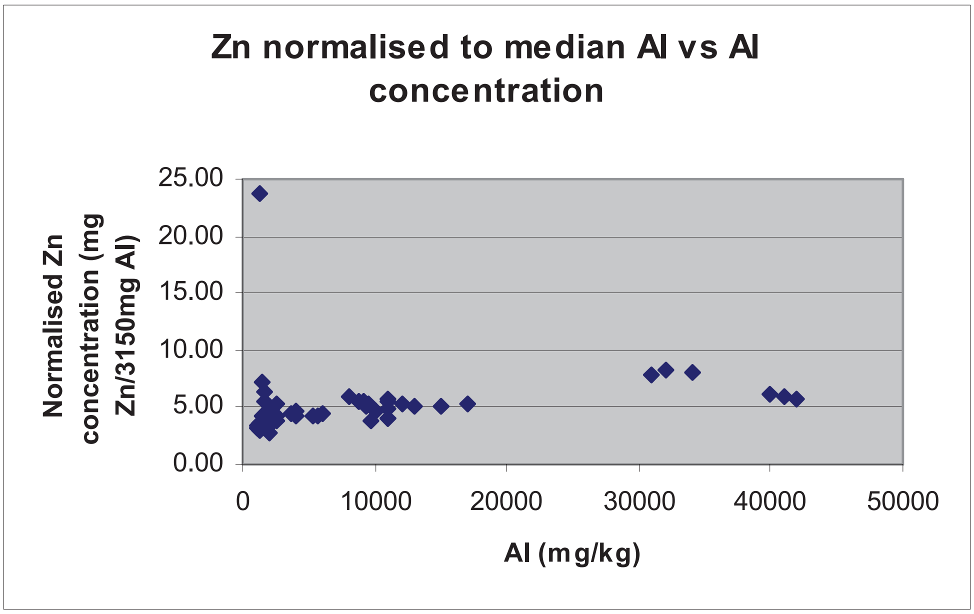







Pb normalised to Al vs Al concentration
Normalised Pb (mg Pb/3150mg Al)
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
10000
20000
30000
40000
50000
Al (mg/kg)


V normalised to median Al vs Al concentration
normalised V concentration (mg V/3150mg Al)
50000
40000
30000
20000
10000
0
0.00
10.00
20.00
30.00
40.00
50.00
Al conc. (mg/kg)


Zn normalised to median Al vs Al concentration
Normalised Zn concentration (mg Zn/3150mg Al)
25.00
20.00
15.00
10.00
5.00
0.00
0
10000
20000
30000
40000
50000
Al (mg/kg)

Appendix F: Sediment metal concentration data used for statistical comparisons

Sites	Ag	Al	As	Cd	Co	Cr normalised	Cu normalised	Ni normalised	Pb normalised	V normalised	Zn normalised	Hg	Se
Ex1a	<1	1200	11	<0.06	24	16.54	1.84	2.89	2.63	34.13	3.68	<0.01	<0.1
Ex1b	<1	1200	10	<0.06	27	15.75	1.58	3.15	2.63	31.50	3.68	<0.01	<0.1
Ex1c	<1	1500	14	<0.06	27	16.17	1.47	2.94	2.10	35.70	3.36	<0.01	<0.1
Ex3a	<1	1900	18	<0.06	22	21.55	1.49	3.15	3.32	36.47	3.48	<0.01	<0.1
Ex3b	<1	1800	19	<0.06	22	21.00	1.58	3.15	3.50	36.75	3.33	<0.01	<0.1
Ex3c	<1	2000	19	<0.06	9.1	20.48	1.26	2.84	3.15	36.23	2.84	<0.01	<0.1
Ex4a	<1	1800	12	<0.06	9.2	21.00	1.40	2.80	1.75	22.75	3.33	<0.01	<0.1
Ex4b	<1	1700	11	<0.06	8.6	20.38	1.48	2.96	1.85	24.09	3.15	<0.01	<0.1
Ex4c	<1	1800	11	<0.06	6.8	21.00	1.40	2.80	1.75	22.75	3.15	<0.01	<0.1
Ex5a	<1	1300	8	<0.06	0.5	16.23	1.70	2.91	2.42	29.08	23.75	<0.01	<0.1
Ex5b	<1	1100	8	<0.06	6.8	17.75	1.43	2.86	2.86	31.50	3.44	<0.01	<0.1
Ex5c	<1	1300	8	<0.06	6.7	15.99	1.45	2.67	2.42	29.08	3.15	<0.01	<0.1
Ar1a	<1	31000	11	<0.06	14	8.64	4.88	4.06	1.42	11.18	7.82	0.03	0.2
Ar1b	<1	32000	11	<0.06	13	8.56	5.22	4.13	1.38	10.83	8.17	0.03	0.3
Ar1c	<1	34000	11	<0.06	8.1	8.34	5.00	3.98	1.39	10.19	8.06	0.03	0.3
Ar2a	<1	40000	20	<0.06	7.7	7.25	3.47	3.39	1.18	8.66	6.06	0.02	0.2
Ar2b	<1	42000	20	<0.06	8.3	6.90	3.30	3.15	1.13	8.25	5.63	0.02	0.2
Ar2c	<1	41000	19	<0.06	5.3	6.99	3.38	3.23	1.08	8.45	5.84	0.02	0.2
Ar3a	<1	12000	21	<0.06	4.9	8.40	2.55	3.15	1.31	12.08	5.25	0.01	0.1
Ar3b	<1	11000	20	<0.06	4.8	8.88	2.72	3.44	1.43	13.17	5.73	<0.01	<0.1
Ar3c	<1	11000	21	<0.06	5	8.88	2.69	3.15	1.43	13.46	5.44	<0.01	0.1
Ar4a	<1	9200	16	<0.06	6	10.96	2.29	3.42	1.71	15.07	5.48	<0.01	0.1
Ar4b	<1	8700	17	<0.06	5.8	11.22	2.28	3.44	1.81	15.93	5.43	0.01	0.1
Ar4c	<1	9600	18	<0.06	6	10.83	2.30	3.28	1.64	14.77	5.25	<0.01	0.1
Ons1a	<1	13000	26	<0.06	9.3	6.78	2.42	2.91	1.21	12.36	5.09	<0.01	0.2
Ons1b	<1	17000	26	<0.06	11	6.67	2.78	2.96	1.11	10.93	5.37	<0.01	0.2
Ons1c	<1	15000	28	<0.06	11	6.51	2.52	2.94	1.05	11.34	5.04	<0.01	0.2
Ons2a	<1	10000	23	<0.06	6.8	10.08	2.05	3.15	1.58	13.86	4.73	<0.01	0.1
Ons2b	<1	9400	23	<0.06	6.4	10.39	2.14	3.35	1.68	14.74	5.03	<0.01	0.1
Ons2c	<1	11000	23	<0.06	6.7	9.16	2.12	3.15	1.43	12.60	4.87	<0.01	0.1
Ons3a	<1	6000	35	<0.06	4.4	10.50	1.84	3.36	2.10	22.05	4.41	<0.01	<0.1
Ons3b	<1	5300	38	<0.06	3.8	10.10	1.72	3.09	1.78	23.77	4.16	<0.01	<0.1
Ons3c	<1	5600	36	<0.06	4.1	10.13	1.74	3.15	1.69	22.50	4.28	<0.01	<0.1

Sites	Ag	Al	As	Cd	Co	Cr normalised	Cu normalised	Ni normalised	Pb normalised	V normalised	Zn normalised	Hg	Se
Ons4a	<1	11000	20	<0.06	4.9	6.87	1.98	2.84	1.15	10.02	4.01	<0.01	0.2
Ons4b	<1	9700	20	<0.06	4.6	7.14	1.95	2.83	1.30	11.04	3.90	<0.01	0.1
Ons4c	<1	11000	20	<0.06	4.9	7.16	2.03	2.86	1.15	10.02	4.01	<0.01	0.2
Da1a	<1	8000	12	<0.06	6.2	16.54	2.40	6.30	1.18	10.24	5.91	<0.01	<0.1
Da1b	<1	8700	13	<0.06	6.8	16.29	2.46	6.16	1.09	9.41	5.43	<0.01	0.1
Da1c	<1	9200	11	<0.06	6.6	15.41	2.36	5.82	1.03	9.24	5.48	<0.01	0.1
Da2a	<1	3700	7	<0.06	1.5	14.47	1.79	4.43	1.70	6.64	4.51	<0.01	0.1
Da2b	<1	4100	8	<0.06	1.6	14.60	1.84	4.84	1.54	6.45	4.69	<0.01	0.1
Da2c	<1	4100	8	<0.06	1.6	14.60	1.84	4.69	1.54	6.53	4.23	<0.01	0.1
Da3a	<1	1700	4	<0.06	0.8	11.67	2.59	3.89	1.85	12.79	3.71	<0.01	<0.1
Da3b	<1	1400	4	<0.06	0.8	11.48	3.15	3.83	2.25	14.85	4.28	<0.01	0.1
Da3c	<1	1900	4	<0.06	0.9	11.61	2.16	3.81	1.66	11.61	3.65	<0.01	0.1
Da4a	<1	1200	6	<0.06	0.5	15.49	1.84	4.20	2.63	24.94	3.41	<0.01	0.2
Da4b	<1	1300	6	<0.06	0.5	15.75	1.94	4.12	2.42	22.78	2.91	<0.01	0.1
Da4c	<1	1100	6	<0.06	0.4	16.32	1.72	4.01	2.86	27.49	3.15	<0.01	<0.1
Pho1a	<1	1500	19	<0.06	2.1	35.70	2.31	8.40	4.20	39.90	7.14	<0.01	<0.1
Pho1b	<1	1700	20	<0.06	2	31.50	2.22	7.97	3.71	35.21	5.56	<0.01	<0.1
Pho1c	<1	1600	20	<0.06	2.2	37.41	2.36	8.27	3.94	39.38	6.30	<0.01	<0.1
Pho2a	<1	2600	26	<0.06	2.8	18.17	2.30	6.66	3.63	27.87	4.24	<0.01	<0.1
Pho2b	<1	2500	25	<0.06	2.5	20.16	2.14	6.05	3.78	27.72	3.91	<0.01	<0.1
Pho2c	<1	1800	16	<0.06	1.8	22.75	2.45	6.48	3.50	26.25	4.03	<0.01	<0.1
Pho3a	<1	2200	17	<0.06	3.3	21.48	2.43	7.88	1.43	24.34	4.87	<0.01	<0.1
Pho3b	<1	2000	16	<0.06	3	22.05	2.36	7.40	1.58	25.20	5.04	<0.01	<0.1
Pho3c	<1	2500	18	<0.06	3.7	20.16	2.90	8.19	2.52	22.68	5.29	<0.01	<0.1
Pho4a	<1	2100	19	<0.06	2.1	19.50	2.10	6.30	3.00	27.00	4.05	<0.01	<0.1
Pho4b	<1	2100	18	<0.06	2	19.50	1.95	6.00	3.00	25.50	3.75	<0.01	<0.1
Pho4c	<1	2000	18	<0.06	1.9	20.48	2.21	6.30	3.15	26.78	3.94	<0.01	<0.1
DP1	<1	3400	13	<0.06	1.8	12.97	1.85	4.26	1.85	12.97	8.25	<0.01	<0.1
DP2	<1	10000	12	<0.06	6	12.92	2.46	4.73	1.58	7.25	8.19	<0.01	0.1
DP3	<1	6700	13	<0.06	3.4	13.16	2.07	4.37	1.88	7.99	7.99	<0.01	0.1
DP4	<1	15000	12	<0.06	6.8	11.55	2.52	4.20	1.05	6.51	4.83	<0.01	0.2

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