Heavy Metals in Marine Biota, Sediments and Waters from the Shark Bay Area, Western Australia

Department of Conservation and Environment
Perth, Western Australia.

Environmental Note 175 August 1985

HEAVY METALS IN MARINE BIOTA, SEDIMENTS AND WATERS FROM THE SHARK BAY AREA, WESTERN AUSTRALIA

D. McCONCHIE[*], A.W. MANN[+], M.J. LINTERN[+], D. LONGMAN[+] AND V. TALBOT[x]

[*]DEPARTMENT OF GEOLOGY, UNIVERSITY OF WESTERN AUSTRALIA,
NEDLANDS, WESTERN AUSTRALIA, 6009.

[+]DIVISION OF MINERALOGY AND GEOCHEMISTRY, CSIRO,
FLOREAT PARK, WESTERN AUSTRALIA, 6014.

[x]DEPARTMENT OF CONSERVATION AND ENVIRONMENT,
1 MOUNT STREET, PERTH, WESTERN AUSTRALIA, 6000.

DEPARTMENT OF CONSERVATION AND ENVIRONMENT
PERTH, WESTERN AUSTRALIA
ENVIRONMENTAL NOTE 175 AUGUST 1985

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

History of the project

During the latter part of 1982 a quantity of pearl oysters (Pinctada carchararium) from Shark Bay, W.A. were sent to Perth to be sold for human consumption. Analysis of a sample of these oysters by the Western Australian Government Chemical Laboratories (W.A.G.C.L.) revealed that they complied with all health standards except that for cadmium (Cd); the Cd content of the oysters was approximately double the legal limit of 2 p.p.m. (wet weight). Analysis of further subsamples of oysters from this consignment by D. McConchie of the University of Western Australia (U.W.A.) and by A. Mann and M. Lintern of the Commonwealth Scientific and Industrial Research Organisation (C.S.I.R.O.) confirmed the findings of the W.A.G.C.L. These results were surprising in view of the isolation of Shark Bay from all known potential industrial or geological sources of Cd.

To investigate the Cd content of these oysters further, a field study was carried out at Shark Bay in June 1983 by A. & M. Gablish (Shark Bay Pearling Co.), R. Lawerence (University of Austin, Texas), M. Lintern, A. Mann and D. McConchie. During this study specimens were digested and analysed within a few hours of collection by anodic stripping voltammetry using a portable digital voltammeter (P.D.V.). These field analyses showed that, on a wet weight basis, most mature specimens of Pinctada carchararium contained well in excess of 2 p.p.m. Cd ($\bar{x}$, 4.5 p.p.m.; S.D., 1.8 p.p.m.) while the mean value for immature specimens was 1.8 p.p.m. Cd; mature specimens of Pinna dollabrata contained an average of 9.6 p.p.m. Cd. The mean Cd content of each species varied between the four localities sampled (Red Bluff/Monkey Mia, Cape Rose, Herald Bight, Denham Sound). The concentrations of all other heavy metals examined [copper (Cu), Lead, (Pb), and zinc (Zn)] were low, each averaging over an order of magnitude less than the maximum levels permitted in Western Australia (W.A.) for molluscs consumed by humans.

In view of the above findings, and because there is a known health risk

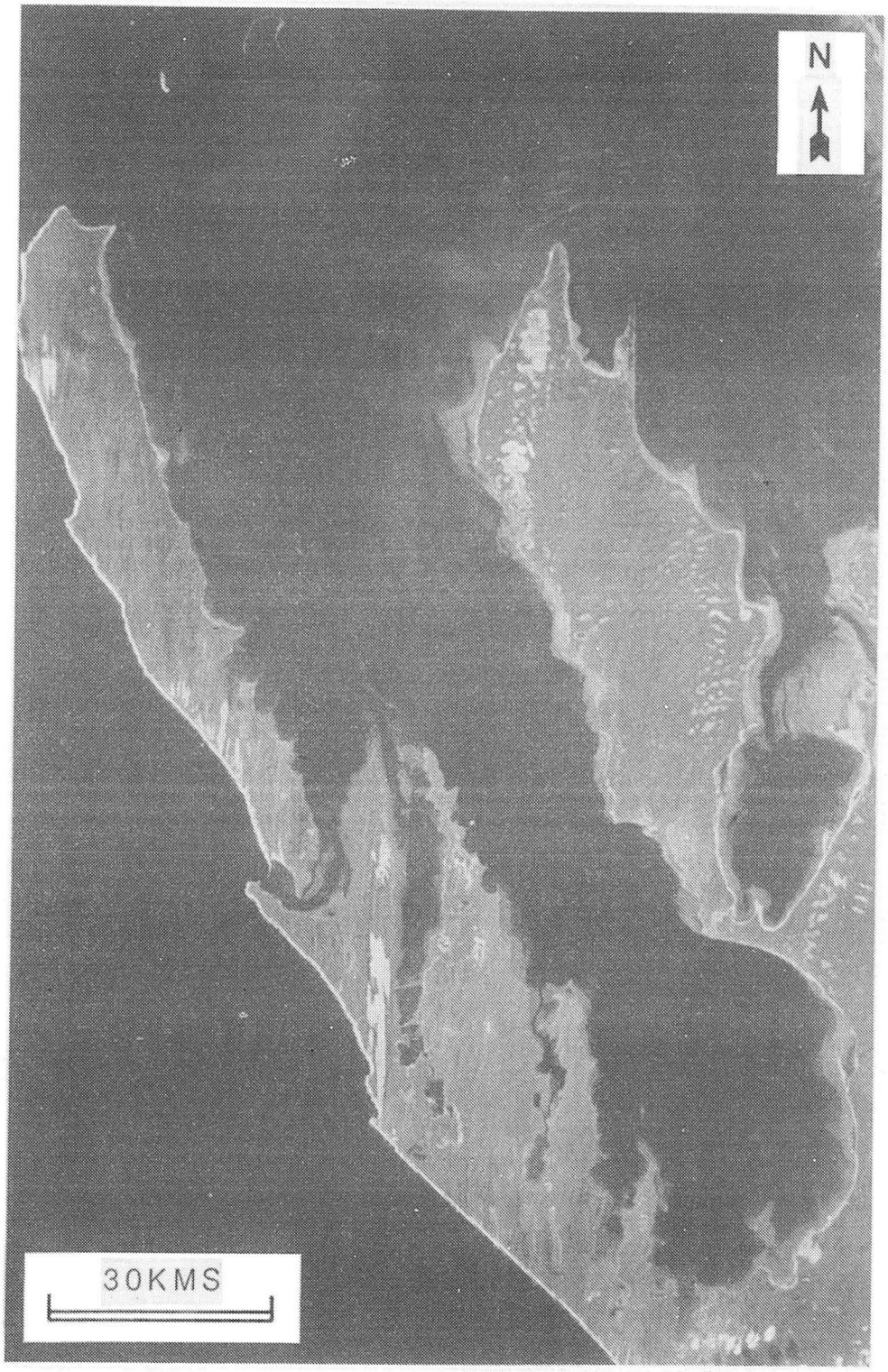

PLATE 1

The Shark Bay area as seen from a space shuttle mission (taken with a conventional camera).

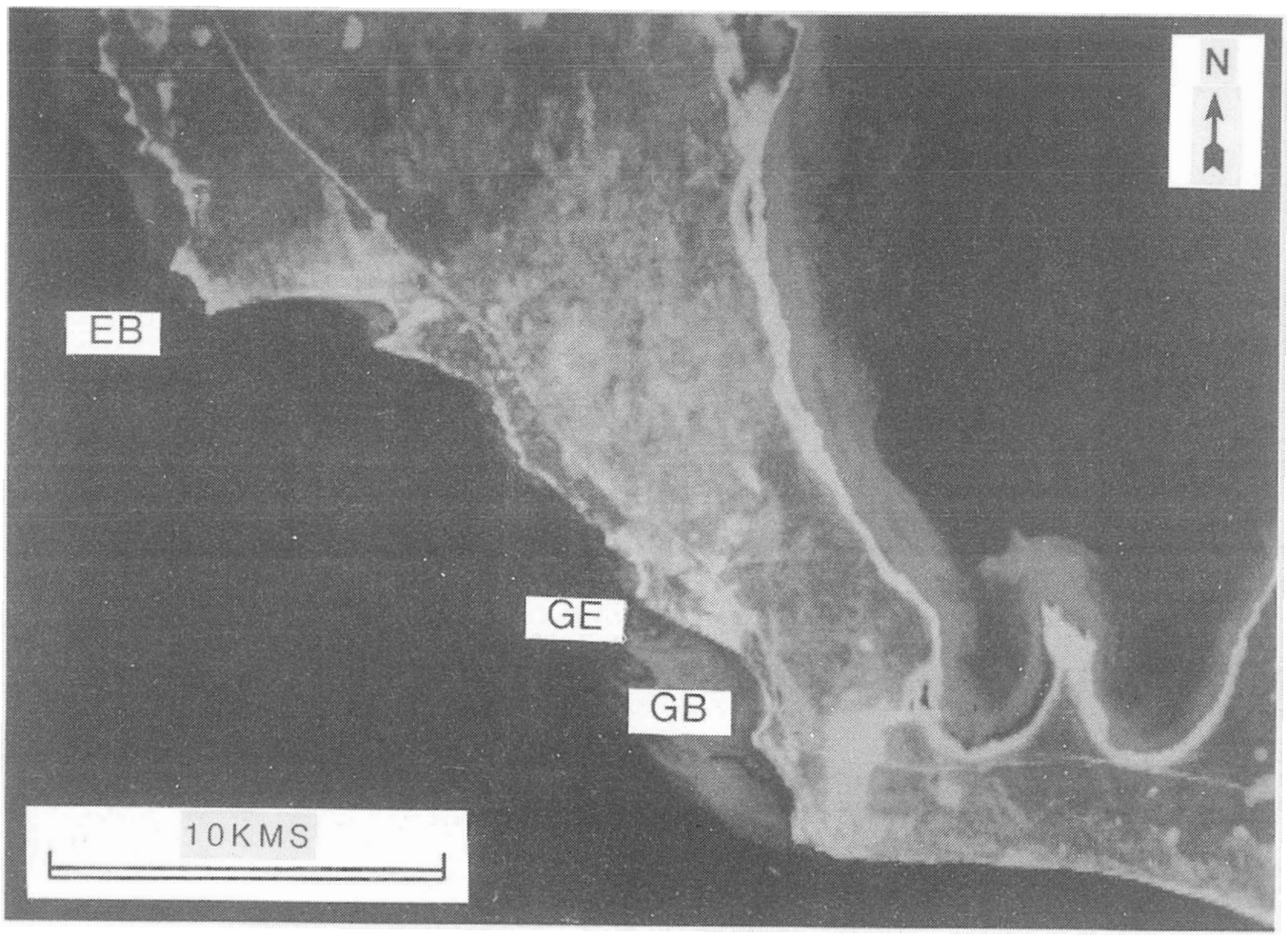

PLATE 2

Landsat imagery of the Taillefer Isthmus of Shark Bay, showing three sampling areas.

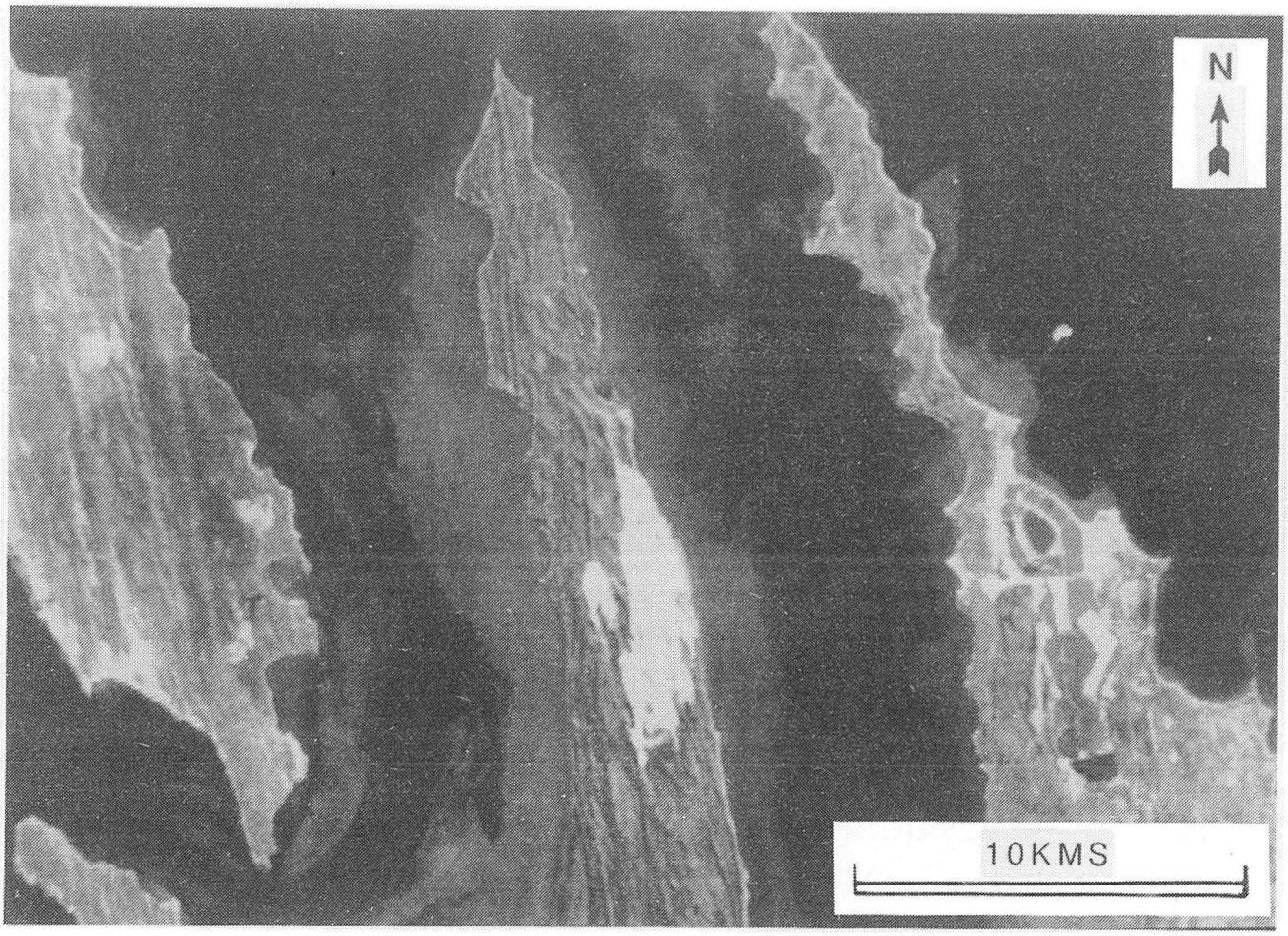

PLATE 3

Landsat imagery showing (from left to right) Dirk Hartog Island, Bellefin Prong and Heirisson Prong.

associated with a high Cd intake in the human diet (e.g., Lauwerys, 1979), the W.A. Department of Conservation and Environment and the W.A. Department of Fisheries and Wildlife were approached to obtain support for further investigation of Cd concentrations in Shark Bay molluscs. With the support of these departments, a larger scale field and laboratory study of Cd in Shark Bay molluscs was carried out in mid 1984. This report documents the findings of the 1984 study.

Shark Bay: geographic setting

Shark Bay is a shallow marine embayment (see Plates 1, 2, 3) of about 8,000 km^2 with an average water depth of 10m; over about 2,000 km^2 the water depth is less than 1m. The climate of the Shark Bay area is semi-arid with a mean annual evaporation potential nearly an order of magnitude higher than the mean annual precipitation of 200-220 mm. Water movement in the embayment is largely controlled by tidal flow (spring tides average <1.5m and neap tides average <0.5m); tidal flow velocities locally reach 0.9m/sec in channels and 0.45m/sec over sublittoral platforms. The combination of the above conditions results in a higher than normal marine salinity in the embayment; salinity increases in a SSE direction across the embayment reaching nearly $50^{o}/oo$ in Freycinet Basin and over $60^{o}/oo$ in Hamelin pool. Further details on the physiography, climate, water conditions and geology of the Shark Bay area can be found in Logan et al. (1970, 1974).

Shark Bay lies about 800 km north of Perth and about 400 km north of Geraldton; it is effectively remote from potential industrial sources of Cd pollution. As such, Shark Bay is in marked contrast with other areas in Australia (e.g., Cockburn Sound, W.A., Talbot and Chegwidden, 1982; Port Pirie, South Australia, Ferguson, 1983) where high concentrations of heavy metals in molluscs have been recorded. In these latter examples, an adjacent authropogenic source for the heavy metals can be identified.

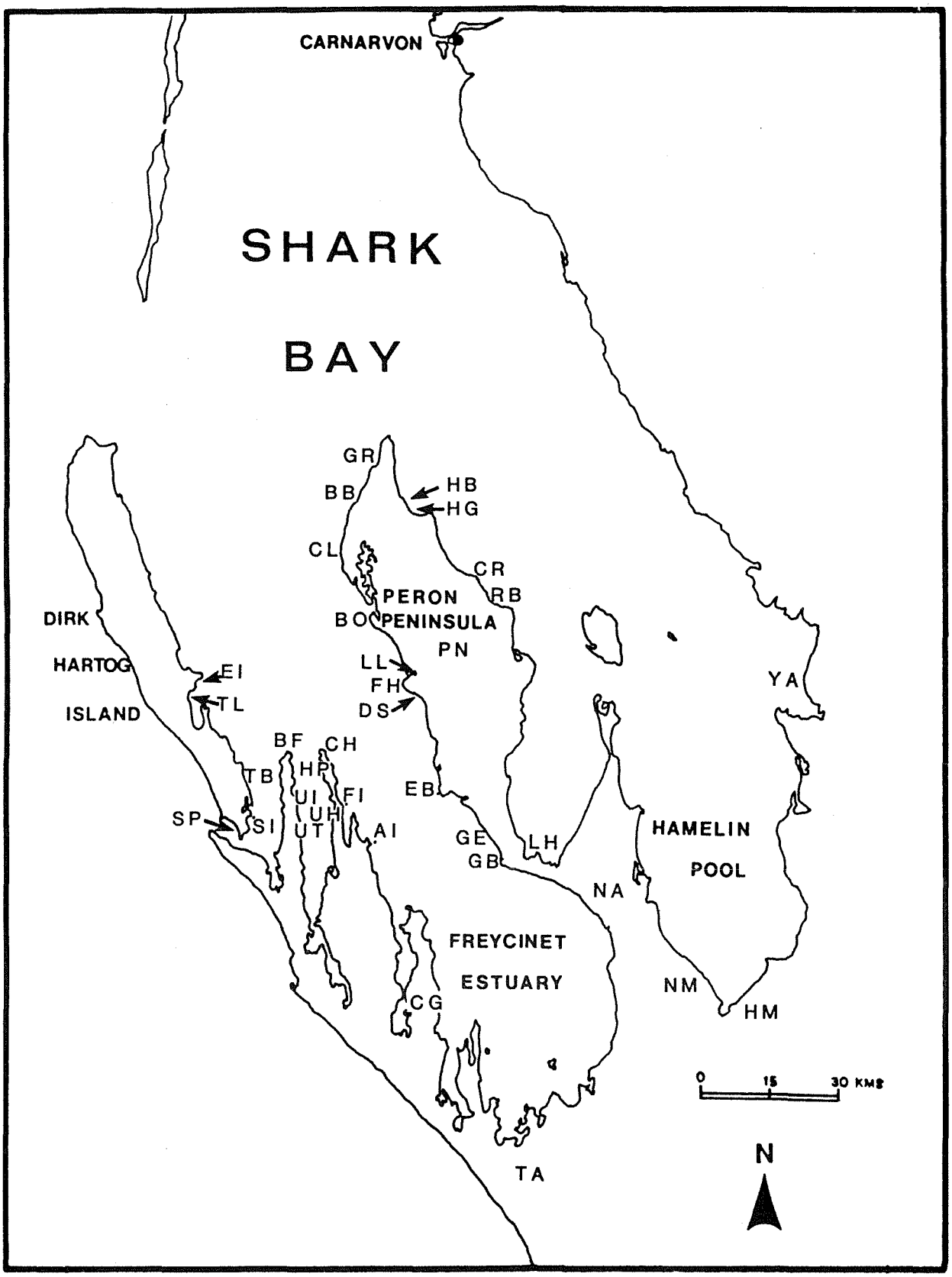

Figure 1: Map of the Shark Bay area showing the location of sample sites.

ANALYTICAL METHODS

Sampling

Sample sites were selected to give extensive coverage of the coastline around the embayment with a separation between successive sites of not more than 25 km (see Fig. 1). The exact position of each sample site was determined by the availability of Pinctada sp. in each area. (Note: no Pinctada sp. were found in Hamelin Pool south of a NE/SW line through Faure Island or in Freycinet Basin, south of an E/W line through Nanga; time and weather conditions prevented sampling the northern section of Dirk Hartog Island).

At each site, marine biological specimens, sediment, and water samples were collected by divers and placed in sterile plastic bags (biological specimens) or air-tight plastic bottles (sediment and water samples). In collecting biological material at each site, emphasis was placed on obtaining specimens of Pinctada sp. and Pinna dollabrata but other species were collected where readily available (see tables 1 - 10). With the exception of very small specimens of Pinctada sp. (D.V.L. see Fig. 2, less than 45 mm) which were returned to the sea immediately, no selection criteria were applied to sampling at any site. At sites where specimens of Pinctada sp. were scarce, all available individuals were taken but not all specimen sizes were always represented. This sampling procedure was designed to approximate the methods which would be used by a private individual or commercial operation harvesting oysters for human consumption. Sampling was not necessarily intended to yield statistically significant biological data on mollusc population density, size distribution, age distribution or species diversity.

Preparation of biological material

The live heel depth (H.D.) and dorso-ventral length (D.V.L.) of all specimens of Pinctada sp. (see Fig. 1) were measured with calipers prior to shucking and any individuals with damaged or defective shells were discarded. The measured individuals were then subdivided into size groups based on H.D., opened (see Plate

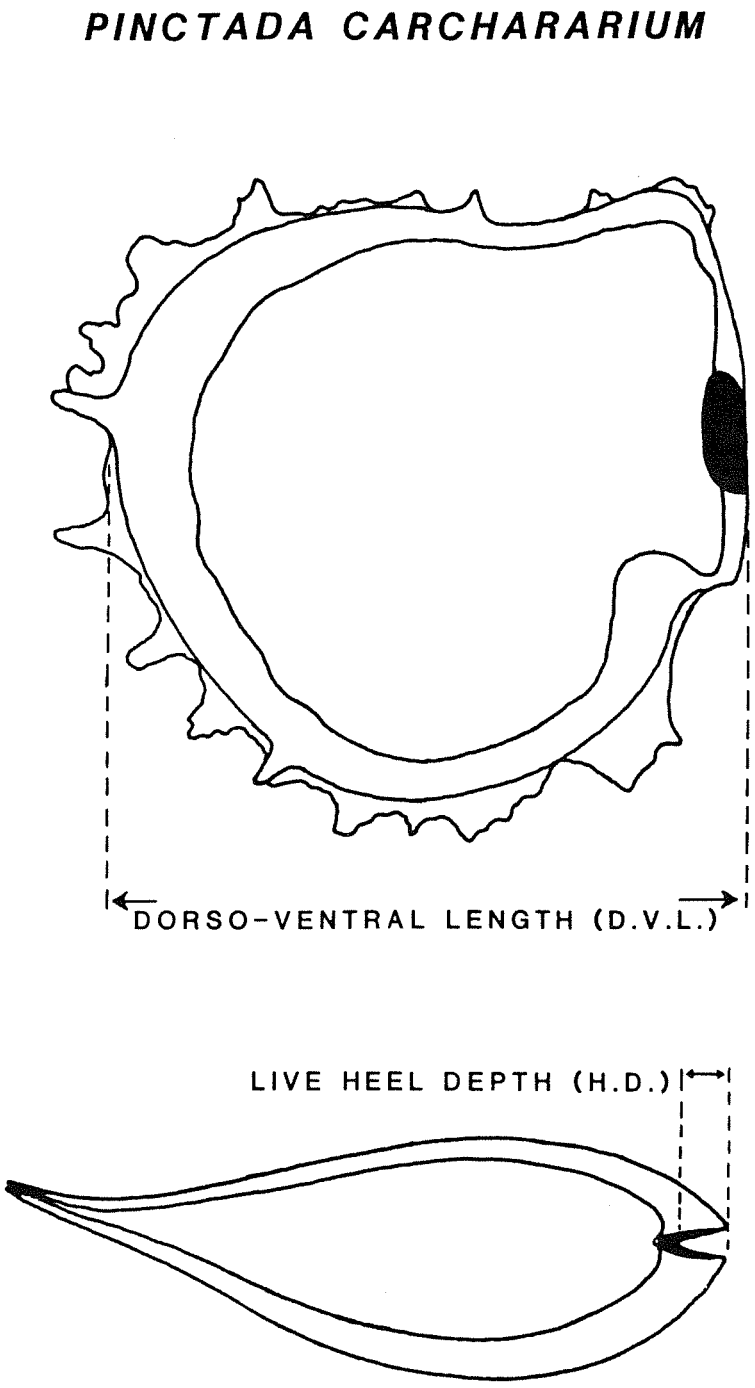

Figure 2: Diagram of the shell of Pinctada carchararium showing where where dorso-ventral length (DVL) and live heel depth (HD) are measured.

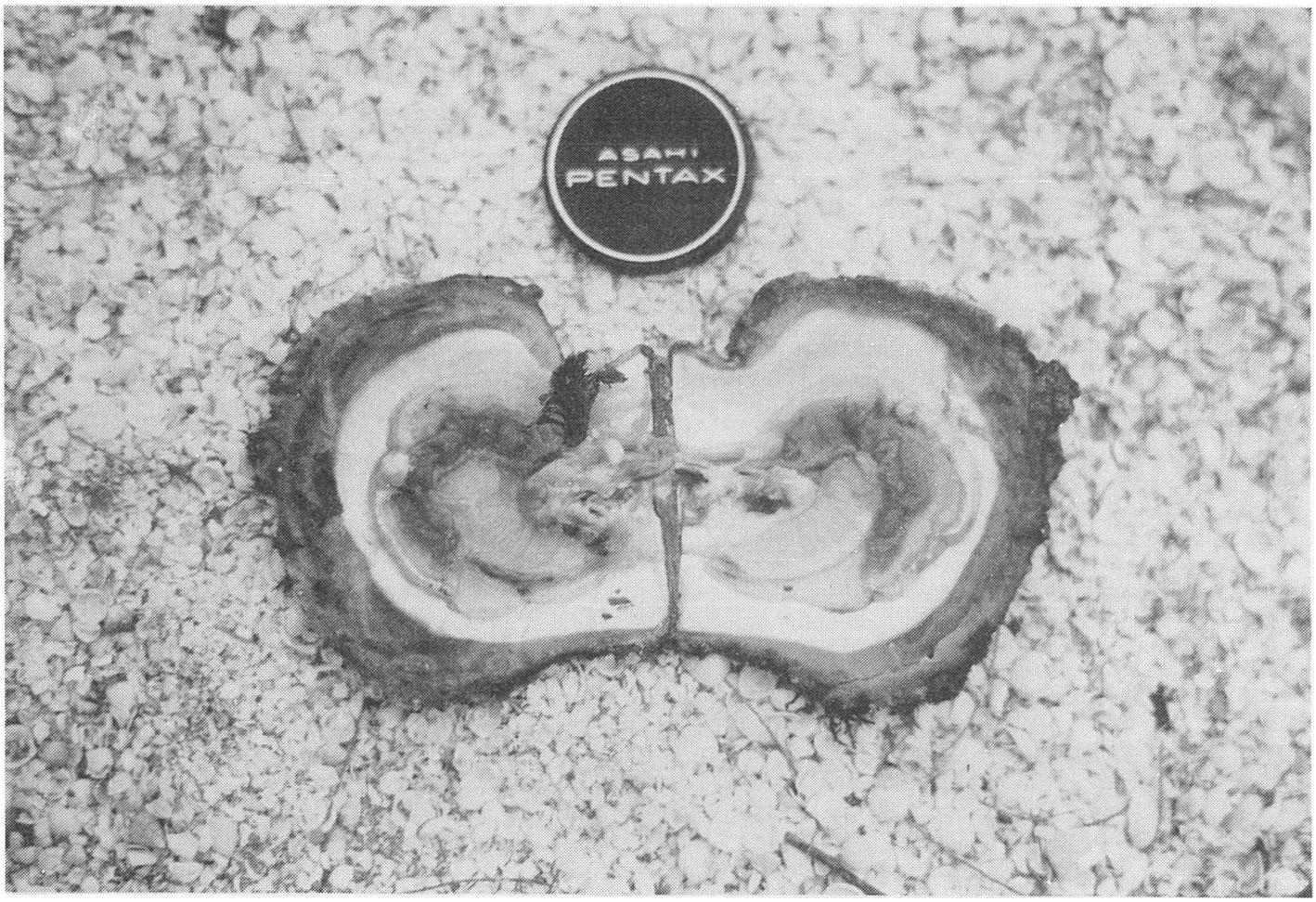

PLATE 4

An opened pearl oyster (Pinctada carchararium), showing internal organs.

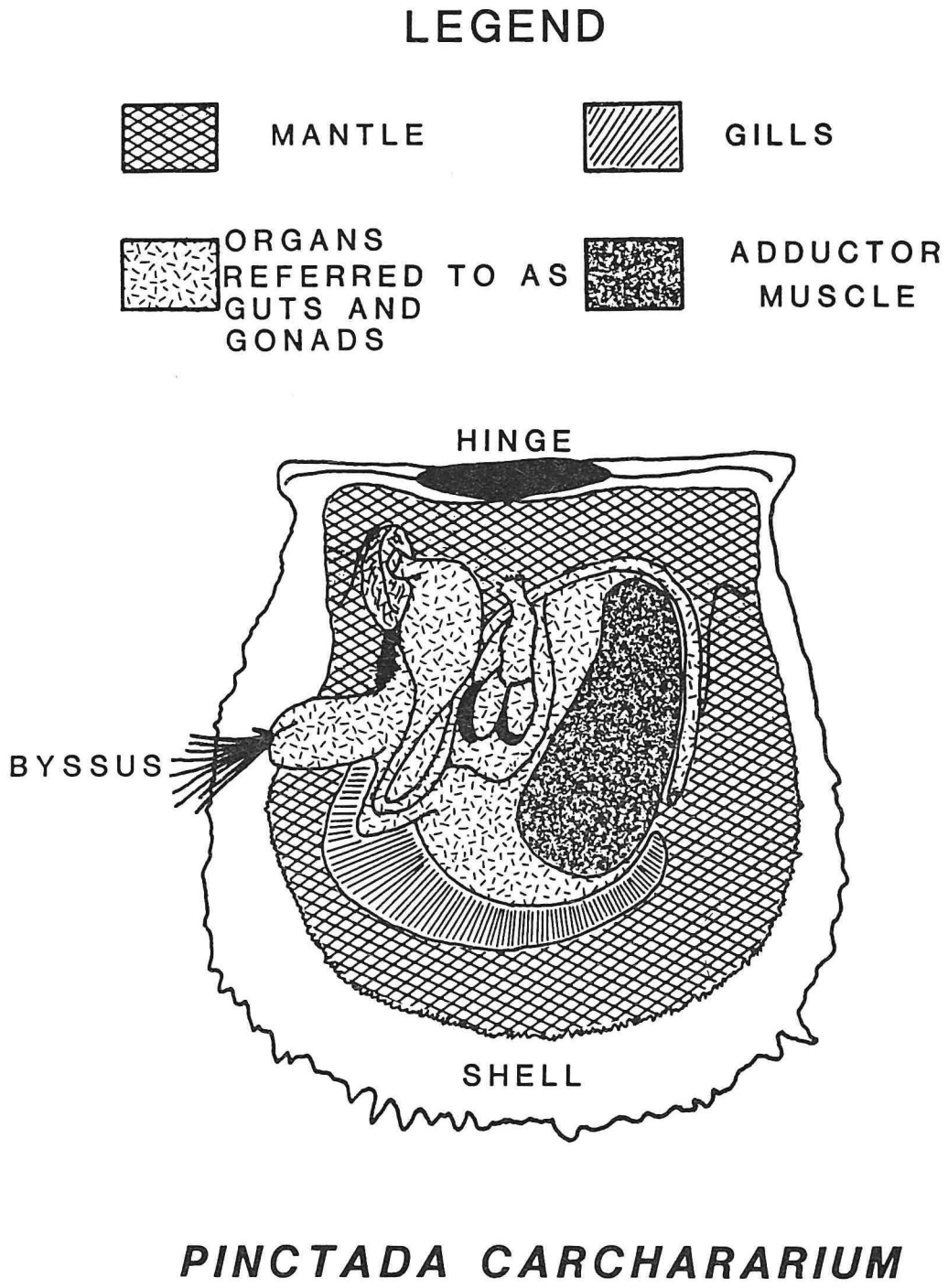

Figure 3: Simplified schematic diagram of Pinctada carchararium showing organs and groups of organs referred to in the text.

4) with a stainless steel knife, relieved of their byssus (the byssus was discarded), blotted dry, weighed on a portable electronic balance, and placed in clean acid rinsed beakers for digestion. The gut of ~~of~~ the organisms was not purged prior to digestion because humans normally consume the entire organism including gut contents (see Harris et al., 1979). Molluscs other than Pinctada sp. were prepared for digestion as above except that no measurements of shell dimensions were made. Green leaf samples of the ribbon weed (Posidonia australis) which were free from visible epiphytes were washed in deionised water, blotted dry and placed in clean acid rinsed beakers for digestion.

All sample weights in this report are wet weights and all heavy metal concentrations are reported on a wet weight basis; the W.A. state health limits are specified on a wet weight basis. Seventeen specimens of Pinctada sp. from site (EB) and seventeen from site (GB) were returned to the Perth laboratory and used to determine a wet weight to dry weight conversion factor. This determination showed the wet to dry weight ratio to be 6.15 ± 0.1 when dried at 105°C for 24 hrs. Drying dissected organs of the organism shows that for the adductor muscle the wet/dry weight ratio is 5.55 ± 0.1, for the guts and gonads it is 6.20 ± 0.1 and for the mantle and gills it is 6.65 ± 0.1.

Specimens of Pinctada sp. from some sample sites and age groups, prepared as above, (see Tables 1-10) were dissected prior to digestion and their adductor muscles, guts and gonads, and mantle and gills were (see Fig. 3 and plate 4) digested and subsequently analysed separately to evaluate the physiological distribution of heavy metals within the organism. A sample of Pinna sp. from sample site (EI) was similarly dissected prior to digestion and analysis.

Digestion of biological material

Digestions were carried out on all biological material within a few hours of collection thereby minimising any errors which may result from bacterial activity, prolonged storage or freeze drying for transport to a laboratory (e.g., Fourie and

Peisach, 1977). Digestion involved the addition of 25 mls of concentrated HNO_3 and 25 mls of 120 vol. H_2O_2 (both AR grade) to each beaker of biological material prepared as above. The beakers of digestion reagent and organic matter were then heated and digestion was complete within 15 mins; the use of 1l beakers and constant stirring with an acid rinsed stirring rod prevented any risk of 'boiling over' during the early stage of digestion when vigorous exothermic reactions take place. After cooling each digest the total fluid volume was measured and 30 mls of the fluid was sealed in an acid rinsed vial for Cd analysis and subsequent return to the laboratory to be analysed for other heavy metals. This method of digestion is both efficient and safe to carry out under field conditions.

All glassware used in the digestions was washed in 'chemsolv' analytical grade detergent and rinsed first in deionised water then in acidified deionised water.Blanks incorporating all reagents involved in the digestions were prepared as a check on reagent purity.

Heavy metal analysis

A) Biological material: Digested samples were analysed for Cd, Cu and Pb in the field by anodic stripping voltammetry using a portable digital voltammeter (Mann and Lintern, 1984), hereinafter referred to as P.D.V. A 0.5 ml aliquot of the HNO_3/H_2O_2 extract of each biological sample was added to 50 ml of 2M NaCl/0.2M ascorbic acid electrolyte in the cell of the instrument. Plating of the metals was carried out for a period of 1 minute, and the stripping peaks recorded digitally. A small measured aliquot of 10 p.p.m. standard solution was then added, and for each sample the increase in peak height was recorded; in this way, peak suppression, which occurs in solutions containing organic matter, was compensated for. The concentration of Cd (or Cu, or Pb) in the biological material was calculated from the formula

$$T = \frac{(B-K) * P \times F}{A-B} \Big/ \frac{V * W * 1000}{(50 + V)} \qquad (1)$$

Where K = peak height of a blank solution at the Cd (or Pb or Cu) peak position

B = peak height of the unknown

A = peak height after the addition of an aliquot of standard

P = concentration of the standard (in p.p.b.)

F = total volume of extract (in mls)

V = volume of aliquot added to cell (in mls)

W = weight of solid material (in grams)

Few biological samples contained sufficient Cu or Pb to record a peak on the P.D.V. instrument (lower detection limit approximately 0.2 p.p.m. for these elements). In contrast, most oyster samples had appreciable concentrations of Cd, and the field use of the P.D.V. instrument enabled maximum flexibility and efficiency to be achieved in the sampling program. Over 160 individual digestions were field analysed in the course of the project.

All digestions were stored in previously acid-washed containers and returned to the laboratory for subsequent routine analysis by A.A.S. of Cu and Zn, and on some 20 samples for Cd, as a cross-check of the accuracy of the P.D.V. instrument. The HNO_3/H_2O_2 digests were aspirated either directly or after dilution into a Varian Techtron AA5 instrument.

B) Sediments: A limited number of sediment and soil samples were analysed for their heavy metal content after drying for 48 hours and crushing to -150#. 2.0 g of each sample were leached with 20 mls of 1M HCl for 2 hrs at 95°C. An aliquot of this solution was taken, and added to the 50 mls of 2M NaCl/0.2M ascorbic acid in the analytical cell. The concentration of Cd, Cu or Pb was calculated by direct comparison of peak height against a standard solution of Cd, Cu and Pb.

X-Ray diffraction analysis was also carried out on the sediments, using a Siemens diffractometer, and CuK_{α} radiation. Samples were mounted on glass, using an alcohol smear, and were examined in the range 4^{o} - 40^{o}, at a scan rate of 1^{o}/minute.

C) Water Samples: Water samples from the Nilemah Embayment-Hamelin Pool area, which contained appreciable concentrations of heavy metals, were analysed using the Portable Digital Voltammeter, and the 2M NaCl/0.2m ascorbic acid electrolyte described above. 25 ml of each water sample was added, after filtering through a 0.45 um filter, to 25mls of 4M NaCl/0.4M ascorbic acid to achieve the desired electrolyte concentration in the cell. Seawater and bore water samples which were expected to contain low (sub p.p.b.) levels of heavy metals, were analysed in the laboratory, using a PAR 174 Polarographic instrument and a model 303 Hanging Mercury Drop Electrode. The instrument was used in the differential pulse mode, with a scan rate of 5mV/sec, after a 2 minute plating period.

RESULTS

Heavy metals in biological material

Tables 1-10 contain the data for Cd concentrations obtained by field analysis, and Cu and Zn concentrations (determined by laboratory A.A.S. analysis) for a series of biological samples taken from different locations around Shark Bay. Locations, and their respective codes, are shown on Figure 1.

Table 1, shows the metal concentrations (in p.p.m. wet weight), for a series of samples from the north-east side of Peron Peninsula, near Monkey Mia; measurements of the dorso-ventral length (D.V.L.), the heel depth (H.D.), and the total flesh weight (T.F.W.) are also shown. At this location a series of individual oysters was analysed to evaluate variance within samples from individual sample sites. Given that two major aims of the project were to examine the distribution of Cd in Pinctada sp. in various localities in the Shark Bay area, and to examine the Cd distribution within different age or size groups of Pinctada sp., the data on

Table 1: Cadmium concentrations of biological material from the Monkey Mia area.

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
RB3A	Pearl oyster	Pinctada sp.	6	87	5.0	92.7	6.5	85	0.4
RB4A	"	"	6	81	2.4	80.0	6.5	67	0.4
RB5A	"	"	8	70	1.6	92.2	3.9	39	0.3
CR4	"	"	1	82	5	12.3	5.8	85	0.3
CR5	"	"	1	72	5	10.0	13.0	135	0.4
CR7	"	"	1	79	5	11.8	11.0	114	0.3
CR8	"	"	1	78	5	7.3	14.3	47	0.3
CR9	"	"	1	70	5	10.4	10.2	44	0.4
CR10	"	"	1	56	5	5.1	8.1	41	0.3
CR11	"	"	1	77	5	9.8	17.7	135	0.4
CR12	"	"	1	76	5	11.6	9.5	154	0.5
CR13	"	"	1	76	5	8.4	9.6	39	0.6
CR14	"	"	1	66	2	5.8	5.4	28	0.4
CR15	"	"	1	52	2	4.2	4.7	26	0.4
CR16	"	"	1	75	4	9.4	5.8	38	0.5
CR17	"	"	1	69	4	8.8	4.7	24	0.6
CR18	"	"	1	83	7	11.0	17.3	92	0.5
CR19	"	"	1	88	7	14.3	8.9	129	0.4
CR20	"	"	6	67	3	48.1	9.4	101	0.6
CR21	"	"	4	80	6	45.5	14.0	100	0.4
RB6A	Adductor muscle		7	80	3.6	16.7	26.1	14	0.1
RB6A	Mantle and gills		7	80	3.6	29.2	2.3	115	0.6
RB6A	Guts and gonads		7	80	3.6	39.5	5.3	131	0.9

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

Table 2: Cadmium concentrations of biological material from the Taillefer Isthmus area.

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
EB17	Weed	Posidonia sp.					<1.0	1.1	0.1
GE3	"	"					<0.4	0.8	<0.1
GB7	"	"					<0.25	0.6	0.1
EB3	Pearl oyster	Pinctada sp.	6	73	4	47.0	20.0	120	0.5
EB4	"	"	6	57	2	31.7	23.0	117	0.6
EB5	"	"	6	55	2	25.1	7.9	31	0.7
GB3	"	"	6	71	4.6	46.2	4.6	118	0.5
GB4	"	"	6	66	3.2	36.4	5.1	124	0.6
GE6	"	"	6	53	2	31.8	3.9	33	0.5
GE7	"	"	3	76	3	27.8	4.7	149	0.6
GB8	Adductor muscle	"				12.7	18.7	22	0.3
GB9	Mantle and gills	"				21.6	0.4	133	0.6
GB10	Guts and gonads	"				23.5	3.0	183	1.7
GE4	Razorfish	Pinna sp.	2			20.8	7.4	27	0.7
GE5	"	"	1			23.0	6.3	178	0.6
EB6	"	"	1			34.9	28.0	152	0.6
EB7	"	"	3			36.1	25.7	4	0.7
EB8	"	"	4			26.5	6.8	5	0.8
GB5	"	"	1			19.8	6.0	44	0.7
GB6	Mussel	Mytilus sp.	4			20.0	1.1	12	0.6
EB10	"	"	3			12.6	0.4	9	0.5
EB9	Bivalve	Costacallista sp.				11.4	<0.2	4	2.4
EB11	"	Hemicardium sp.				7.5	0.7	4	0.4

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

Table 3: Cadmium concentrations of biological material from the Useless Loop area.

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
AI6	Pearl oyster	Pinctada sp.	6	59	5.3	34.8	7.4	95	0.5
AI7	"	"	4	67	3	30.8	10.5	108	0.6
AI8	"	"	6	60	3	33.2	6.8	61	0.5
FI5	"	"	6	50	2	26.8	3.7	33	0.7
FI6	"	"	1	73	4	8.7	8.2	171	0.5
FI3	Razorfish	Pinna sp.	1			16.1	12.3	7	0.6
AI5	"	"	1			37.0	16.6	10	0.5
AI3	Mussel	Mytilus sp.	1			5.0	<0.5	11	0.5
AI4	"	"	5			4.2	0.5	5	0.3
FI4	"	"	4			26.1	1.8	17	0.5

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

Table 4: Cadmium concentrations of biological material from the Herald Bight area.

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
HB10	Weed	Posidonia sp.					<0.14	0.8	0.1
HB11	Pearl oyster	Pinctada sp.	4	79	4.3	60.9	7.9	77	0.4
HB13	"	"	5	82	3.8	60.2	9.1	68	0.5
HB15	"	"	6	52	1.9	28.9	4.6	21	0.6
HG5	"	"	2	84	4.2	29.5	7.5	21	0.8
HG6	"	"	6	57	2.2	41.7	4.6	14	0.6
HB12A	Adductor muscle	"	8	84	5.3	23.8	37.8	17	0.1
HB14A	"	"	8	81	3.6	21.2	26.4	17	0.1
HB16A	"	"	11	53	1.9	38.0	8.8	7	0.2
HB12B	Mantle and gills	"	8	84	5.3	47.4	8.9	143	0.5
HB14B	"	"	8	81	3.6	35.7	4.9	157	0.5
HB16B	"	"	11	53	1.9	43.0	3.5	19	0.7
HB12C	Guts and gonads	"	8	84	5.3	49.0	6.0	112	0.7
HB14C	"	"	8	81	3.6	41.3	4.9	126	0.8
HB16C	"	"	11	53	1.9	52.0	2.6	22	0.9
HB6	Razorfish	Pinna sp.	2			69.4	32.4	10	0.6
HB7	"	"	2			28.1	18.4	21	0.6
HG1	"	"	1			43.3	28.9	5	0.5
HG2	"	"	3			46.3	20.3	8	0.8
HB8	Mussel	Mytilus sp.	2			34.2	1.9	8	0.4
HB9	"	"	3			26.7	2.5	13	0.7
HG3	"	"	1			14.7	3.3	9	0.7
HG4	"	"	3			27.0	2.3	8	0.6
HB17	Salt bush						<0.1	<1	0.1

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

Table 5: Cadmium concentrations of biological material from the Useless Inlet area.

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
UT3	Weed	Posidonia sp.					<0.5	1.5	<0.1
UH3	"	"					<0.3	1.5	<0.1
HP3	"	"					<0.4	<1.5	<0.1
UI3	Pearl oyster	Pinctada sp.	6	74	3	82.6	5.4	4	0.3
UI4	"	"	6	58	2	40.3	3.9	7	0.5
UH4	"	"	1	49	1	4.2	1.4	7	0.4
UH5	"	"	2	62	3	15.9	9.6	17	0.5
HP5	"	"	3	57	2	16.9	5.3	13	0.5
HP6	"	"	2	66	3.5	16.8	7.2	14	0.5
UT4	"	"	6	51	2	27.7	2.3	5	0.7
UT5	"	"	2	65	3	18.7	5.3	5	0.9
UT6	Razorfish	Pinna sp.	1			14.5	2.6	4	0.8
UT7	"	"	1			42.6	20.3	9	0.8
HP4	"	"	1			9.5	4.6	7	0.8
UI5	"	"	1			7.5	4.9	3	1.0
UI6	"	"	2			89.3	10.3	5	0.5
UH6	"	"	2			41.5	10.0	5	0.6
UH7	Mussel	Mytilus sp.	1			6.5	1.8	6	0.9
UI8	"	"	2			21.8	3.7	4	0.8
UI7	Hairy mussel	Stavelia sp.	1			85.1	0.2	3	0.9

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

Table 6: Cadmium concentrations in biological material from the South Passage (SP) and Blind Strait (SI, TB) areas

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
SI3	Weed	Posidonia sp.					<0.2	<1.5	0.5
SI6	Pearl oyster	Pinctada sp.	6	72	3	66.2	15.2	17	0.5
SI7	"	"	4	94	6.5	57.7	16.1	66	0.5
TB3	"	"	6	86	5.5	79	19.6	36	0.5
TB4	"	"	6	68	3	46	10.9	56	0.5
SP4	"	"	3	54	2.8	14.8	11.2	80	0.5
SP5	"	"	2	70	7	11.6	20.5	128	0.6
SI5	Razorfish	Pinna sp.	1			40.6	48.8	16	0.8
SI4	Mussel	Mytilus sp.	2			16.0	5.4	5	0.5
SP3	Clam	Tridacna sp.	1			95.1	9.1	11	0.6

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

Table 7: Cadmium concentrations in biological material from Cape Bellefin (BF) and Cape Heirisson (CH).

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
CH3	Weed	Posidonia sp.					<0.8	<1.5	<0.1
CH6	Pearl oyster	Pinctada sp.	6	58	2	34.3	7.2	118	0.7
CH7	"	"	6	66	3.3	48.7	10.2	74	0.6
BF5	"	"	6	52	1.7	58.2	5.3	6	0.6
CH4	Razorfish	Pinna sp.	1			28.2	5.8	21	0.6
CH5	"	"	1			9.7	4.4	11	0.6
BF3	"	"	2			60.4	10.9	5	0.5
BF4	"	"	1			49.9	13.8	4	0.6
BF6	Mussel	Mytilus sp.	1			13.8	2.1	10	0.4
BF7	"	"	5			8.5	1.2	5	0.5

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

Table 8: Cadmium concentrations of biological material from the Tetrodon Loop area.

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
TL12	Weed	Posidonia sp.					<0.4	<0.5	0.1
EI12	"	"					<0.3	<0.5	0.2
TL8	Pearl oyster	Pinctada sp.	1	108	6.5	22.0	14.4	11	0.4
TL9	"	"	2	60	1.8	12.6	4.7	4	0.6
EI8	"	"	2	60	1.8	14.2	5.3	6	0.8
EI9	"	"	5	81	3.3	65.6	8.2	6	0.6
EI10	"	"	3	95	6.5	46.8	17.7	58	0.6
TL3	Razorfish	Pinna sp.	1			39.8	18.7	2	0.7
TL4	"	"	1			40.3	10.3	4	0.8
EI3	"	"	1			41.0	15.1	8	0.8
EI4	"	"	1			10.3	24.2	5	1.8
EI5	Adductor muscle	"				12.7	4.6	3	0.2
EI6	Gut and granules	"				18.4	42.6	7	1.2
EI7	Gill and mantle	"				19.2	1.8	4	0.3
TL5	Mussels	Mytilus sp.	3			45.8	6.1	5	0.7
EI11	"	"	2			12.8	6.8	8	0.7
TL11	Bivalve	Tapes sp.				13.6	6.0	3	0.9
TL6	Rock oysters	Saccostrea sp.	7			18.4	2.3	180	5.8
TL7	Mullet (guts)	Mugil sp.				11.6	0.2	88	31.8
TL10	" (tail)	"				7.9	1.8	4	0.9
TL13	" (flesh)	"				11.2	<0.2	3	0.5

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

Table 9: Cadmium concentrations in biological material from the Denham area.

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
FH7	Weed	Posidonia sp.					<0.2	3	0.1
DS1	"	"					0.2	7	0.1
FH3	Pearl oyster	Pinctada sp.	6	63	4	33.5	11.7	333	0.6
FH4	"	"	6	59	2.2	38.0	7.4	307	0.6
FH5	"	"	6	57	2.2	28.4	5.6	215	0.7
FH6	Razorfish	Pinna sp.	3			24.0	3.9	113	1.4
DS2	"	"	1			13.8	2.1	297	0.9
FH8	Mussels	Mytilus sp.				12.0	0.7	89	0.7
FH9	Bivalve	Costacallista sp.				9.1	<0.2	4	0.9
LL2	"	"	4			7.9	0.3	8	1.3
FH10	"	Gomphina sp.				6.3	<0.4	31	0.7
LL3	"	Pitarina sp.	4			11.5	0.2	2	0.7

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

Table 10: Cadmium concentrations in biological material from the east Denham Sound area.

SAMPLE NUMBER	SAMPLE TYPE	SCIENTIFIC NAME	N	SIZE D.V.L. (mm)	SIZE H.D. (mm)	SIZE T.F.W. (g)	METAL CONCENTRATION (p.p.m.) Cd	Zn	Cu
BB3	Weed	Posidonia sp.					<0.6	<0.5	0.1
BO3	Pearl oyster	Pinctada sp.	6	49	1.5	22.7	3.2	152	0.6
BO4	"	"	6	55	3.5	27.7	3.9	176	0.5
BO5	"	"	4	57	6.5	18.7	4.2	175	0.5
BO6	"	"	1	61	4	4.3	3.2	158	0.6
BO7	"	"	1	56	4	4.6	4.0	125	0.4
BO8	"	"	1	54	4	3.3	2.3	188	0.3
BO9	"	"	1	71	4	6.1	3.9	330	0.5
BO10	"	"	1	60	4	6.1	2.6	214	0.4
BO11	"	"	1	68	4	5.3	3.7	257	0.5
BO12	"	"	1	64	4	7.0	2.3	148	0.6
BO13	"	"	1	54	4	4.3	6.7	144	0.5
BO14	"	"	1	79	4	7.7	3.2	140	0.6
BB6	"	"	6	59	3	32.9	4.9	13	0.5
BB7	"	"	5	68	6	38.0	13.0	104	0.5
GR4	"	"	1	45	2	2.1	6.8	15	0.8
GR5	"	"	1	74	5	7.9	12.1	40	0.7
CL3	"	"	6	69	4	47.1	7.4	86	0.5
CL4	"	"	4	79	6	37.7	12.1	152	0.5
CL5	Razorfish	Pinna sp.	1			32.5	17.0	29	0.7
CL6	"	"	1			44.3	16.3	86	0.5
GR6	"	"	4			12.6	8.9	12	0.9
BB5	"	"	3			39.2	9.3	7	0.5
BB4	Mussel	Mytilus sp.	9			19.9	0.5	6	1.2
GR7	Hairy mussel	Stavelia sp.	1			37.7	0.5	6	1.0
GR8	"	"	1			49.5	0.2	6	2.4
CLC	Crayfish (flesh)	Panulirus sp.					<0.1	12	3.9

NOTE: D.V.L. Dorso-ventral length.
H.D. Heel depth.
T.F.W. Total flesh weight.
N. Number in sample.

individual animals, (Table 1), clearly show that because of the wide variation within each age/size group, some kind of averaging technique is required. In addition, since health limits are based on Cd content per wet weight of oyster flesh, an arithmetic mean of Cd concentration in individual samples is inappropriate in the present context; the misuse of the arithmetic mean in environmental data is well described (Talbot & Simpson, 1983). The weighted mean (defined as:- the sum of the mass of Cd in all individuals in the sample divided by the T.F.W. for all individuals) of individual samples within a given age/size group in the present study, compiled from analysis of individual specimens, could be usefully and meaningfully used for comparison purposes. However, if error in the chemical analysis is less than the "natural" variation in metal content, as is likely in the present case, it is equally rigorous to group a number of specimens of a given age/size before digestion and analysis to reduce the effect of atypical individuals. In the present example this can be illustrated; the calculated weighted average of 13 individual samples CR4 - CR17, in the heel depth range 2 mm - 5 mm was 9.5 p.p.m. Cd (N.B. the arithmetic mean of the same samples is 9.2 p.p.m. Cd), and the analytical value obtained for a single group of 6 specimens in the same age/size range (sample CR20) was 9.4 p.p.m. Cd. Because of the appreciable savings in the number of chemical analyses required, this latter method was used to obtain weighted mean Cd concentrations in various age/size groups, and in various localities in the Shark Bay area. Depending on weight and availability, the number of samples in each group was usually $3 < N < 7$, giving a total flesh weight of oyster analysed between 20 g and 100 g. Three samples coded RB6A, at the foot of Table 1, show that for 7 dissected individuals of Pinctada sp., the group containing adductor muscles, contained a higher concentration of Cd (26.1 p.p.m.) compared to mantle and gills (2.3 p.p.m.) and guts and gonads (5.3 p.p.m.). This observation was repeated in several other locations, and will be discussed in detail, later.

Table 2, displays the heavy metal concentration in biological material from the Taillefer Isthmus area, of the Peron Peninsula (see Figure 1, also Plate 2). Mature

specimens from Eagle Bluff (EB3) contained 20 p.p.m. Cd, whilst those from Goulet Bluff (GB3) contained 4.6 p.p.m. Cd. Samples (GE) between these two locations, show Cd concentrations of 3.9 p.p.m. and 4.7 p.p.m. Samples of Pinna sp. taken from locations GE and EB showed Cd concentrations of 7.4 p.p.m. and 28.0 p.p.m. respectively. The significance of these apparent variations between two geographically similar locations will be discussed later; differences in the type of substrate at each location, and in proximity to major banks of ribbon weed (see Plate 2) were evident. This is an obvious area for further investigation. Cd concentrations in mussels (Mytilus edulis), and other bivalves (Costacallista impar and Hemicardium tumoriforum) are close to the lower detection limit (approx. 0.1-0.2 p.p.m.). Mytilus sp. samples from the Useless Loop area (Table 3) also showed very low Cd concentrations in comparison to concentrations in Pinctada sp. from the same locations (3.7 - 10.5 p.p.m. Cd).

In the group of samples (Table 4) from Herald Bight, on the north-east side of the Peron Peninsula (see Figure 1), 27 individuals of Pinctada sp. were dissected, and grouped according to heel depth (groups 5.3 mm, 3.6 mm, 1.9 mm heel depth). Groups contained a minimum of 8 samples, and analysis again showed the adductor muscle of each age/size group to contain the highest concentrations of Cd (37.8 p.p.m. Cd, 26.4 p.p.m. Cd, and 8.8 p.p.m. Cd in each group respectively). Highest Zn concentrations were not, however, found in the adductor muscle (17 p.p.m. Zn, 17 p.p.m. Zn and 7 p.p.m. Zn respectively) but in the mantle and gills (143 p.p.m. Zn, 157 p.p.m. Zn and 19 p.p.m. Zn). The reasons for this differential partitioning of heavy metals is not known. Samples of Pinna sp. from this location were found to contain concentrations in excess of 20 p.p.m. Cd, samples of Pinctada sp., 4.6 p.p.m. - 9.1 p.p.m. Cd, and samples of Mytilus sp. less than 3.3 p.p.m. Cd.

Samples of Pinna sp. from the Useless Inlet area between Bellefin and Heirisson Prongs (Figure 1), contained between 2.6 and 20.3 p.p.m. Cd (Table 5). Grouped samples of Pinctada sp. in this area contained between 2.3 and 9.6 p.p.m. Cd; a single small (D.V.L. = 49mm) Pinctada sp. from this area contained 1.4 p.p.m. and

was one of the few Pinctada sp. samples in the Shark Bay area, found in this study, to have a Cd concentration less than the State Health Limit of 2 p.p.m. Cd wet weight.

Samples of Pinctada sp. from South Passage and Blind Strait (Table 6) were found to have high concentrations of Cd (between 11.2 and 20.5 p.p.m. Cd), whilst the single Pinna sp. specimen examined contained 48.8 p.p.m. Cd, the highest recorded bulk flesh value of any animal in the survey. This is higher than the maximum (8.5 p.p.m.) recorded for Pinna bicolor in Spencer Gulf (Ward et al 1982). A specimen of the clam Tridacna sqamosa contained 9.1 p.p.m. Cd. Samples of Pinctada sp. from Cape Bellefin and Cape Heirisson (Table 7) contained much lower concentrations of Cd (5.3 - 10.2 p.p.m. Cd), and the Pinna sp. sampled in this area contained low concentrations of Cd (4.4 - 13.8 p.p.m. Cd) relative to samples of this species in other locations.

In Table 8 heavy metal concentrations in Pinctada sp. and Pinna sp. specimens from the Tetrodon loop (TL) and Egg Island (EI) areas of the east side of Dirk Hartog Island are shown. Pinctada sp. contain up to 17.7 p.p.m. Cd and Pinna sp. up to 24.2 p.p.m. Cd. Some of the Pinna sp. samples from this area were dissected, and analysed separately; unlike Pinctada sp., the highest concentration of Cd in Pinna sp. is found in the gut and granules (42.6 p.p.m.), with a much smaller concentration (4.6 p.p.m.) in the adductor muscle. The texture of the adductor muscle of Pinna sp. is noticeably different from that of Pinctada sp., and much more closely resembles that of the commercially viable scallop, Amusium balotti.

Samples of both Pinctada sp. and Pinna sp. from the Denham area, were found to contain high concentrations of Zn relative to samples from other locations in this study; however, Zn concentrations, relative to Cd, are low when compared to the ratio in other species of oysters and mussels Australia-wide (e.g., Harris et al., 1979, Ward et al., 1982). Concentrations of Cd in Pinctada in these samples were in the range 5.6 - 11.7 p.p.m. Cd, and in Pinna were the lowest recorded in this study (2.1 - 3.9 p.p.m. Cd) for this species. Several samples of of other bivalves

(Mytilus sp., Costacallista sp., Gomphina undulosa, and Pitarina citrina) were digested and analysed and found to have low concentrations of Cd, Cu and Zn.

Samples of Pinctada sp. from the north-west side of Peron Peninsula, (East Denham Sound), were subjected to group and individual chemical analysis (Table 10). Cd concentrations in the 9 samples subjected to individual analysis ranged from 2.3 - 6.7 p.p.m. Cd. The weighted mean of these individuals, 3.5 p.p.m. Cd (The arithmetic mean is also 3.5 p.p.m.) compares with 3.9 p.p.m. Cd (Sample BO4) for the single group of 6 individuals analysed of this age/size group. A sample of crayfish (Panulirus sp.) flesh from this locality was found to contain less than the lower detection limit (0.1 p.p.m.) of Cd. Samples of Mytilus sp. and Stavelia horrida from this area posessed Cd concentrations not exceeding 0.5 p.p.m.

Metal concentrations in a series of individually dissected adductor muscles from sample sites EB and GB, were determined in the laboratory (Table 11). The adductor muscles show concentrations of Cu, Pb and Zn which are low in comparison to Cd concentrations; the latter show an extremely wide variation, from 5.4 to 70.9 p.p.m. Cd for animals of similar total flesh weight. The reasons for this wide variation are not known, and in combination with the general biochemical problem of why the adductor muscle of Pinctada sp. contains high concentrations of Cd relative to other organs, and to the adductor muscle in other species (e.g., Pinna sp. and Amusium sp.) in Shark Bay, constitutes an important area for possible future study (see suggestions in Lake, 1979). Because the total flesh weight (T.F.W.) of the GB samples reported in Table 11 is, on average, some 44% greater than that of the EB samples, a meaningful comparison of concentrations in the adductor muscles from the two localities cannot be made directly.

Leaching cadmium from molluscs with brine solutions

A series of brine (4M NaCl) pickling experiments were carried out on dissected Pinctada sp., to ascertain the percentage of Cd which could be easily removed, at ambient temperatures. The results are shown in Table 12. Two sets of experiments

were performed - one set with the brine initially acidified to pH3 with acetic acid (the brine pH rose to pH6 after 24 hours), and the other set carried out at a brine pH of 6. Results in columns B for each metal, show the metal load (µg) extracted into 400 ml of brine, and in columns A the load of metal (in µg) remaining in the oyster (this was calculated by subsequent total digestion and analysis of the brined material). The brine takes up a considerable but variable proportion of Cd and Zn - this will be discussed later in this report. Cd and Zn (and Pb) form very strong chloride complexes in saline solutions (Mann & Deutscher, 1980) and this factor may be important to the general geochemical behaviour of these elements in the Shark Bay area, in relation to groundwater, sediments and biological material.

Heavy metals in Shark Bay sediments

Hot acid extracts using 100 mls of 1M HCl on 10g of dried sediment from marine environments at sites EB and GB, and from dried soil, drill spoil and sediments from Hamelin Pool, (Table 13) did not contain measurable concentrations of Cd. Pb concentrations were near the detection limit but showed some variation; the highest Pb concentration in sediment was from a marine sediment at site EB. In future, if detection limits were to be improved, it is likely that a geochemical study of sediments, (particularly of substrates on which pearl oysters were growing) could prove to be relevant (e.g., see Warren, 1981), although the use of marine calcareous sediments as direct indicators of heavy metal pollution has been recommended against (Talbot & Chegwidden, 1982).

Heavy metals in seawater, groundwater and bore-water

Table 14 shows trace metal concentrations in seawaters and bore-waters from the Shark Bay area. As expected most seawaters contained less than 1 p.p.b. Cd and Pb; the only notable exception was Herald Bight where seawater was found to contain 4.6 p.p.b. Pb. By comparison, some groundwater samples from the Nilemah Embayment, Hamelin Pool (see Table 15), contained nearly 8 p.p.m. Pb. Appreciable

Table 11: Metal concentration values of a series of pearl oyster adductor muscles from the Goulet Bluff (G.B.) and Eagle Bluff (E.B.) locations.

SAMPLE NUMBER	SIZE				METAL CONCENTRATION (p.p.m.)			
	D.V.L. (mm)	H.D. (mm)	T.F.W. (g)	A.W. (g)	Cd	Pb	Zn	Cu
EB28	65	3.7	5.0	1.2	9.1	3.7	25	0.3
EB29	64	3.6	5.5	1.8	15.6	2.3	39	0.9
EB30	66	2.6	6.7	2.0	31.7	0.2	30	0.4
EB31	61	2.3	5.4	1.6	12.1	3.0	18	1.1
EB32	70	4.1	5.8	1.6	11.0	1.1	27	1.4
EB33	64	2.5	4.2	1.0	13.7	6.1	32	0.5
EB34	64	3.0	5.1	1.3	15.9	1.9	25	0.1
EB35	68	3.1	6.9	1.9	14.0	4.7	15	0.3
EB36	72	5.0	6.2	1.4	9.1	4.0	56	0.5
EB37	65	3.6	6.9	2.0	12.8	2.8	32	0.1
GB28	68	3.5	7.2	2.0	5.4	1.6	22	0.2
GB29	70	3.8	6.2	1.7	9.4	1.9	31	0.4
GB30	68	5.7	5.9	1.7	70.9	0.9	25	1.1
GB31	70	3.0	7.9	2.8	13.7	<0.9	30	0.1
GB32	70	3.8	7.1	2.6	13.5	1.2	23	0.3
GB33	74	4.1	8.9	3.0	13.4	0.2	23	0.4
GB34	75	3.1	7.2	2.3	8.2	1.2	24	0.3
GB35	74	3.6	6.6	2.2	25.7	2.4	33	0.5
GB36	70	3.0	6.1	2.0	22.8	1.2	32	0.7
GB37	78	5.6	8.6	2.4	10.5	1.1	33	0.4

NOTE: T.F.W. Total flesh weight
A.W. Adductor weight
D.V.L. Dorso-ventral length
H.D. Heel depth.

Table 12: Metal amounts (expressed in μg) in a series of 400 ml brine extracts (4M NaCl) performed on pearl oyster parts at two different acid strengths over a period of 24 hours.

SAMPLE NUMBER	SAMPLE TYPE	pH	WET WEIGHT (g)	METAL AMOUNT (μg) Cd B	Cd A	Zn B	Zn A	Pb B	Pb A	Cu B	Cu A
EB22	Adductor muscle	3-4	13.3	91	79	160	100	-	-	-	6.3
EB23	Guts and gonads	"	17.8	98	23	920	460	-	-	-	14.1
EB24	Mantle and gills	"	16.5	49	<2	760	100	-	-	-	11.4
GB22	Adductor muscle	"	18.6	91	105	280	300	-	-	-	7.6
GB23	Guts and gonads	"	19.2	49	74	1120	6100	-	-	-	13.8
GB24	Mantle and gills	"	22.6	56	5	800	410	-	-	-	10.8
EB25	Adductor muscle	6-7	12.3	35	56	80	210	-	-	-	4.2
EB26	Guts and gonads	"	15.3	21	9	200	720	-	-	-	18.8
EB27	Mantle and gills	"	14.9	<7	9	120	430	-	-	-	8.2
GB25	Adductor muscle	"	21.1	88	114	160	360	-	-	-	4.9
GB26	Guts and gonads	"	22.1	23	28	480	3800	-	-	-	11.5
GB27	Mantle and gills	"	24.1	<9	14	440	670	-	-	-	9.2

NOTE: B - Amount of metal (in μg) in the brine solution after the exposure to the oyster material.

A - Amount of metal (in μg) in the oyster material after pickling in the brine solution.

Table 13: Metal concentrations in a selection of sediment and soil samples from the Shark Bay area. A hot acid extract (1M HCl for two hours in a boiling water bath) was performed on each.

SAMPLE NUMBER	SAMPLE TYPE	METAL CONCENTRATION (p.p.m.) CADMIUM	LEAD
PN11	Soil	<0.2	1.6
HM121	Drill spoil	<0.2	1.2
HM116	Sediment	<0.2	0.4
HM114	"	<0.2	1.0
GR3	Soil	<0.2	0.9
NA3	"	<0.2	0.9
GB2	Sediment	<0.2	0.4
EB2	Sediment	<0.2	1.7
EB13	Lagoon sediment	<0.2	0.6
EB14	Sediment	<0.2	7.8
EB15	Sediment	<0.2	2.2

Table 14: Trace metal concentrations in waters from the Shark Bay area - Sea and bore water samples.

SAMPLE NUMBER	LOCATION	WATER SAMPLE TYPE	METAL CONCENTRATION (ppb) Zn	Cd	Pb	Cu
PN5	North Peron	Salt lake	<5	0.11	0.33	0.42
PN4	"	Salt lake	-	0.16	0.73	1.67
PN8	Big Lagoon	Lagoon	-	<0.28	1.33	1.35
PN16	Goulet Bluff	Lagoon	-	<0.05	0.14	0.95
EB12	Eagle Bluff	Lagoon	-	<0.07	0.21	0.76
HB4	Herald Bight	Salt lake	-	<0.12	0.77	2.56
CG4	Depuch loop	Lagoon	-	0.14	0.64	1.6
CG1	Carrarang	Well	-	0.21	0.29	-
CG2	"	Bulgoo Well	-	0.12	0.73	-
TA1	Tamala	Well	-	0.15	0.09	2.8
TA2	"	"	-	<0.13	0.38	-
NA1	Nanga	Bore	<1	0.14	0.5	0.13
NA2	"	"	<5	<0.22	0.95	0.66
PN1	Peron	"	<1	0.18	0.33	0.68
PN9	"	"	-	<0.06	0.12	1.33
PN10	"	"	<2	0.22	<1	0.68
PN13	"	"	-	0.28	0.18	0.58
PN15	"	"	-	<0.11	<0.10	0.51
SI1	Sunday Island	Sea water	<2	0.12	1.38	0.82
TB1	The Beacons	"	-	0.22	1.36	2.04
AI1	Ant Island	"	-	<0.07	0.12	0.36
EI1	Egg Island	"	-	0.06	0.33	0.35
GB1	Goulet Bluff	"	<5	0.33	1.25	1.04
EB1	Eagle Bluff	"	<5	0.37	0.71	1.35
GE1	Taillefer Isth	"	-	0.06	0.33	0.33
BO1	Middle Bluff	"	<2	0.17	2.7	1.44
PN14	Lharidon Bt.	"	<5	0.29	0.58	1.97
YA1	Yannga	"	-	0.14	0.77	1.58
SP1	South Passage	"	<3	<0.16	0.82	1.25
GR1	Gregorys	"	-	<0.06	<0.12	0.93
UT1	Useless Inlet	"	-	0.06	1.15	0.16
HB1	Herald Bight	"	<1	0.5	4.57	2.92

Table 15: Trace metal concentrations in water samples from the Nilemah Embayment area of Hamelin Pool, Shark Bay.

SAMPLE NUMBER	SAMPLE TYPE	T.D.S. (°/oo)	METAL CONCENTRATIONS (p.p.b.) Zn	Cd	Pb	Cu
HM98	Groundwater	17	-	2.4	0.3	3.0
HM102	"	74	-	10	30	30
HM110	"	123	-	1.9	7900	-
HM114	"	74	-	0.2	5.2	2.1
HM115	Sea water	63	-	<0.3	1.7	1.3
HM116	Surface water	48	<5	<0.4	5	2.5
HM121	Groundwater	59	6	5	110	-

NOTE: T.D.S. - Total dissolved solids.

Table 16: Comparison of Portable Digital Voltammeter Cd analysis and AAS analysis of a selection of biological material. (Concentrations reported as found in analytical solutions).

SAMPLE NUMBER	SAMPLE TYPE	Cd CONCENTRATION (p.p.m.) P.D.V.	A.A.S.
HB8	Mytilus sp.	0.14	0.15
HB9	"	0.17	0.14
EI11	"	0.21	0.20
SI4	"	0.26	0.24
GR6	Pinna sp.	0.30	0.29
EB8	"	0.32	0.31
TL4	"	0.63	0.64
BO15	"	0.93	0.64
BB5	"	1.02	1.07
AI5	"	1.37	0.78
EI3	"	1.54	1.86
HG2	"	1.56	1.59
UT7	"	1.52	1.24
BF3	"	1.50	1.70
GR5	Pinctada sp.	0.23	0.24
HP6	"	0.26	0.23
TL8	"	0.95	0.83
GB8	" (adductor)	0.63	0.68
HB14A	" "	1.02	0.91
HB12A	" "	1.51	1.16

concentrations of Cd (up to 10 p.p.b.) were also recorded in some of these waters; the Cd (and Pb) concentration is greater than can be attributed to simple evaporative concentration of seawater. As such these samples constitute the only non-biological source of anomously high concentrations of heavy metals encountered in the survey; they will continue to be the subject of further investigation. The presence of high concentrations of heavy metals in similarly saline groundwaters from salt lake systems in Western Australia has been documented (Mann, 1983).

Comparison of P.D.V. and A.A.S. analytical techniques

Table 16 shows comparative analytical results for the P.D.V. instrument and a laboratory A.A.S. instrument, for a selection of digests of biological material examined during the project. The selection of material for comparison included samples of Mytilus sp. and Pinna sp. as well as Pinctada sp., and contained samples with Cd concentrations varying by an order of magnitude. P.D.V. results were neither systematically higher or lower than A.A.S., with a mean absolute difference of 12.4%. Part of this difference can be attributed to the A.A.S. technique, particularly since dilutions were also required, and standards could not be exactly matrix-matched.

Since errors in weighing and in measuring volumes during preparation of the extract are small, it is estimated that the likely error in Cd results reported for field-analysed biological material, quoted on a wet weight basis, is 10%.

DISCUSSION

Organism and shell size

In Pinctada carchararium, relationships between shell dimensions, total flesh weight, and organism age are not well known and may be ill-defined due to local variations in nutritional factors, parasite activity, substrate stability, water salinity, the existence of sub-species, etc. In this study, it was noted that large individuals from some locations had very thin (almost transluscent) shells while

smaller specimens from other locations had very thick shells suggesting local variations in any age/size relationship. Thus, relationships between shell dimensions, total flesh weight, and organism age must be treated with some caution. Despite the above limitations, however, if comparisons of heavy metal concentrations between oysters from different parts of the embayment are to be made, it is essential to have some means of allowing for variations in population structure.

In this study we have assumed that there is a relationship between live heel depth, dorso-ventral length (see Fig. 2), total flesh weight, and age but we make no attempt to quantify the relationship. Hynd (1961) has shown that there is an exponential relationship between live heel depth and dorso-ventral length in Pinctada albina albina (P. caracharium is synonymous with P. albina albina of Hynd, 1961) from Shark Bay, a proposal which is consistent with our observations (see Fig. 4). However, data points on our plot show considerable scatter, a line of best fit slightly displaced from but parallel to that of Hynd (1961), and the suggestion of subdivision into two slightly different trends. If one line of best fit is drawn for each of our possible sub-populations, one would lie slightly above our overall line of best fit and the other would lie slightly below that of Hynd (1961). Hynd (1961) also noted that plots such as Figure 4 may reveal genotypic and phenotypic variations and it remains possible that the two sub-populations in Figure 4 reflect the existence of two sub-species of Pinctada in Shark Bay. Other morphological evidence (A. Gabelish, Shark Bay Pearling Co., pers. comm.) also suggests the existence of two subspecies in the embayment and the existence of hybrids between them. In this study, we note that samples from sites (see Fig. 1) BF, EI, HB, HG, RB, SI, TB, TL and UI plot above our line of best fit, while samples from AI, BB, BO, CL, FI, GB, GR, SP, and UT plot below the line; samples from CH, CR, EB, FH, GE, HP and UH plot both sides of the line but near to it. However, the location of these groups of sites does not show any recognisable regional pattern nor any correlation with heavy metal content or substrate composition.

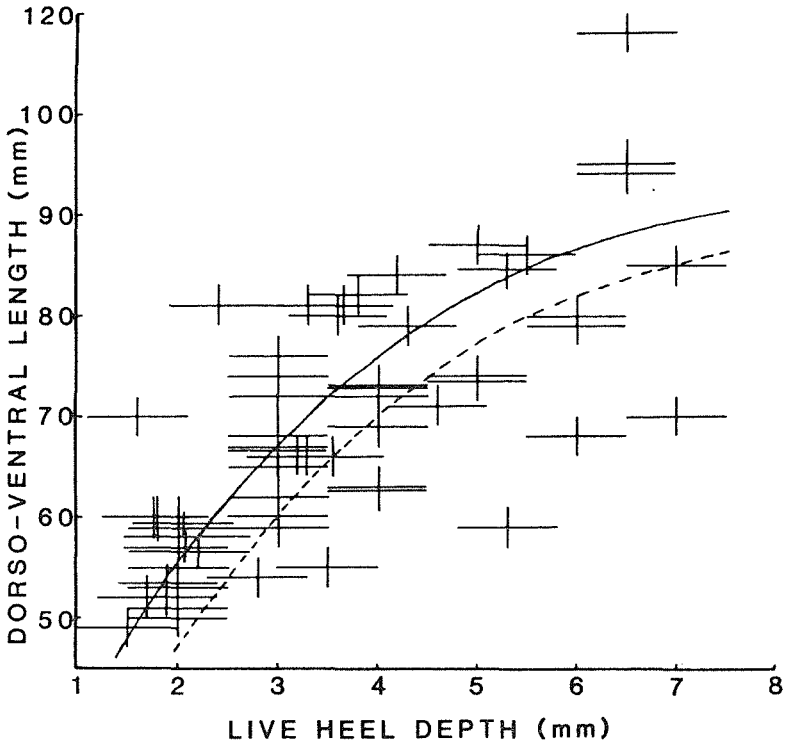

Figure 4: Plot of dorso-ventral length against live heel depth for Pinctada carchararium

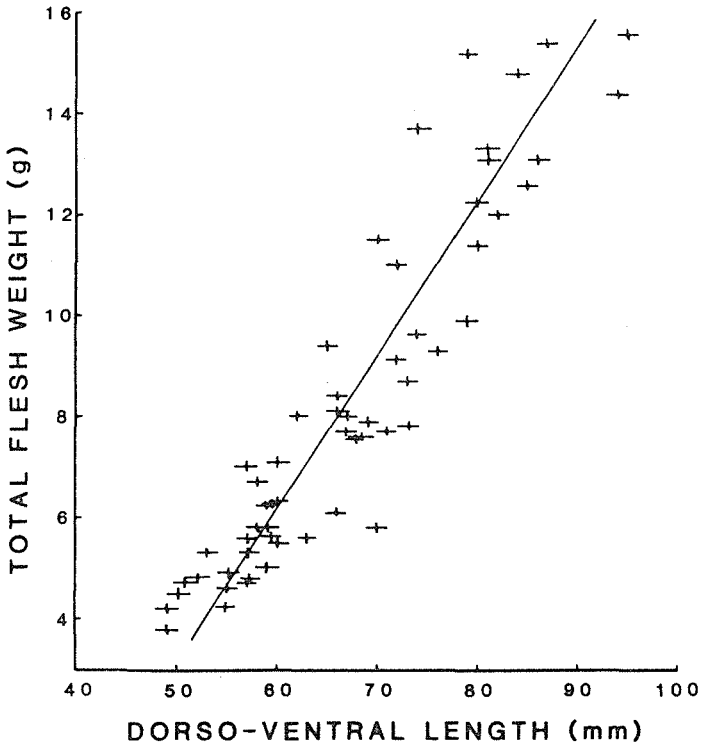

Figure 5: Plot of dorso-ventral length against total flesh weight for Pinctada carchararium

A plot which shows much less data point scatter and appears linear for dorso-ventral lengths greater than 50 mm is obtained by plotting dorso-ventral length against total flesh weight (see Fig. 5). Because this plot shows a good correlation between dorso-ventral length (which in turn is related to live heel depth see Fig. 4) and total flesh weight, it is evident that several potential age indicator parameters are linked and we could choose any one for use in correcting heavy metal analyses for local variations in population structure. Because only total flesh weight and dorso-ventral length show a linear relationship over the range of interest and because total flesh weight is the most accurately and consistently measured of the three parameters, total flesh weight was chosen as the 'age dependent' parameter for use in interpreting heavy metal analytical data.

Cadmium concentration as a function of total flesh weight

As expected, the Cd concentration in Pinctada sp. generally increases with total flesh weight (see Fig. 6a,b). For each sample site, the gradient of a line (G_{Cd}) through points on a plot of Cd concentration against T.F.W. appears to be characteristic of that location; gradient vary from 0.49 at sites BF and UI up to 2.76 at sites EB and SP. The gradient for each site (Fig. 6a) was determined by visual inspection because data points were too few for the application of statistical procedures; each data point on figure 6a is a weighted mean for 4-8 individual animals. All gradients are defined to pass through the origin. In figure 6b plots of total flesh weight against Cd concentration for individual animals from two sample sites are presented to show the variation which could be expected to give rise to each data point in figure 6a. The greater number of data points for each sample site in figure 6b permits the use of statistical methods to assess the significance of the fitted line which determines the gradient (G_{Cd}) at each locality. The mathematically determined values of G_{Cd} are 0.98 for site CR and 0.58 for site BO which compare very favourably with the values determined by visual inspection (fig. 6a) of 0.96 and 0.70 respectively and give confidence in the other

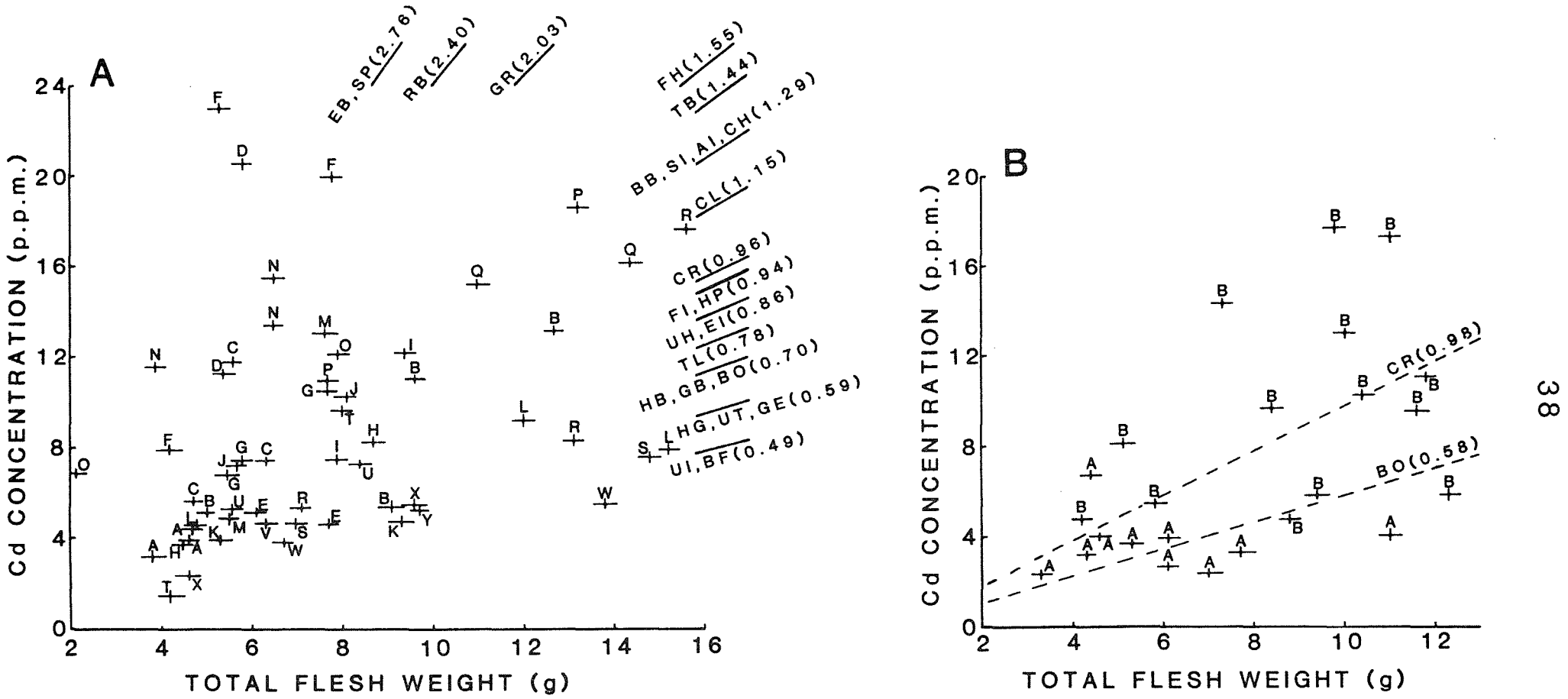

Figure 6: Plots of cadmium concentration against total flesh weight for Pinctada carchararium in Shark Bay. Gradients for the line of best fit to data points from each sample locality are shown; in A, each plotted point represents a weighted mean for 4-8 individual specimens. Sample sites are represented by letters as follows: A = BO, B = CR, C = FH, D = SP, E = GB, F = EB, G = AI, H = FI, I = CL, J = CH, K = GE, L = HB, M = BB, N = RB, O = GR, P = TB, Q = SI, R = EI, S = HG, T = UH, U = HP, V = TL, W = UI, X = UT, Y = BF.

values of G_{Cd} in figure 6a. Statistical assessment of the data in fig 6b yields a correlation (r) for the CR data of 0.63 and for the BO data of 0.55 with the one tailed (t) statistic indicating that both are significant at above the 95% confidence level. However, despite the favourable comparison between the gradients in Figure 6a and 6b and despite the satisfactory statistics for the figure 6b data we suggest that the value of G_{Cd} for each site may be in error by up to 25%. The variation in G_{Cd} between many sample sites is sufficiently large that even an error of 50% would not conceal the observation that there is a marked regional variation in the rate of Cd uptake by the oysters. Because the calculated values for G_{Cd} incorporate both the Cd concentration and an allowance for size ('age') they can be used for direct comparisons between sample sites (each value is based on 12-24 individual animals).

The values of G_{Cd} can also be used in reverse to calculate the maximum total flesh weight (T.F.W.) which an oyster at each sample site is likely to attain before it exceeds 2 p.p.m. Cd. Such a calculation indicates that oysters from areas EB, SB, RB, GR, FH, TB, BB, SI, AI, CH and CL would be likely to exceed this value before they reached 2.0 gms (T.F.W.), oysters from areas CR, FI, HP, UH and EI would exceed it at between 2.0 and 2.5 gms (T.F.W.), those from TL, BO, HB and GB would exceed between 2.5 and 3.0 gms T.F.W., and those from HG, UT, GE, UI and BF would exceed it between 3.0 and 4.2 gms T.F.W.. It is also possible using figure 5 to convert these total flesh weights to dorso-ventral lengths (D.V.L.) which show that all oysters would be likely to exceed 2 p.p.m. Cd before their D.V.L. reached 45 mm except those from TL, BO, HB, GB, HG, UT, GE, UI and BF and even these would exceed this value before their D.V.L. reached 55 mm. Thus, all specimens of Pinctada sp. from the Shark Bay area which are above the minimum size for commercial fishing (i.e. D.V.L. > 60 mm) would be likely to exceed the maximum Cd concentration of 2 p.p.m.

Cadium distribution within Pinctada carchararium

Previous studies of the distribution of Cd between various organs in molluscs (e.g., Ostrea sinuata, Brooks and Rumsby, 1967) have shown that Cd concentrates in organs which in this study have been collectively classed as guts and gonads. (In Pinna sp. most of the Cd is concentrated in gut granules). Generally, the adductor muscle contains the lowest Cd concentration with higher concentrations present in the mantle and gills and the highest in the guts and gonads. The distribution of Cd in the single Pinna sp. dissected during this study (see Table 8) is consistent with that described above but the same does not apply to the numerous specimens of Pinctada sp. examined.

In all 37 specimens of Pinctada sp. examined, the adductor muscle contains by far the highest concentration of Cd found in any part of the organism. The remainder of the animal contains on average, less than one fifth of the concentration found in the adductor muscle. Weighted means calculated for all the dissected specimens of Pinctada sp. analysed indicate that slightly over 60% of all the Cd contained in the organisms is in the adductor muscle.

In contrast to Cd, the Zn concentration in the adductor muscle is very low and accounts for little more than 5% of the total Zn in the organisms. The Zn is approximately evenly distributed between the mantle and gills, and the guts and gonads. Hence, despite the similarity in chemical behaviour of Zn and Cd these oysters can clearly segregate these two elements and concentrate them in different organs.

Zinc and copper concentrations in Pinctada carchararium

Cu concentrations in all specimens examined averaged about 0.5 p.p.m.; very few contained < 0.3 p.p.m. or > 0.8 p.p.m.) and show no systematic variation between sample sites. Zn concentrations, on the other hand, vary markedly between sample sites ranging from less than 10 p.p.m. at some sites to over 300 p.p.m. at others.

Because Zn concentrations (like Cd concentrations) show a marked increase with

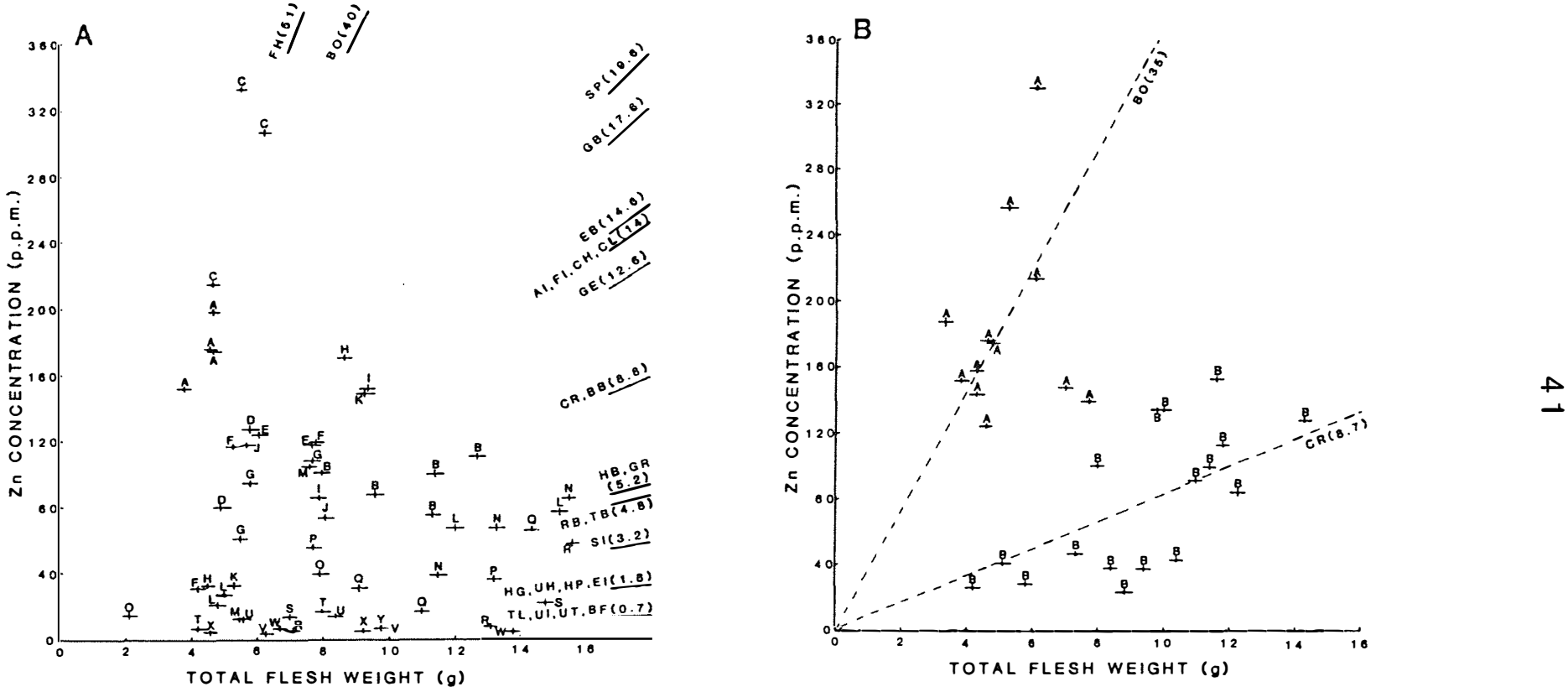

Figure 7: Plots of zinc concentration against total flesh weight for Pinctada carchararium in Shark Bay. Gradients for the line of best fit to the data points from each sample locality are shown; in A, each plotted point represents a weighted mean for 4-8 individual specimens. Sample sites are represented by letters as follows: A = BO, B = CR, C = FH, D = SP, E = GB, F = EB, G = AI, H = FI, I = CL, J = CH, K = GE, L = HB, M = BB, N = RB, O = GR, P = TB, Q = SI, R = EI, S = HG, T = UH, U = HP, V = TL, W = UI, X = UT, Y = BF.

the size ('age') of the organisms examined, intersite comparisons are best achieved using the gradients for plots of Zn concentration against total flesh weight for each sample site. These plots for Zn concentrations (figures 7a and 7b) show the large variation between sites; the gradients differ by up to two orders of magnitude between some sites. As with the similar plots for Cd, gradients in figure 7a are determined by visual inspection because although each point plotted is a weighted mean for several individual organisms (4-8) few points can be plotted for each sample site. The gradients in figure 7b were determined by linear regression (the regression line was required to pass through the origin) and analysed statistically. The correlation (r) for the samples (fig 7b) from BO is 0.58 and for the samples from CR is 0.75; the one tailed (t) statistics show both are significant above the 95% confidence level. The mathematically determined gradients for Zn p.p.m./T.F.W. are 8.7 for samples from CR and 35 for samples from BO; both of these compare favourably with the gradients determined by visual inspection in figure 7a (8.8 for CR and 40 for BO). However, despite this agreement between the methods we suggest that, as for Cd, error limits of ± 25% should be applied to each gradient recorded in figure 7a.

The regional variation in zinc uptake by Pinctada sp. can readily be shown by plotting the gradients (G_{Zn}) determined above on a map of the embayment. Such a map (fig 8) shows high values of G_{Zn} between Denham and the Big Lagoon, near the Useless Loop salt works and in South Passage, relative to other areas sampled in this study. These Zn anomalies are clearly defined and the inference that they reflect human activity seems inescapable. Although the Pinctada sp. appears to be a very efficient detector of extraneous sources of Zn, it is important to note that no mollusc sample analysed during the study had a Zn content near the maximum level of 1000 p.p.m. wet weight set by the W.A. department of health for molluscs for human consumption. Similar results were noted for the concentrations of Cu and Pb; Cd is the only element in Shark Bay molluscs known to exceed the health department limits for human consumption.

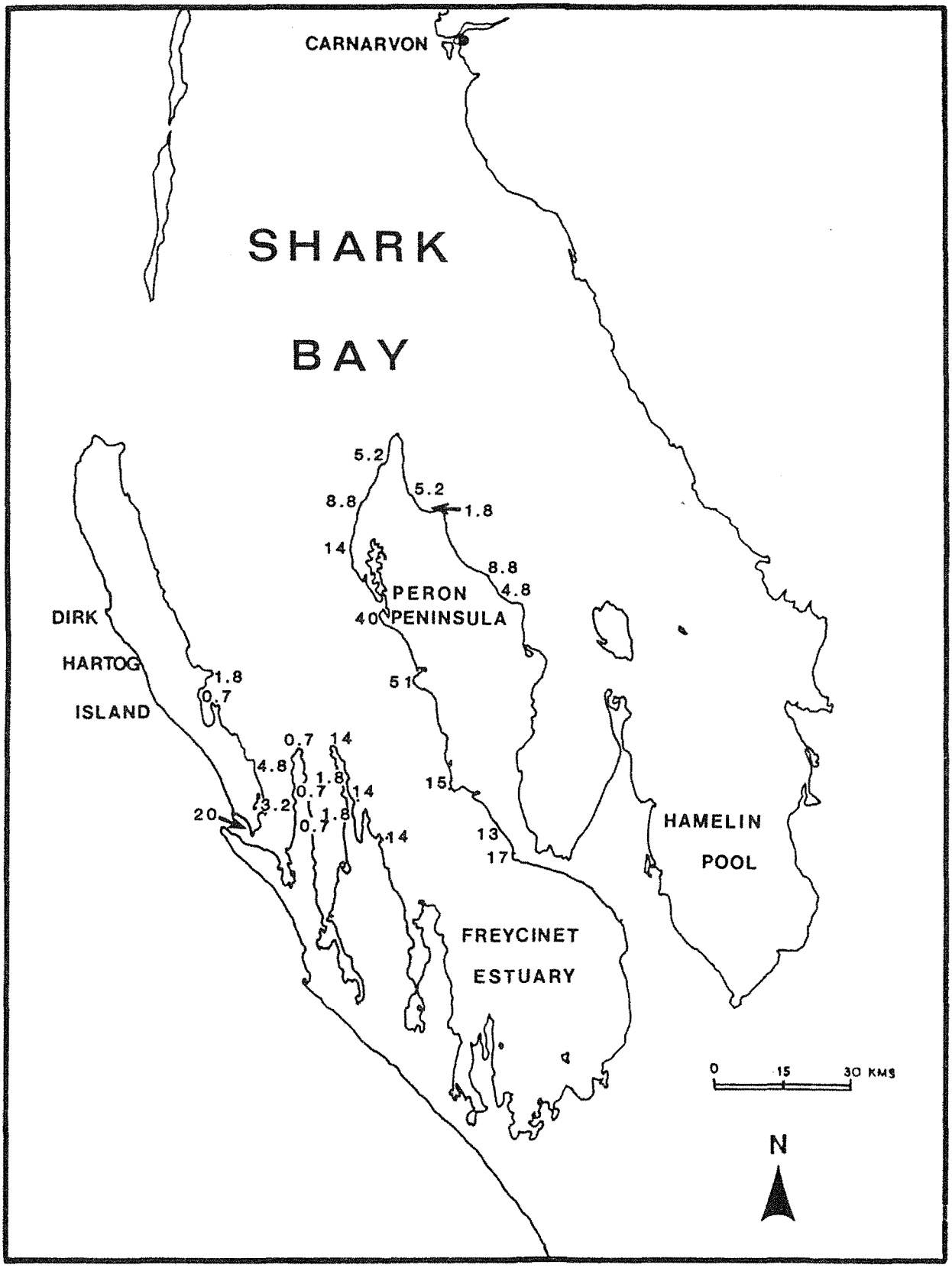

Figure 8: Map of the Shark Bay area showing regional variation in the gradient of the line of best fit to plots of zinc concentration against total flesh weight for Pinctada carchararium at each sample locality.

Cadmium in species other than Pinctada carchararium

Various species of marine fauna other than Pinctada sp. were analysed during this study and the results of these analyses are shown in tables 1 to 10. However, many of these species (e.g. the mullet, Table 8; the crayfish, Table 10; the clam, Table 6 and several others) were only obtained at single localities and few individuals were examined. Hence, these samples cannot be used in regional assessment of heavy metal distribution but they may suggest species worth investigating during follow-up work.

Pinna sp. and Mytilus sp. both appear to show variations in Cd concentration with sample location but for neither species do we have sufficient data either to correct Cd concentrations for animal size ('age') or to draw definitive conclusions from these organisms alone.

Data from Pinna sp. analyses appear to support the conclusions derived from the Pinctada sp. data and indicate that the variation in Cd concentration with location in the embayment is not a feature peculiar to Pinctada sp. Of all the species examined, the specimens of Pinna sp. contain the highest mean Cd concentrations, are widely dispersed within the embayment, and probably have the greatest potential of any species other than Pinctada sp. as an indicator of variations in Cd availability in the Shark Bay area.

Leaching from molluscs with brine solutions

Two simple experiments were conducted during this study to determine whether any Cd could be leached from samples of Pinctada sp. by 400 mls of near neutral (pH 6-7) or slightly acid (pH 3-4) brine solutions (4m NaCl) in 24 hrs. The results of these experiments, each of which involved 6 specimens of Pinctada sp., are summarised in Table 12.

From Table 12 it is clear that soaking the oysters in brine does leach out a substantial quantity of Cd and that the acidified brine is more effective than the near neutral brine. If weighted means are calculated for all oysters leached in the

acidified brine it is apparent that about 70% of the Cd originally present in the oysters is removed into the brine; in the near neutral brine a little under 50% of the Cd is transferred to the brine. These figures suggest that 'pickling' the oysters in brine may be an effective means of reducing their Cd content prior to human consumption but more work is required to determine optimum brine composition and leaching conditions.

It can also be seen from the data in Table 12 that the brine is more effective at removing Cd from the guts and gonads and the mantle and gills of the oysters than it is at removing it from the adductor muscle. Weighted means show that in the acid brine about 80% of the Cd is removed from the guts, gonads, mantle and gills while only 50% is removed from the adductor muscle; in the near neutral brine a little less than 50% is removed from the guts, gonads, mantle and gills while only 40% is removed from the adductor muscle. Hence, the efficiency of Cd removal by 'pickling' the oysters in brine could be further enhanced by discarding the adductor muscle (the least palatable part of the organism) before pickling. Because about 60% of the total Cd in the oysters is concentrated in the adductor muscles, if the adductor muscle is discarded and 80% of the remainder can be removed by leaching in acidified brine, then a sample of oysters with a pre-treatment content of 10 p.p.m. should contain less than 1 p.p.m. after treatment. Alternatively, it could be argued that if both of these treatments were carried out then almost all oysters from the Shark Bay area should have Cd contents below 2 p.p.m. Either of the treatments above would bring oysters from many areas of Shark Bay within the limits on Cd content set for human consumption.

Metals in marine flora

During this study specimens of ribbon weed (Posidonia sp.) which is abundant in the Shark Bay area were collected and analysed. Cd concentrations in this weed range between 0.1 p.p.m. and 1 p.p.m.; the highest level of about 1 p.p.m. was found in weed from site EB. Cd concentrations in the weed are all near the lower limit of

detection for the P.D.V. equipment; analysis of a larger number of samples at lower levels of sensitivity would be required to assess whether regional study of the Cd content of weed in Shark Bay could add significantly to the assessment of regional variation in Cd availability. As reported by Ferguson (1983) for Port Pirie, marine flora may play an important part in the biogeochemical cycle of Cd in the Shark Bay area and may influence its availability for uptake by molluscs.

Metals in water samples from the Shark Bay area

Several water samples were analysed during this study (see Tables 14, 15 and Figs 9, 10, 11) a) to determine the heavy metal content of sea water at each mollusc sample site and the waters in salt lakes, bores, and wells and b) to determine whether there is any relationship between heavy metal content and total dissolved solids (TDS).

In all samples (Table 14 and Fig 9), the Zn concentration is low (< 5 p.p.b.) and near to the lower limit of detection of the analytical procedure used with the result that no meaningful conclusions about the regional variation in Zn concentration can be drawn. Also common to all water samples is the observation that there is no apparent relationship between TDS and heavy metal concentration in the water or (for the seawater samples) in molluscs. Hence, salinity variation within the embayment can be ruled out as a direct control on the variation in the concentration of heavy metals.

Cd concentrations for seawater samples range from 0.06 p.p.b. to 0.37 p.p.b. (average 0.18 p.p.b.), for bore- and well-waters range from 0.06 p.p.b. to 0.28 p.p.b. (average 0.17 p.p.b.) and from salt-lake-water range from 0.05 p.p.b. to 0.28 p.p.b. (average 0.13 p.p.b.) compared with a value of 0.06 p.p.b. for average open ocean waters (Eaton, 1976). Thus, possible sources of dissolved Cd which could directly or indirectly influence Cd uptake by molluscs are elevated relative to average ocean water by a factor of 2-3 times. Regression analysis of the data shows no significant correlation ($r = 0.08, P < 0.05$) between dissolved Cd concentration

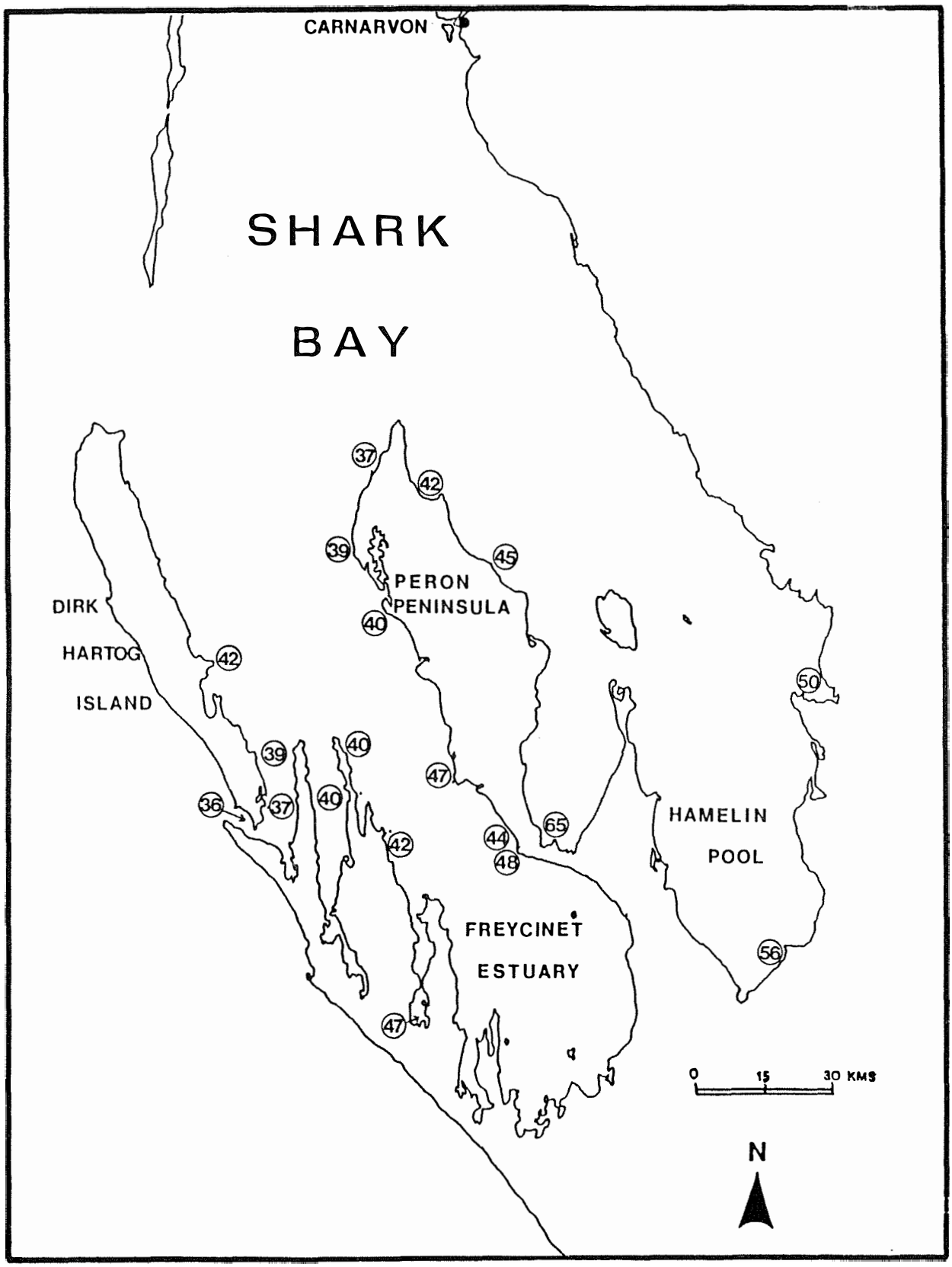

Figure 9: Map of the Shark Bay area showing regional variation in the concentration of total dissolved solids in seawater and lagoon-water. All values are in parts per thousand.

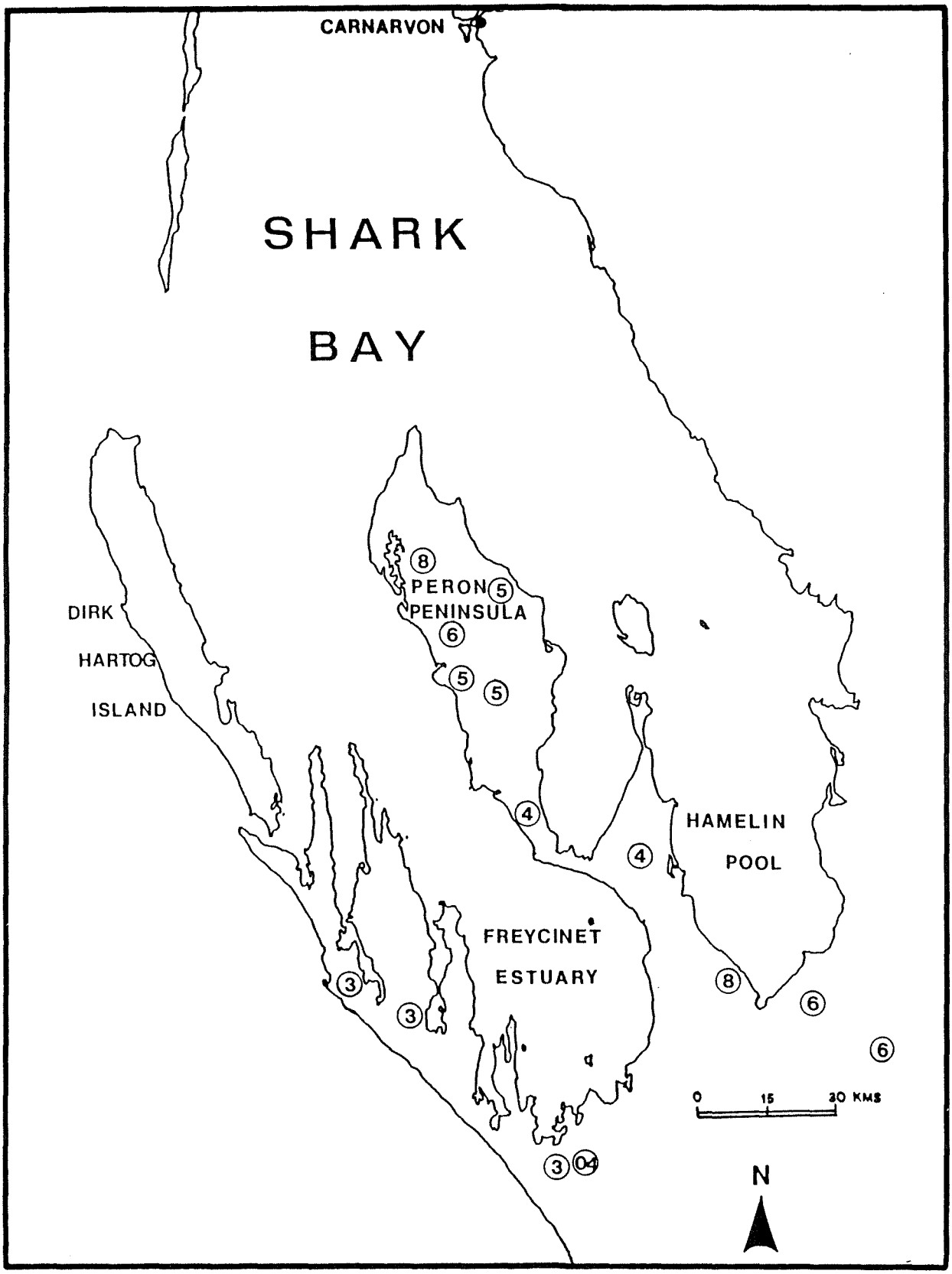

Figure 10: Map of the Shark Bay area showing the concentration of total dissolved solids in bore and well-waters. All values are in parts per thousand.

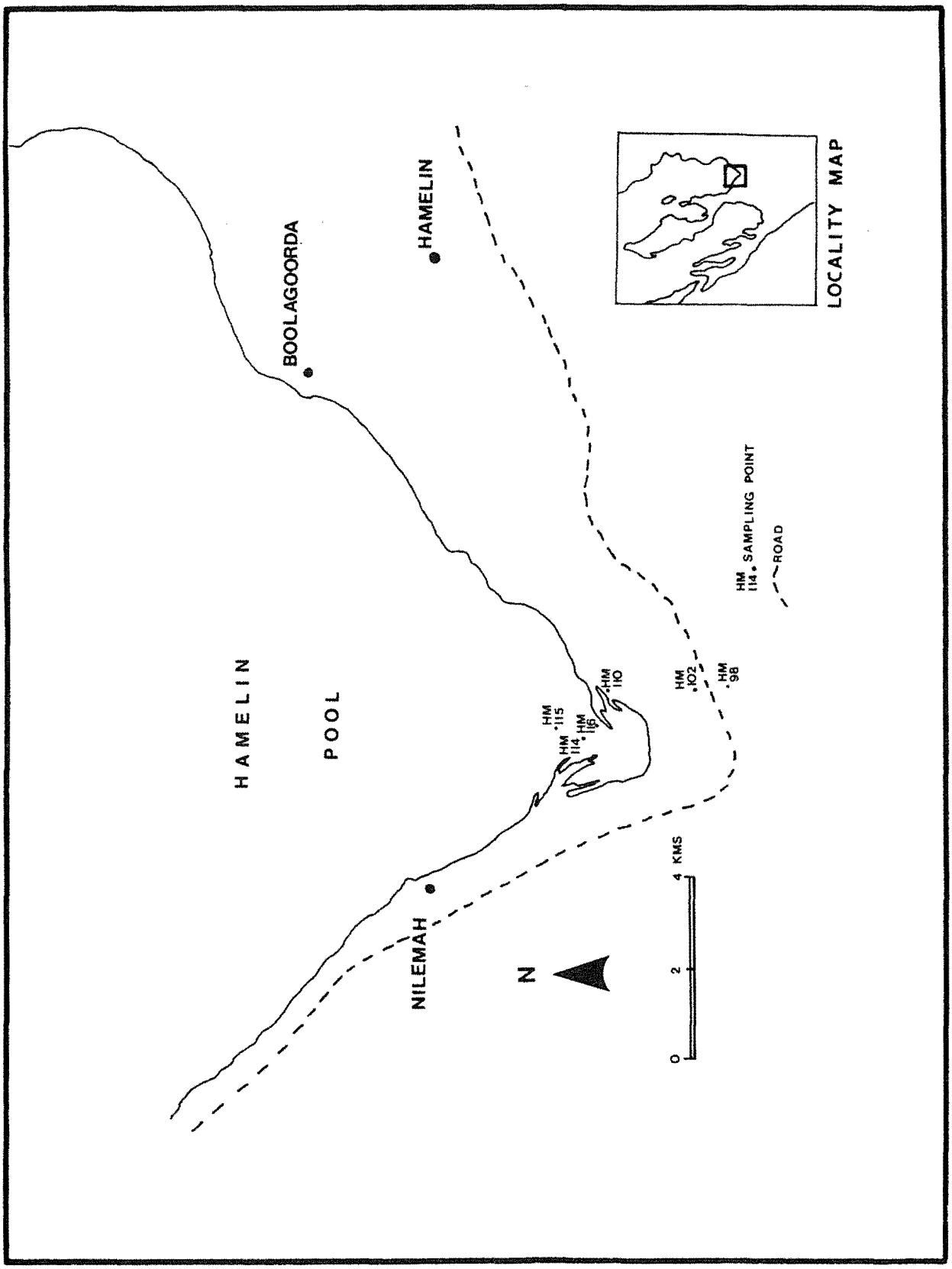

Figure 11: Map of the southern end of Hamelin pool showing the location of groundwater sample sites.

and the Cd concentration gradients (Fig 6a) for oysters. Hence, the Cd content of the molluscs examined cannot be a simple reflection of the availability of dissolved Cd at each sample site although the high Cd concentrations in some Shark Bay molluscs may in part reflect the fact that the dissolved Cd content in the embayment is higher than that of the average for open ocean water.

Cu and Pb lead concentrations in the molluscs examined were near or below the lower limits of detection for the procedures used in this study, except for Pb in the adductor muscles (Table 11) of Pinctada sp., and hence cannot be compared with the dissolved Cu and Pb concentrations in Table 14. However, the concentrations of both dissolved Cu and Pb in seawater do correlate with the concentration of dissolved Cd ($r = 0.68$ for Pb vs Cd and $r = 0.83$ for Cu vs Cd; both are significant at above the 95% confidence level) and similar factors may influence regional variation in the concentration of all three elements.

The concentrations of Cd, Cu, and Pb in groundwater from the Nilemah embayment (see Table 15 and Fig. 11) constitute a special case because they represent the highest levels yet recorded in waters in the Shark Bay area. Cd occurs in concentrations up to 10 p.p.b., lead Pb up to > 7900 p.p.b. and Cu to 30 p.p.b.; if similar levels are attained in this type of sedimentary environment elsewhere in Shark Bay, then the existence of these potential sources may contribute toward explaining the high Cd concentrations in seawater in Shark Bay relative to the mean oceanic concentration (Eaton, 1976) of 0.06 p.p.b. and the high concentrations in some species of mollusc. The reason for the high heavy metal concentrations in groundwater in the Nilemah embayment is unknown and further investigation of them must form part of any future investigations of heavy metals in the Shark Bay area.

Heavy metals in sediments

No variation in the amount of Cd released from a selection of sediment samples (Table 13) by digestion with hot 1M HCl was detected because for all samples the concentration of Cd in the digest was below the lower limit of detection for the

procedure used. For Pb, however, we note that the amount released from sediment from site EB is over 4 times higher than that released from sediment from site GB, a difference which relates well to the much higher Pb levels in Pinctada sp. adductor muscles for specimens from site EB relative to those from site GB (see Table 11). Although the data are few, the above suggestion of a relationship between heavy metal concentrations in molluscs and acid leachable metals in substrate sediment in the Shark Bay area should be worth following up during future investigations.

X-ray diffraction studies of sediment from each mollusc sample site were carried out; for each site the ratio of quartz to carbonates (calcite + aragonite) was determined from measurements of peak areas on the diffraction scan. There is a tendency for the ratio of quartz to calcite + aragonite in the sediment to be higher at localities where the Cd content of the molluscs is highest. The mean quartz to calcite + aragonite ratio is 10.6 at sites where G_{Cd} (Fig. 6) exceeds 1.4,3.9 where G_{Cd} is between 0.9 and 1.4, and 1.7 where G_{Cd} is less than 0.9. However, despite this apparent relationship between the Cd content of molluscs and substrate composition, the suggested link is tentative because only a sample of the top 3cms of sediment was taken at each locality. The possible link needs to be investigated further but such investigations will require that several short core samples be obtained at each locality. It was also observed that the substrate sediment at sites where the G_{Cd} ratio is high frequently contains feldspar, ilmenite, almandine and hematite in concentrations exceeding 0.5% each; these may be significant. No correlation ($P < 0.05$) between aragonite/calcite ratio or high magnesium/low magnesium calcite ratio and Cd concentration in molluscs was found. Hence, although it appears likely that there is a significant relationship between the Cd content of some molluscs and substrate composition, the nature of the relationship is not yet clear; it may be a complex relationship involving micro-organisms, marine flora etc.

Variation in cadmium concentration between sites

Regional variation in the Cd content of Pinctada sp. in the Shark Bay area is

shown in figure 12 where the mapped values are those for the gradients of plots G_{Cd} of Cd concentration against T.F.W. for each locality (see fig. 6). This method of deriving regional variation data is the most appropriate for the analyses carried out here because it incorporates data from all specimens of Pinctada sp. analysed and allows for variation in the size ('age') range at each sample site. From figure 12 it is clear that the Cd concentration in Pinctada sp. varies within the embayment but the distribution of sites with high and low values of G_{Cd} gives no definitive indication of the cause of the variation. Some possible explanations for the regional variation in Cd concentration in Pinctada sp. are summarised as follows:-

1. It reflects regional variation in the abundance of subspecies of Pinctada sp. and hybrids of these subspecies. Against this suggestion is the observation that the regional variation in the Cd concentration of Pinna sp. matches that of Pinctada sp. indicating that the variation is not species or subspecies specific.

2. It reflects regional variation in salinity within the embayment. Against this suggestion is the observation that there is no evidence for a statistically significant correlation between salinity and Cd concentration (compare Fig. 12 with Fig. 9).

3. It reflects regional variation in the dissolved Cd concentration in the seawater. Against this suggestion is the observation that there is no statistically significant correlation between dissolved Cd concentrations and the gradients in figure 6. However, in the embayment as a whole, the dissolved Cd concentration averages 2-3 times higher than that in mean ocean water (see previous discussion) which may help explain the generally high Cd concentrations in Shark Bay molluscs.

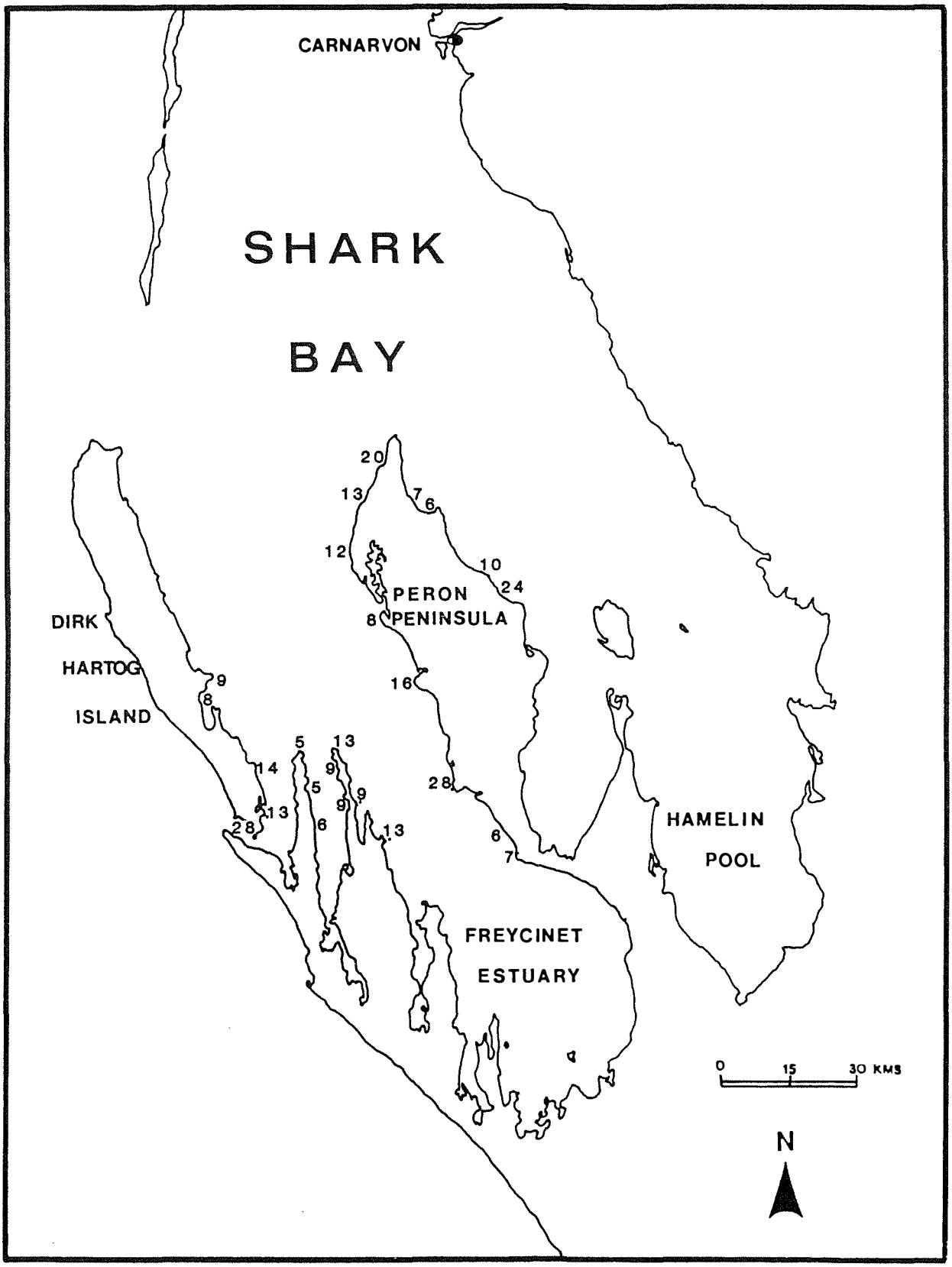

Figure 12: Map of the Shark Bay area showing regional variation in the gradient of the line of best fit to plots of cadmium concentration against total flesh weight for Pinctada carchararium at each sample site. All gradients have been multiplied by a factor of ten.

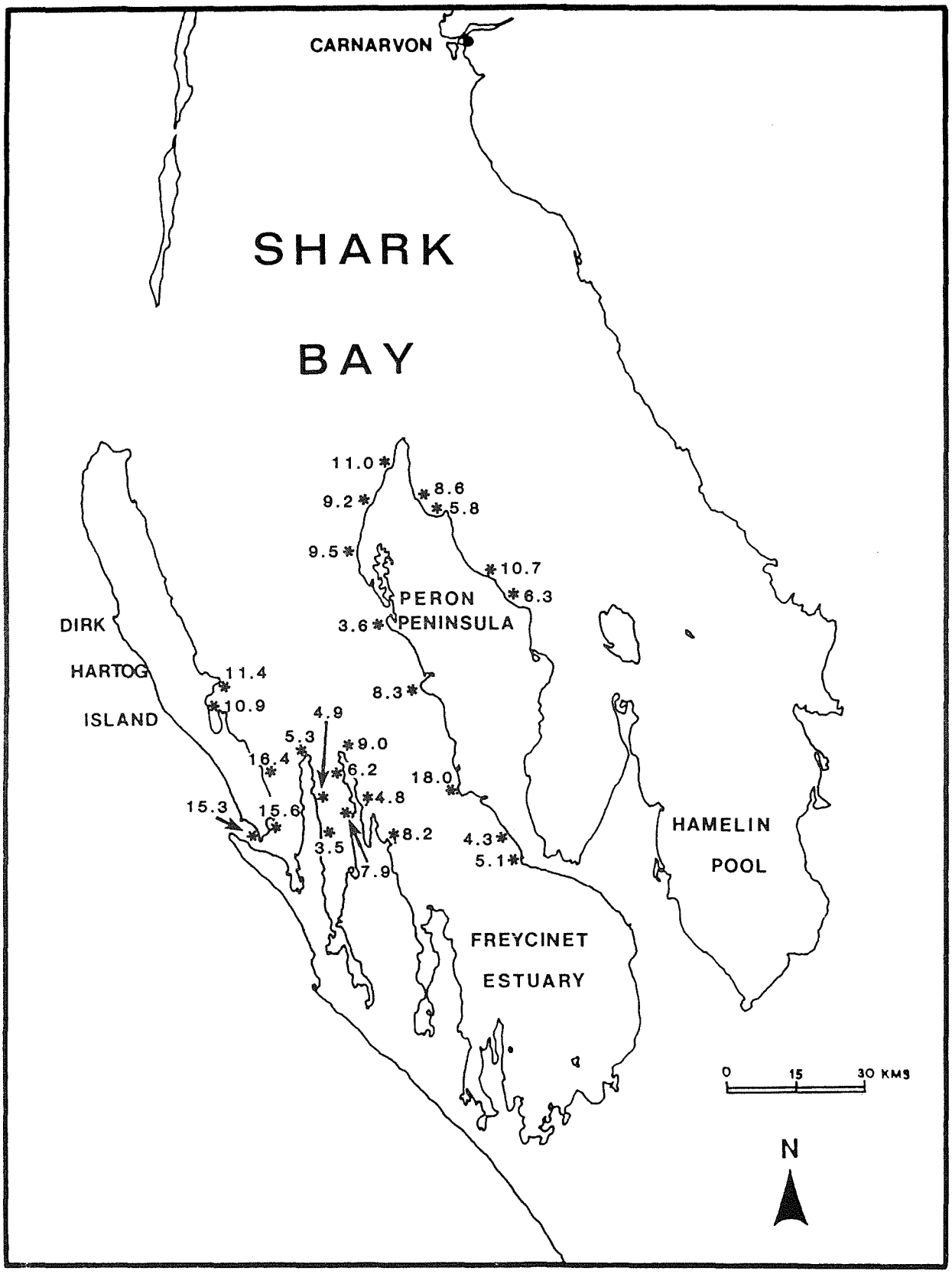

Figure 13: Map of the Shark Bay area showing regional variation in the weighted mean cadmium concentration for a random sample of Pinctada carchararium from each sample site. Concentrations are in p.p.m.

4. It reflects variations in heavy metal concentrations in super-saline groundwaters, in or adjacent to the supra-tidal zone. This argument would become more credible if groundwaters similar to those observed at the Nilemah Embayment (which were found to contain high concentrations of heavy metals) were also located adjacent to areas with high concentrations of Cd in oysters.

5. It reflects regional variation in sediment substrate composition. This suggestion may form a substantial part of any explanation for the regional variation in Cd concententrations in the molluscs because there does appear (see discussion in preceeding section) to be a relationship between the Cd concentration in oysters and substrate composition but more detailed sediment sampling would be necessary before this suggestion can be more than tentative. Any relationship between the Cd concentrations in molluscs and substrate composition may not be a simple direct relationship and this would also need to be investigated during any further studies. For example, the sediment itself or micro-organisms living in the upper layers of it may influence carbonate ion activity, water pH, etc. near the sediment/water interface and may as a result influence the behaviour of Cd (e.g., adsorption and desorption of Cd in the sediment). Alternatively substrate composition may directly effect Cd availability.

6. It reflects the presence, type and abundance of microbiota and/or marine flora (principally Posidonia sp.). This possibility cannot be confirmed with the available data but is not inconsistent with any findings of this study. Many species of microorganisms can have a marked influence on the geochemistry of microenvironments they have colonised (e.g., Berner, 1971), particularly the sulphur metabolising bacteria, and may preconcentrate Cd in their cell structure. If any microorganisms do preconcentrate Cd then clearly any molluscs which ingest these micro-organisms will accumulate Cd more rapidly

than those which don't.

7. It reflects current patterns and velocities in various parts of Shark Bay. This suggestion also remains possible but is only likely to have an indirect effect through its influence on substrate sediment composition and microbiotic ecosystems, etc.

8. It may reflect a combination of two or more of the above possibilities.

Clearly, there is no simple explanation for the regional variation in G_{Cd} values for Pinctada sp. in the Shark Bay area and more work will be necessary before a convincing explanation can be proposed.

Another way of looking at the regional variation in the Cd concentration in oysters is shown in figure 13. This figure shows the mean Cd concentration of a random sample of Pinctada sp. from each locality, where the sample from each site represents the assemblage which would be likely to be obtained by an individual or commercial concern harvesting Pinctada sp. for human consumption. Because the values in figure 13 were not corrected for organism size (i.e. they are not based on values of G_{Cd}), they represent the combined effects of regional variation in Cd uptake and regional variation in the size ('age') structure of Pinctada sp. populations at each site. Regional variation in figure 13 shows a close relationship to that in figure 12 and supports the suggestion made earlier that it is unlikely that a random sample of Pinctada sp. with a minimum dorso-ventral length of 45 mm and a maximum mean Cd concentration of 2 p.p.m. could be obtained anywhere in Shark Bay. However, the Cd concentrations in figure 13 are also consistent with the suggestion that discarding the adductor muscle from the oysters and/or 'pickling' the oysters in acidified brine may reduce the Cd content of animals to less than the 2 p.p.m. limit set for human consumption.

CONCLUSIONS

Summary

The Cd concentration in specimens of Pinctada carchararium in Shark Bay is high generally above the W.A. State Health Department limits for molluscs for human consumption and varies regionally within the embayment. However, to permit the comparison of Cd concentrations between oysters from different sample sites it is necessary to make allowance for variation in the size ('age') of individual animals obtained at each site because it is shown here that the Cd concentration increases as a direct function of specimen size. To allow for the increase in Cd concentration with organism size, sample sites must be compared using the gradient (G_{Cd}) of a plot of concentration against T.F.W., for a suite of oysters from each sample site rather than using mean Cd concentrations.

A map showing the variation in values for G_{Cd} between sites (Fig. 12) shows that there is a substantial difference between sites but gives few clues as to the cause of the variation. Four possible causes for the regional variation in G_{Cd} can largely be ruled out;

a) an anthropogenic source of Cd can probably be excluded because sites with high G_{Cd} values do not coincide with sites of human activity,

b) variation in G_{Cd} due to regional variation in the abundance of sub-species (and their hybrids) of Pinctada sp. is improbable because regional variation in the Cd concentration in Pinna dollabrata shows a close match with values of G_{Cd} for Pinctada sp.,

c) variation in G_{Cd} as a function of salinity variation is largely ruled out by the poor agreement between values of G_{Cd} and salinity (fig. 9) and

d) variation in G_{Cd} due to variations in the concentration of dissolved Cd in the seawater can be excluded because there is a very poor correlation between G_{Cd} and the dissolved Cd concentration.

Several possible explanations for the regional variation in G_{Cd} remain but it is not feasible with the present data to do more than list the viable

explanations. These possible explanations involve:

a) variation in the heavy metal concentrations in groundwaters in the supra-tidal zone,

b) variation in substrate sediment composition,

c) variations in microbiotic ecosystems near the sediment/water interface,

d) variation in the abundance of the ribbon weed (posidonia australis)

e) variation in water currents between sites, or

f) a combination of these possibilities.

In evaluating regional variation in Cd concentration in molluscs, no species was found other than Pinna sp., which could usefully add to the data obtained from Pinctada sp.

The only metal other than Cd examined in Pinctada sp. which was found to show marked regional variation in concentration is Zn. Values for G_{Zn} (determined as for G_{Cd}) vary by nearly two orders of magnitude with sites which have high G_{Zn} values coinciding very closely with sites of human activity at Denham and Useless Loop. The data support an anthropogenic cause for the locally high Zn concentrations but it is noted that even the highest Zn concentration detected is still well below the maximum permitted in molluscs for human consumption by the W.A. Health Department.

Analysis of dissected parts of Pinctada sp. reveals that, on average, about 60% of the Cd in each oyster is contained in the adductor muscle. This observation is unusual; because in other species of mollusc heavy metals, including Cd, tend to be concentrated in parts of the organism collectively referred to here as the guts and gonads (including gut granules). We have no explanation as to why the Cd is selectively concentrated in the adductor muscle. By contrast, the Zn concentration in Pinctada sp. adductor muscles is low. Because over half the Cd in the oysters is in the adductor muscle (the least desirable part of the organism to eat), discarding the adductor muscle (about 25% of the mass of the organism) during preparation will significantly reduce the Cd content of the oyster meat for human consumption.

A second method of reducing the Cd content of oyster meat is to leach the

oysters with a brine solution; slightly acidified brine (pH 3-4) is more efficient than near neutral brine. Leaching in the cold acidified brine (4M NaCl) for 24 hours was found to remove about 50% of the Cd from the adductor muscle and about 80% of the Cd from the rest of the oyster. Thus, if the adductor muscle is discarded during preparation and the remainder is 'pickled' in brine, then oysters with a pre-treatment Cd content of 10 p.p.m. should contain less than 1 p.p.m. after treatment.

Overall, both the plots of G_{Cd} and the data for random samples of Pinctada sp. show that samples of Pinctada sp.from anywhere in Shark Bay are likely to contain more than the 2 p.p.m. maximum Cd concentration set for molluscs for human consumption by the W.A. State Health Department. If the sample sites are selected on the basis of low G_{Cd} values then it is possible to collect oysters with an average Cd concentration of less than 2 p.p.m. by excluding specimens with a dorso-ventral length greater than 55 mm. For those oysters which exceed the 2 p.p.m. Cd limit most of the Cd can be removed by a) discarding the adductor muscle and b) 'pickling' the oysters in slightly acidified brine solution. If collection of Pinctada sp. in Shark Bay is to be undertaken for human consumption then not only will the areas to be fished need to be selected on the basis of G_{Cd} values (Fig 12) but an upper limit may need to be applied to the size of the oysters taken, adductor muscles may need to be discarded, and for some oysters 'pickling' in brine may be necessary if the limit of 2 p.p.m. Cd is not to be exceeded.

Further work

Several areas of investigation relevant to the high Cd concentration in Shark Bay molluscs warrant further investigation; these are summarised as follows:-

1. The extent and distribution of saline, supra-tidal groundwaters of the type which were observed to contain high concentrations of heavy metals in the Nilemah embayment need further investigation. Their effective contribution to the heavy metal balance in Shark Bay, and to marine biota in the bay needs to

be determined.

2. Examination of the Cd content of Pinna sp. should be expanded to enable comparisons to be made between Cd concentrations in molluscs from Shark Bay and those from other parts of Australia; Pinctada carchararium is not common outside the Shark Bay area.

3. An investigation as to why Cd is selectively concentrated in the adductor muscle of Pinctada sp. is a problem of some biochemical interest.

4. If the 'pickling' of oyster meat is to be used as a method of reducing its Cd content for human consumption, further investigations should be conducted to determine optimum brine leaching conditions.

5. To obtain a better understanding of the controls influencing the regional variation in G_{Cd} it will be essential to carry out more detailed investigations of substrate sediment composition involving more samples from each site and the use of short core samples and marine sediment collection or "seston". Eagle and Goulet Bluffs which are geographically close to each other but have very different G_{Cd} values would be ideal sites to commence this type of study.

6. Because the role of microbiota and larger algae in influencing values of G_{Cd} at each sample site is not yet established and may be important, it will be necessary to examine this possible relationship during any future study.

ACKNOWLEDGEMENTS

The authors are indebited to A and M Gabelish for their assistance with all

aspects of the field work which forms the basis of this study. Without their assistance, efficiency and effectiveness would have been greatly reduced. We also thank G. Wright for his services as an unpaid field assistant. The W.A. department of Conservation and Environment and the W.A. department of Fisheries and Wildlife are thanked for their financial support which made this project possible. C. Sfreddo is thanked for typing the manuscript and attending to all the stylistic modifications of early drafts which inevitably result where numerous authors are involved.

REFERENCES

Berner, R.A., 1971: Principles of chemical sedimentology. McGraw-Hill, N.Y., 240 pp.

Brooks, R.R. and Rumsby, M.G., 1967: Studies on the uptake of cadmium by the oyster Ostrea sinuata (Lamarck). Aust. J. Mar. Freshw. Res., 15, 53-61.

Eaton, A., 1976: Marine geochemistry of cadmium. Marine chemistry 4, 141-154.

Ferguson, J., 1983: Concentrations and speciation of lead, zinc and cadmium in seawater-like smelter effluent and adjacent marine environments, Port Pirie, South Australia. Aust. J. Mar. Freshw. Res., 34, 375-385.

Fourie, H.O. and Peisach, M., 1977: Loss of trace elements during dehydration of marine zoological material. Analyst (London) 102, 173-200.

Harris, J.E., Fabris, G.J., Statham, P.J. and Tawfik, F., 1979: Biogeochemistry of selected heavy metals in Western Port, Victoria, and use of invertebrates as

indicators with emphasis on Mytilus edulis planulatus. Aust. J. Mar. Freshw. Res. 30, 159-178.

Hynd, J.S., 1961: An analysis of variation in Australian specimens of Pinctada albina (Lamarck) (Lamellibranchia). Aust. J. Mar. Freshw. Res., 11, 326-366.

Lake, P.S., 1979: Accumulation of cadmium in aquatic animals. Chem. in Australia, 46, 26-29.

Lauwerys, R., 1979: Cadmium in man. In M. Webb. (ed) The chemistry, biochemistry and biology of Cadmium. Elsevier, p. 433-455.

Logan, B.W., Davies, G.R., Read, J.F. and Cebulski, D.E., 1970: Carbonate sedimentation and environments, Shark Bay, Western Australia. Am. Assoc. Pet. Geologists, Mem 13, 232 pp.

Logan, B.W., Read, J.F., Hagan, G.M., Hoffman, P., Brown, R.G., Woods, P.J. and Gebelein, C.D., 1974: Evolution and diagenesis of Quaternary carbonate sequences, Shark Bay, Western Australia. Am. Assoc. Pet. Geologists, Mem. 22, 358 pp.

Mann, A.W., 1983: Hydrogeochemistry and weathering on the Yilgarn Block, Western Australia - ferrolysis and heavy metals in continental brines. Geochim. Cosmochim. Acta., 47, 181-190.

Mann, A.W. and Deutscher, R.L., 1980: Solution geochemistry of lead and zinc in water containing carbonate, sulphate and chloride ions. Chemical Geol., 29, 293-311.

Mann, A.W. and Lintern, M., 1984: Field analysis of heavy metals by portable digital voltammeter. J. Geochem. Explor., 22. (in press).

Talbot, V. & Chegwidden, A., 1982: Heavy metals in the sediments of Cockburn Sound, Western Australia, and its surrounding areas. Environ. Poll., B, 5, 187-205.

Talbot, V. & Simpson, C., 1983: The validity of using arithmetic means to summarize environmental pollution data. Chem. in Australia, 50, 156-158.

Ward, T.J., Warren, L.J., and Swaine, D.J., 1982: Effects of heavy metals on aquatic life. I.L.S.Z.R.O. Project Report CH-6/ZH-212, 112 pp.

Warren, L.J., 1981: Contamination of sediments by lead, zinc and cadmium: A review. Environ. Poll., B, 2, 401-436.