Heavy Metal Concentrations in the Oysters

Saccostrea cuccullata and *Saccostrea sp.*

(probably *S. commercialis*) from the Dampier Archipelago,

Western Australia

Department of Conservation and Environment

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ABSTRACT

Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn concentrations in oysters S. cuccullata and Saccostrea sp. (probably S. commercialis) of the Dampier Archipelago are low, with the exception of Cu and Zn concentrations in oysters from a localised area adjacent to the Dampier township and iron ore exporting terminals at Dampier and Cape Lambert. Although the shape of S. cuccullata is very irregular, length significantly correlates with wet weight ($P<0.001$) and Cu and Zn ($P<0.01$).

While iron ore spillages occur at the exporting terminals this is not reflected very strongly in the Fe concentrations in the oysters throughout the archipelago. Further, Fe concentration did not correlate significantly with oyster length or wet weight thus indicating that oysters may be able to regulate their concentrations of Fe.

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INTRODUCTION

The sheltered, sufficiently deep waters (up to 20 m) of Mermaid Sound (300 km^2) within the Dampier Archipelago (3,600 km^2) (Fig 1) have enabled the development of port facilities over the past 20 years to handle the export of salt and iron ore. Recently, further development has commenced as a result of the discovery of offshore hydrocarbons. This development will include the treatment of natural gas for domestic purposes and the construction of a liquified natural gas (LNG) plant.

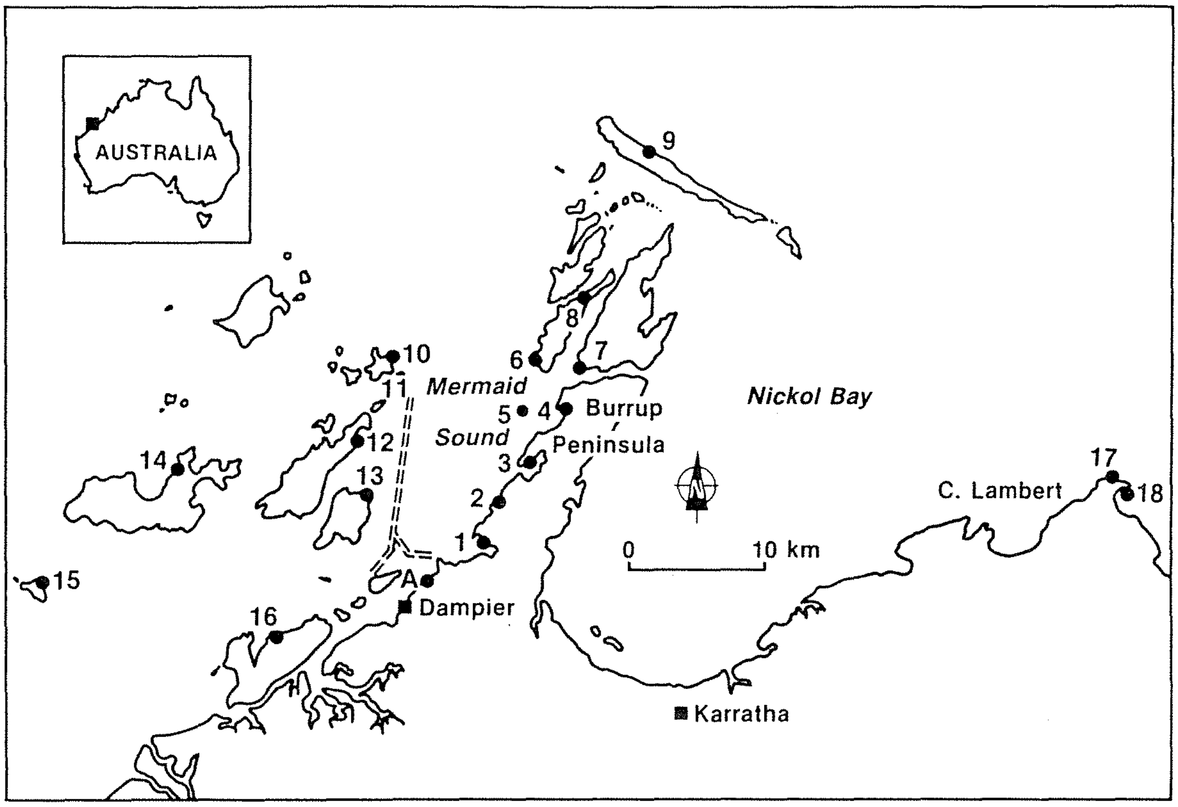

Figure 1 : The Dampier Archipelago Showing Oyster Sampling Sites

It is envisaged that the discharge of warm, chlorinated seawater to Mermaid Sound from any new development would increase the concentrations of some heavy metals in the biota of the region. Eaton (1979) and Harrison et al. (1979) have shown that coolant waters from power-generating stations contain increased concentrations of Cu at discharge points. Waslenchuk (1982) has reported that the Millstone nuclear power station in Waterford, Connecticut, discharges Cu, Ni and Zn in coolant waters. The source of the metals is considered to be the Cu-Ni alloyed condensers and the Cu-Ni-Zn alloyed auxiliary heat exchanger containing sacrificial Zn blocks as corrosion inhibitors.

In order to detect any increase in heavy metal concentrations in the biota during and after development of this area, oysters have been used as a heavy metal monitor species. Little is known, however, about the most common intertidal oyster, S. cuccullata, of this area.

A synopsis on the use of bivalves as heavy metal monitoring organisms has been given by Forstner and Wittmann (1979). They point out that oysters can be used as monitoring organism as all are filter feeders and are only slightly mobile.

They show that most siderophiles (periodic groups VIIa and VIII), chalcophiles (periodic groups Ib : except Au; IIb, IIIb, IVb : except C and Si; Vb : except N; and groups Ia, IIa, IIIa, IVa, Va and VIa) are present in most species of oyster and that the concentration of many elements is largely a function of the water quality of the sampling site rather than of the oyster species sampled.

The concentrations of heavy metals in oysters, however, like most bivalves, are also functions of seasonal factors, temperature, salinity, diet, spawning and individual variation (Forstner and Wittmann 1979). It has also been shown that the concentrations of several heavy metals can increase in oysters to many orders of magnitude above background concentration (Bloom 1975, Forstner and Wittmann 1979), thus demonstrating the potential of oysters as sentinel accumulators of heavy metals. Bloom (1975) showed that the range of concentrations of Zn in the oyster Ostrea angasi in the polluted Derwent River, Tasmania, was 3700–38700 mg kg^{-1} dry weight on one occasion and Forstner and Wittmann (1979) has shown that the Cu and Zn concentrations in the oyster Crassostrea gigas can vary between 18.5 and 6480, and 100 and 35120 mg kg^{-1} dry weight, respectively. In this paper, the background concentrations of Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the oysters S. cuccullata and Saccostrea sp. sampled in 1980–83 from 17 and 4 sampling sites respectively, in the Dampier Archipelago are reported. The relationships between concentrations of Cu, Fe and Zn and the size of S. cuccullata were also investigated.

METHODS AND MATERIALS

Species Identification

Some confusion has arisen in the past concerning the identification of S. cucullata. MacKay et al. (1975) have wrongly equated S. cucullata with Crassostrea commercialis. The species studied in this paper have been identified by S.M. Slack-Smith, Western Australian Museum, who also indicated strong similarities between Saccostrea sp. and S. commercialis.

Oyster Collection and Associated Problems

Both S. cucullata and Saccostrea sp. grow naturally in clusters, although some isolated specimens of S. cucullata occur. These isolated specimens are often irregular in shape (Fig 2), as a result of which, it is extremely difficult to select a suitable oyster size for heavy metal determinations. S. cucullata used in this survey were 40–60 mm long and 25–35 mm wide; the vertical surface of Saccostrea sp. being 25–35 mm long and 12–25 mm wide. Although the irregular shape of S. cucullata presents sampling problems, it will be shown later that the length of the oyster is still a good index of its wet weight.

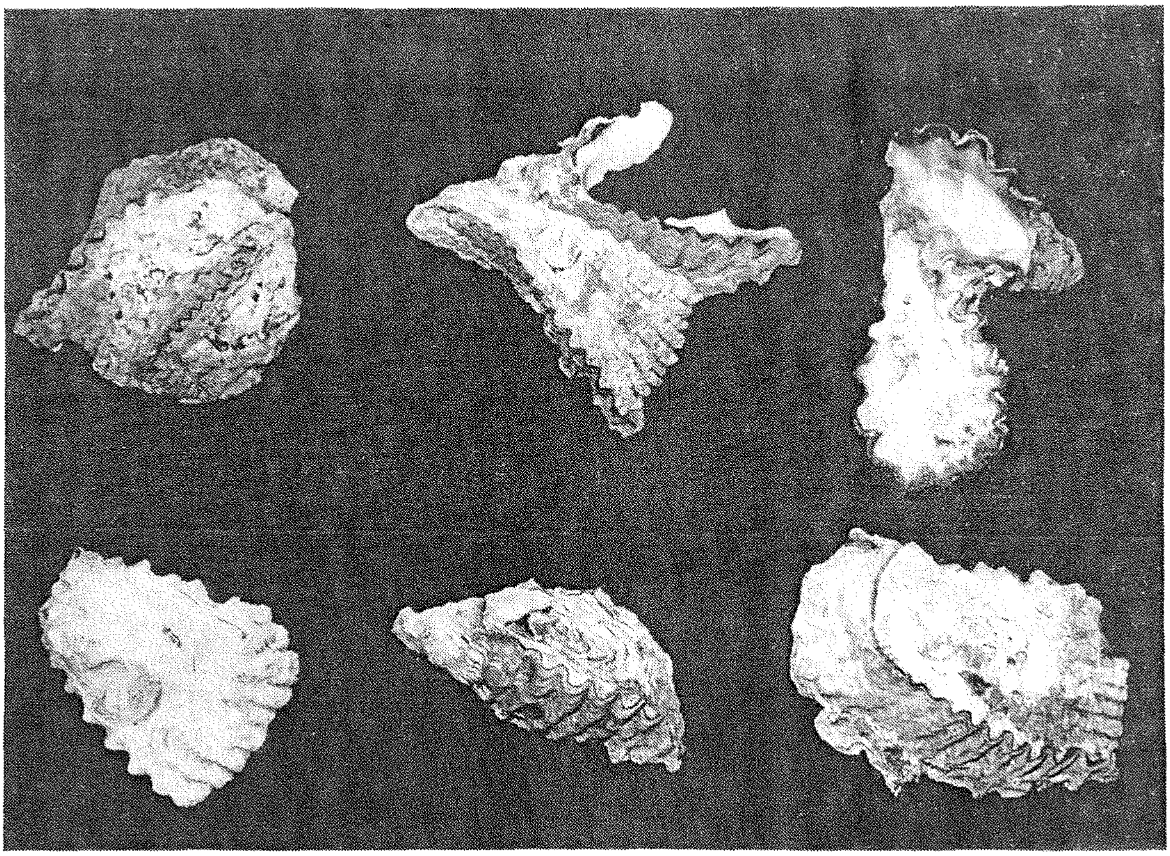

Figure 2 : Examples of variation in external shell morphology of the oyster S. cucullata which results in sampling problems.

The oysters were collected whole at 19 sampling sites, S. cucculiata at sites 1–15, 17–18 and A, and Saccostrea sp. at sites 2–4 and 16 (Fig 1), and stored frozen until analysed as in Talbot and Chegwidden (1982).

Although the heavy metal concentrations vary considerably as a function of sampling site and time, this does not negate the validity of the values as a measure of background concentrations: oysters are capable of accumulating heavy metals in concentrations up to many orders of magnitude above background in polluted waters (Forstner and Wittmann 1979). The data, however, are not sufficient to allow detailed statistical examination of variations. Much of the variance in concentrations could be attributed to some individual oysters accumulating heavy metals beyond the norm thus resulting in the intermittent elevations of geometric mean values.

Sampling Preparation, Chemical Analysis of Samples and Standard Reference Material

Fifteen oysters (three pooled samples each of five specimens) of each species from each sampling site were analysed for Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, following the procedure of Talbot and Chegwidden (1982).

Primary and secondary standards of orchard leaves (NSB 1971), bovine liver (NBS 1577) and mussel (Department of Conservation and Environment, W.A.) were analysed in conjunction with the samples of this study following the procedure of Chegwidden (1979) and Talbot and Chegwidden (1982).

Results are expressed in terms of wet weight because most health standards for metals in human foodstuffs are expressed this way; however, the author recognises that there are problems associated with using wet weight, such as the dehydration of samples during storage.

Relationships of Size and Cu, Fe and Zn Concentration in S. cucculiata

The length frequency distributions of this oyster varies between leptokurtic to negatively skewed with a modal length of 45–60 mm, depending on sampling site. Consequently, small and large oysters are hard to find. Nevertheless, 200 solitary specimens were sampled from the complete range of oyster sizes available at the time from Site A (Fig 1). Their height (H), length (L), width (W), "basal area" (LW), "longitudinal cross sectional area" (LH), "latitudinal cross sectional area" (WH), "volume" (LWH), shucked wet weight (WW) and Cu, Fe and Zn concentrations were measured. Although these oysters were not rectangular in shape, these combinations of measurements can still be used in correlation analyses.

Linear regression correlation coefficients were calculated to see if any significant ($P<0.001$) relationships existed so that future work could be standardised. To this end, the data were processed using the statistical package (Statistical Package for Social Scientists) developed by Nie et al. (1975).

Further, all measurements were transformed to logarithms and processed with the same package to determine whether any significant ($P<0.001$) log-log or log-normal correlation coefficients between these parameters were higher than their respective linear correlation coefficients. Significant values in the lower range of $P<0.001$ were treated initially as being unimportant as r values can be elevated due to anomalies in experimental procedure (Talbot and Simpson 1983).

Schulz-Baldes (1973) has shown that when trace element concentrations in shellfish are expressed on a weight-specific basis (as ug g^{-1}), highest values are often recorded in the smallest individuals. The 24 smallest oysters and the 22 largest oysters were selected from the 200 sampled oysters using shell length as the body measurement and their metal concentration expressed on a weight-specific basis, for similar comparisons. The comparisons were made using ranges and geometric mean for each Cu, Fe and Zn in both classes.

RESULTS

Analytical Results for Standard Reference Materials

Standard reference materials showed that Pb analysis was unreliable near the detection limit of 0.4 mg kg^{-1} using flame AAS. This problem is enhanced if background correction is not used.

More reliable results for Cu, Pb and Zn were obtained when the sample to be digested was allowed to digest in acid for six hours before heating. This probably allows most of the low molecular weight organometallic compounds to be oxidised to less volatile inorganic compounds before heating.

Regional Survey

S. cuccullata was more widespread than *Saccostrea sp.* throughout the Archipelago. The former favoured more exposed less turbid areas than *Saccostrea sp.* which was more prevalent in embayments and sheltered areas.

Table 1a shows that Ag, Cd, Co, Cr, Mn, Ni and Pb concentrations are low in both species of oyster. For this reason only range values are given: any other statistical analysis is meaningless. Concentrations of Cu, Fe and Zn are given in Tables 1b and 1c.

Table 1a

Concentration ranges of some heavy metals in two species of oyster collected in the Dampier Archipelago between October 1980 and September 1983. These ranges comprise three measurements. Each measurement is the result for a pool of five oysters.

	Concentrations (mg kg^{-1} wet wt) Ag	Cd	Co	Cr	Mn	Ni	Pb
S. cuccullata	0.0–0.1	0.0–0.8	ND*	0.0–0.7	0.4–3.0	0.2–1.7	0.0–0.8
S. commercialis	0.0–0.4	0.2–0.4	ND*	0.0–0.8	1.4–3.2	0.3–1.5	0.0–1.7

Lower limit for operating ranges for Ag, Cd, Co, Cr, Mn, Ni and Pb and 0.8, 0.3, 2.0, 1,3, 1.0, 1.0, 1.6 mg L^{-1}, respectively.

*ND = Not Detected.

Table 1b

Concentrations of the three prominent heavy metals in oysters (S. cuccullata) of similar size sampled at the Dampier township (Site A) in May 1982.

	CONCENTRATION ($mg\ kg^{-1}$ wet wt)				SHELL SIZE (mm)		
	Parameters	Cu	Fe	Zn	Length	Width	Height
May 1982	X	87	80	1004	58.9	34.0	18.7
	s.d.	66	73	473	3.4	3.2	2.7
	Range	31–200	39–280	370–1800	53.9–64.8	30.5–38.7	14.5–23.5
	Geometric mean	71	65	899	58.8	33.8	18.5

Lower limit of operating ranges for Cu, Fe and Zn are 0.8, 1.2 and 0.3 $mg\ L^{-1}$, respectively.

X = Mean of ten specimens

Table 1c

Concentrations of Cu, Fe and Zn in two species of oyster in the Dampier Archipelago (October 1980 – September 1983). The geometric mean and range of three measurements are given. Each measurement is the result for a pool of five oysters.

Site	Date	Species		Concentration ($mg\ kg^{-1}$ wet wt.) Cu	Fe	Zn
1	Oct 1980	S. cuccullata	G*	38.4	26.4	689
			Range	37.8–39.9	23.7–29.4	677–698
1	Feb 1981	"	G	23.8	48.6	412
			Range	17.9–35.3	39.8–72.0	277–671
1	Jun 1981	"	G	13.9	32.3	430
			Range	12.2–16.0	21.7–57.1	349–571
1	Oct 1981	"	G	23.8	18.4	455
			Range	14.9–29.4	12.7–29.3	401–503
1	Nov 1981	"	G	34.3	16.7	526
			Range	25.1–46.6	12.7–19.5	440–665
2	Feb 1981	"	G	14.9	16.3	110
			Range	9.9–19.2	10.8–25.0	80–133
2	Feb 1981	Saccostrea sp.	G	18.3	39.5	386
			Range	14.8–24.3	29.2–51.3	274–503

Table 1c (Cont'd)

Site	Date	Species		Cu	Fe	Zn
2	Jun 1981	S. cuccullata	G	4.8	15.7	137
			Range	2.9- 7.3	11.8-21.3	91-149
2	Jun 1981	Saccostrea sp.	G	13.6	28.4	346
			Range	9.4-18.7	21.6-39.8	253-460
2	Nov 1981	S. cuccullata	G	16.7	13.4	492
			Range	11.6-21.4	9.6-18.1	386-593
3	Feb 1981	Saccostrea sp.	G	25.7	21.1	390
			Range	18.3-29.2	18.3-28.1	341-486
3	Feb 1981	S. cuccullata	G	14.1	21.8	473
			Range	12.6-16.3	16.7-27.3	386-594
3	Jun 1981	"	G	14.7	33.7	367
			Range	11.6-19.5	25.4-46.3	318-406
3	Oct 1981	"	G	28.3	24.6	331
			Range	14.7-38.4	19.2-28.9	245-406
3	Oct 1981	Saccostrea sp.	G	15.7	14.9	273
			Range	12.2-19.6	12.3-20.4	194-386
3	Nov 1981	S. cuccullata	G	21.1	20.7	369
			Range	16.3-28.4	17.7-27.6	331-408
3	Nov 1981	Saccostrea sp.	G	7.2	11.8	265
			Range	4.9-11.3	8.4-14.6	243-297
4	Feb 1981	"	G	10.9	12.1	223
			Range	4.6-19.9	5.5-18.6	163-302
4	Jun 1981	S. cuccullata	G	11.3	26.4	213
			Range	10.0-12.3	18.7-30.4	176-255
4	Oct 1981	"	G	14.1	15.6	420
			Range	6.8-21.1	11.8-20.7	374-446
4	Nov 1981	"	G	32.6	16.3	301
			Range	27.9-37.8	11.7-23.7	264-327
5	Feb 1981	"	G	2.8	9.0	183
			Range	1.6- 4.1	6.0-13.1	164-252
5	Jun 1981	"	G	1.9	12.0	207
			Range	1.4- 3.8	8.7-19.0	160-270
5	Oct 1981	"	G	13.9	12.8	260
			Range	12.1-15.6	7.8-14.6	230-319

Table 1c (Cont'd)

Site	Date	Species		Cu	Fe	Zn
5	Nov 1981	S. cuccullata	G	30.6	10.9	443
			Range	26.2–39.1	10.7–11.4	386–483
6	Jun 1981	"	G	37.9	37.4	238
			Range	34.8–40.1	30.9–42.0	214–254
7	Jun 1981	"	G	8.3	24.8	73.4
			Range	7.6– 9.2	12.9–34.0	64.5–85.3
8	Jun 1981	"	G	12.0	64.3	132
			Range	11.4–13.1	50.1–73.7	93–152
9	Feb 1981	"	G	10.4	15.0	191
			Range	9.4–12.7	9.9–21.1	176–200
10	Jun 1981	"	G	8.3	13.7	90
			Range	3.5–12.6	4.2–18.3	55–138
11	Feb 1981	"	G	10.4	15.0	191
			Range	9.4–12.7	9.9–21.1	176–200
12	Jun 1981	"	G	7.4	11.7	167
			Range	6.5– 8.1	11.3–11.9	160–171
13	Feb 1981	"	G	8.2	35.8	107
			Range	5.7–10.3	19.3–50.5	90–134
14	Feb 1981	"	G	25.6	29.4	367
			Range	24.1–28.3	25.9–33.2	354–375
15	Jun 1981	"	G	16.6	20.7	132
			Range	14.7–18.5	17.1–22.8	115–148
16	Jun 1981	Saccostrea sp.	G	11.2	39.6	270
			Range	10.7–12.0	29.6–53.2	247–293
17	July 1983	S. cuccullata	G	335	447	1021
			Range	229– 453	291– 633	724–1232
17	Sept 1983	"	G	151	386	459
			Range	109– 265	231– 547	380–621
18	July 1983	"	G	428	1173	693
			Range	219– 555	739–1629	589–793
18	Sept 1983	"	G	248	351	729
			Range	190– 365	247– 589	583–876

G = Geometric Mean

The data for site A in Table 1b have been arranged to highlight the difference between the use of arithmetic and geometric means when the data are skewed: this subject has been previously discussed at length by Talbot and Simpson (1983) who explained the validity of using geometric means to summarise environmental data. In this case, the arithmetic means for Cu and Zn concentrations exceed the National Health and Medical Research Council's recommended standards of 70 and 1000 mg kg^{-1} wet weight, respectively, for foodstuff (shellfish) (Anon. 1981).
The geometric means, however, for Cu and Zn concentrations are more acceptable.

Table 1c shows the geometric means and ranges for Cu, Fe, Zn concentrations in S. cuccullata and Saccostrea sp. throughout the archipelago. For S. cuccullata the ranges were 1.4–555, 4.2–1629 and 55–1232 mg kg^{-1} wet weight respectively, while for Saccostrea sp. they were 4.6–29.2, 5.5–51.3 and 165–503 mg kg^{-1} wet weight respectively.

The highest mean Cu and Zn concentrations in S. cuccullata of 428 and 1021 mg kg^{-1} respectively were found at sites 18 and 17 respectively where an iron ore exporting terminal, an electric power generation station and some banded iron formations are found. Similar plant facilities exist near site 1 where high Cu and Zn values were also noted, however, sewage discharges also take place due south of this location.

Relationships of Shell Size and Cu, Fe and Zn Concentration in S. cuccullata

Interpretation of significant ($P<0.001$) low r values in the statistical analyses will not be attempted because not enough is known about the frequency distribution of each parameter. Low r values may be a result of the correlation of data derived from two dissimilar frequency distributions, and elevated r values may be due to the correlation of data derived from two similarly skewed distributions.

Data from 200 specimens were analysed (Table 2). Higher significant correlations (based on the two-tailed t-test) were WW-LW (0.840), L-W (0.836), WW-L (0.813), WW-W (0.808). The wet weight of an oyster was significantly related to basal parameters at the time of sampling. The equations relating these highly significant correlations are given in Table 3.

Table 2

Correlation coefficients (r) between (L) (length), W (width), H (height), WW (wet weight), Cu, Fe, Zn and functions of basal area (LW), external volume (LWH), longitudinal cross section (LH), latitudinal cross section (WH) of the oyster S. cuccullata based on the analyses of 200 individual oysters from site A taken in May 1982.

W	*0.836*						
H	*0.533*	*0.573*					
WW	*0.813*	*0.808*	*0533*				
Cu	0.442	0.390	0.135	0.313			
Fe	−0.110	−0.125	−0.210	−0.209	−0.053		
Zn	*0.511*	0.460	0.312	0.346	*0.526*	−0.095	
LW			*0.572*	*0.840*	0.453	−0.136	*0.509*
LWH				*0.702*	0.330	−0.168	0.443
LH		*0.733*		*0.715*	0.269	−0.203	0.432
WH	*0.652*			*0.647*	0.283	−0.161	0.427
	L	W	H	WW	Cu	Fe	Zn

r (P<0.001) = 0.51 Significant values are given in italics
r values are omitted where a parameter appears in both variables

Table 3

Statistical data associated with the four highest correlations found in Table 2

Parameter	Sample No	Median	Range	Regression Equation	95% Confidence Intervals	Estimated Error of Dependent Variable
WW	200	1.6 g	0.1–2.7 g			
LW	200	1610 mm^2	80–4060 mm^2	WW=0.0065LW +0.149	0.0057–0.0074 −0.006=+0.304	0.351
L	200	54 mm	18–86 mm	L=17.74 WW +28.00	14.86–19.88 24.63–31.53	8.01
W	200	32 mm	8.6–50.8mm	W=11.62 WW +17.14	9.91–13.33 14.79–19.45	5.45

Shell measurements also showed that the H:W ratio decreased with size, i.e. the height of unusually wide oysters was small. This may explain why correlations involving height and wet weight were poor.

Concentrations of Zn and to a lesser extent Cu had lower, but still significant correlations ($P<0.01$) with LW, L, W and WW. This indicates that the Cu and Zn concentrations are cumulative.

Further testing of the data using null hypotheses showed that no specific length range of oyster could significantly improve the correlation between length and Cu, Fe and Zn concentrations.

The log-log and log-normal relationships for all the data from these oysters were less with the exception of log (Cu) - log (Zn), which was slightly lower than that for the linear regression coefficient.

The results for the analysis of Cu, Fe and Zn concentrations on a weight-specific basis showed that for the group of smaller oysters, concentrations were Cu, geometric mean = 24.9, range 15.0-92.9; Fe, 28.1, 8-90.0; and Zn, 473, 208-1380. For the group of larger oysters, concentrations were Cu 75.2, 54.1-98.3; Fe 24.1, 18.2-47.4, and Zn 947, 544-1458. Unlike the result of Schulz-Baldes (1973), the higher concentrations were found in the larger oysters. These metal concentrations, however, varied considerably in specimens of S. cuccullata of one size (Table 1b). It can be concluded that Cu and Zn correlates significantly ($p<0.01$) with length despite sampling problems.

DISCUSSION

Of the two major intertidal oyster species (S. cucculata and Saccostrea sp.) in the Dampier Archipelago, the most convenient for use in heavy metal pollution monitoring is S. cucculata as it is widely distributed in clusters, with some individuals growing alone.

Whilst the concentrations of heavy metals in S. cucculata throughout the area are relatively low, this oyster does accumulate Cu, Zn and to a far lesser extent Fe at sites A, 1, 17 and 18 where industrial development has taken place. Consequently, this oyster shows potential for use in the monitoring of some heavy metals in the area.

Although the morphology of S. cucculata is very irregular in the natural state, wet weight is a significant ($P<0.001$] function of either length, width or basal area. Cu and Zn concentrations, however, significantly correlate with these size parameters at $p<0.01$.

The modal length of the S. cucculata specimens sampled at site A adjacent to the Dampier township is between 45–60 mm and the length frequency distribution varies between leptokurtic to negatively skewed. The modal length of this oyster, however, as sampled throughout the archipelago is 50–60 mm.

The significant correlations for the chalcophiles Cu and Zn (Table 2) are consistent with the isolation of metal-binding proteins from this oyster (Talbot unpublished work). The correlations involving Fe were all negative but insignificant at the 0.001 probability level (Table 2). This oyster may be able to regulate its uptake of iron by the use of a high molecular weight metal-binding protein, similar to ferritin. Consequently r values tending towards zero would be expected. The Cu, Cd, Pb and Zn values in both species were similar to those in Sydney rock oysters collected from 19 relatively unpolluted areas along the coast of New South Wales (MacKay et al. 1975).

The objective of obtaining background concentration ranges for several heavy metals in these two species of oysters throughout the Dampier Archipelago was achieved. Extrapolation of these results should, however, be avoided as the size range selected was probably too wide. It was difficult to choose a suitable index and index range for size when sampling, since these oysters are very irregular in shape. As the concentrations of Cu and Zn vary considerably within S. cucculata of the same size, and there is a positive correlation between concentrations of these metals with oyster length, it could be concluded that the selection of an index range of 20 mm was too wide for calculations such as seasonal variation. Had a much smaller index range been chosen, however, it may have been difficult to get samples throughout the archipelago as the modal class of this oyster and availability as isolated specimens varies between sample sites.

A second problem arose during the sampling and storage of S. cucculata. As these oysters cement themselves to their substrates their shells crack upon removal. This allows superficial water to escape from the soft tissue while some dehydration may also take place during storage in the field. This could affect the results which are expressed in wet weight. The results are expressed in this form to be consistent with the standards for heavy metals in foodstuffs.

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