

The Origin of High Cadmium Loads in Some Bivalve Molluscs from Shark Bay, Western Australia: A New Mechanism for Cadmium Uptake by Filter Feeding Organisms

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Abstract. Although Shark Bay is remote from all known industrial and geological sources of heavy metals, the cadmium content of several species of Shark Bay molluscs may exceed 10 mg/kg. The cadmium load in these molluscs varies geographically within the bay, but possible explanations for cadmium distribution involving variation in salinity, saline groundwater influx, the dissolved cadmium concentration, the cadmium concentration in substrate sediments, species, or an anthropogenic source are not supported by analytical data. The cadmium concentration is normal in Shark Bay seawater (0.04 µg/L to about 0.35 µg/L), rarely exceeds 0.25 µg/L in ground waters, bore waters, and salt lake brines, and very seldom exceeds 1 mg/kg in sediments. No direct link between the cadmium loads in molluscs and its concentration in the water or substrate sediment is evident, but the cadmium load in molluscs is usually highest where turbulence is high and the substrate sediment contains fine hematite. Over about 2,000 km², the water depth in Shark Bay is less than 1 m and fine sediment is readily suspended by strong winds. The iron-oxides (superfine hematite) are eroded from the Peron Sandstone exposed in some coastal cliffs and constitute up to 2% of substrate sediments near these cliffs.

This study reveals that cadmium in the water adsorbs extremely efficiently onto the surface of the hematite, which is negatively charged at the prevailing seawater pH of 8.15, and that suspended hematite particles are ingested by the molluscs. Inside the molluscs, lower pH conditions cause reversal of the hematite charge and the cadmium is released and accumulated by the organism. Effectively, the hematite is pre-concentrating the cadmium and acting like a chemical conveyor-belt in enhancing metal transfer to the molluscs. A link between cadmium uptake by molluscs and hematite in the sediment is supported by the observation that in water with a depth of 3 m, bottom dwelling oysters contain up to 10 times more cadmium than oysters grown in baskets suspended near the surface at the same site.

This mechanism for the transfer of cadmium to filter feeding organisms is new, but we have no doubt that it operates in similar environments elsewhere, and that at some sites

where cadmium “pollution” has been reported, high metal loads in molluscs may be natural rather than anthropogenic. Conversely, in some environments the discharge of cadmium-free hematite could induce a rise in the cadmium load in the resident mollusc population.

Background

Although Shark Bay, Western Australia, is geographically remote from all known industrial and geological sources of heavy metals, in 1982, 500 kg of pearl oyster flesh (*Pinctada carchariarium*; *P. carchariarium* is synonymous with *P. albina albina*) from Shark Bay was declared unfit for human consumption by the Western Australian health authorities, because its cadmium content was more than twice the legal limit of 2 mg/kg (wet weight); the cadmium content was also notably higher than that in molluscs from areas of recognized cadmium pollution. The concentrations of all other toxic metals in the oyster flesh were well below the limits adopted in Western Australia for mollusc products. Subsequent investigations (McConchie *et al.* 1988) revealed that a) *P. carchariarium* was not the only species of Shark Bay mollusc with a high cadmium content, b) the cadmium/zinc ratios in the molluscs were unusually high, and c) in Shark Bay, the cadmium load in the oysters varied widely depending on where the sample was obtained.

McConchie *et al.* (1988) were unable to discover the reason for the curiously high cadmium load in the Shark Bay molluscs despite a thorough survey of the molluscs and all potential sources of cadmium in or near Shark Bay. They were, however, able to rule out many possible explanations, and developed procedures and an initial data base which provided a foundation for further studies, the results of which we report here. Possible explanations for the high cadmium load in the molluscs, and its geographic variation within the Shark Bay area, which were rejected by McConchie *et al.* (1988) include: an anthropogenic source, possible hybridization between *Pinctada carchariarium*, *P. margaritifera* and *P. fucata*, salinity variation, local groundwater

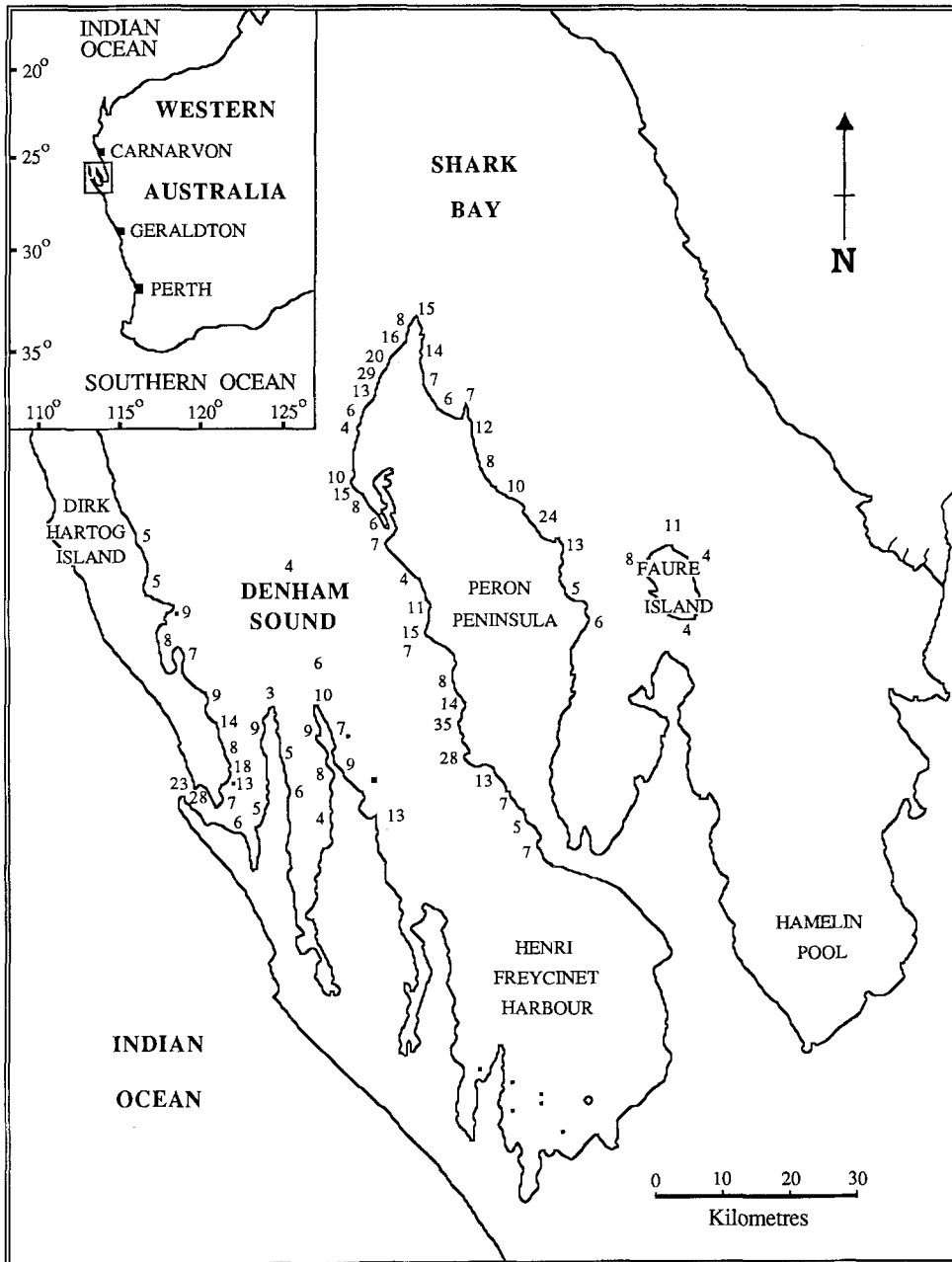


Fig. 1. Map of the Shark Bay area showing regional variation in G_{Cd} values for all samples of *P. carchiarium*. Note: all G_{Cd} values are multiplied by 10 so that decimal points do not reduce plot clarity

influx, variation in the dissolved cadmium concentration, and variation in the cadmium concentration in substrate sediments. The data obtained from over 400 sediment, soil, and water samples by McConchie *et al.* (1988) and during follow-up work indicate that the concentration of cadmium in Shark Bay seawater is normal (ranging from 0.04 $\mu\text{g/L}$ to about 0.35 $\mu\text{g/L}$; c.f. mean oceanic concentration of 0.06 $\mu\text{g/L}$, Eaton 1976), the concentration in ground waters, bore waters, and salt lake brines rarely exceeds 0.25 $\mu\text{g/L}$, and the concentration in substrate sediments and near-shore lithologies very seldom exceeds 1.0 mg/kg.

In this paper we report on the findings of investigations which followed the work of McConchie *et al.* (1988), describe the cadmium uptake mechanism revealed by this work, and outline some implications of the mechanism for future work on heavy metals in marine ecosystems.

Geographic and Geologic Setting

Shark Bay (Figure 1) is a shallow marine embayment of about 8,000 km² with an average water depth of 10 m; over about 2,000 km² the water depth is less than 1 m. The topographic relief of the surrounding landmass is low and presents no barrier to strong southerly winds which are common throughout the year, particularly during summer (November–May); there are also periodic cyclonic storms and strong westerly sea breezes during summer. The climate in 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. In southern reaches of sub-embayments in the area the climate, combined with shallow water bars and low tidal exchange vol-

umes, results in higher than normal marine salinities (reaching nearly 50‰ in Henri Freycinet Harbour and over 60‰ in Hamelin Pool). Further details on the physiography, climate and water conditions of the Shark Bay area can be found in Logan *et al.* (1970, 1974).

The nearest potential industrial sources of cadmium pollution to Shark Bay are Perth (about 800km south) and the smaller town of Geraldton (about 400km south); thus, Shark Bay differs from other areas in Australia (*e.g.*, Cockburn Sound, Western Australia, Talbot & Chegwidgen, 1982; Port Pirie, South Australia, Ferguson, 1983; Princess Royal Harbour, Western Australia, Talbot, 1983) where high heavy metal loads in molluscs can be linked to a local industrial source.

Dirk Hartog Island and the area of the mainland between the Indian Ocean and Henri Freycinet Harbour are composed largely of calcareous aeolianite (Tamala Aeolianite) dunes with local concentrations of siliceous sand; both lithologies have very low heavy metal contents, but some phosphatic sedimentary grains near small guano covered islands on the eastern side of Dirk Hartog Island have cadmium contents which exceed 10 mg/kg. The Peron Peninsula which extends up the middle of Shark Bay is dominated by red ferruginous quartz sands (Peron Sandstone) but calcretes are locally well developed and evaporite pans (birridas) are numerous on the northern part of the peninsula. About 30% of beaches around the northern part of Peron Peninsula consist of white quartzose and calcareous sands with the rest having a distinct reddish color due to the presence of iron-oxides reworked from Peron Sandstone cliffs; very few beaches around the southern part of the peninsula contain the reddish iron-oxides. Cadmium concentrations in the Peron Sandstone and the other lithologies on the peninsula rarely exceed 50 µg/kg; small localized beach accumulations of heavy minerals (particularly garnet, ilmenite and iron-oxides) have slightly higher heavy metal contents (metals leachable with hot 30% HCl) but cadmium concentrations remain below 200 µg/kg (McConchie *et al.* 1988). No rocks with high heavy metal contents have yet been recognized along the eastern margins of Shark Bay or in any other nearby strata. Further details of the geology of the region can be obtained from Logan *et al.* (1970, 1974) and Butcher *et al.* (1984).

Procedures

Sample sites (Figures 1,2,3) in this study were selected to expand the coverage of the coastline around Shark Bay beyond that of McConchie *et al.* (1988) and many of the (McConchie *et al.* 1988) sites were resampled (no specimens of *P. carchariarium* were found in the more saline waters south of the southernmost data points shown on Figure 1). Routine sampling, sample preparation, and sample digestion, procedures follow the methods described by McConchie *et al.* (1988). The method, developed by McConchie *et al.* (1988), of analyzing pooled samples of animals belonging to pre-defined size classes, for each sample site, then plotting the weighted mean metal concentration for each pool against mean individual flesh weight for the pool proved to be an efficient means of quantifying regional variation in the rates of metal uptake while compensating for variation in the size/

age distribution of animals collected at each site. This method of normalizing data for samples with differing animal size/age distributions was shown to be statistically valid by McConchie *et al.* (1988), and is considered to be less damaging to mollusc populations than the traditional method of collecting and analysing numerous specimens from a single size/age class. Heavy metal analysis procedures also follow the methods described by McConchie *et al.* (1988) except that a later model PDV instrument (the *Chemtronics* "PDV2000") was used for most of the cadmium, lead, and copper analyses and this provided a small improvement in sensitivity and a reduction in the sample volume required for each analysis. In total, over 800 individual analyses were carried out on biota, sediment, and water samples. All biological sample weights and heavy metal concentrations are reported on a wet weight basis; the wet weight/dry weight ratio for specimens of *P. carchariarium* is 6.15 ± 0.1 for the whole organism after drying at 105°C for 24 h (McConchie *et al.* 1988).

Mollusc analyses are restricted to *P. carchariarium*, because they are the most widely distributed and abundant species in Shark Bay suitable for this type of study (McConchie *et al.* 1988); alternative sentinel species either do not carry similarly high cadmium loads, or are not widely distributed, or are rare.

Additional procedures involved sampling and analyzing specimens of *P. carchariarium* grown in baskets suspended near the surface (at three of the benthic sample sites) and a detailed study of iron-oxides present in sediments at all sample sites. The iron-oxides were separated from the sediment by wet sieving at 6φ, dried at 50°C for 48 h, and examined by X-ray diffraction, using a Philips PW1700 system with a graphite monochromator and $\text{Cu}_{K\alpha}$ radiation; samples were pressed into aluminium holders and scanned from 5° 2θ to 50° 2θ at a scan rate of 1° 2θ/min. Further examination of selected samples of the iron-oxides involved:

1. Room temperature Mössbauer spectroscopy, using a horizontally aligned apparatus with sinusoidal drive, a ^{57}Co in rhodium source with a line width of 0.108 mm/sec and a recoilless fraction value of 0.78 and standardization relative to natural iron at 298°K.
2. Determination of the iso-electric point for the oxides, using a Rank Bros. (Cambridge) electrophoretic mobility cell, electrical and optical system.
3. Estimation of the iron-oxide content of the top 5 cm of the substrate sediment at each sample site by digestion with aqua regia and determination of the iron concentration by standard atomic absorption methods.
4. Determination of the cation exchange capacity for the iron-oxides by extraction (shaking with BaCl_2 at pH = 7) and analysis of major adsorbed cations by atomic absorption (Al, Ca, and Mg) and flame photometry (Na and K).
5. Determination of the cadmium adsorption efficiency for the iron-oxides in sea water samples (pH = 8.1) spiked with cadmium chloride to 0.1, 5, 10, 25, 50, and 100 mg Cd/L.

Results

Values of G_{Cd} and G_{Zn} for all specimens of *P. carchariarium* from all sample sites are shown in Figures 1 and 2 respectively. G_{Cd} for each site is defined as the gradient of the line

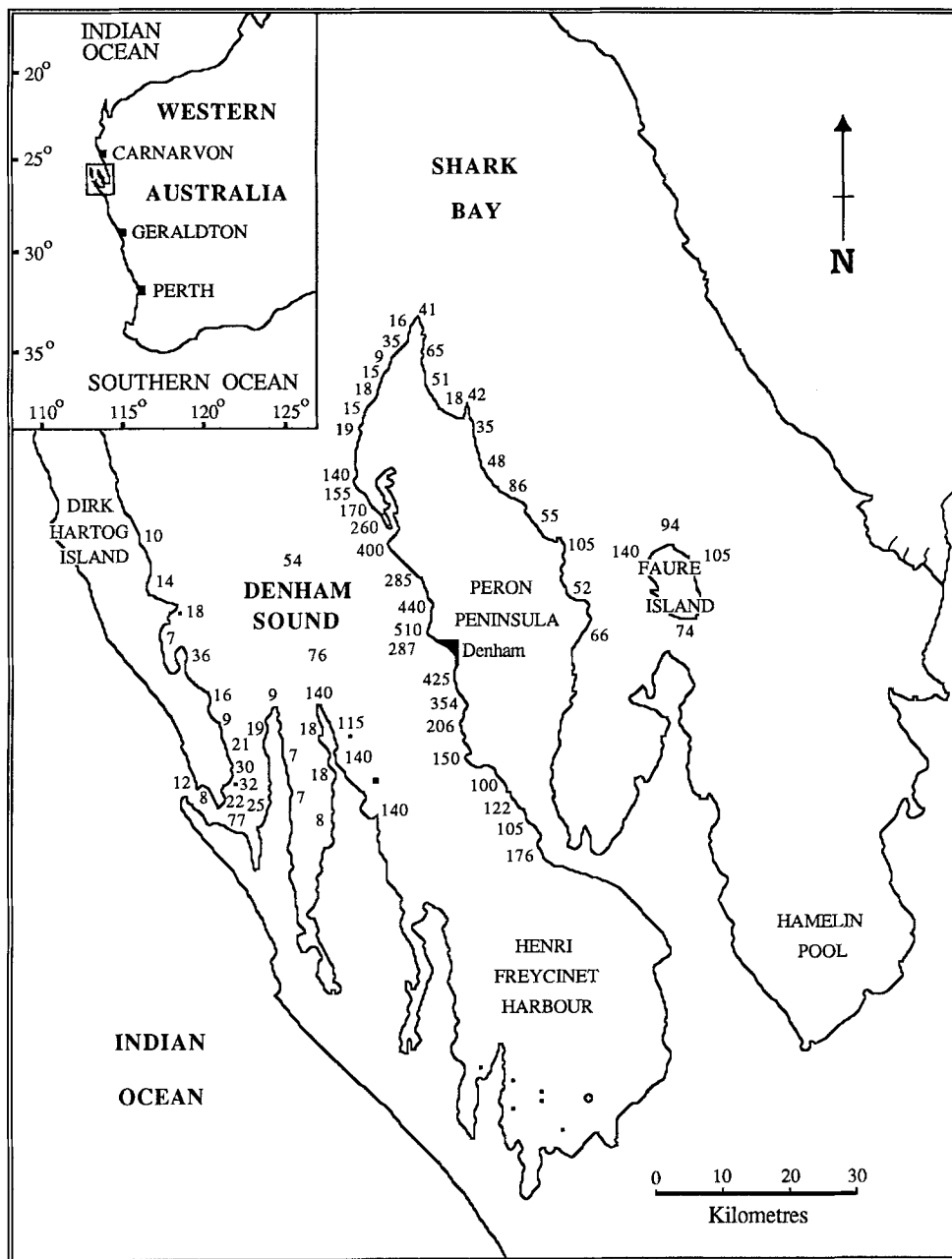


Fig. 2. Map of the Shark Bay area showing regional variation in G_{Zn} values for all samples of *P. carchariarium*. Note: all G_{Zn} values are multiplied by 10 so that decimal points do not reduce plot clarity

of best fit to a plot of the weighted mean cadmium concentration for each sample pool from the site against the mean individual flesh weight for the pool (McConchie *et al.* 1988); G_{Zn} plots are similar but apply to zinc. Several age related parameters for *P. carchariarium* (including: live heel depth, dorso-ventral length and individual flesh weight) were evaluated by McConchie *et al.* (1988) for use in establishing G_{Cd} and G_{Zn} values and, although all were found to be usable, mean individual flesh weight was selected as the principal 'age dependent' parameter because it is the most accurately measured of the alternatives. The weighted mean for specimens within a given size/age group is defined as the total mass of cadmium for all individuals in the sample group divided by their total flesh weight; the statistical validity of using weighted means and of pooling samples based on size/

age groups before digestion and analysis was demonstrated by McConchie *et al.* (1988).

The use of G_{Cd} and G_{Zn} provides an efficient means of quantifying differences in the rate of metal uptake between sites (metal uptake rates at a particular site reflect the bio-availability of the metal to the species analysed) while compensating for variation in the size/age distribution of animals collected at each site. Resampling of the McConchie *et al.* (1988) sites indicates that values of G_{Cd} and G_{Zn} remain constant for each site over a three year period to within $\pm 25\%$; six of the twelve resampled sites differed by less than 10% over the three year period. Interestingly, the seven sites which were resampled during summer (when the water was more turbulent) returned higher G_{Cd} values than the McConchie *et al.* (1988) value, determined during the calmer winter

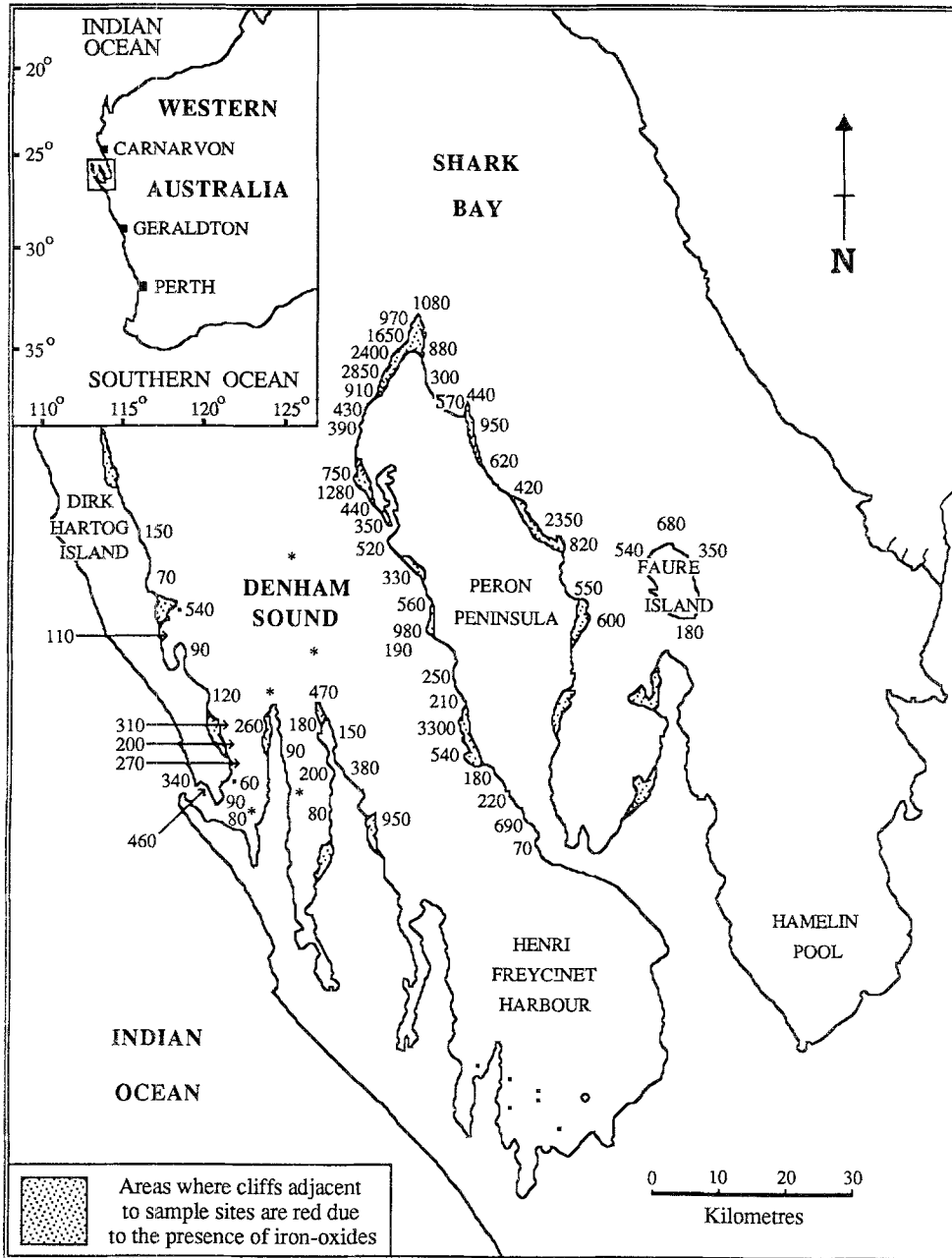


Fig. 3. Map of the Shark Bay area showing regional variation in the iron-oxide content of the top 5 cm of substrate sediment at all *P. carchariarium* sample sites. All iron-oxide concentrations are in mg/kg of dry sediment; no iron-oxides were detected at sites marked*

months, and showed the greatest deviation from the original values. The five sites resampled during winter months returned G_{Cd} values which were all within $\pm 10\%$ of the originally reported values and were neither consistently higher nor lower. Thus, the value of G_{Cd} for each site appears to be characteristic of that location and the difference in G_{Cd} values between sites is sufficiently great (ranging between 0.3 and 3.5) that even large errors in G_{Cd} determinations would not hide regional variations in the rate of cadmium uptake by the oysters.

G_{Cd} values can also be used in reverse to calculate the mean individual flesh weight which an oyster from a particular sample site is likely to attain before it exceeds the 2 mg/kg cadmium limit. Mean individual flesh weight (M.I.W.) which would have a cadmium concentration of L mg/kg at

any particular site is given by $M.I.W. = L/G_{Cd}$ (where M.I.W. is in gms and L is in mg/kg); the value of L can be converted to a dorso-ventral length (D.V.L.) measurement using the plot of M.I.W. vs. D.V.L. presented by McConchie *et al.* (1988). If this calculation is applied to the Shark Bay pearl oysters using the G_{Cd} values in Figure 1, and $L =$ the limit of 2 mg/kg cadmium, it is clear that it would be rare to find oysters in Shark Bay which contain less than 2 mg/kg cadmium but are over the minimum size for commercial fishing (i.e. D.V.L. >60mm).

Whereas values of G_{Cd} vary widely within Shark Bay (Figure 1) without showing an obvious systematic pattern, variation in the values of G_{Zn} (Figure 2) does show a systematic pattern. Values of G_{Zn} range over nearly two orders of magnitude and show a distinct rise with increasing proximity of

the sampled site to the town of Denham (Figure 2) and a minor rise near the small town of Useless Loop (G_{Zn} values of 14 on the peninsula southwest of Denham, Figure 2). The values of G_{Zn} probably reflect an anthropogenic source of zinc (e.g., sacrificial anodes on boats, runoff from galvanized iron roofing, etc.) but the same explanation cannot be applied to G_{Cd} values and cannot explain the cadmium/zinc ratios in Shark Bay oysters which are curiously high in comparison to those in other species of oysters and mussels Australia-wide (e.g., Harris *et al.* 1979; Ward *et al.* 1982). It is also noted that even at the site where G_{Zn} is highest no oyster has yet been found with a zinc content in excess of the 1000 mg/kg (wet weight) limit applied in Western Australia to molluscs for human consumption.

At three sample sites, with water depths at mean low tide of about 3 m, values of G_{Cd} for the normally sampled bottom dwelling oysters were 2.4, 1.5, and 0.9 but for oysters grown for 18 months in floating rope baskets (suspended 0.25 to 0.5 m below the water surface), values of G_{Cd} were 0.36, 0.15, and 0.12 respectively. These data support the suggestion of McConchie *et al.* (1988) that the mechanism responsible for the high cadmium loads in the Shark Bay oysters is linked to the substrate sediments and not to the dissolved cadmium concentration. It is also interesting to note that whereas about 60% of the mass of cadmium in bottom dwelling Shark Bay oysters is contained in the adductor muscle (McConchie *et al.* 1988), in oysters grown in the baskets, less than 12% of the mass of cadmium was contained in the adductor muscle; this difference is consistent with the experimental findings of Francesconi (1989). The tendency for cadmium to concentrate in the adductor muscle of bottom dwelling Shark Bay oysters is unusual for molluscs (Brooks & Rumsby 1965; Segar *et al.* 1971; Ishii *et al.* 1985) and may also be related to an unusual cadmium uptake mechanism.

X-ray diffraction studies of the $<6\phi$, fraction of the sediment reveals that it contains two ferruginous minerals, hematite ($\alpha - Fe_2O_3$) and maghemite ($\gamma - Fe_2O_3$) with an average hematite: maghemite ratio of about 4:1; no other ferruginous minerals were detected in the sediments except where rare localized heavy mineral concentrations (including magnetite, ilmenite and garnet) were present. The aqua regia extractable iron content of the top 5 cm of sediment from each mollusc sample site is thus assumed to reflect the concentration of iron present as Fe_2O_3 ; there are probably traces of iron in some of the biogenic carbonates in the sediment and in the traces of sulphides formed as a result of the bacterial reduction of sulphate, but these appear to account for a very small proportion of the iron present. The concentration of iron-oxides in the sediment shown in Figure 3 is therefore calculated from the aqua regia extractable iron content assuming all iron is present as Fe_2O_3 ; the concentration of iron-oxides determined using this assumption ranges from not detectable to over 3,000 mg/kg.

Mössbauer studies of the Shark Bay iron-oxides reveal that most are superparamagnetic hematite with a spectrum which suggests a mean particle diameter of about 120 Å (c.f. data of Kündig *et al.* 1966) and a very high surface area to volume ratio of $5 \times 10^8 \text{ m}^{-1}$ (assuming spherical particles). The high surface area of the oxide particles ties in well with the very high cation exchange capacity of 180 meq/100 g oxide measured by Lawrance (1985). Determinations of the electrophoretic mobility of five samples of Shark Bay iron-

oxides over the pH range of 5–9 indicates that their iso-electric point (I.E.P.) is at a pH of between 7.2 and 7.8.

In the experiments to assess the capacity of Shark Bay iron-oxides to adsorb cadmium from spiked solutions of natural Shark Bay sea water (Lawrance 1985), the oxides proved capable of adsorbing cadmium remarkably efficiently. More importantly, the adsorption efficiency (measured as the proportion of the cadmium in the spiked solution extracted by the oxides) increases dramatically as the cadmium concentration initially present in the spiked solution is decreased; at cadmium concentrations in the initial solution of less than about 0.1 mg/L and 4 g of oxide in 20 mL of solution, over 90% of the cadmium initially present is adsorbed onto the iron-oxides. Speciation models indicate that over 95% of the cadmium in Shark Bay sea water will be present as chloride complexes which should favor high adsorption efficiencies (Lawrance 1985). Kinetic studies of cadmium adsorption onto iron-oxides (Gadde and Laitinen 1974; Millward 1980) indicate that an initially rapid phase of adsorption (during the first hour) is followed by a second much slower step which probably involves solid state diffusion; similar adsorption kinetics would be expected to apply in Shark Bay. Both the high adsorption capacity and the probable high adsorption rates favor cadmium adsorption from sea water by the Shark Bay iron-oxides whenever turbulence causes the resuspension of fine sediment particles. Thus, even at the low concentrations of cadmium present in Shark Bay sea water, cadmium transfer from the water to the oxides may be very efficient.

Discussion

Although this study is not focused on zinc in *P. carcharia-rum*, the map of G_{Zn} values (Figure 2) shows how effectively G_{Cd} and G_{Zn} values can reveal a point source of metals and that, whereas zinc concentrations in the oysters are influenced by anthropogenic factors, cadmium concentrations are not. There is no evident natural or anthropogenic point source for cadmium in the Shark Bay area which could explain the regional variation in G_{Cd} values shown in Figure 1. Although the cadmium concentration in Shark Bay sea water averages 2–3 times higher than that in mean ocean water and is likely to contribute to the generally high cadmium concentrations in Shark Bay molluscs, variation in the dissolved cadmium concentration does not correlate with G_{Cd} values (McConchie *et al.* 1988) and therefore cannot be the factor controlling the regional variation in G_{Cd} values. Similarly, there is no significant correlation between G_{Cd} values and the cadmium concentration in substrate sediments at each mollusc sample site. However, McConchie *et al.* (1988) did note that as the proportion of allogenic grains in the substrate sediment increased relative to authigenic and biogenic minerals, there was a general increase in the value of G_{Cd} . They further suggested that this relationship would probably form a substantial part of any final explanation for the regional variation in G_{Cd} values in the molluscs and that a minor component in the sediment may provide an important link.

In finding the explanation for the regional variation in the values of G_{Cd} , the best clue was the observation that coastal cliffs near sites with high G_{Cd} values had a distinct red colour

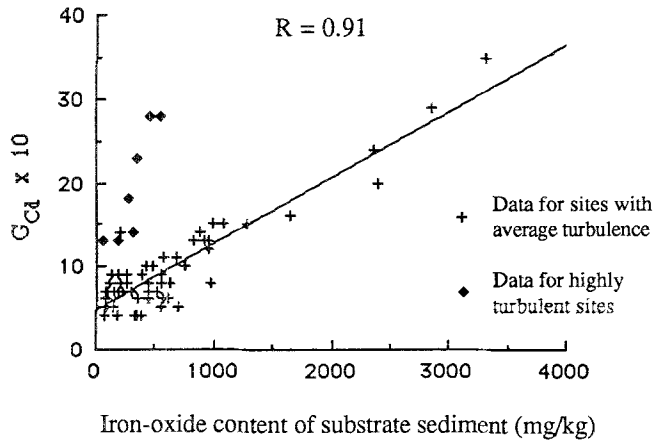


Fig. 4. Plot of G_{Cd} values for all *P. carchariarium* sample sites against the iron-oxide content of the top 5 cm of substrate sediments at each site. Data for sites characterized by particularly high turbulence, and data for sites where no iron-oxides were detected, were excluded from the calculation of R

due to the presence of iron-oxides (Figures 1 and 2) and that some of these iron-oxides were eroded from the cliffs and could be found as a trace component in the substrate sediment where the oysters were collected. The relationship is more clearly demonstrated by Figure 4 which combines the data in Figures 1 and 3 and shows that there is a strong correlation between G_{Cd} and the iron-oxide concentration in the substrate sediment. Furthermore, the largest deviations from the plot (Figure 4) are for sample sites which are characterised by higher than average turbulence such as at the southern end of Dirk Hartog Island. Thus, in the Shark Bay area, oysters with high cadmium loads are found where turbulence is high and the substrate sediment contains fine hematite.

Work on this project has shown that cadmium in the sea water adsorbs very efficiently onto the surface of the very fine hematite in the sediment even though the concentration of cadmium in the water and the concentration of iron-oxides in the sediment are both low; the hematite is negatively charged at the prevailing seawater pH of 8.15 (the I.E.P. for the hematite is at a pH of between 7.2 and 7.8). Over about 2,000 km² the water depth in Shark Bay is less than 1 m and fine sediment (which includes the hematite) is readily suspended by the strong winds which are common in the area. While in suspension the iron-oxides can adsorb cadmium from the sea water and can be ingested by filter feeding organisms such as the pearl oyster, thereby transferring cadmium to the molluscs. Once inside the molluscs, lower pH conditions prevail, the hematite becomes positively charged, and the cadmium is released and accumulated by the organism. Effectively, the fine iron-oxides in the sediment are pre-concentrating the cadmium and acting like a 'chemical conveyor belt' in increasing the efficiency of metal transfer to the molluscs. For areas with a similar turbulence, the correlation between the concentration of iron-oxides in the substrate sediment and G_{Cd} (an indicator of the rate of cadmium uptake by the molluscs) is $R = 0.91$ (Figure 4); where turbulence is higher, G_{Cd} is higher than expected for the iron-oxide content of sediment at the site and where turbulence is low G_{Cd} values are lower than expected.

The above model for the transfer of cadmium to molluscs in Shark Bay is consistent with the slightly higher G_{Cd} values recorded during the more turbulent summer months at sites which were previously sampled during winter if, as suggested by other data (Francesconi 1989), there is some loss of cadmium from the animals when the rate of supply is reduced. Confirmation of a link between cadmium uptake by the oysters and iron-oxides in the sediment lies in the observation that the oysters grown in baskets suspended near the surface for 18 months contained seven to ten times less cadmium than oysters collected from the bottom at the same site; despite the much lower G_{Cd} values for the oysters in the basket they remain marginal for harvesting for human consumption. The unusual tendency for the Shark Bay oysters to concentrate up to about 60% of their total mass of cadmium in their adductor muscles may also be related in some way to this new mechanism for the uptake of cadmium by molluscs. Previous studies of the distribution of cadmium between various organs in molluscs (e.g., *Ostrea sinuata*, Brooks and Rumsby 1967; *P. albina albina*, Francesconi 1989) have shown that where cadmium is taken directly from the water as dissolved cadmium it concentrates in various organs in the order viscera > gills > mantle > adductor. In experiments carried out on Shark Bay oysters held in filtered sea water spiked with up to 20 $\mu\text{g Cd/L}$ (Francesconi 1989) the distribution of cadmium between the various organs in the animals changed over 88 days from adductor > viscera > mantle > gills to viscera > gills > mantle > adductor. This finding is consistent with our observations that in the oysters grown in floating baskets less than 12% of the mass of cadmium was contained in the adductor muscle compared with about 57% for bottom dwelling oysters at the same sites. Francesconi (1989) suggested that this change in cadmium distribution between organs may indicate two different metal uptake mechanisms are operating. The tendency for cadmium to concentrate in the adductor muscle of bottom dwelling Shark Bay oysters is unusual and may indicate that cadmium taken up by the new mechanism described here is metabolized in a manner different from dissolved cadmium taken directly from sea water.

Conclusions

Although Shark Bay is remote from all known industrial and geological sources of cadmium, the cadmium load in specimens of the pearl oyster *Pinctada carchariarium* is generally above the W.A. State limits set for molluscs for human consumption and is commonly higher than the load in molluscs from areas of recognized cadmium pollution. In analyses involving over 2,000 animals, oysters which contained less than 2 mg/kg cadmium but were over the minimum size for commercial fishing (i.e. D.V.L. > 60 mm) were notably rare.

The cadmium load in the oysters and the rate of cadmium uptake (indicated by values of G_{Cd}) vary by about an order of magnitude between sample sites within Shark Bay but show no correlation with any obvious source of cadmium. The cadmium concentration is normal in Shark Bay seawater (0.04 $\mu\text{g/L}$ to about 0.35 $\mu\text{g/L}$), rarely exceeds 0.25 $\mu\text{g/L}$ in ground waters, bore waters, and salt lake brines, and very rarely exceeds 1 mg/kg in sediments. However, there is a strong correlation between G_{Cd} and the concentration of

iron-oxides in the substrate sediment on which the oysters are growing. It appears that fine hematite particles, which are eroded from the Peron Sandstone exposed in some coastal cliffs, and are readily suspended by strong winds, are an important link in the transfer of cadmium to the oysters.

This study reveals that cadmium in the water adsorbs extremely efficiently onto the surface of the hematite, which is negatively charged at the prevailing seawater pH of 8.15, and that suspended hematite particles are ingested by the molluscs. Inside the molluscs, lower pH conditions cause the hematite charge to be reversed and the cadmium is released and accumulated by the organism. Thus, the cadmium load in oysters is highest at sites where the iron-oxide concentration in the substrate sediment is high and fine particles in this sediment are frequently resuspended by wind induced turbulence. Effectively, the hematite is pre-concentrating the cadmium and acting like a chemical conveyor-belt in enhancing metal transfer to the molluscs. This mechanism for the transfer of cadmium to filter feeding organisms probably operates in parallel with the conventional mechanism involving uptake of dissolved cadmium directly from the sea water, but appears to be the dominant mechanism for *P. carchariarium* in Shark Bay. The link between cadmium uptake by molluscs and iron-oxides in the sediment is supported by the observation that in water with a depth of 3 m, bottom dwelling oysters contain up to 10 times more cadmium than oysters grown in baskets suspended near the surface at the same site.

We have no doubt that this new mechanism for the transfer of cadmium to filter feeding organisms operates effectively in similar environments elsewhere where water turbulence is high and the sediment contains very fine iron-oxides; there may also be other common constituents of sediments which can act as metal transfer agents in the same way that iron-oxides do in Shark Bay. This finding has two important implications for scientists investigating heavy metals in the environment:

1. At some sites where the cadmium load in filter feeding organisms is unexpectedly high, the elevated metal loads may be wholly or partly a result of natural conditions and not due to anthropogenic pollution as might initially be suspected.
2. Where iron-oxides in suspension or ferrous iron in solution (which will rapidly form hydrated iron-oxides in normal marine environments) are discharged into a marine environment where regular resuspension is likely, the cadmium load in molluscs in that environment may rise even if the discharged waters are cadmium-free. A similar outcome may arise where low cadmium ferruginous sediment is deposited in shallow marine environments during land reclamation or similar operations.

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