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Geochemical Partitioning of Trace Metals in the Potential Culture-Bed of the Marine Bivalve, *Anadara granosa*

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The relative distribution of trace metals in coastal sediment geochemical phases has received considerable attention as a mean of assessing the degree of trace metal pollution (Rosental et al. 1986; Abaychi and Douabul 1986; Rule and Alden 1992; Abu-Hilal 1993). Metals in the non-residual fraction (exchangeable, carbonate, easily reducible, moderately reducible and organic phases) have been demonstrated to be strongly correlated with tissue-metal concentrations in various benthic organisms (Luoma and Bryan 1978; Langston 1982; Bourgoin et al. 1991).

Among these phases, the oxides of manganese (easily reducible phase) and iron (moderately reducible phase) and organic matter have been emphasized as important scavengers of available trace metals (Arakel and Hongjun 1991; Young and Harvey 1992; Abu-Hilal 1993). Therefore, these phases are undoubtedly among the criteria that should be considered explicitly when assessing the potential bioavailability of metals.

The marine bivalve *Anadara granosa* is commercially cultured in the tidal mudflats along the western coast of the Peninsular Malaysia. The purpose of this study was to provide an assessment of the geochemical partitioning of trace metals in sediments collected from a culture-bed of *A. granosa*. The selected area is thought to receive minimal or restricted impacts of trace metal pollution. The present investigation is of significance as a baseline of information for comparative studies with other aquaculture areas in the region.

MATERIALS AND METHODS

Tidal mud flats along the Straits of Tuba separating the Island of Dayang Bunting and the Island of Tuba of Langkawi Archipelago, Peninsular Malaysia were selected as study sites (Fig. 1). These areas have been designated by the Fisheries Department of Malaysia as the potential culture-bed for *A. granosa*.

Surficial sediments (upper 5 cm) were manually sampled with acid-washed plastic tubes from four stations between the mean high water and low water neap tide levels. Three pooled samples approximately 300 m apart were designated for each station. The sediments are texturally homogeneous and at least partially anaerobic due to the presence of a black-sulphide rich layer about 3-5 cm below the sediment-water interface. However, attempts were not made to purge the atmospheric air with nitrogen during the sampling period.

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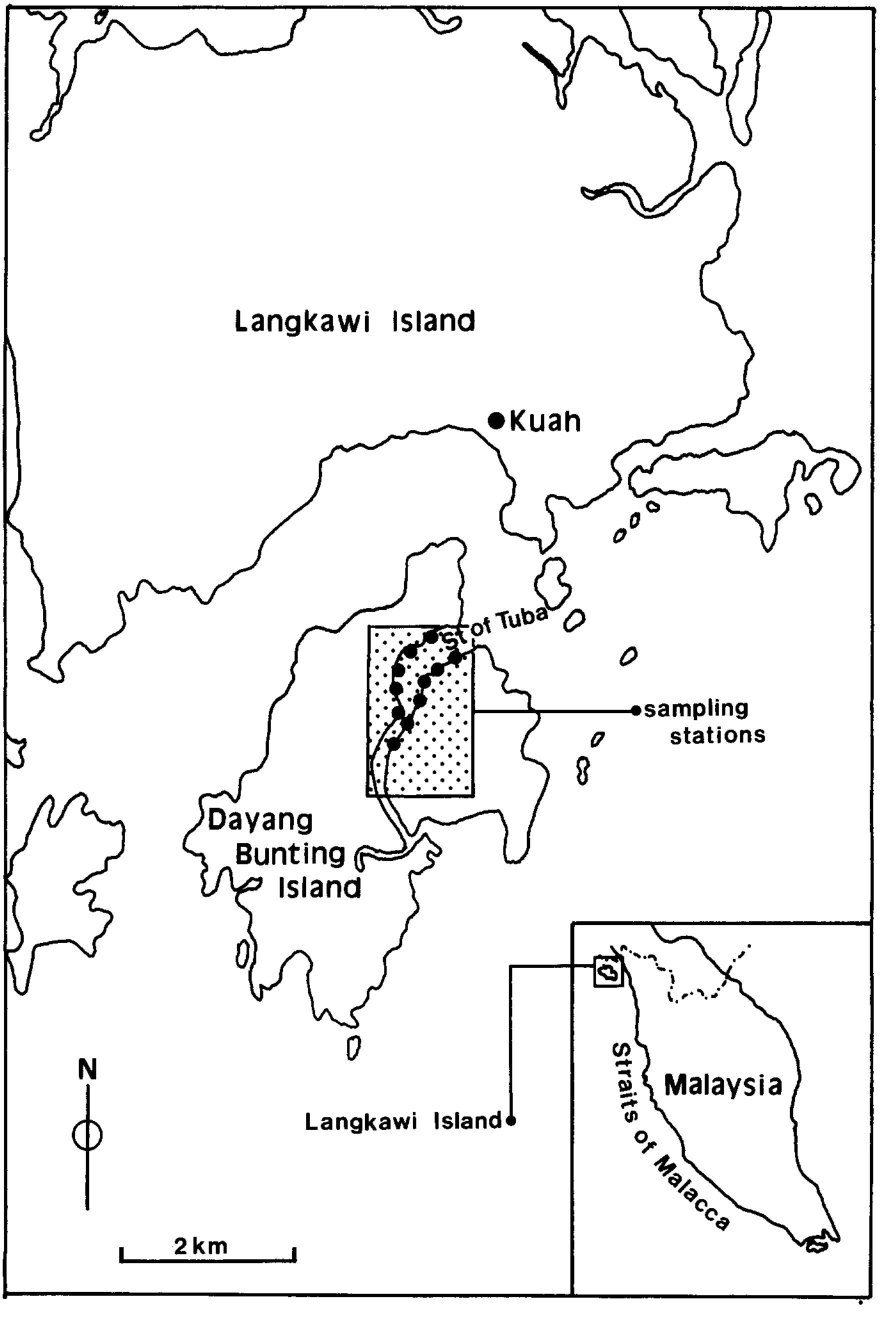

Figure 1. Location of study area where sampling stations were designated.

Upon reaching the laboratory, the upper sediment layer (5 cm) was scooped with a plastic spoon and cleaned of visible debris before wet sieving to < 210 μm grain size with artificial seawater. After oven drying (110 ^{o}C for 8 hr), the sediments were ground and subjected to trace-metal extraction.

Trace metals in the non-residual fraction (associated with the exchangeable, easily reducible, moderately reducible and organic phases) were sequentially extracted following the methods adopted by Rule and Alden (1992). Trace metals associated with the residual fraction, on the other hand, were extracted with the methods described by Peerzada and Rohaza (1989).

Elemental analysis was performed by the Inductively Coupled Plasma method (Baird ICP-AES 2000). Reagent washes were discarded due to the undetectable level of trace metals. An estimate of the precision of the methods employed was provided by analyzing triplicates of one sample. The results were within 10% of the mean values.

The numerical summation of each metal concentration in the exchangeable, easily reducible, moderately reducible and organic-sulphide phases is referred to as the total metal in the non-residual fraction. Trace metals in both the non-residual and residual fractions, on the other hand, made up the total leachable trace-metal concentrations.

RESULTS AND DISCUSSION

Trace-metal concentrations in various geochemical phases are given in Table 1. There were no substantial elevated levels of Cd, Cu, Ni, Pb or Zn at any station. This observation is substantiated by the low standard deviations and, consequently, small coefficients of variation for all metals (Table 2). With the exception of Ni, the relative abundance of Cd, Cu, Pb and Zn in the non-residual fraction may be considered to be very low (Fig 2). As metals in the non-residual fraction are normally associated with polluted waters (Chester and Voutsinou, 1981), it may be concluded that this area is relatively unimpacted with trace metals.This is not unexpected as this area is only dotted with small villages where fishing and subsistence agriculture are the main economic activities.It may be suggested that the trace metal levels recorded from this area may serve as a baseline in assessing trace-metal contamination in other aquaculture areas in this region.

As the relative abundance of trace metals in the non-residual fraction was very small (Fig. 2), there is a possibility that the potential availability of these metals to the commercially important bivalve *A. granosa* and other benthic dwelling organisms may be minimal.

With the exception of Pb, the relative abundance of Cd, Cu, Ni and Zn in the exchangeable phase was low and geochemically insignificant (Fig. 3). The greater abundance of Pb in the exchangeable phase may be attributed to the heavy traffic flow of fishing and leisure boats ferrying tourists to various small islands in the Langkawi Archipelago.

Trace metals associated with the oxides of Fe and Mn either extracted in combination or singly assume a relatively important role in scavenging available metals from pollution sources (Waldichuk 1985; Arakel and Hongjun 1991). The moderately reducible phase (oxides of Fe) in sediments from the Straits of Tuba (Fig. 3) assumed a greater role in scavenging the available Cd, Cu and Zn than the

Table 1. Trace metal concentrations (ppm, dry wt) in various geochemical phases in pooled sediments from four stations in the Straits of Tuba. EP, ERP, MRP, OSP, NR and R represent exchangeable phase, easily reducible phase, moderately reducible phase, organic-sulphide phase, non-residual fraction and residual fraction respectively.

Stations	Phase	Cd	Cu	Ni	Pb	Zn
1	EP	0.03	0.07	0.32	1.61	0.88
	ERP	<0.01	<0.01	<0.01	<0.01	<0.01
	MRP	0.19	0.09	<0.01	<0.01	4.74
	OSP	0.06	0.76	6.41	1.22	3.64
	NR	0.28	0.92	6.73	2.83	9.26
	R	1.63	4.50	4.82	26.44	26.12
	total	1.91	5.42	11.55	29.27	35.38
2	EP	0.02	0.08	0.32	1.52	0.76
	ERP	<0.01	0.03	<0.01	<0.01	0.26
	MRP	0.16	0.08	<0.01	<0.01	4.91
	OSP	0.07	0.62	5.64	1.52	3.73
	NR	0.25	0.81	5.96	3.04	9.66
	R	1.44	3.82	8.63	22.11	25.24
	total	1.69	4.63	14.59	25.15	34.90
3	EP	0.02	0.06	0.24	1.33	0.86
	ERP	<0.01	0.09	<0.01	<0.01	0.41
	MRP	0.19	0.18	<0.01	<0.01	3.83
	OSP	0.23	1.11	6.82	2.82	4.03
	NR	0.44	1.44	7.06	4.15	9.13
	R	1.34	3.96	5.34	21.16	21.42
	total	1.78	5.40	12.40	25.31	30.55
4	EP	0.01	0.03	0.26	1.33	0.69
	ERP	< 0.01	0.05	<0.01	<0.01	0.33
	MRP	0.14	0.46	<0.01	<0.01	4.64
	OSP	0.25	0.99	6.82	3.55	4.44
	NR	0.40	1.53	7.08	4.88	10.10
	R	1.62	4.13	5.52	23.16	30.34
	total	2.02	5.66	12.60	28.04	40.44

Table 2. Trace metal concentrations (ppm, dry wt) in the total, residual and non-residual fractions pooled from all stations.

	Total	% cv	Residual	% cv	Non-residual	% cv
Cd	1.85 ± 0.14	7.8	1.51 ± 0.14	9.3	0.13 ± 0.9	26.5
Cu	5.28 ± 0.45	8.5	4.10 ± 0.29	7.1	1.18 ± 0.36	30.5
Ni	12.79 ± 1.29	10.0	6.08 ± 1.73	28.5	6.71 ± 0.52	7.8
Pb	26.94 ± 2.04	7.6	23.22 ± 2.30	9.9	3.73 ± 0.96	25.7
Zn	35.31 ± 4.03	11.4	25.78 ± 3.66	14.2	9.54 ± 0.44	4.6

n = 4; mean ± s.d.

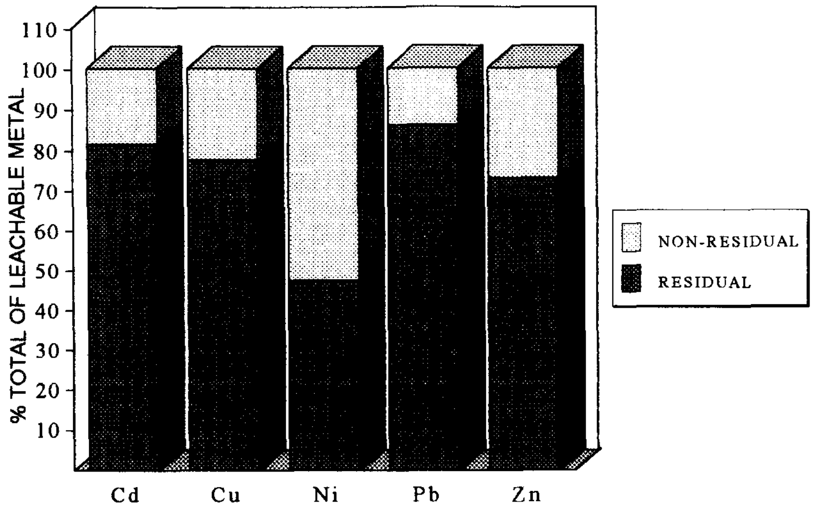

Figure 2. The percentage of total leachable metal in both the residual and non-residual fractions. Pooled data from four stations.

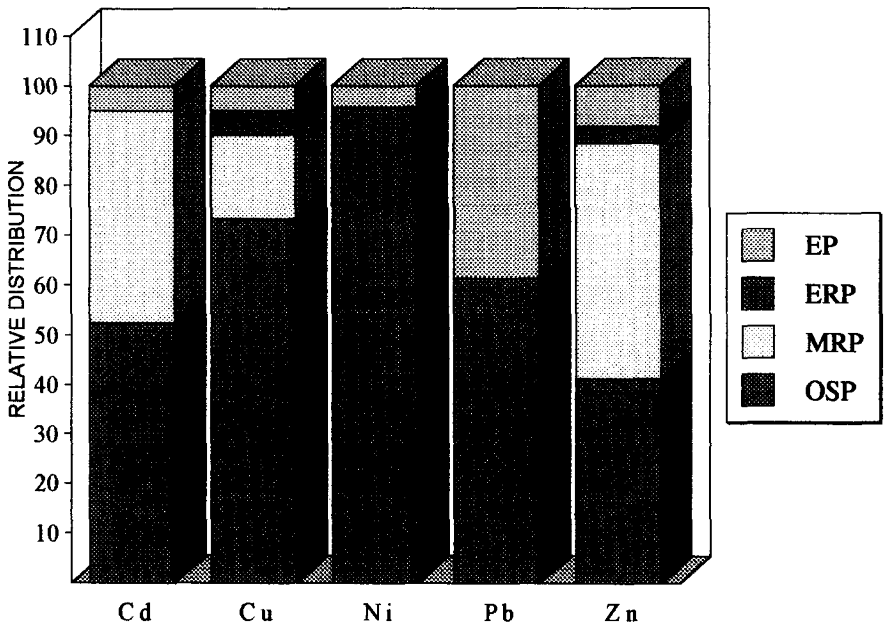

Figure 3. Relative distribution of trace metals in various non-residual geochemical phases. EP, ERP, MRP and OSP represent the exchangeable phase, easily reducible phase, moderately reducible phase and organic-sulphide phase, respectively. Pooled data from four sampling stations.

easily reducible phase (oxides of Mn).The present study supports suggestions made earlier by Young and Harvey (1992) that the oxides of Mn and Fe and the organic matter may compete among each other relative to their abundance in providing binding sites for the sorption of available trace metals. This phenomenon is further supported by the results of Luoma and Bryan (1981) where the organic component assumed a greater role in the sorption of Cu, Pb and Zn in sediments of low iron content.

Sediments from the Straits of Tuba appear at least to be partially anaerobic. The presence of high organic matter (7-9% based on ignition loss at 450 ^{o}C) may further enhance the sediments to be more anoxic. It may be concluded that the organic-sulphide phase assumes a greater role than the easily and moderately reducible phases in sediments from the Straits of Tuba as an efficient scavenger and may also serve as a reservoir of trace metals to be made available under favorable prevailing conditions. This conclusion is supported by the observation that more than 50% of the total non-residual Cu, Ni and Pb were associated with this phase (Fig. 3). It is also noteworthy that trace metals must be in the form that are biologically available to have an impact on aquatic organisms (Waldichuk 1985).

Biologically available trace metals may occur primarily in one phase or may be most of the loosely bound portion of various geochemical phases (Rule 1985). Trace metals in these phases (exchangeable phase and easily reducible phase) are assumed to be easily biologically available (Rule and Alden 1990). As the observed concentrations and the relative abundance of these metals are very low in both of these phases, marine bivalves such as *A. granosa* cultured in this area are possibly unlikely at risk of being contaminated with trace metals of toxicological significance.

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