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Concentration of heavy metals in sediments and bivalves (*Soletellina* sp.) in the mangrove environments of Tok bali, Kelantan, Malaysia

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ABSTRACT

An assessment on marine contamination due to heavy metals was conducted in the mangrove areas based on marine bivalves and sediments collected from Tok Bali, Kelantan. The sediments were collected at the intertidal zone during low tide. Six sampling stations were randomly chosen for sampling in the whole study area. The sediments collected were analyzed for sedimentological characteristics using particle size analyzer (PSA) for sediments <63 mm, organic carbon, using wet dichromate method and heavy metals using Inductive Couple Plasma-Mass Spectroscopy (ICP-MS). Results on the sedimentological characteristics revealed that the sediments ranged from fine sand (2.43Φ) to silt (6.97Φ), moderately sorted (0.66Φ) to poorly sorted (1.65Φ) and strongly negatively skewed (-0.06 Φ) to positively skewed (0.11Φ). Organic carbon contents ranged from 0.9% to 1.3%. For heavy metals in sediments, results revealed that the average concentrations for Cr is 83.8µg/g; 139.4µg/g for Mn; 11.5µg/g for Cu; 82.9µg/g for Zn; 45.1µg/g for Sr; 31.5µg/g for Ba and 35.1µg/g for Pb. For the bivalve on the other hand, Cr has an average concentrations of 2.1µg/g; 47.8µg/g for Mn; 4.7µg/g for Cu; 80.0µg/g for Zn; 34.4µg/g for Sr; 1.4µg/g for Ba and 1.6µg/g for Pb. Results from normalization revealed that the heavy metals were derived from natural source and no anthropogenic input was observed

Key words: Heavy metals, Sediments, Bivalaves, Mangroves, Malaysia.

INTRODUCTION

The environment consists of numerous metals from natural and anthropogenic sources. Most of the metals accumulate in the environment such as in the sediment, water and in organisms. Metals enter the marine environment through natural process such as weathering of rock, leaching of soils, and eruption of volcanoes and emission of hydrothermal vent. The metals played a critical role in industrial development and technological advance. High concentration of metals is a source of pollution and pollution by metals is a serious problem due to toxicity and the ability to accumulate in the biota.

Marine bivalves are proven bioindicator of stress in marine ecosystems because they have a tendency to accumulate very high concentration of metals than their surrounding environment. They are recognized as good monitors of ecosystem changes. Bivalves are widely used as bioindicators of heavy metals pollution because they are known to concentrate these elements, providing a time integrated indication of environmental contamination. Contaminant levels in the tissues of bivalves more accurately reflect the magnitude of environmental contamination compared to fish and crustacean, for bivalves have a very low level of enzyme activity capable of metabolizing pollutants.

Heavy metal pollution of sediments, however, is frequently difficult to determine. The approached most often used is to compare metal concentration of surface sediment sample with a deep sample from the same area or a surface sample from a more distant area which is thought to be unpolluted. Contaminant concentrations in bottom sediments represent a critical measure of health contamination. There are many cases in which catastrophic events against human health have occurred. In order to avoid such incidents, monitoring toxic metal concentrations in the environments should be employed.

Information on the levels of heavy metals in the mangrove environment is scarce and limited. Studies were focused on the coastal areas and rivers. Unlike other environmental media, the use of biomonitors to study heavy metal pollution in the Malaysian environment has received widespread attention. Bivalves (*Perna viridis* and *Saccostrea* sp.) and gastropods (*Thais* sp.) were frequently used while fish were used mainly in relation to health concerns as a result of fish consumption rather than an as indicators of heavy metal contaminations. The aim of this study is to assess heavy metal pollution using bivalves as bioindicator and to find out any relationships between heavy metals and the sediments.

MATERIAL AND METHODS

Study Area and sampling

Sediment and bivalves were collected at the Tok Bali lagoon which has undergone increasing development like shipping and fishing activities. The sediments and bivalves were collected at the .intertidal zone during low tide. Sampling of 6 bottom sediments samples was done by means of scooping the sediments using plastic. The upper 2–3 cm was recovered and placed in acid-cleaned labeled plastic bags, then homogenized and stored in the freezer before analysis. The sampling stations were defined as an harbor, human settlements, lagoon channels, and coastal area on the basis of their location and the activities undertaken therein (Fig. 1).

A total amount of 30 specimens of bivalve (*Soletellina* sp.) were collected from 6 sediment sampling sites. The bivalves were rinsed with distilled water and frozen until analysis. The samples were thawed out and the soft tissue of the bivalve was dissected with plastic forceps and the wet weight of the samples was recorded. Soft tissue was dried subsequently in an oven at 95^{o}C for 24 hours or until constant weight had been attained. Then, the dry weight was recorded. Samples were homogenized and ground to powder using mortar and pestle. The homogenized sample was processed for digestion and the digests was stored until injection to Inductive Couple Plasma-Mass Spectroscopy (ICP-MS) for heavy metal contents determination.

Analytical procedures

Sediments were treated with concentrated hydrogen peroxide for 48 h, organic debris and shell fragments were removed by sieving (<63 µm) and grain-size analysis was performed by a laser diffraction size (Malvern Mastersizer 2000 coupled with Hydro 2000s sampler unit). Sediments were classified in accordance with Shepard (1954). Organic carbon (Corg) in sediments was determined using Wet Dichromate Oxidation method (Holme and McIntyre, 1984). Corg was determined after removal of carbonates with concentrated HCl 1 N (Hedges and Stern, 1984). Analytical precision of measurements was 2.5% for Corg. Sediments (150 mg) and biota (1500 mg) were mineralized using a microwave oven (MLS 1200mega, Milestone) in a teflon vessel with super pure concentrated HCl, HNO_3 and HF mixture (2 : 0.5 : 0.1 v/v) for dried sediments (adapted from Mester et al.,1999), and with concentrated HNO_3 (Navarro et al.,1992) for the dried biota soft tissue. Reagent blanks were processed simultaneously. The certified reference materials for marine sediment (Standard Reference Material (SRM) "estuarine sediment (National Bureau of standards (NBS 1646a)) and bivalve tissue DOLT-3 (Dogfish liver from National Research and Council of Canada) were used to control accuracy of the analytical method for sediments and biota. Recovery values found were 105% for sediments and 80.57% for biota (Tables 2 & 4). All concentrations were based on dry weight (d. wt.).

RESULTS AND DISCUSSION

Fine silts constituted the predominant textures (stations 1, 4, 5 and 6) inside the mangroves environment except for stations 2 and 3 which are coarse sands. Grain size progressively decreased from the tidal outlet outward the inner areas of the mangroves and in the lower energy zones. Very fine silts were found prevalent in the mangrove environment (Table 1). Other sedimentological characteristics revealed that the sediments are moderately sorted (0.66Φ) to poorly sorted (1.65Φ) and strongly negatively skewed (-0.06Φ) to positively skewed (0.11Φ). Results indicated that the surrounding environment experienced moderate tidal influenced.

Heavy Metals in Surface Sediments

Table 3 shows the results on the heavy metal contents in surface sediments of the study area. Results revealed that the average concentrations for Cr is 83.8µg/g; 139.4µg/g for Mn; 11.5µg/g for Cu; 82.9µg/g for Zn; 45.2µg/g for Sr; 31.5µg/g for Ba and 35. 1µg/g for Pb. Based on the results, the levels of heavy metals are relatively low. Heavy metal concentrations in marine sediment is affected by reactions at particle surfaces that influence the quantity of metal adsorbed, reduction or oxidation reactions and adsorption or desorption of metals (Luoma, 1990). The variations in the distribution of heavy metals are influenced by the type of sediment, particle size and organic carbon content (Calvert et al., 1993).

Recovery test of Sediments

Evaluation on the precision and acceptability of analysis was done using the "Standard Reference Material (SRM) estuarine sediment. Table 2 shows the recovery test in sediments which range from 79.93% to 105.48%.

Heavy Metals in Bivalves

Table 5 shows the results on the heavy metal contents in bivalves collected in the study area. Results revealed that the average concentrations for Cr is 2.1µg/g; 47.8µg/g for Mn; 4.7µg/g for Cu; 80.0µg/g for Zn; 34.4µg/g for Sr; 1.4µg/g for Ba and 1.6µg/g for Pb. Based on the results, the levels of heavy metals are relatively low. Generally, bivalve can accumulate pollutants in their tissues to elevate levels reaching concentrations that are much higher than that of the ambient water concentrations. It also accumulates high concentrations of heavy metals in their soft tissues. In this study, the bivalves are still not accumulating these heavy metals therefore, are still safe for consumption. According to Phillips (1993), organisms that live in the estuaries have higher level of adaptation to stand presence of stress and disruptions. However, if the levels are more than they can take, it will bring harmful effects if consumed.

Recovery test of bivalve

Evaluation on the acceptability of analysis was done using the Standard Reference Material (SRM) from Dogfish Liver (DOLT 3). Table 4 shows

Table 1: Sedimentological Characteristics ((Ø)

Station	Mean	Sorting	Skewness	Kurtosis
1	6.84	1.29	0.33	2.45
2	2.27	0.74	-1.19	5.97
3	2.43	0.66	-1.99	8.4
4	6.8	1.44	0.11	2.18
5	6.97	1.47	-0.08	2.06
6	6.56	1.65	-0.06	2.1
Maximum	6.97	1.65	0.33	8.4
Minimum	2.27	0.66	-1.99	2.06
Average	5.31	1.21	-0.48	3.86

Table 2: Recovery test of sediment

Element	Certified value	Analyzed value	Recovery
Mn	234.50	207.09	88.31
Cu	10.01	10.56	105.48
Zn	48.90	48.21	98.59
Pb	11.70	11.86	101.39
Ba	210.00	174.34	83.02
Cr	40.90	32.69	79.93
Sr	68.00	63.42	93.26
Fe	2.02	1.85	91.56

Table 3: Heavy metal contents in sediment (µg/g dry weight)

Station	Cr	Mn	Cu	Zn	Sr	Ba	Pb	Fe (%)
1	20.5	15.1	18.4	179.3	20.2	83.5	23.4	2.4
2	144.3	408.3	1.0	47.5	48.3	11.2	25.8	4.1
3	118.4	291.5	1.8	48.8	68.9	10.1	25.7	3.5
4	36.8	17.6	12.8	61.5	43.1	23.7	40.3	3.0
5	60.0	69.6	22.5	69.3	26.8	37.3	49.8	5.5
6	122.6	34.2	12.3	91.1	63.7	23.0	45.5	3.1
Average	83.8	139.4	11.5	82.9	45.2	31.5	35.1	3.6

Table 4: Recovery test of bivalve

Element	Certified value	Analyzed value	Recovery
Cu	31.2	26.83	85.99
Zn	86.6	89.95	103.87
Pb	0.319	0.308	96.55
Cr	3.5	2.82	80.57

Table 5: Heavy metal contents in bivalves (µg/g)

Station	Cr	Mn	Cu	Zn	Sr	Ba	Pb	Fe (%)
1	2.1	45.6	4.1	84.2	35.2	1.1	1.5	0.2
2	1.6	54.6	4.3	88.5	32.4	1.7	1.7	0.3
3	3.2	50.0	5.6	86.4	32.6	2.0	1.6	0.2
4	2.3	42.2	6.4	80.5	33.7	1.7	1.7	0.3
5	2.0	62.8	4.0	75.4	41.6	1.2	1.8	0.2
6	1.6	31.9	3.5	65.0	30.8	0.8	1.5	0.2
Average	2.1	47.8	4.7	80.0	34.4	1.4	1.6	0.2

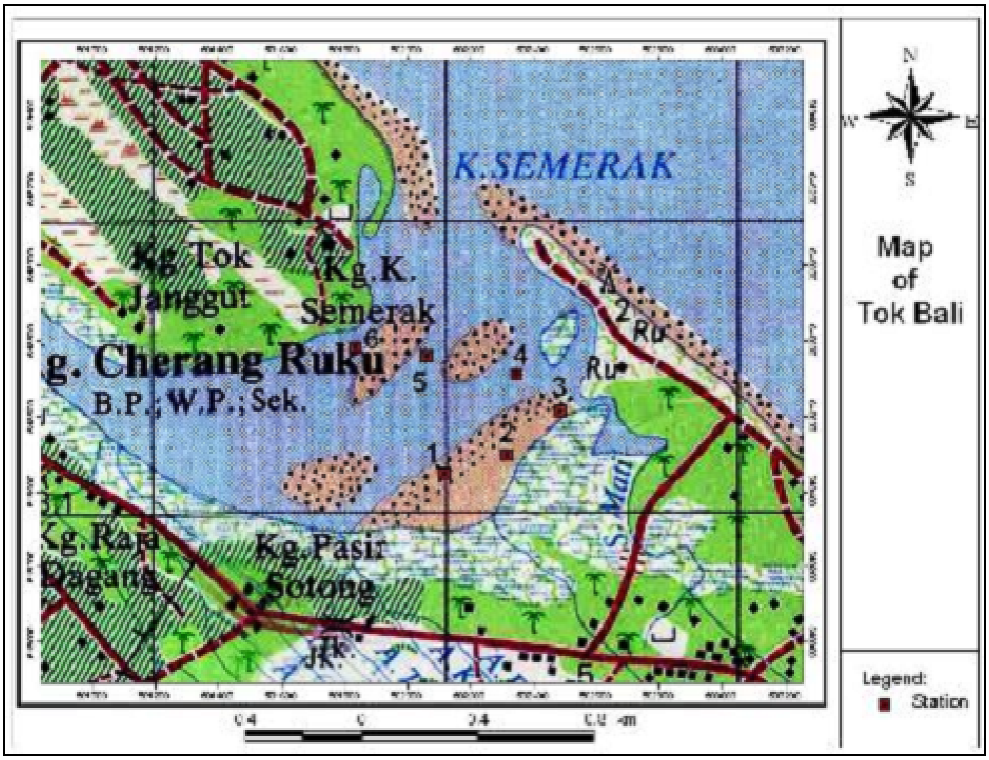

Fig. 1: Sampling location of the study area

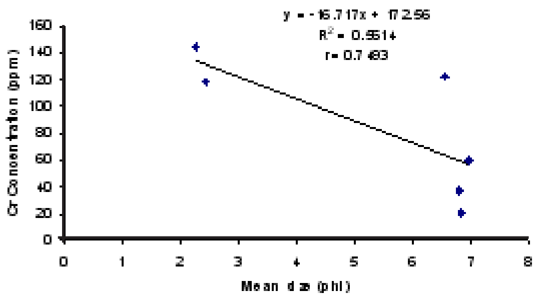

Fig. 2: Correlation beatween Cr and mean size

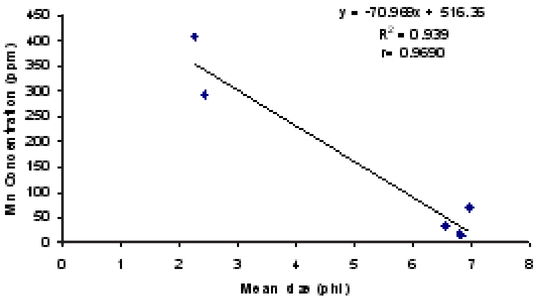

Fig. 3: Correlation between Mn and mean size

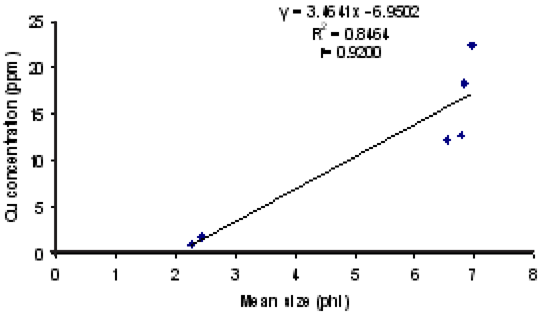

Fig. 4: Correlation between Cu and mean size

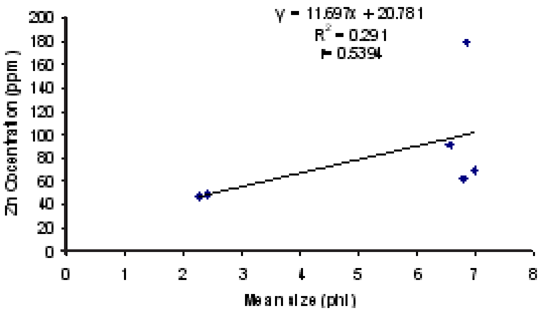

Fig. 5: Correlation between Zn and mean size

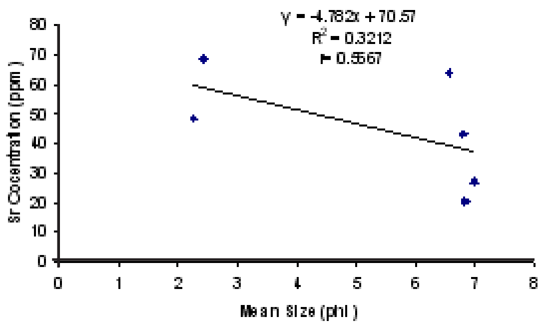

Fig. 6: Correlation between Sr and mean size

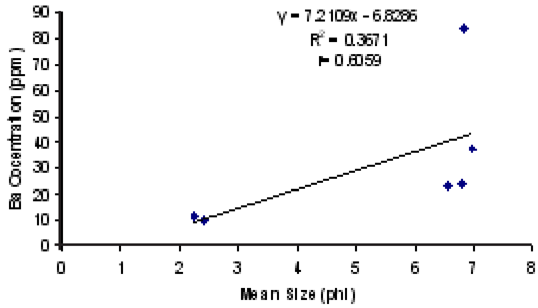

Fig. 7: Correlation between Ba and mean size

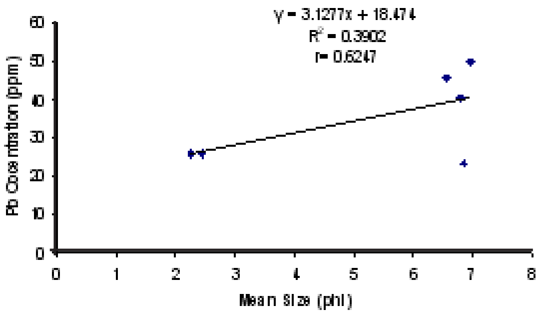

Fig. 8: Correlation between Pb and mean size

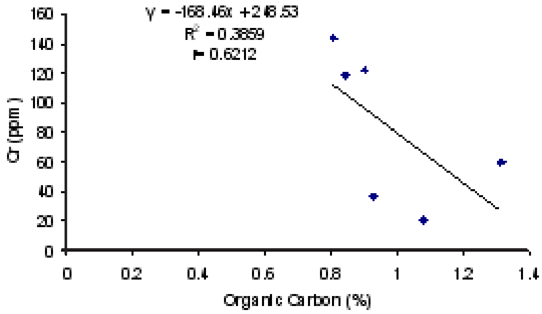

Fig. 9: Correlation betweaen Cr & organic carbon

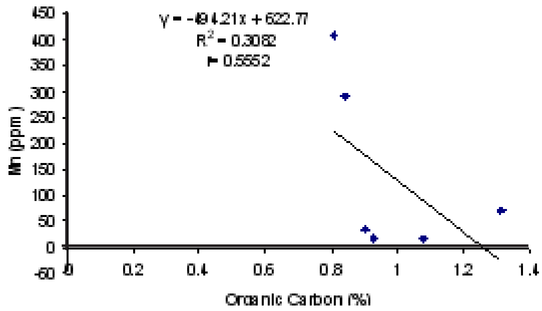

Fig. 10: Correlation between Mn and organic carbon

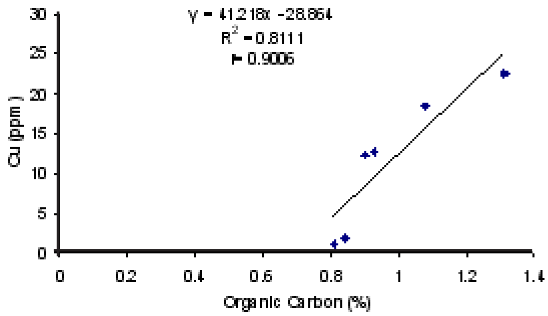

Fig. 11: Correlation between Cu and organic carbon

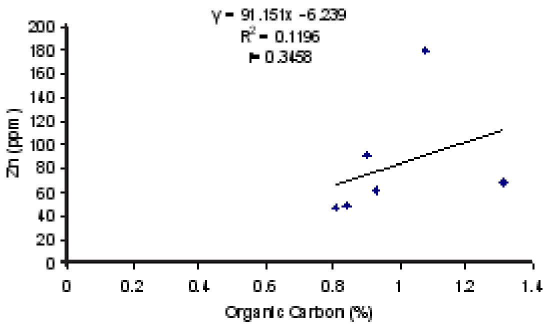

Fig. Correlation between Zn and organic carbon

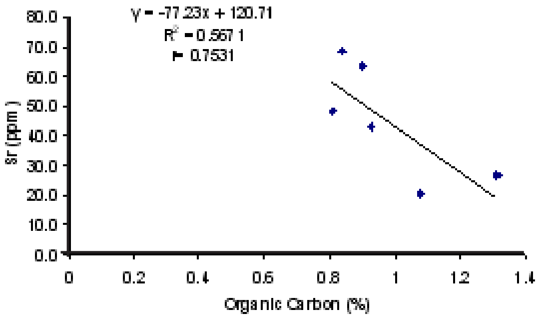

Fig. 12: Correlation between Sr and organic carbon

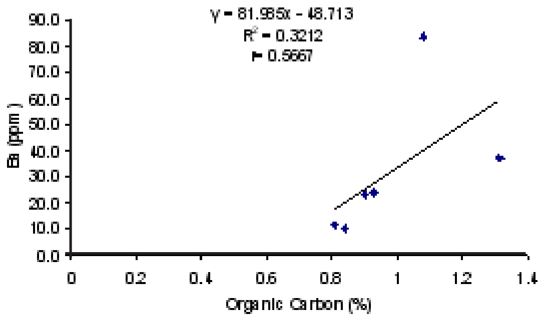

Fig. 13: Correlation between Ba and organic carbon

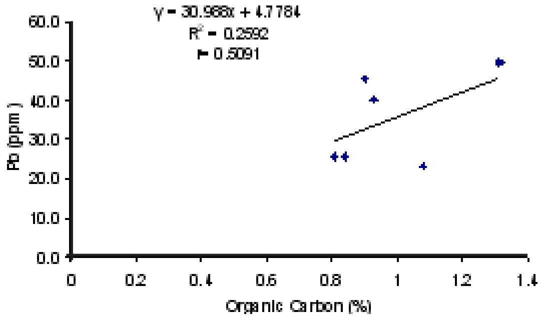

Fig. 14: Correlation between Pb and organic carbon

the recovery test which ranged from 80.57% and 103.87%.

Correlation between Heavy Metals in sediments and Particle Size

Correlation analysis was done to determine if there is a relationship between heavy metals and particle size in sediments. Results showed that Cr (r=0.749), Mn (r= 0.969) and Cu (r= 0.920) showed high correlation with particle size (Figures 2, 3 & 4) while other heavy metals such as Zn (r= 0.5394), Sr (r= 0.5667), Ba (r= 0.6247) and Pb (r= 0.6247) showed moderate correlation with particle size (Figures 5 to 8). Increasing heavy metal contents in sediments depends on the size of particles (Kamaruzzaman, 1999). The finer the particle size the probability for heavy metals to be attached or adsorbed is higher due to specific surface area.

Correlation between heavy metals and organic carbon

Organic carbon is an important component of sediments and considered as a binding agent for heavy metals. In this study there are four heavy metals which show moderate correlation with organic carbon such as Cr, Mn, Ba and Pb while Cu and Sr show high correlation (r value 0.9 and 0.7 respectively). Only Zn shows low correlation and definite but small relationship. Figures 9 to 14 show the correlation between heavy metals and organic carbon. Knowing the r values indicate the strength of relationships with these two parameters.

CONCLUSION

Considering the results on the levels of heavy metals in sediments and bivalves, the heavy metals in sediments are derived from natural source and no anthropogenic input is observed although there are lots of activities taking place in the study area. The bivalves are still safe for human consumption.

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