

Assessment Cu, Ni and Zn Pollution in the Surface Sediments in the Southern Peninsular Malaysia using Cluster Analysis, Ratios of Geochemical Nonresistant to Resistant Fractions, and Geochemical Indices

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Abstract

The intertidal sediment samples collected in May 2007 from 12 sampling sites in the southern part of Peninsular Malaysia, were determined for the total concentrations of Cu, Ni and Zn and their four geochemical fractions. The total concentrations ($\mu\text{g/g}$ dry weight) of Cu, Ni and Zn ranged from 9.48 to 115.82, 12.95 to 36.18 and 45.35 to 136.56, respectively. The ratios of nonresistant to resistant fractions based on geochemical analysis revealed that the Pantai Lido and Senibong had > 1.0 , indicating $> 50\%$ of the total concentrations of Cu, Ni and Cu were contributed by anthropogenic sources. This is well complemented by the cluster analysis in which Pantai Lido and Senibong are clustered together based on the three metals clustering pattern. By using Fe as a normalizing element, Cu found at Pantai Lido and Senibong showed > 1.5 for the enrichment factor (EF), which indicated that the Cu was delivered from non-crustal materials or anthropogenic origins while all sampling sites showed Ni and Zn may be entirely from crustal materials. Based on the geoaccumulation index (Igeo) (Müller, 1981), similar pattern was also found for Pantai Lido and Senibong in which again only Cu concentrations ranged from 1-2, indicating 'moderate pollution' (Igeo $1 < 2$; Class 2). while other sites can be considered as 'unpolluted' (Igeo < 0 ; Class 0) by Cu, Ni and Zn. Ratios of NR/R exhibited better in the assessment of polluted sites while EF and Igeo should be revised according to Malaysian sedimentary characteristics. This study should prompt more biochemical and molecular studies on the intertidal molluscs from the Straits of Johore since the identified two sites are located in the Straits of Johore, especially the commercial mussel *Perna viridis*.

Keywords: heavy metals; surface sediments; geochemical indices; geochemical fractions

1. Introduction

Metal contamination in the sediment cannot be simply evaluated by examining metal concentrations alone (Zhang *et al.*, 2009). It should be complemented by speciation of the metals. Sediment is believed to be the final metal repository in aquatic environments and only a minor fraction of materials escapes back into the water. However, heavy metal levels in sediments are often analyzed based on the total metal content, and this proves insufficient understanding of the environmental behaviour and origins of these heavy metals in the sediments (Badri and Aston, 1983; Martin *et al.*, 1987; Tack and Verloo, 1995). Therefore, geochemical study is conducted to estimate the nonresistant fractions of metals which are related to anthropogenic sources. Besides the statistical analysis on the metal data to ease the interpretation, calculation of some geochemical indices and comparison with sediment quality values can help in the assessment of heavy metal pollution of the study area.

Cluster analysis is one of the multivariate analyses that aims to summarize all the variables into different

clustering patterns according to sites receiving anthropogenic sources. However, sometimes it is difficult to understand the clustering patterns without the correlation analysis and other supporting data. Ratios of geochemical nonresistant to resistant fractions (NR/R), and geochemical indices are important information that can help understand the anthropogenic sampling sites with different sources. In this study, the nonresistant (NR) geochemical fraction is a summation of easily, freely, leacheable or exchangeable (EFLE), acid-reducible and oxidisable-organic fractions generated by sequential extraction technique in the surface sediment, in which these three geochemical fractions are related to anthropogenic sources (Badri and Aston, 1983; Yap *et al.*, 2002). The last fraction is resistant (R) which is natural-origin related. Therefore, the ratio NR/R can be potentially used as an indicator of anthropogenic-related sampling site.

The geochemical normalization has been used extensively to obtain enrichment factor (EF) and to assess anthropogenic contributions of metals in sediments being studied (Acevedo-Figueroa *et al.*, 2006). In the calculation of EF, we used Fe as a normalizer

since Fe is also an abundant element in the structure of clay minerals and several authors have successfully used iron to normalize heavy metals contaminants (Feng *et al.*, 1998; Mucha *et al.*, 2003). This is due to Fe in the estuarine sediment is mainly from natural weathering processes and has been broadly used to normalize the metal concentrations in order to reduce particle grain size influence because variations in Fe concentration could be explained by particle grain size differences, with fine-grained sediments having high Fe concentrations, besides its geochemistry is similar to that of many trace metals and its natural sediment concentration tends to be uniform. (Daskalakis and O'Connor 1995; Feng *et al.*, 1998). Although there is no such study reported from Malaysia, at least there is ground for us to use Fe as a normalizer in this study. Therefore, we believe it is reasonable to use Fe to calculate metal enrichment factor. The assessment criteria for EF used in this study followed those suggested by Zhang and Liu (2002) and Acevedo-Figueroa *et al.* (2006). Another criterion to evaluate the heavy metal pollution in the surface sediments is the geoaccumulation index (Igeo) by Müller (1981). This index is to determine and define metals contamination in sediments, by comparing current

concentrations with pre-industrial levels. The Igeo index can assess to the estimation of these pollution process. Müller (1981) has distinguished seven classes of Igeo.

The objective of this study was to assess the contamination of Cu, Ni and Zn collected from southern intertidal area of Peninsular Malaysia by comparing to EF and Igeo values besides the ratios of nonresistant to resistant geochemical fractions.

2. Materials and Methods

The sediment samples for this study were collected between 8-11 May 2007. It comprised of 12 sampling sites located in the southern part of Peninsular Malaysia (Fig. 1). The positions, sampling dates and site descriptions are given in Table 3. The top 3-5 cm of surface sediments were collected at each sampling site. Each sediment sample was put in a plastic bag and frozen prior to analysis.

Sediment samples were dried by using an oven at 60°C until constant dry weights. Later, the dried sediments were pounded by using a clean pestle and mortar and were sieved through a 63 µm stainless steel

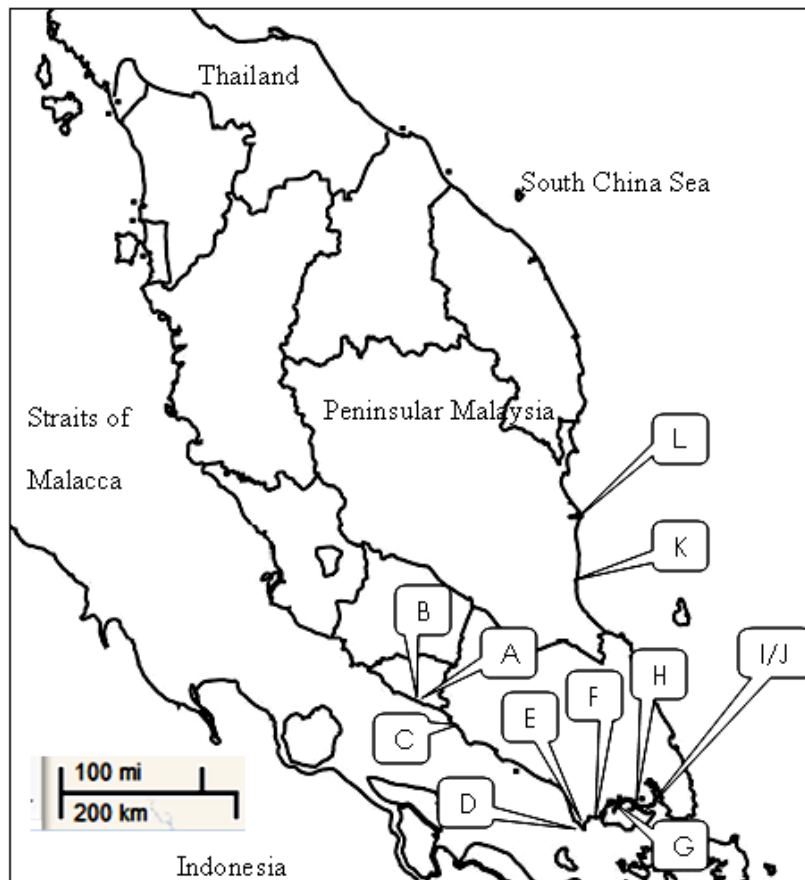


Figure 1. Sampling map showing the sampling sites for surface sediments in the intertidal area of the southern part of Peninsular Malaysia.

aperture. While sifting, the sieve was shaken vigorously to produce homogeneity (Yap *et al.*, 2002) and stored in clean and new plastic bags.

The direct aqua-regia method was used to determine the concentrations of Cu, Ni and Zn in the dried sediment samples. Firstly, about 1 g of each dried sample was weighed and digested in a combination of concentrated nitric acid (HNO₃, AnalaR grade, BDH 69%) and perchloric acid (HClO₄, AnalaR grade, BDH 60%) in the ratio of 4: 1. After that, the tubes were put into the digestion block at the low temperature (40°C) for 1 hour and then the temperature was increased to 140°C for at least 3 hours. The digested samples were diluted to 40 ml by double distilled water and filtered through Whatman No.1 (filter speed: medium) filter paper in a funnel into acid washed pillboxes. They were stored until metal determination.

Geochemical fractions of Cu, Ni and Zn in the sediment were obtained by using the Sequential Extraction Technique (SET) which was described by Badri and Aston (1983) and modified by Yap *et al.* (2002). They are four fractions considered in this method: ‘easily, freely, leacheable or exchangeable’ (EFLE), acid-reducible, oxidisable-organic and resistant fractions.

Before the next fractionation, the residue for each fraction was weighed. Residue was rinsed by 20 ml

double distilled water. After that it was filtered through a Whatman No.1 (Filter speed: medium) filter paper in a funnel and the filtrate were stored for the next step. For each fraction of the sequential extraction procedure, a blank was employed by using the same procedure to ensure that the samples and chemicals used were free of contamination.

After filtration, the sample was determined for Cu, Ni and Zn by using an air-acetylene flame Atomic Absorption Spectrophotometer (AAS), an inorganic analytical instrument made by Perkin-Elmer Model AAnalyst 800. All the data were presented in µg/g dry weight basis.

The quality of the method used was checked with a Certified Reference Material (CRM) for Soil (International Atomic Energy Agency, Soil-5, Vienna, Austria). The agreement between the analytical results for the reference material and its certified values for each metal was satisfactory with the percentages of recovery being between 88.3% for Cu (certified value: 77.1 µg/g; measured value: 68.1 µg/g), 106.4% for Ni (Certified value: 13 µg/g dry weight and Measured value: 12.3±3.0 µg/g dry weight) and 87.8% for Zn (certified value: 368 µg/g; measured value: 323 µg/g). Procedural blanks and quality control samples made from the standard solutions for Cu, Ni and Zn were prepared from 1000 mg/L stock solution (MERCK Titrisol) of each metal,

Table 1. Positions, sampling dates, and descriptions of the sampling sites.

	Sampling sites	Latitude-North	Longitude-East	Sampling date	Description of sampling site
A.	Malacca-1 (Telok Mas), Malacca	2°45.686'	101°46.769'	8 May 2007	A small fishing village.
B.	Malacca-2 (Crystal Bay), Malacca	2° 10.026'	102° 18.419'	8 May 2007	Residential development area
C.	Parit Jawa, Johore	1°57.013'	102°37.967'	9 May 2007	Fishing village.
D.	Kukup-1 (Offshore), Johore	1°19.507'	103°26.364'	9 May 2007	Fish aquaculture area.
E.	Kukup-2 (Inshore), Johore	1°19.557'	103°26.503'	9 May 2007	Restaurant and residential area.
F.	Tg. Kupang, Johore	1°22.766'	103°38.106'	10 May 2007	Fishing village.
G.	Pantai Lido, Johore	1°28.146'	103°46.895'	10 May 2007	Urban area.
H.	Senibong, Johore	1°29.106'	103°49.020'	10 May 2007	Mussel aquaculture, fishing and industrial area.
I.	Kg. Pasir Puteh-1, Johore	1°29.108'	103°49.003'	10 May 2007	Mussel aquaculture, fishing and industrial area.
J.	Kg. Pasir Puteh-2, Johore	1°29.108'	103°49.003'	10 May 2007	Mussel aquaculture, fishing and industrial area.
K.	Kuala Pontian, Pahang	2°45.636'	103°31.176'	11 May 2007	A fishing village.
L.	Nenasi, Pahang	3°08.153'	103°26.598'	11 May 2007	Fisherman's landing site.

Note: The sampling sites followed the alphabets in Fig. 1.

were analyzed for every five to ten samples in order to check for sample accuracy.

For the statistical analysis, the data were \log_{10} (mean + 1) transformed before correlation and cluster analysis in order to reduce the variance (Zar, 1996). The cluster analysis based on Single Linkage Euclidean distances, on the metal concentrations in the four geochemical fractions and non-resistant fractions for the surface sediments collected from 12 sampling site, was done by using STATISTICA 99 edition.

In this paper, we used a metal enrichment factor (EF) according to Ergin *et al.* (1991), as follows:

$$EF = \frac{\left(\frac{Me}{Fe}\right)_{Sample}}{\left(\frac{Me}{Fe}\right)_{Background}}$$

where (Me/Fe)_{Sample} is the metal to Fe ratio in the samples of interest; (Me/Fe)_{Background} is the natural background value of metal to Fe ratio. As we do not have metal background values for our study area, we adopt the values from crust material, which gives 32 µg/g for Cu, 50 µg/g for Ni, 127 µg/g for Zn and 35900 µg/g for Fe (Martin and Whitfield, 1983). The above equation used in the present study can estimate the EF of Cu, Ni and Zn in the sediments of the sampling sites using Fe as a normalizer to correct for differences in sediments grain size and mineralogy.

The Igeo index can be calculated by the following equation:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right)$$

where C_n is the measured concentration of the examined metal (n) in the sediment and B_n is the geochemical background concentration of the metal (n). Factor 1.5 is the background matrix correction factor due to lithogenic effects. Because we did not have the background values of the metals of interest, same as we did in EF calculation, we adopt the earth crust values (Martin and Whitfield, 1983) in Igeo calculation.

3. Results and Discussion

The total metal concentrations (µg/g dry weight) and their respective geochemical fractions are given in Table 2. The total Cu concentrations of the sediment samples ranged from 9.48 to 116. Most of the sites registered a Cu concentration of less than 40.0, with only two sites having Cu concentrations of higher than 100. The total Zn concentrations of the sediment samples ranged from 45 to 136, with five sites exceeding 100. The total Ni concentrations of the sediments collected ranged from 12.9 to 36.2.

The present ranges for Cu, Ni and Zn were lower than those reported for polluted drainage sediments from Peninsular Malaysia (Cu: 1019 µg/g dry weight; Zn: 484 µg/g dry weight; Ni: 121 µg/g dry weight) (Yap *et al.*, 2007). To compare with the marine sediments, Cu and Zn ranges from this study were higher than those for the offshore sediments in the Straits of Malacca (Cu: 0.25-13.8 µg/g dry weight; Zn: 4.00–79.05 µg/g dry weight) (Yap *et al.*, 2002, 2003) and a proclaimed Ramsar wetland site at Tg. Piai (Cu: 3.43-3.81 µg/g dry weight; Zn: 40–43 µg/g dry weight) (Yap *et al.*, 2006a). For Ni ranges, our data was also higher than that for Tg. Piai (Ni: 10-11 µg/g dry weight) (Yap *et al.*, 2006a). The present levels of Cu, Ni and Zn were also higher than those reported for the Dumai coast in Indonesia (Cu: 1.61-13.8 µg/g dry weight; Zn: 31–87 µg/g dry weight; Ni: 7–19.9 µg/g dry weight) (Amin *et al.*, 2009). On the other hand, the Cu and Zn ranges from this study were lower than those for the intertidal sediments in the west coast of Peninsular Malaysia (Cu: 0.40-315 µg/g dry weight; Zn: 3-306 µg/g dry weight) (Yap *et al.*, 2002; 2003). Our Ni levels were also lower than Pearl River Estuary (China) (Ni: 13-318 µg/g dry weight) (Li *et al.*, 2007).

The correlation coefficients between geochemical fractions for Cu, Ni and Zn are presented in Table 3. It is found that the nonresistant fractions for Cu are significantly ($P < 0.05$) related to F1, F2, F3 and F4 of the Cu while the nonresistant fractions for Zn and Ni are significantly ($P < 0.05$) related to F1, F2 and F3 for both metals. Therefore, the contribution of the nonresistant fractions for Zn and Ni are expected since F1, F2 and F3 formed the nonresistant fraction. This again was well supported by the ratios of NR/R which are significantly ($P < 0.05$) correlated with F1, F2 and F3 for Zn and Ni. This was not found for Cu in which ratios of NR/R are significantly ($P < 0.05$) correlated with F1, F3 and F4 for Cu.

The EF and Igeo values for all sampling sites are given in Table 2. By using Fe as a normalizing element, all the sampling site showed < 1.5 for the Cu EF. According to Zhang and Liu (2002)'s criterion, sites at Pantai Lido and Senibong had exceeded 1.5 value, which suggested that a significant portion of Cu is delivered from non-crustal materials or non-natural weathering processes (Feng *et al.*, 1998). However, for Ni and Zn, all the sampling sites exhibited EF values lower than 1.5, indicating unpolluted condition or natural weathering processes. Based on the Igeo values, similar pattern is also found for Pantai Lido and Senibong in which the Cu concentrations ranged from 1-2, indicating 'moderate pollution' (Igeo 1<2; Class 2). while other sites can be considered as 'unpolluted' (Igeo<0; Class 0) by Cu, Ni and Zn.

Table 2. Concentrations ($\mu\text{g/g}$ dry weight) of Cu, Ni and Zn in the four geochemical fractions, ratios (NR/R) of nonresistant (NR) to resistant (R) fractions, enrichment factor (EF) and index of geoaccumulation (Igeo) in the surface intertidal sediments collected from southern part of Peninsular Malaysia.

Cu	F1	SE	F2	SE	F3	SE	F4	SE	NR	NR/R	SUM	AR	SE	Fe	EF	Igeo
A. Malacca-1	0.25	0.01	0.44	0.01	2.03	0.16	13.74	0.06	2.72	0.20	16.46	17.81	0.05	39277	0.51	-1.43
B. Malacca-2	0.15	0.02	0.44	0.01	1.67	0.15	13.09	1.00	2.25	0.17	15.35	16.35	0.26	39772	0.46	-1.55
C. Parit Jawa	0.23	0.00	0.45	0.03	5.75	0.45	17.01	2.15	6.42	0.38	23.44	24.52	0.29	31390	0.88	-0.97
D. Kukup-1	0.17	0.00	0.51	0.03	1.01	0.01	12.18	0.49	1.69	0.14	13.87	15.65	0.11	34450	0.51	-1.62
E. Kukup-2	0.17	0.01	0.49	0.02	3.07	0.42	12.60	0.05	3.73	0.30	16.33	17.73	0.40	31129	0.64	-1.44
F. Tg. Kupang	0.15	0.01	0.40	0.02	3.88	0.21	13.80	0.30	4.43	0.32	18.23	19.46	0.46	29206	0.75	-1.30
G. Pantai Lido	1.30	0.02	0.63	0.00	69.64	3.09	52.36	2.43	71.57	1.37	123.93	109.06	0.62	29511	4.15	1.18
H. Sembong	0.99	0.01	0.55	0.00	69.54	2.72	51.75	0.93	71.08	1.37	122.83	115.82	2.51	38664	3.36	1.27
I. Kg. Pasir Puteh-1	0.29	0.00	0.53	0.01	13.71	0.02	28.20	0.66	14.53	0.52	42.73	42.20	0.56	47353	1.00	-0.19
J. Kg. Pasir Puteh-2	0.38	0.00	0.77	0.03	10.38	0.73	31.95	0.18	11.53	0.36	43.48	38.52	0.25	33742	1.28	-0.32
K. Kuala Pontian	0.08	0.00	0.38	0.02	1.50	0.18	5.50	0.83	1.96	0.36	7.46	9.48	0.19	44218	0.24	-2.34
L. Nenasi	0.30	0.11	0.40	0.00	3.02	0.39	11.58	0.15	3.73	0.32	15.30	16.18	0.18	36119	0.50	-1.57
Ni	F1	SE	F2	SE	F3	SE	F4	SE	NR	NR/R	SUM	AR	SE	Fe	EF	Igeo
A. Malacca-1	0.58	0.03	1.05	0.02	5.00	0.10	17.45	0.46	6.63	0.38	24.08	22.11	0.21	39277	0.404	-1.762
B. Malacca-2	0.61	0.04	0.97	0.00	4.65	0.05	21.39	1.63	6.23	0.29	27.62	24.38	0.27	39772	0.440	-1.621
C. Parit Jawa	0.53	0.01	0.81	0.08	5.58	0.16	15.51	1.05	6.92	0.45	22.43	16.85	0.16	31390	0.385	-2.154
D. Kukup-1	0.65	0.00	1.32	0.01	9.31	0.01	22.30	0.83	11.28	0.51	33.58	26.45	0.69	34450	0.551	-1.504
E. Kukup-2	0.53	0.00	0.94	0.02	6.68	0.10	14.51	0.63	8.15	0.56	22.66	18.05	0.30	31129	0.416	-2.055
F. Tg. Kupang	0.41	0.02	0.65	0.04	6.01	0.20	9.39	0.48	7.08	0.75	16.46	12.95	0.66	29206	0.318	-2.534
G. Pantai Lido	1.11	0.06	1.71	0.04	29.94	0.13	12.80	0.43	32.77	2.56	45.56	33.87	0.51	29511	0.824	-1.147
H. Sembong	1.23	0.01	2.63	0.11	28.17	0.58	11.78	0.33	32.02	2.72	43.81	36.18	0.59	38664	0.672	-1.052
I. Kg. Pasir Puteh-1	0.73	0.05	1.45	0.01	12.85	0.18	12.88	0.93	15.03	1.17	27.91	23.14	0.25	47353	0.351	-1.697
J. Kg. Pasir Puteh-2	0.97	0.02	2.65	0.00	16.66	0.68	19.57	2.88	20.27	1.04	39.85	27.01	0.23	33742	0.575	-1.474
K. Kuala Pontian	0.24	0.03	0.34	0.06	2.48	0.00	13.28	1.43	3.06	0.23	16.34	13.67	0.82	44218	0.222	-2.456
L. Nenasi	0.23	0.17	0.34	0.03	2.91	0.02	15.11	0.77	3.47	0.23	18.59	13.15	0.56	36119	0.261	-2.512

Zn	F1	SE	F2	SE	F3	SE	F4	SE	NR	NR/R	SUM	AR	SE	Fe	EF	Igeo
A. Malacca-1	0.00	0.00	8.15	0.26	17.66	1.77	73.05	0.82	25.82	0.35	98.86	84.91	1.16	39277	0.611	-1.166
B. Malacca-2	0.00	0.00	7.67	0.15	17.52	0.93	64.58	1.58	25.19	0.39	89.77	76.16	0.83	39772	0.541	-1.323
C. Parit Jawa	0.00	0.00	12.89	0.11	25.83	0.83	63.06	3.54	38.73	0.61	101.78	94.21	0.85	31390	0.848	-1.016
D. Kukup-1	0.00	0.00	16.85	0.90	33.98	0.27	97.76	0.29	50.84	0.52	148.59	131.65	1.38	34450	1.080	-0.533
E. Kukup-2	0.00	0.00	10.04	0.11	27.83	0.95	59.20	0.15	37.87	0.64	97.07	88.57	1.10	31129	0.804	-1.105
F. Tg. Kupang	0.00	0.00	11.35	0.33	27.07	0.47	37.45	1.42	38.42	1.03	75.87	71.11	0.91	29206	0.688	-1.422
G. Pantai Lido	1.51	0.05	21.75	0.14	43.18	0.07	36.49	0.11	66.44	1.82	102.93	126.34	0.18	29511	1.209	-0.593
H. Senibong	4.67	0.01	31.00	0.01	39.24	0.21	36.63	0.04	74.92	2.05	111.54	135.08	2.34	38664	0.987	-0.496
I. Kg. Pasir Puteh-1	0.00	0.00	20.12	1.00	40.10	0.93	53.91	0.07	60.22	1.12	114.13	121.83	1.27	47353	0.727	-0.645
J. Kg. Pasir Puteh-2	0.89	0.34	3.78	0.74	44.18	0.04	76.71	0.09	48.85	0.64	125.56	130.13	1.02	33742	1.089	-0.550
K. Kuala Pontian	0.00	0.00	3.85	0.19	9.46	0.39	38.08	1.66	13.31	0.35	51.39	45.35	0.41	44218	0.290	-2.071
L. Nenasi	0.10	0.09	6.76	0.19	13.43	0.52	44.95	0.69	20.29	0.45	65.24	56.89	0.69	36119	0.445	-1.744

Note: F1= easily, freely, leacheable or exchangeable, F2= acid-reducible, F3= oxidizable-organic, F4= resistant. SE= standard error. AR= direct digestion by using aqua-regia method; SUM= summation of F1, F2, F3 and F4.

The ratios of NR/R values are also given in Table 2. Major contribution (> 50%) of anthropogenic sources, as indicated by ratio NR/R > 1.0, is shown at Pantai Lido and Senibong for Cu. For Ni, strongly contribution by anthropogenic sources (NR/R > 2.0) was evidenced at Pantai Lido and Senibong while two sites at Kg. Pasir Puteh also indicated major contribution of anthropogenic inputs (NR/R > 1.0). Lastly, for Zn, ratios NR/R > 1.0 were also found at Tg. Kupang, Pantai Lido, Senibong and Kg. Pasir Puteh-1. Therefore, comparing among ratios of NR/R, EF and Igeo, it seems that ratios of NR/R can better categorize the polluted sites by Zn and Ni contributed by anthropogenic sources while a thorough revision on EF and Igeo calculations for Zn and Ni are needed in order to suit local sedimentary characteristics.

Finally, based on the cluster analysis in Fig. 2, it can be summarized that sites at Pantai Lido and Senibong are grouped into a same sub-cluster, indicating that these two sampling sites received more contamination of Cu, Ni and Zn as shown in Table 3. Since these sites also had higher (>50%) non-resistant fractions of these metals than the resistant ones. These localized elevated metal concentrations could be related to point source discharges related to rapid urbanization and industrial development at the two sites. The rest of sites are clustered differently, indicating lesser contamination by Cu, Ni and Zn. Therefore, the dendrogram based on cluster analysis supports the findings by using the assessment of ratios of NR/R and EF.

In order to estimate possible environmental consequences of the analyzed metals at the studied sites,

Table 3. Correlation coefficients between geochemical fractions for each metal. N= 12. Based on log₁₀ (mean +1).

Cu	F1	F2	F3	F4	NR	NR/R
F1	1.00	0.57	0.93	0.87	0.94	0.93
F2		1.00	0.60	0.76	0.61	0.43
F3			1.00	0.93	0.99	0.95
F4				1.00	0.93	0.80
NR					1.00	0.96
NR/R						1.00
SUM						
AR						
Zn	F1	F2	F3	F4	NR	NR/R
F1	1.00	0.48	0.51	-0.41	0.60	0.79
F2		1.00	0.62	-0.21	0.78	0.78
F3			1.00	0.14	0.97	0.70
F4				1.00	0.03	-0.56
NR					1.00	0.80
NR/R						1.00
SUM						
AR						
Ni	F1	F2	F3	F4	NR	NR/R
F1	1.00	0.96	0.95	0.04	0.97	0.87
F2		1.00	0.90	0.14	0.92	0.77
F3			1.00	-0.16	0.99	0.95
F4				1.00	-0.12	-0.42
NR					1.00	0.94
NR/R						1.00
SUM						
AR						

Note: values in bold are significantly correlated at p < 0.05. F1= easily, freely, leacheable or exchangeable, F2= acid-reducible, F3= oxidizable-organic, F4= resistant, AR= digestion based on direct aquaegia method.

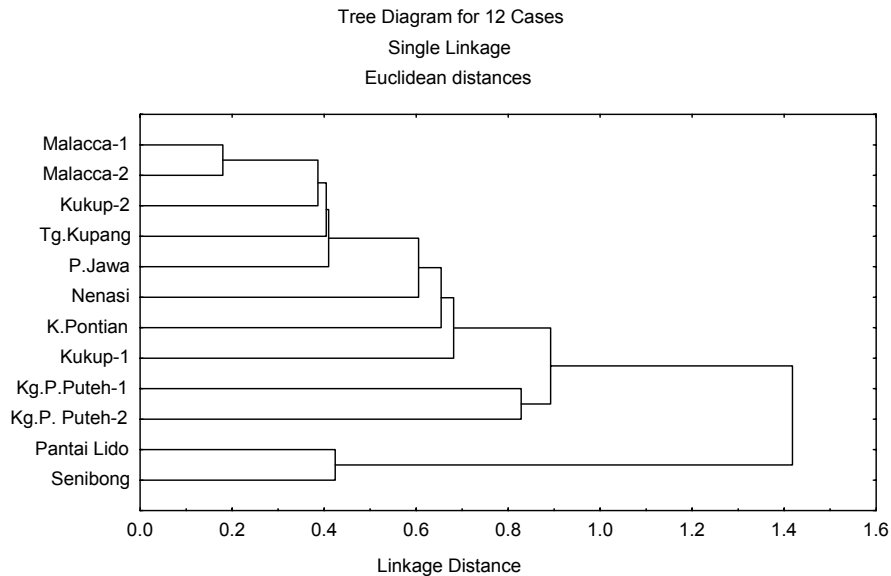


Figure 2. Cluster analysis based on Single Linkage Euclidean distances, on the Cu, Ni and Zn concentrations in the four geochemical fractions and non-resistant fractions for the surface sediments collected from 12 sampling sites, based on $\log_{10}(\text{mean} + 1)$ transformed data.

concentrations of Cu, Ni and Zn were compared to the Sediment Quality Guidelines of Effect Range Low (ERL) and Effect Range Median (ERM) proposed by Long *et al.* (1995, 1997). For Cu, all sampling sites except for Pantai Lido, Senibong, Kg. Pasir Puteh-1 and -2, were still below the ERL value (34.0) and the ERM value (270 $\mu\text{g/g}$). In particular, Pantai Lido and Senibong also exceeded the ERM values (270 $\mu\text{g/g}$). For Ni, only five sampling sites were still below the ERL value (20.9 $\mu\text{g/g}$) and the ERM value (51.6 $\mu\text{g/g}$) while the other seven sites, including the above four mentioned sites, exceeded Ni ERL but were still below Ni ERM value. Zn concentrations in all stations (45-136 $\mu\text{g/g}$) were still well below the values for ERL (150 $\mu\text{g/g}$) and ERM (410 $\mu\text{g/g}$). Nonetheless, the comparison of the present data with other established sediment quality values (SQV) is not included in this paper because most of the SQVs are established based on localized sedimentary characteristics. This is argued that the assessment of heavy metal pollution based these non-Malaysian SQVs could be misleading and questionable.

Since all these identified sampling sites are located in the Straits of Johore, this finding should be of much relevance on the commercial aquaculture of the green-lipped mussel *Perna viridis* (Yap *et al.*, 2006b), in which they are massive-cultured by long-lined technique on both sites of the Johore Causeway. Since previously Pantai Lido was reported as a relatively uncontaminated site based on our sampling done in January 2000 (Yap *et al.*, 2002; 2003), this study should prompt more biochemical and molecular studies on the intertidal molluscs from the Straits of Johore.

4. Conclusions

The concentrations of Cu, Ni and Zn in most surface sediments collected from the southern part of Peninsular Malaysia were found to be lower than the heavy metal levels reported by other studies from Malaysia and the surrounding region. However, Pantai Lido and Senibong had elevated Cu levels that were higher than the other sites in this study. Sampling sites at Pantai Lido and Senibong were found as contaminated sites based on the ratios of NR/R and EF values. From monitoring point of view, further biomonitoring studies should be continuously done in the future.

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References

- Acevedo-Figueroa D, Jimenez BD, Rodrí'guez-Sierra CJ. Trace metals in sediments of two estuarine lagoons from Puerto Rico. *Environmental Pollution* 2006; 141: 336-42.
- Amin B, Ismail A, Arshad A, Yap CK, Kamarudin MS. Anthropogenic impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. *Environmental Monitoring and Assessment* 2009; 148(1-4): 291-305.
- Badri MA, Aston SR. Observation on heavy metal geochemical associations in polluted and nonpolluted estuarine sediments. *Environmental Pollution (Series B)*, 1983; 6: 181-93.

- Daskalakis KK, O'Connor TP. Normalization and elemental sediment contamination in the coastal United States. *Environmental Science & Technology* 29, 47-477. Schi., K.C., Weisberg, S.B., 1999. Iron as a reference element for determining trace metal enrichment in Southern California coast shelf sediments. *Marine Environmental Research*, 1995; 48: 161-76.
- Ergin M, Saydam C, Basturk O, Erdem E, Yoruk R. Heavy metal concentrations in surface sediments from the two coastal inlets (Golden Horn Estuary and Izmit Bay) of the northeastern Sea of Marmara. *Chemical Geology* 1991; 91: 269-85.
- Feng H, Cochran JK, Lwiza H, Brownawell B, Hirschberg DJ. Distribution of heavy metal and PCB contaminants in the sediments of an urban estuary: the Hudson River. *Marine Environmental Research*, 1998; 45: 69-88.
- Li QS, Wu ZF, Chu B, Zhang N, Czi SS, Fang JH. Heavy metals in the coastal wetland sediments of the Pearl River Estuary, China. *Environmental Pollution* 2007; 149: 158-64.
- Long ER, MacDonald DD, Smith SC, Calder FD. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 1995; 19(1): 81-97.
- Long ER, Field LJ, MacDonald DD. Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environmental Toxicology Chemistry* 1997; 17(4): 714-27.
- Martin JM, Whitfield M. The significance of the river input of chemical elements to the ocean. In: *Trace Metals in Sea Water* (Eds: Wong CS, Boyle E, Brul KW, Burton JD, Goldberg ED). Plenum Press, New York. 1983; 265-96.
- Martin JM, Nirel P, Thomas AJ. Sequential extraction techniques: promises and problems. *Marine Chemistry* 1987; 22: 313-41.
- Mucha AP, Vasconcelos MTSD, Bordalo AA. Macrobenthic community in the Doura estuary: relations with trace metals and natural sediment characteristics. *Environmental Pollution* 2003; 121: 169-80.
- Müller G. Die Schwermetallbelastung der sedimente des Neckars und seiner Neben.usse: eine Bestandsaufnahme. *Chemical Zeitung* 1981; 105: 157-64.
- Tack FMG, Verloo MG. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *International Journal of Environmental Analytical Chemistry* 1995; 59: 225-238.
- Yap CK, Choh MS, Edward FB, Ismail A, Tan SG. Comparison of heavy metal concentrations in surface sediment of Tanjung Piai wetland with other sites receiving anthropogenic inputs along the southwestern coast of Peninsular Malaysia. *Wetland Science* 2006a; 4(1): 48-57.
- Yap CK, Ismail A, Edward FB, Tan SG, Siraj SS. Use of different soft tissues of *Perna viridis* as biomonitors of bioavailability and contamination by heavy metals (Cd, Cu, Fe, Pb, Ni and Zn) in a semi-enclosed intertidal water, the Johore Straits. *Toxicological and Environmental Chemistry* 2006b; 88(4): 683-95.
- Yap CK, Ismail A, Tan SG. Cd and Zn concentrations in the straits of Malacca and intertidal sediments of the west coast of Peninsular Malaysia. *Marine Pollution Bulletin* 2003; 46: 1341-58.
- Yap CK, Ismail A, Tan SG. Concentrations of Cu and Pb in the offshore and intertidal sediments of the west coast of Peninsular Malaysia. *Environment International* 2002; 28: 467-79.
- Yap CK, Pang BH, Fairuz MS, Hoo YI, Tan SG. Heavy metal (Cd, Cu, Ni, Pb and Zn) pollution in surface sediments collected from drainages receiving different anthropogenic sources from Peninsular Malaysia. *Wetland Science* 2007; 5(2): 97-104.
- Zar JH. *Biostatistical analysis*. 3rd ed. NJ, USA: Prentice-Hall. 1996.
- Zhang J, Liu CL. Riverine composition and estuarine geochemistry of particulate metals in China - Weathering features, anthropogenic impact and chemical fluxes. *Estuarine, Coastal and Shelf Science* 2002; 54: 1051-70.
- Zhang W, Feng H, Chang J, Qu J, Xie H, Yu X. Heavy metal contamination in surface sediments of Yangtze River intertidal zone: An assessment from different indexes. *Environmental Pollution* 2009; 157: 1533-43.

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