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Comparative Studies of Concentrations of Cu and Zn in the Surface Intertidal Sediments Collected from East, South and West Coasts of Peninsular Malaysia

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Abstract: Malaysia is one of the fast economic developing nations in the region. From the ecotoxicological points of view, many environmental concerns are expected to continually rise up due to the potential anthropogenic inputs such as industries and urbanization. Although the heavy metal concentrations had been reported in the sediments from the west coast of Peninsular Malaysia, the east coast receives lesser attention since it is not as populous and industrialized as in the west coast. In this study, concentrations of Cu and Zn for surface sediments were determined and the samples were collected between 2002 and 2004, from west (five sites), south (five sites) and east (10 sites) intertidal area of Peninsular Malaysia. Total Cu concentrations ranged from 3.80 to 117 µg/g dry weight with south coast recording the highest mean concentration (38.8 µg/g dry weight), followed by west (31.13 µg/g dry weight) and east coasts (12.96 µg/g dry weight). Total Zn concentrations ranged from 36.6 to 395 µg/g dry weight with west coast recording the highest mean concentration (137 µg/g dry weight), followed by south (111 µg/g dry weight) and east coasts (73.8 µg/g dry weight). Apart from the comparison based on the conventional total concentrations of metals, three geochemical fractions (EFLE, acid-reducible and oxidisable-organic) were also useful in identifying the polluted sites in which the three geochemical fractions in the sediments of the west and south coasts of Peninsular Malaysia had significantly ($P < 0.05$) higher concentrations of Cu and Zn when compared to those in the east coastal sediments. This had strengthened our previous assumption that the east coast is less polluted by anthropogenic Cu and Zn when compared to the west and south coasts of Peninsular Malaysia.

Key words: West and east coasts of Peninsular Malaysia, Cu and Zn concentrations, surface sediments.

Introduction

Tropical Southeast Asian countries are now a fast growing region with their rapid economic and population growths. In particular, the economic expansion involving industries are the driving force to make a country rich. Following that, rapid urbanization in the localized area, mainly concentrated in cities, are sources where potential anthropogenic inputs arise due to domestic wastes and dumping. Among the Southeast Asian countries, Malaysia receives Gross Domestic Product (GDP) as 207.2 billion for the year 2003, as compared to Singapore's GDP as 109.1 billion for the same year (CIA World Fact Book, 2004) and this figure means Malaysia is one of the fast economic developing nations in the region. In the literature, industries and urbanization would potentially create environmental problems but how are these problems becoming significant? This is usually highlighted in local newspapers when massive death of fish is reported or how if humans are among the unfortunates? Therefore, monitoring the intertidal environment for its pollution level is necessary since it is important to predict if we are exposed to toxic contaminants in our surrounding or not.

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Our previous studies (Yap et al., 2002, 2003a, 2003b, 2005), based on the sediment samples collected during 1999-2001, signified that the heavy metal pollution in the intertidal area of the west coast of Peninsular Malaysia are (1) localised and (2) near to anthropogenic sources. These findings seem to be typical of many developing nations in the world. However, what is the heavy metal pollution status during 2002-2004, awaits further investigation and this has been the focal point of this study. From the monitoring point of view, the trends of heavy metal variations temporally and spatially are important information to predict any possible outcomes due to the potentially anthropogenic discharges.

Previous studies mainly focussed on the west coast of Peninsular Malaysia but the east coast of the Peninsula receives less attention in the study of heavy metal pollution, based on the reports in the literature (Mushrifah et al., 1995; Shazili et al., 1997), when compared to the west and south coasts of the Peninsula. Therefore, the objective of this study is to determine the pollution status of concentrations of Cu and Zn in the surface sediments collected from east coast (Tumpat to Mersing) by comparing with a few known polluted sites in the west and south coasts of Peninsular Malaysia.

Methods and Materials

Sampling and Storage

The sampling area covered the west, south and east coasts of Peninsular Malaysia (Figure 1). The descriptions of all sampling sites are presented in Table 1.

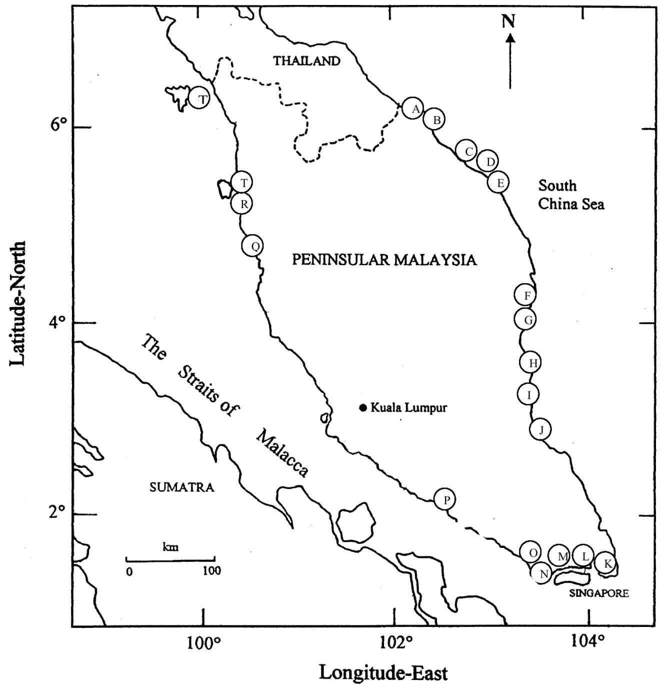

Figure 1: Sampling sites along the coastal area of Peninsular Malaysia. Names of sampling sites represented by alphabets follow those in Table 1.

Table 1: Sampling dates, sediment types and descriptions of sampling sites for the intertidal sediment collected from the west coast of Peninsular Malaysia

	Sampling sites	*Dates of sampling*	*Site descriptions*
A	Pantai Sri Tujuh, Tumpat	6 April 2004	Fish aquacultural sites
B	Tok Bali	7 April 2004	Beach
C	Jetty to Pulau Redang	7 April 2004	Jetty
D	Kertih	7 April 2004	Fishing area
E	Jetty Tanjung Api	8 April 2004	Fishing area
F	Sg. Pahang	8 April 2004	Pristine area
G	Kampung Tanjung Batu	8 April 2004	Pristine area
H	Kuala Nenasi	8 April 2004	Pristine open sea
I	Jetty Kuala Pontian	8 April 2004	Mussel cultured site
J	Pantai Mersing	8 April 2004	Fishing area
K	Kuala Belungkor	18 April 2002	Pristine area
L	Kampung Pasir Puteh	18 April 2002	Industrial, mooring activities and urban area
M	Pantai Lido	18 April 2002	Urban area and jetty
N	Tanjung Piai	17 April 2002	A Ramsar site
O	Jetty Kukup	17 April 2002	Jetty and boating activity
P	Sebatu	17 April 2002	Mussel cultured site
Q	Kuala Kurau	9 April 2002	Fishing village
R	Bukit Tambun	9 April 2002	Receiving domestic wastes
S	Kuala Juru	9 April 2002	Receiving industrial effluents
T	Teluk Ewa, Langkawi	10 April 2002	Cement factory in the nearby

The sampling procedure for the intertidal sediments was similar to that reported by Yap et al. (2002, 2003a) viz., an Ekman grab and a plastic spatula were used during the sampling. The top 3 to 5 cm of surface sediments were collected at each sampling site. Each sediment sample was placed in a clean plastic bag and was frozen (–10°C) prior to analysis. Triplicates from each sampling site were analysed.

Sample Preparation

Sediment samples were dried at 60°C for at least 96 hours until a constant dry weight (dw) (Fichet et al., 1999) by using an air-circulating oven. Afterwards, the samples were crushed to powder by using a mortal and pestle and sieved through a 63 mm stainless steel aperture sieve. During the process, the sieve was shaken vigorously to produce homogeneity (Yap et al., 2002, 2003a).

Speciation of Cu and Zn of Sediment Samples

Geochemical fractions of Cu and Zn in the sediments were obtained by using the modified SET (Badri and Aston, 1983; Yap et al., 2002). The four fractions considered were: 1. Easy, freely, leachable or exchangeable (EFLE), 2. 'Acid-reducible', 3. 'Oxidisable-organic' and 4. Resistant. The extraction solutions and the conditions employed for each fraction used in this study followed those reported by Yap et al. (2002).

The prepared samples were determined for Cu and Zn by an air-acetylene flame atomic absorption spectrophotometer (AAS) Perkin-Elmer Model AAnalyst 800. The data were presented in µg/g dry weight basis.

Quality Control

To avoid possible contamination, all glassware and equipment used were acid-washed. A quality control sample was routinely run through during the period of metal analysis. Percentages of recoveries were 95% for Cu and 110% for Zn. 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 Cu and Zn analytical results for the reference material and their certified values for the metals were satisfactory (certified Cu: 77.1 ± 4.7 µg/g, measured Cu: 80.0 ± 5.0 µg/g; certified Zn: 368 µg/g, measured Zn: 389 µg/g).

Statistical Analysis

Based on the geographical factor, the sampling sites in the coastal sediments of Peninsular Malaysia were divided into west (five sites), south (five sites) and east (10 sites) coasts. The Pearson's product moment correlation coefficient on the $\log_{10}$ (mean + 1) transformed data (Zar, 1996) was applied, by using the Statistical Analysis System (SAS) for Windows (Release 6.12 software), to determine the strength and levels of significance of the relationships.

Results and Discussion

The total concentrations of Cu and Zn of all sampling sites are presented in Figure 2. Total Cu concentrations by using direct aqua-regia method ranged from 3.80 to 117 µg/g dry weight with south coast recording the highest mean concentration (38.8 µg/g dry weight) (the highest Cu concentration at Kg. Pasir Puteh with 117 µg/g dry weight). This is followed by west (31.13 µg/g dry weight) and east coasts (12.96 µg/g dry weight). Total Zn concentrations ranged from 36.6 to 395 µg/g dry weight with west coast recording the highest mean concentration (137 µg/g dry weight) (the highest Zn concentration at Kuala Juru with 395 µg/g dry weight). This is followed by south (111 µg/g dry weight) and east coasts (73.8 µg/g dry weight).

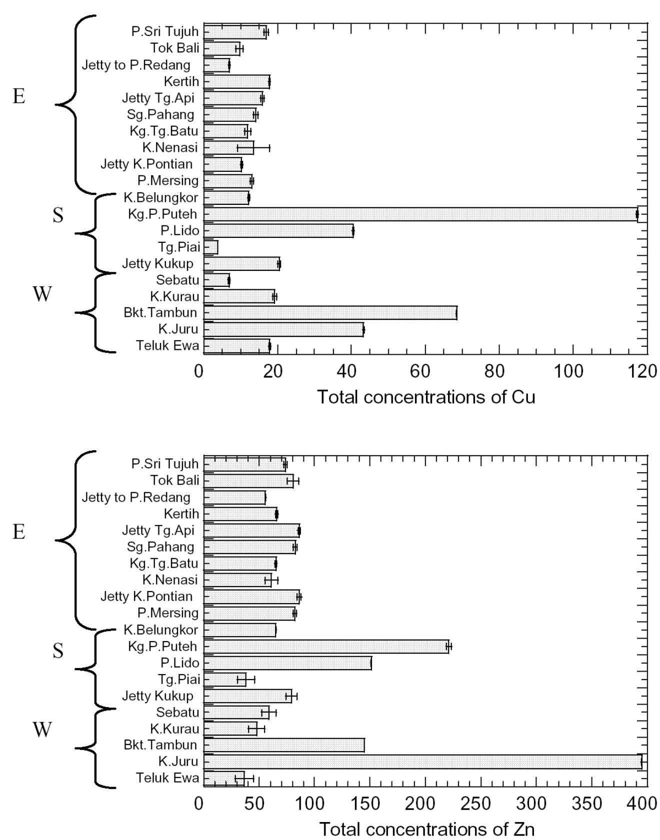

Figure 2: Total concentrations (mean µg/g dry weight ± standard error) of Cu and Zn, based on aqua-regia method, of the surface sediment collected from the west (W), east (E) and south (S) coasts of Peninsular Malaysia.

Concentrations of Cu and Zn in each fraction of EFLE, acid-reducible and oxidisable-organic are compared among all the sampling sites, as shown in Figures 3, 4 and 5. For EFLE Cu and Zn (Figure 3), three sites from K. Juru, Kg. Pasir Puteh and Bukit Tambun were found to be significantly elevated, followed by the rest of the sampling sites. For acid-reducible Zn (Figure 4), K. Juru was found to be significantly elevated, followed by Bukit Tambun and the rest of the sampling sites but for acid-reducible Cu (Figure 4), no consistent pattern with known polluted sites are identified. For oxidisable-organic Cu (Figure 5), Kg. Pasir Puteh was found to be significantly elevated, followed by Bukit Tambun and the rest of the sampling sites while for oxidisable-organic Zn, K. Juru, Kg. Pasir Puteh, Bukit Tambun and P. Lido were found to be significantly elevated, followed by the rest of the sampling sites (Figure 5).

Spearman's rank correlation coefficients among EFLE, acid-reducible, oxidisable-organic, resistant and nonresistant fractions based on all the sediment data are

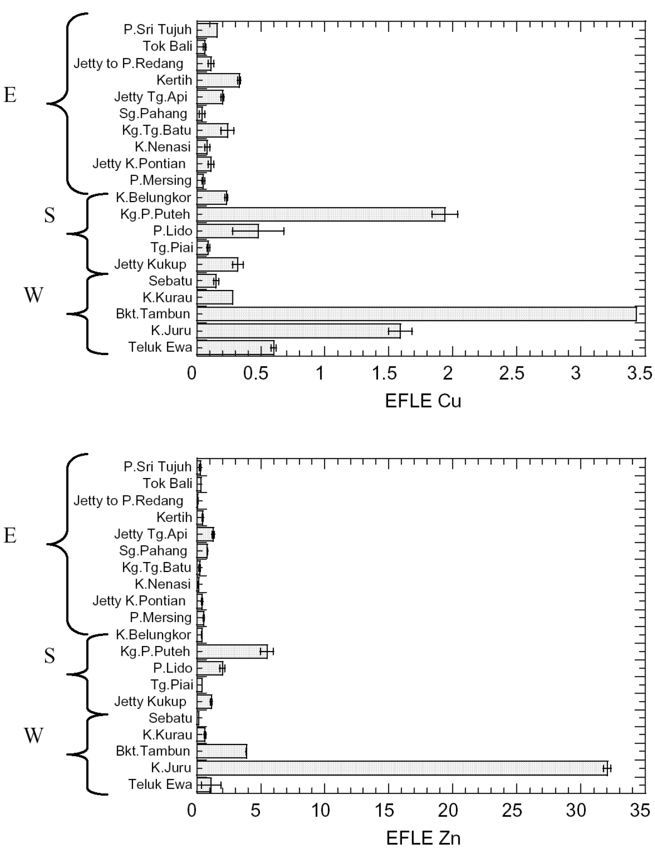

Figure 3: Concentrations (mean µg/g dry weight ± standard error) of easily, freely or leachable (EFLE) fraction of Cu and Zn in the surface sediment collected from the west (W), south (S) and east (E) coasts of Peninsular Malaysia.

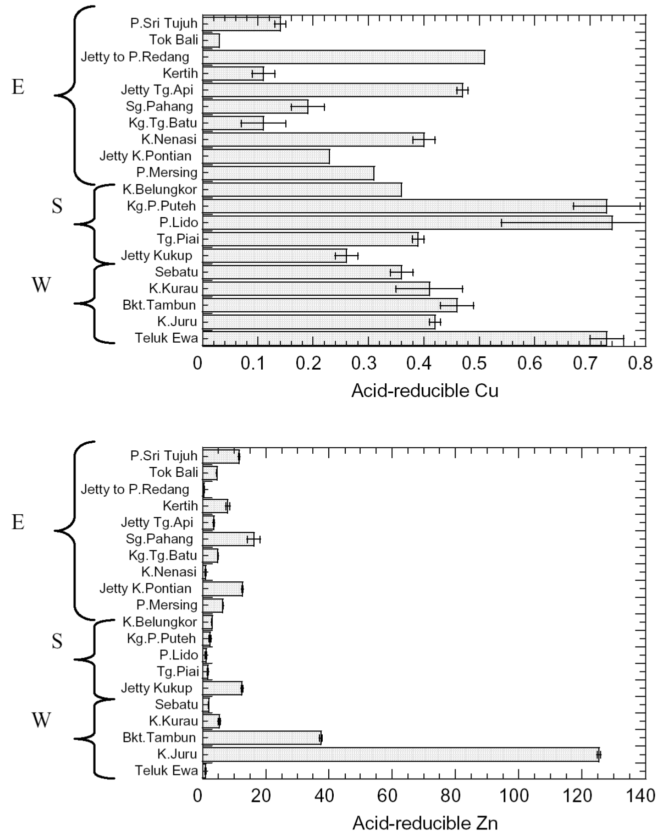

Figure 4: Concentrations (mean µg/g dry weight ± standard error) of acid-reducible fraction of Cu and Zn in the surface sediment collected from the west (W), south (S) and east (E) coasts of Peninsular Malaysia.

presented in Table 2. All pairwise are significantly correlated (R = 0.46-0.96; at least $P < 0.05$) except for 'acid-reducible'-resistant fractions of Cu and Zn. Similar results (low R values with acid-reducible fractions) are generated based on Zn concentration collected in offshore and intertidal sediments of west coast of Peninsular Malaysia, collected during 1999-2001, as reported by Yap et al. (2005).

Two interesting patterns can be concluded from the correlation coefficients based on correlation analysis in Table 2. First, total concentration of Cu is highly correlated with resistant Cu indicating that when the total concentration was high, high concentration of naturally occurring Cu would be high too (with $R = 0.96$; $P < 0.001$ in Table 2). This indicated that the Cu polluted sites do not exhibit high percentages of nonresistant Cu. Second, in contrast to Cu, total Zn concentration is not significantly ($P < 0.05$) correlated with resistant Zn. This indicated that the supposedly high Zn polluted sites were also recorded to have low percentage of nonresistant Zn.

A comparison of the west, south and east regions was made and this is presented in Table 3. Summation of all

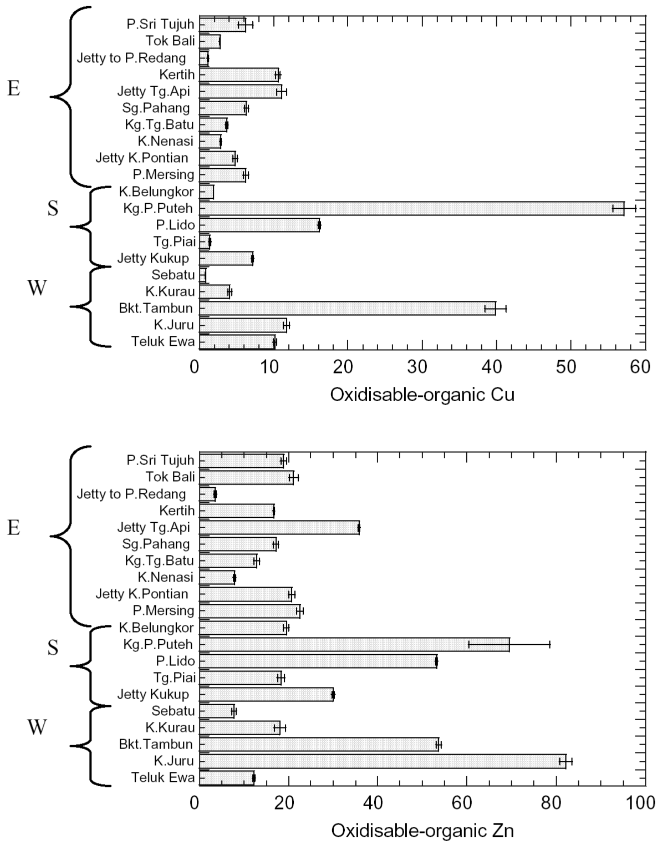

Figure 5: Concentrations (mean µg/g dry weight ± standard error) of oxidisable-organic fraction of Cu and Zn in the surface sediment collected from the west (W), south (S) and east (E) coasts of Peninsular Malaysia.

geochemical fractions of Cu and Zn concentrations in the west coastal sediments also showed the highest levels of Cu and Zn when compared to south and east regions.

When compared to background levels and established sediment quality criteria of Cu and Zn (Table 4), concentrations of Cu and Zn in the east coast sediments are all below the levels of sediment quality criteria and close to or below background levels reported from China and Hong Kong. However, some sites recorded elevated concentrations of Cu and Zn which were higher than the Action Levels of these metals established by the Hong Kong Sediment Quality Criteria (Lau Wong and Rootham, 1993) and the Interim Sediment Quality Values-low (ISQVs-high) for Hong Kong (Chapman et al., 1999). The highest concentrations of Cu and Zn were all below the Interim Sediment Quality Values-high (ISQVs-high) for Hong Kong (Chapman et al., 1999).

For the west coast sediments, only sites at Kg. Pasir Puteh, Kuala Juru and Bukit Tambun fell in the ranges for Action Level of Hong Kong Sediment Quality Criteria. Also, generally, the mean concentration of Zn was higher than the Zn background levels of Chinese and Hong Kong coastal waters. Therefore, the above sites are regarded as 'hotspot' sites in Peninsular Malaysia.

Three patterns can be seen from the present data based on the aqua-regia and sequential extraction of surface sediments collected from the intertidal area of Peninsular Malaysia. First, the trend of Cu and Zn pollution in the west coast of Peninsular Malaysia are similar and consistent with those previously reported by Yap et al. (2002, 2003a) viz., localized and elevated concentrations of metals were also found at sites close to urban and industrial areas. Second, the west coast of Peninsular Malaysia has more anthropogenic inputs of Cu and Zn when compared to the east coast. Third, the present results indicated that proper management and control measures are needed to mitigate the anthropogenic inputs of Cu and Zn in these 'hotspot' sites in Peninsular Malaysia.

Table 2: Spearman's correlation coefficients of intertidal sediments based on 20 sampling sites along the coastal area of Peninsular Malaysia

	TOTCu	*Cu1*	*Cu 2*	*Cu3*	*Cu4*	*TOTZn*	*Zn1*	*Zn2*	*Zn3*	*Zn4*
TOTCu	1.00	0.78***	0.43 ^{ns}	0.89***	0.96***	0.53*	0.82***	0.35 ^{ns}	0.60**	0.28 ^{ns}
Cu1		1.00	0.48*	0.67***	0.84***	0.28 ^{ns}	0.64**	0.13 ^{ns}	0.42 ^{ns}	0.49*
Cu2			1.00	0.37^{ns}	0.37 ^{ns}	0.10 ^{ns}	0.46*	-0.46*	0.23 ^{ns}	0.50*
Cu3				1.00	0.83***	0.72***	0.89***	0.39 ^{ns}	0.69***	0.25 ^{ns}
Cu4					1.00	0.49*	0.79***	0.32 ^{ns}	0.61**	0.33 ^{ns}
TOTZn						1.00	0.66***	0.54**	0.83***	0.21 ^{ns}
Zn1							1.00	0.41 ^{ns}	0.79***	0.37 ^{ns}
Zn2								1.00	0.47*	-0.13 ^{ns}
Zn3									1.00	0.33 ^{ns}
Zn4										1.00

Note: 1 = EFLE, 2 = acid-reducible, 3 = oxidisable-organic and 4 = resistant.
Based on 30 stations in the offshore. Levels of significance: *P< 0.05; **P< 0.01; ***P< 0.001; ^{ns}P> 0.05.

Table 3: Mean concentrations (µg/g dry weight) of total based on aqua-regia method and four geochemical fractions based on sequential extraction technique, of Cu and Zn in the surface sediments along the intertidal area of Peninsular Malaysia, separated into west, south and east coasts sediments

	Cu				*Zn*			
Region	*Min*	*Max*	*Mean*	*SE*	*Min*	*Max*	*Mean*	*SE*
East coast (10 sites)								
Total concentration-based aqua-regia methods	6.90	17.79	12.96	1.08	55.55	86.13	73.83	3.55
EFLE	0.04	0.33	0.14	0.03	0.08	1.28	0.45	0.11
Acid-R	0.03	0.51	0.25	0.05	0.48	16.17	6.89	1.63
Ox-Organic	1.15	11.07	5.56	1.03	3.54	35.82	17.71	2.78
Resistant	8.63	17.43	12.73	0.80	41.67	60.91	48.59	1.90
South coast (five sites)								
Total concentration-based aqua-regia methods	3.80	117.34	38.82	20.55	38.05	221.2	110.91	33.35
EFLE	0.09	1.94	0.61	0.34	0.40	5.48	1.88	0.95
Acid-R	0.26	0.74	0.50	0.10	1.04	12.47	4.07	2.13
Ox-Organic	1.40	57.15	16.74	10.44	18.27	69.51	38.09	10.05
Resistant	6.79	116.63	40.56	20.11	44.05	156.9	75.87	20.62
West coast (five sites)								
Total concentration-based aqua-regia methods	6.87	68.51	31.13	11.08	36.57	394.9	136.59	67.38
EFLE	0.15	3.43	1.21	0.61	0.16	32.05	7.57	6.15
Acid-R	0.36	0.73	0.48	0.07	0.93	125.2	34.14	23.75
Ox-Organic	0.84	39.86	13.33	6.92	7.74	82.15	34.75	14.36
Resistant	10.16	62.58	29.75	9.34	44.76	188.23	106.38	27.80

Table 4: Comparison of the concentrations of Cu and Zn obtained in this study with some background levels and actions levels of sediment quality criteria

Description	*Cu*	*Zn*	*Reference*
Background values of Chinese coastal areas	30	80	Zheng et al. (1992)
Background values of the marine sediments in Hong Kong	15	94	Tanner et al. (2000)
Background values of the estuary sediment in Hong Kong	10	70	Tanner et al. (2000)
Action level of Hong Kong Sediment Quality Criteria	65	200	Lau Wong and Rootham (1993)
Interim ISQV- Low sediment quality values	65	200	Chapman et al. (1999).
Interim ISQV-High sediment quality values	270	410	Chapman et al. (1999).
East coast of Peninsular Malaysia (10 sites)	12.9 (6.90-17.8)	73.8 (55.6-86.1)	This study
South coast of Peninsular Malaysia (five sites)	38.8 (3.80-117)	111 (38.1-221)	This study
West coast of Peninsular Malaysia (five sites)	31.1 (6.87-68.5)	137 (36.6-395)	This study

Finally, the 'So what?' question can be asked after the presentation of the present data. Two points can be given: first, these data are important for future reference and second, the present work sets important milestones to be followed for future endeavours or for similar monitoring work in this region.

Conclusion

The geochemical partitioning of Cu and Zn provides us with a better understanding of the dominance of Cu and Zn concentrations found in the intertidal sediments of Peninsular Malaysia. The higher concentrations of Cu and Zn in the intertidal sediments collected from the west and south coasts of Peninsular Malaysia indicated contamination of both metals due to anthropogenic inputs. The present data supported our earlier assumption that the west and south coasts of Peninsular Malaysia, having more industries and urban areas, showed higher metal contamination when compared to the east coast. This also indicated that observation of the sampling sites for any possible sources of anthropogenic sources are important in the interpretation of heavy metal concentrations found in the sediments.

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