Spatial and Vertical Metals Distribution in Sediment Cores from Kongkong Laut Estuary, Masai, Johor

Sara Azuana Khalidah Khalid[1], Ferdaus Mohamat Yusuff[1,2]*, Faradiella Mohd Kusin[1,2], Aziz Arshad[3] and Zulfa Hanan Asha'ari[1]

[1]Department of Environmental Sciences, Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[2]Environmental Forensics Research Unit (ENFORCE), Faculty of Environmental Studies, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[3]Department of Aquaculture, Faculty of Agriculture, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

ABSTRACT

Sediment has been widely used as a means for assessing the impact of anthropogenic activities on aquatic environment, with metal pollution being the most well-known threat to aquatic environments. Therefore the aim of this study is to identify and determine metal concentrations, specifically that of copper (Cu), chromium (Cr), cadmium (Cd), iron (Fe), and zinc (Zn) on four sediment cores samples of KongKong Laut Masai Johor. The aqua regia method had been used to analyze Cu, Cr, Cd, Fe and Zn concentrations in sediment samples. Metal concentrations had then been determined through the use of flame atomic absorption spectrometry. The degree of metal contamination in sediment core samples had been determined through using Enrichment Factors (EF) and Geoaccumulation Indices (I_{geo}). From this study, the mean and standard deviation of metal concentrations in each sediment core sample were shown to be lower than the average shale concentration and lower than both the effects-range low (ERL) and effects-range median (ERM) parameters for aquatic toxicity. This information could be useful, serving as a baseline for evaluating the potential impacts of future development in the area.

INTRODUCTION

Metal contamination in sediment is a worldwide concern, due to its potential to remobilization, bioaccumulation and

biomagnification in aquatic ecosystems (Al-Mur et al., 2017). Metals can be divided into essential and non-essential elements, both having the potential to be toxic to living organisms when their concentration exceeds from the permissible limit, since both are persistent, which can be bioaccumulated and biomagnified through the food chain (Lim et al., 2012; Saraee et al., 2011).

The determination of metals distribution in core sediment samples can provide information about previous and present levels of contamination in aquatic environments (Al-Najjar, 2011; Cho et al., 2015). Therefore, the study of core sediment samples could provide historical evidence and historical records of metals distribution over the time (Williams & Block, 2015).

Agricultural activities such as palm oil plantations, and increasing interest in eco-tourism sectors in KongKong Laut Masai, have led to the vigorous development such as jetty, restaurants and raft houses along the KongKong Laut River, which can have a negative impact on the area's aquatic ecosystem in this area and directly expose risks to the food chain. Therefore the study of metal in the core sediment sample is needed, so as to provide useful information regarding anthropogenic activities along the KongKong Laut River.

Several studies have been conducted on surface sediment along the KongKong Laut River (Wan & Mohamat-Yusuff, 2014; Zulkifli et al., 2010). However, no study has yet been conducted on sediment cores along the KongKong Laut River. Therefore, the goal of the present study is to assess the spatial and vertical distribution of Zinc (Zn), Cadmium (Cd), Iron (Fe), Copper (Cu) and Chromium (Cr) in sediment cores, providing information which may serve as a baseline for evaluating potential impacts of future development in the study area.

MATERIALS AND METHODS

Sample Collection and Analytical Procedure

The sampling for sediment core samples was conducted in December 2016, involving four sampling stations points along the KongKong Laut River (Figure 1). Each sampling station was adjacent to a different type of human activity which it was believed could release significant amounts of anthropogenic pollution, such as metal pollution (Table 1).

Core samples were collected at a distance ranging from 1.5m to 2m from the low tide mark. The core sample lengths from each station varied due to the stratum differences existing in each station. Each core was sliced into 3cm sections. The core samples were then placed in a pre-labeled zip lock plastic bag, and kept in an icebox during transportation. At the laboratory, all samples were kept frozen at -20°C for further analysis. All reagents used were analytical-reagent grade certified. Samples were oven dried at 60°C, until a constant weight was obtained. Samples were then grained and sieved through a 63µm mesh size.
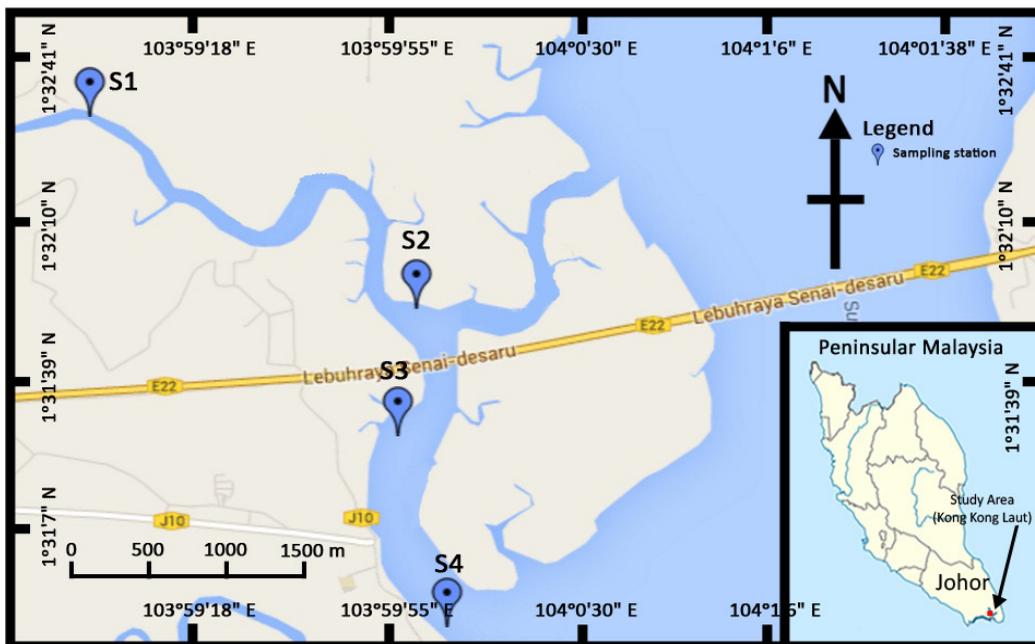
Figure 1. Sampling station for sediment core samples along the KongKong Laut River

Table 1
Coordinates and descriptions of the sampling sites

Sampling station	Abbreviation	Coordinate	Site description
Serai River	**S1**	1° 32' 31.0"N 103° 58' 57.1"E	A site near to palm oil plantation
Serai River	**S2**	1° 31' 51.1"N 103° 59' 58.4"E	A site near to waterway transportation and fishing activities
Mendana Strait	**S3**	1° 31' 28.0"N 103° 59' 59.0"E	A site near to raft house and jetties
Mendana Strait	**S4**	1° 30' 49.9"N 104° 00' 05.0"E	A site near to restaurants and abandon ship

The aqua regia method was used to determine the pseudototal trace metals in sediment samples (Wan & Mohamat-Yusuf, 2014; Zulkifli et al., 2010). The aqua regia solution (12 ml), consisting of a 3:1 ratio of hydrochloric acid to nitric acid, was added to one gram of the 63µm size sediment sample, which was then left to stand overnight. Afterwards, the sample was heated to 50°C in the digestion block for 1 hour. Then the temperature was increased to 140°C for 3 hours. The extract was filtered through a 0.45µm Whatman No.1 filter paper, and diluted in 50ml milli-Q water. All glassware and equipment were acid-soaked with 10% HNO_3 for 24 hours prior to use. The quality of the method used was checked through using the Standard Reference Material 1646a (SRM 1646a). Samples were stored at 4°C prior to analysis using an atomic absorption spectrophotometer (AAS) (Perkin-Elmer Model AAnalyst 800 series, USA). The recoveries of measured elements ranged from 99.6% to 100.54% (Table 4).

Organic matter was determined through the loss on ignition method (Al-Trabulsy et al., 2013). Particle size analysis was conducted through the pipet method (Gee & Bauder, 1986). In this study, statistical analysis was performed using the statistical package for the social sciences (SPSS) version 22, and Microsoft Office Excel 2010 (Microsoft Corporation, USA). The degree of trace metal contamination in the sediment core samples was assessed through using the Enrichment Factor (EF) (Zulkifli et al., 2010) and the Index of Geoaccumulation (I_{geo}) (Muller, 1969).

Calculation of Enrichment Factor and Geo-aAccumulation Index

$$EF = \frac{(C_x/C_{Fe})sample}{(S_x/S_{Fe})shale}$$

Where;

C_x = concentration of the measured trace element in the study area (in mg/kg)

C_{Fe} = concentration of the measured Iron in the study area (in mg/kg)

S_x = concentration of the reference trace elements in the reference environment (in mg/kg)

S_{Fe} = concentration of the Iron in the reference environment (in mg/kg)

Iron (Fe) was chosen as the reference element for this present study, because it is associated with a fine solid surface, such as the mangrove sediment found in this study area. This is due to its geochemistry being close to many trace metals, and also due to its natural concentration which tends to be uniform in natural sediment (Daskalakis & O'Connor, 1995; Naji & Ismail, 2011). The EF result can be classified into five enrichment categories, as presented in Table 2, whereas the I_{geo} result can be classified into seven categories shown in Table 3.

Table 2
The degree of metal enrichment based on EF categories

Enrichment factor (EF) value	Enrichment categories
< 2	Depletion to minimal enrichment
2-5	Moderate enrichment
5-20	Significant enrichment
20-40	Very high enrichment
>40	Extremely high enrichment

$$I_{geo} = \frac{log_2 \, C_x}{1.5 \cdot S_x}$$

Where:

C_x = Measured trace element in the sample (in mg/kg)

S_x = Background or pristine value of the trace element (in mg/kg)

1.5 = Factor introduced in order to minimize the effect of possible variation in the background value that may be attributed to lithologic variations in the sediments (Stoffers et al., 1986)

Table 3
The degree of trace metal contamination based on I_{geo} contamination classification

I_{geo} value	I_{geo} Class	Designation of sediment quality
≤0	0	Uncontaminated
0-1	1	Uncontaminated to moderately contaminated
1-2	2	Moderately contaminated
2-3	3	Moderately to strongly contaminated
3-4	4	Strongly contaminated
4-5	5	Strongly to extremely contaminated
>5	6	Extremely contaminated

RESULTS AND DISCUSSIONS

Results of the descriptive analysis of trace element concentrations from four sediment core samples have been presented in Table 4. From the five trace elements that have been studied, the highest mean concentration was Fe (3.80 ± 0.45% dry weight), as Fe is a vital element for flora and fauna in maintaining metabolic and cellular functions. This is followed by Zn (75.07 ± 5.67 mg/kg), Cu (18.34 ± 2.07 mg/kg), Cr (13.22 ± 2.72 mg/kg), and Cd (0.21 ± 0.08 mg/kg). All mean and standard deviations of trace metal concentration were still generally lower than the average shale concentrations, as reported by Turekian and Wedepohl (1961), and were also lower than the effects range low (ERL) and effects range median (ERM) values (Long et al., 1995).

Table 4
Mean and standard deviation of trace metal concentration in sediment core samples from all locations at KongKong Laut River are expressed in units of mg/kg with the exception of Fe (%)

Site	Zn	Cd	Fe[a]	Cu	Cr
S1 (n=7)	64.85 ± 2.68	0.19 ± 0.05	4.26 ± 0.40	23.06 ± 3.19	19.73 ± 3.73
S2 (n=13)	78.41 ± 7.23	0.21 ± 0.07	3.73 ± 0.61	17.55 ± 1.10	8.99 ± 2.97
S3 (n=9)	81.69 ± 4.98	0.22 ± 0.08	3.35 ± 0.20	18.37 ± 1.80	12.86 ± 2.16
S4(n=7)	75.32 ± 7.78	0.23 ± 0.1	3.82 ± 0.52	14.38 ± 2.17	11.30 ± 2.03
Average	75.07 ± 5.67	0.21 ± 0.08	3.80 ± 0.43	18.34 ± 2.07	13.22 ± 2.72
Average shale[b]	95	0.3	4.72	45	90
ERL[c]	150	1.2	na	34	81
ERM[c]	410	9.6	na	270	370
Recovery of analysis (%)	100.22	100.54	99.6	99.74	100.43

Notes: [a] % dry weight; [b] Turekian and Wedepohl (1961); [c] Long et al., (1995); na = not available; n = number of sub-samples

The spatial distribution of metals in the upper surface samples (0-3 cm depth) from all sites is presented in Figure 2. Cu concentration is higher at S1, which may be derived from the fertilizer used on the palm oil plantation near this site. The Zn concentration is higher at S3 when compared to other stations, which might be derived from the water transportation activities conducted at this sampling station, located near to water ways and jetty operations. Cd concentration is higher at S4, which may be the result of untreated sewage effluent, as this is located near the restaurant and the raft-house. However, when compared to the average shale, ERL and ERM, all metals concentrations are still lower than the threshold limit.
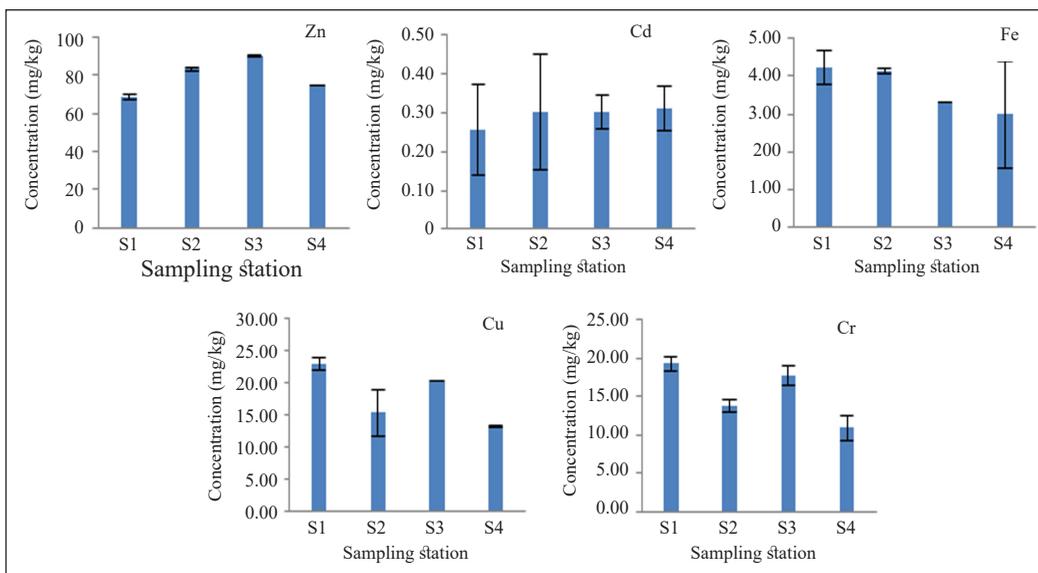
Figure 2. Metal concentration in the surface samples (0-3 cm depth) from all four sites

The vertical profiles of the Zn, Cd, Fe, Cu, and Cr concentrations from the four cores are shown to have a fluctuating pattern in regards to depth, without showing obvious increasing or decreasing trends (Figure 3). The vertical distribution of Cd in all cores showed a decreasing pattern from upper part toward the bottom part indicating an increasing enrichment of this element at all cores. This might be derived from the combustion of fuel used for water transportation and the burning of waste such as plastics, batteries, construction material and other matter by local people near the estuary, which may enter the estuary during the rainy time season. The vertical profile for Cu showed an increasing pattern of concentration downward in all cores, except for core S3. Cu is an essential nutrient and is required by organisms in small amounts (White & Rainbow, 1985). Due to the biological requirements of aquatic organisms, the concentration of Cu in surface sediment is lower than that of the bottom sediment. However, at S3 the concentration of Cu was

higher in the surface sediment, which might be due to anthropogenic activities occurring in this area, such as jetty operations and heavy water transportation. The distribution pattern of Cr at all core sites showed a decreasing trend from the upper part to the lower part, indicating a reduced discharge of the Cr effluent source in the study area.

To determine the relationship between metals and sediment texture, a Pearson correlation analysis was performed. Fe shows strong positive correlations with Cr at core S1 (see Table 5) indicating that the sources of both elements come from the same sources which are believed to come from the natural sources as the average concentrations of both elements is lower than the permissible limit shown in Table 4. From the correlation analysis, there is a significant, strong positive correlation between Zn and Fe from the cores S2 (see Table 6) and S4 (see Table 8), indicating that it is scavenged by Fe oxides. This correlates with the findings of Laluraj and Nair (2006), who determined that geochemical variations in metal distribution was associated with the precipitation or dissolution of Fe oxides, acting as a source or sink for metal. Correlation analysis had shown that sand was significantly,
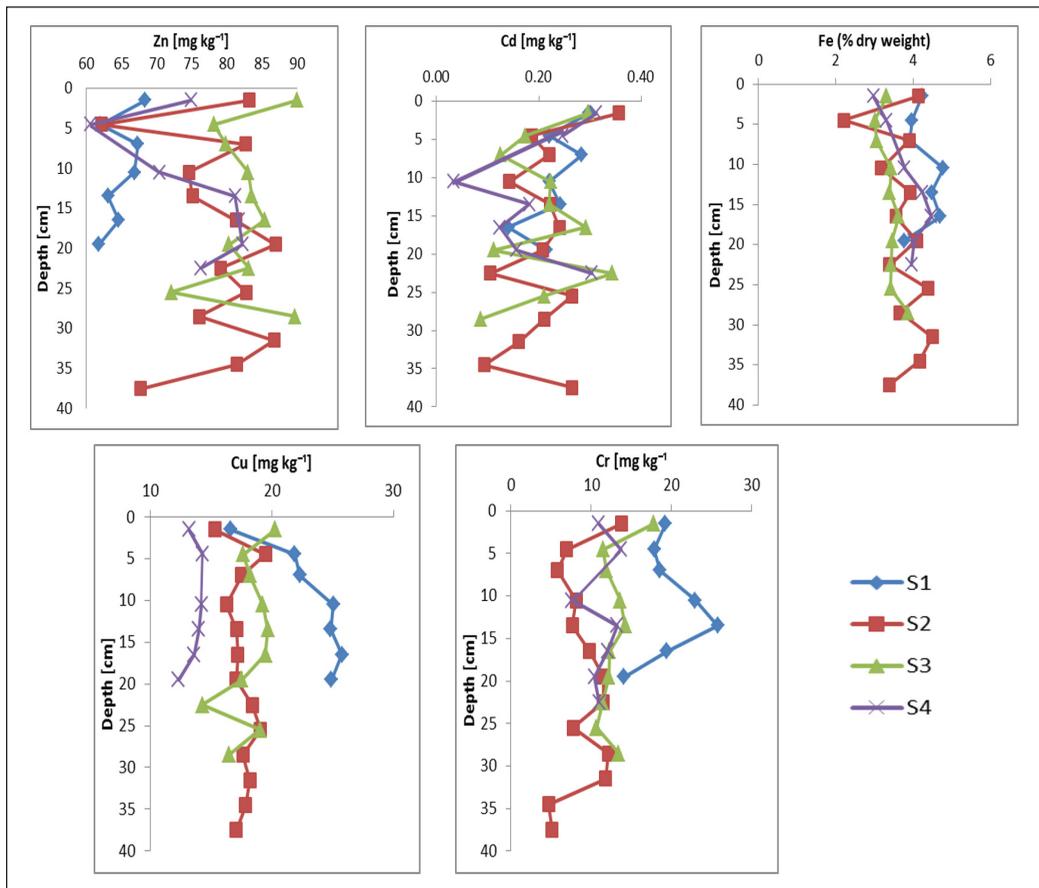
Figure 3. Depth profiles of Zn, Cd, Fe, Cu and Cr concentrations from station S1, S2, S3 and S4

negatively correlated with silt and clay in all cores, except for S2 and S3. This showed that an increased percentage of silt and clay would lead to a decreased percentage of sand. Cd and Cr had shown significant, positive correlations with Zn at core 3 (see Table 7), indicating that the source of Cd and Cr at S3 came from both anthropogenic and natural. A strong positive correlation between Fe and Cu from core S4 indicates that Cu elements are believed to be derived from a natural source.

Table 5
Pearson correlation coefficient values between metals, organic matter, clay, silt and sand for core 1

	Zn	Cd	Fe	Cu	Cr	OM	Clay	Silt	Sand
Zn	1								
Cd	0.63	1							
Fe	0.32	-0.22	1						
Cu	-0.07	-0.67	0.12	1					
Cr	0.36	0.11	0.86*	0.43	1				
OM	0.04	0.58	-0.29	-0.64	0.07	1			
Clay	0.29	0.23	0.32	-0.36	0.29	0.61	1		
Silt	0.07	-0.18	0.50	0.11	0.61	0.57	0.79*	1	
Sand	0.00	-0.07	-0.40	0.11	-0.50	-0.68	-0.86*	-0.94**	1

Notes: *significant level of p<0.05, **significant level of p<0.01

Table 6
Pearson correlation coefficient values between metals, organic matter, clay, silt and sand for core 2

	Zn	Cd	Fe	Cu	Cr	OM	Clay	Silt	Sand
Zn	1								
Cd	0.09	1							
Fe	0.81**	0.17	1						
Cu	-0.06	-0.36	0.05	1					
Cr	0.45	0.12	0.19	0.20	1				
OM	0.29	-0.00	0.35	-0.03	0.15	1			
Clay	0.37	-0.19	0.07	-0.07	0.13	0.42	1		
Silt	-0.30	0.20	-0.07	-0.08	-0.07	0.13	0.42	1	
Sand	-0.17	-0.23	0.10	0.39	-0.59*	0.50	0.23	-0.33	1

Notes: *significant level of p<0.05, **significant level of p<0.01

Table 7
Pearson correlation coefficient values between metals, organic matter, clay, silt and sand for core 3

	Zn	Cd	Fe	Cu	Cr	OM	Clay	Silt	Sand
Zn	1								
Cd	0.70*	1							
Fe	0.31	0.24	1						
Cu	0.58	0.33	-0.09	1					

Table 7 *(continue)*

	Zn	Cd	Fe	Cu	Cr	OM	Clay	Silt	Sand
Cr	0.77*	0.25	0.04	0.77*	1				
OM	-0.8	0.40	-0.51	0.13	-0.15	1			
Clay	-0.27	-0.18	0.31	-0.58	-0.23	-0.22	1		
Silt	0.27	0.18	-0.31	0.58	0.23	0.22	-1.0**	1	
Sand	-0.43	-0.32	0.02	-0.10	-0.45	0.07	0.07	-0.07	1

Notes: *significant level of $p<0.05$, **significant level of $p<0.01$

Table 8
Pearson correlation coefficient values between metals, organic matter, clay, silt and sand for core 4

	Zn	Cd	Fe	Cu	Cr	OM	Clay	Silt	Sand
Zn	1								
Cd	-0.25	1							
Fe	0.79*	-0.54	1						
Cu	-0.61	0.14	-0.18	1					
Cr	-0.14	0.32	-0.18	0.36	1				
OM	-0.61	0.29	-0.64	-0.07	0.32	1			
Clay	0.50	-0.04	0.40	0.21	0.14	-0.71	1		
Silt	0.00	-0.11	-0.14	-0.46	-0.50	0.18	-0.79*	1	
Sand	-0.46	0.07	-0.64	0.04	-0.18	0.50	-0.07	-0.32	1

Note: *significant level of $p<0.05$

Enrichment factors and index geoaccumulation were used to determine the differences of metals from anthropogenic activity and natural sources. In the present study, the trace elements considered have been lower than the EF value and I_{geo} value.

Table 9
Enrichment factors (EF) and Index of geoaccumulation (I_{geo}) of trace metals at location in KongKong Laut River

	Zn		Cd		Fe		Cu		Cr	
Site	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}	EF	I_{geo}
S1	0.8	0.14	0.9	0.15	N/A	0.18	0.6	0.10	0.2	0.04
S2	1.0[a]	0.17	0.9	0.03	N/A	0.16	0.5	0.09	0.2	0.02
S3	1.2[a]	0.19	1.5[a]	0.23	N/A	0.15	0.6	0.09	0.3	0.04
S4	1.0[a]	0.16	0.8	0.13	N/A	0.16	0.4	0.06	0.2	0.03

Notes: [a] minor enrichment; N/A = not calculated

Table 9 shows EF and I_{geo} values from four locations along the KongKong Laut River. All four elements show the EF value under the group of the depletion to minimal enrichment. Although all elements show depletion to minimal enrichment, the EF value for Cd at S3 is higher than that of the other stations. This might be due to the enrichment

of these elements coming from natural and anthropogenic sources, such as the restaurant, raft house and jetty near to the sampling location. The I_{geo} value for Fe in all four stations was shown to be close to zero, indicating that Fe behaved conservatively in the estuarine area, and therefore could be used for normalization in EF analysis (Williams & Block, 2015). As shown in Table 8, the I_{geo} value for trace metal concentration from the four sampling locations at KongKong Laut River are practically in the class of uncontaminated to moderately contaminated.

CONCLUSIONS

From the data gained, all trace metal concentrations in this study have been shown to be lower than the average shale concentration, lower than the effects-range low (ERL), and also lower than the effects-range median (ERM) parameter for aquatic toxicity. Although the data of trace metals in this study had shown low levels of concentration, continuous development without proper management might contribute to the elevation of trace metals in the study area, therefore having an impact on the aquatic ecosystem and food chain. This information could be useful, serving as a baseline for evaluating the potential impacts of future development in the area.

ACKNOWLEDGEMENTS

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