

ASSESSMENT OF SELECTED HEAVY METALS IN SEAWATER AND SEDIMENT AT KLANG COASTAL AREA MALAYSIA

(Penilaian Kandungan Logam Berat Terpilih di dalam Air Laut dan Sedimen di Kawasan Pesisir
Pantai Klang, Malaysia)

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Received: 23 November 2014; Accepted: 27 June 2015

Abstract

Sediments are capable of transporting loads of adsorbed nutrients, pesticides, heavy metals, and other toxins. In this study, the samples of sediment were collected from four sampling points (Kapar, Sungai Puloh, Sementa and North Port) using sediment core sampler. The cores then was sub-sampled by slicing into 1 cm slices and dried at 60 °C until mass become constant and the weight recorded. The samples were pulverized and sieved through 220 µm stainless steel sieves. Each sub-sample digested using aqua regia acids. For seawater, the samples were evaporated using the hotplate at 60 °C. The concentration of heavy metals was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The highest concentration of copper, zinc, iron and lead was observed from seawater samples obtained from Sementa while highest concentration of cadmium was found from Kapar samples). Most of the bottom seawater gives high concentration of the heavy metal compare to the surface. For sediment, the overall concentration of heavy metal in each layer was fluctuated. From the analysis, there is a significant correlation for overall selected heavy metals and the samples (seawater and sediment) that study in this area.

Keywords: heavy metals, sediments, seawater, enrichment factor, pollution

Abstrak

Sedimen mampu mengangkut beban nutrien terjerap, racun perosak, logam berat dan toksin lain. Dalam kajian ini, sampel sedimen telah dikumpulkan daripada empat titik persampelan (Kapar, Sungai Puloh, Sementa dan Pelabuhan Utara) menggunakan teras sampler sedimen. Sample tersebut di potong (setiap 1 cm panjang) kepada sub-sampel dan dikeringkan pada suhu 60 °C sehingga berat sampel menjadi konsisten lalu direkodkan. Sampel dikisarkan dan diayak dengan menggunakan pengayak keluli tahan karat yang bersaiz 220 µm. Setiap sub-sampel dicerna dengan menggunakan cairan asid regia. Untuk air laut, sampel disejatkan dengan menggunakan plat panas pada suhu 60 °C. Kepekatan logam berat ditentukan oleh plasma induksi optik pelepasan spektrometri (ICP-OES). Kepekatan tembaga, zink, besi dan plumbum dalam sampel air laut yang diperolehi daripada Sementa adalah tinggi manakala kepekatan kadmium dari Kapar adalah yang tertinggi. Kebanyakan bahagian bawah air laut memberikan kepekatan logam berat yang tinggi berbanding permukaan air laut. Untuk sedimen, kepekatan keseluruhan logam berat dalam setiap lapisan adalah berubah-ubah. Dari analisa, secara keseluruhannya terdapat hubungan yang signifikan bagi logam berat terpilih dan sampel (air laut dan sedimen).

Kata Kunci: logam berat, sedimen, air laut, faktor pengayaan, pencemaran

Introduction

Pollution of various environments was a consequence of population growth and industrialization. Coastal seas form part of marine environment and were very rich in minerals, crude oil, fishes and others. Nowadays, heavy metal contamination of the coastal environment was pull in the attention of environmental researchers due to its increasing

input to the coastal waters, especially in the developing countries. Heavy metals could be introduced into the coastal environments by several pathways including disposal of liquid effluents, runoff carrying chemicals originating from a variety of urban, industrial and agricultural activities as well as atmospheric deposition [1].

Other sources of heavy metals in environment are from natural occurrence or as a result of anthropogenic activities. Industrial activity had led to very high heavy metal concentrations on the environment, which were in general 100–1000 fold higher than those in the Earth’s crust, and locally, living organisms can be exposed to even higher levels [2]. These phenomena have caused adverse impacts on the health of the ecosystem and man, resulting in increased costs of new and remedial infrastructures in both social and health service areas [3]. Uptakes of toxicants into food are influenced by toxicant concentrations in sediment. Pollutants which settle out with bottom sediments exist in an equilibrium state with the water phase which may be altered by natural and anthropogenic environmental disturbances. Contaminated sediment with toxic organics, metals and nutrients caused a complex long-term environmental quality and habitat degradation problem.

The quality of coastal waters of Klang was deteriorated due to the raise of wastes dumping into upstream catchment activities, especially from housing and industrial areas, as well as discharges from agricultural and urban areas [3]. The existence of trace metals in aquatic systems that come from the natural interactions between the water, sediments and atmosphere with which the water is in contact. The concentrations fluctuate as a result of natural hydrodynamic chemical and biological forces. Most significant among these associations is the interaction between metals and organic compounds in water and sediment [4]. The aims of this study are to determine the concentration of heavy metals in seawater and sediment of Klang coastal area, to compare the level of heavy metals concentration between surface and bottom layer of seawater and profile layer for sediment and to determine the sediment enrichment factor (EF) of Klang coastal area.

Materials and Methods

Study Area

The study area for the sampling is located at Kuala Selangor, which is in the west coast of Peninsular Malaysia. The analysis of heavy metal in seawater and sediment was conducted at four point locations of Klang coastal area as shown in Figure 1. First sampling point was located at Sg. Puloh in which located at coordinate N03°03.274’ E101°21.337’. Second location was at Kapar in which located at coordinate N02°06.050’ E101°19.579’. Third location was at North Port in which located at coordinate N 03° 02’.035’ E 101°21.017’ and the last sampling point was at Sementa located at coordinate N 03° 04’.520’ E 101°21.172’.

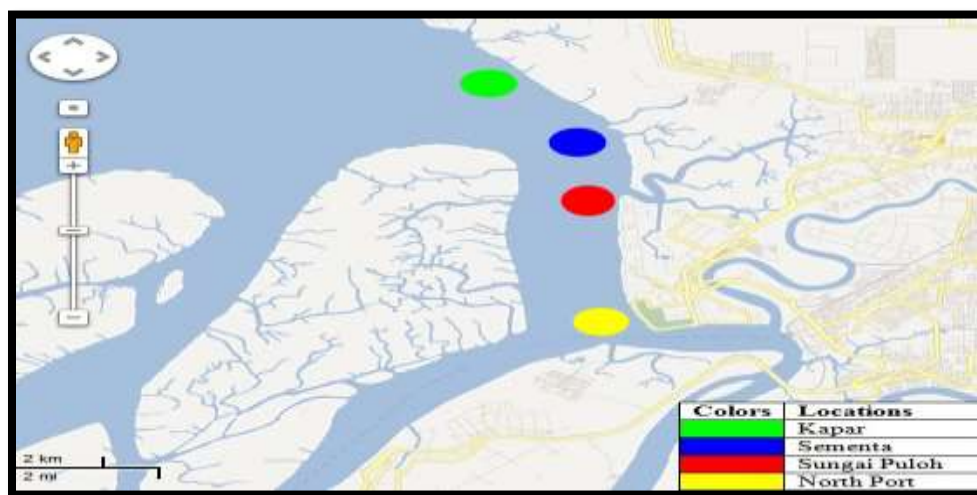


Figure 1. Locations of Sampling Area at Klang Coastal Area. Source: Google Maps, (2012)

Sample Collection

The seawater samples were collected using water sampler and sediment samples by using sediment core sampler with PVC core tube of 50 mm inner diameter at four sampling points (Kapar, Sementa, Sg. Puloh and North Port).

Sample Preparation and Data Analysis

Seawater samples were acidified using nitric acid (HNO₃). Then, samples were filtered using whatman filter paper (125mm) by applying vacuum pump. Filtered sample (1 L) was placed into a beaker and was evaporated using hotplate at 60°C until the volumes remain about 20 mL to 50 mL. After that, sample (1 mL) was diluted with 9 mL 1% nitric acid [5] and proceeds for the analysis by ICP-OES.

For sediment samples, the core tube was sub-sampled by slicing into 1 cm slices. The aggregates were weighed, oven-dried at 60°C until the constant weigh was obtained. Then, the samples were pulverized and sieved through 220 µm stainless steel sieves [6]. For each dried powdered sediment sample, about 0.5 g of samples were weighed and placed in a Teflon digestion vessel with 9 mL of 37% HCl and 3mL of 65% HNO₃. The microwave digester (Milestone ETHOS PLUS with MPR-300/125 medium pressure rotor) was equipped with the TFM (fluoroplastic) closed vessels along with the fume extraction system. The samples were digested at high temperature (140°C). Then, the digested samples were diluted with distilled water. After that, digested volumes were brought up to 25ml with the deionized water in acid washed standard flasks. To avoid any possible contamination to the samples, all glassware and equipment used were acid-washed.

Data obtained was analyzed based on analysis of variance (ANOVA), correlation functions (CF) and enrichment factors (EF) analysis using statistical functions in Microsoft Excel and Statistical Packages for the Social Sciences (SPSS).

The ICP Multi Element Standard solution was as working standard. The preparations of desired standard solutions of the heavy metals were done by diluting each heavy metal's standard solution (1000 mg/L) with appropriate dilution. From the stock solution, it was diluted to obtain the small volume.

Quality Control and Quality Assurance

Seawater samples must be preserved and acidified with nitric acid and stored in the freezer prior to analysis. Standard sample and blank sample were prepared and underwent the same processes and ran together with the samples in the ICP-OES. The sample would increase the reliability and accuracy of the result. Before further analysis were conducted, all the glassware that had been used for this experiment must be washed and rinsed with deionized water, then the glassware were pre-soaked in the 5 percent nitric acid solution for 24 hours. After that, the glassware were once again washed and rinsed with deionized water. All the glassware was allowed to dry in the drying cupboard before used. The sample was analysed in triplicate.

Results and Discussion

Analysis of Seawater

Table 1 shows the concentration of heavy metals obtained in seawater samples at surface and bottom layers.

Different place shows different concentration between surface and bottom of the seawater. For surface layer, Cd was higher in Kapar and lowest in Sementa. Based on the previous study, state that cadmium emission come from the coal fire power plant was different based on their types of coal and technologies use [7]. So, that it was supported that the concentration of cadmium highest in Kapar. The lowest reading was because Sementa is a residential area and away from industrial areas. For bottom layer, Cd was also higher in Kapar and lowest in Sg. Puloh. Otherwise, Sementa was higher in Cu at surface layer and lowest at Sg. Puloh. Conversely, Sementa higher of Cu in bottom layer and Kapar was the lowest. According to the Waste dumping from residential area, piping activities and steel industries nearer these areas cause the high concentration of copper in surface of the seawater.

Table 1. Concentration of heavy metals in seawater layers (surface and bottom)

Sampling Location	Layer	Concentration of Heavy Metal (mg/L) (n=8)				
		Cd	Cu	Zn	Fe	Pb
North Port	Surface	0.006± 0.018	0.007± 0.200	0.045± 1.254	0.375± 0.980	0.018± 0.002
	Bottom	0.003± 0.001	0.007± 0.328	0.111± 1.040	0.846± 0.023	0.015± 0.003
Kapar	Surface	0.001± 0.090	0.007± 0.028	0.077± 3.822	0.518± 3.263	0.008± 0.001
	Bottom	0.006± 0.012	0.008± 0.011	0.093± 1.524	3.338± 0.018	0.017± 0.120
Sg. Puloh	Surface	0.003± 0.020	0.005± 0.394	0.066± 4.100	0.232± 0.362	0.020± 0.002
	Bottom	0.007± 0.023	0.024± 0.015	0.278± 3.210	13.186± 0.010	0.024± 0.032
Sementa	Surface	0.002± 0.011	0.008± 0.047	0.143± 2.121	4.552± 0.014	0.028± 0.012
	Bottom	0.005± 0.001	0.055± 0.010	0.224± 3.241	9.018± 5.420	0.014± 0.014

Zn in surface layer was highest at Kapar and lowest in North Port. Bottom layer of Zn was lowest at Kapar and highest at Sg. Puloh. The wastes from the industries make the concentration of zinc higher than the other. In the other hand, most of the result shows the high concentration in the bottom of the seawater except in Kapar the result shows the higher concentration in the surface. This is according to the ships that come to the Kapar Power Station to transfer the coal from the ship to the power station. The waste from the ship will disturb the surface seawater.

Sementa was higher of Fe at surface layer and lowest at Sg. Puloh. Whereas for bottom layer, Sg. Puloh was highest and North Port was the lowest. most of the result obtained the high concentration for the bottom seawater compare to surface of the seawater Sg Puloh get the highest concentration due to the waste from steel industries such as Star Shine corporation which was operation near the Sg Puloh. The wastes from the industries make the concentration of zinc higher than the other. Sementa gives the high concentration of iron in the surface seawater and the others show high concentration in the bottom of the seawater. This is according to the dumping waste from the residential areas that throw the waste through the river and then the river was connected to the sea. So that, the waste will float in the surface of the seawater make the reading high. Lastly, for Pb it shows that Sg. Puloh was higher at surface layer and lowest at North Port. Then, for bottom layer Pb was higher at Sg. Puloh and lowest at Sementa. According to the result it shows the result high in the bottom of the seawater rather than surface of the seawater. This is due to the physical characteristic of the seawater itself and because of the oil split from the ship that pass through these areas and turbulence happen in the surface of the seawater according to the particle from atmospheric that come from precipitation [8].

Analysis of sediment

Table 2 shows the concentration of heavy metals in sediment sample at different profile (layer).

Table 2. Concentration of heavy metals in sediment at different profile (layer)

Sampling Location	Layer (cm)	Concentration of Heavy Metal (mg/Kg)				
		Cd	Cu	Zn	Fe	Pb
Sungai Puloh	SP ₁ (0-1)	0.3± 0.012	10.2± 0.408	73.2± 2.928	14180±567.2	25.7± 1.028
	SP ₂ (1-2)	0.3± 0.012	9.5± 0.380	388.6±2.501	14050± 562	16.2± 0.648
	SP ₃ (2-3)	0.2± 0.009	8.8± 0.352	78.7± 3.148	15520±620.8	17± 0.680
	SP ₄ (3-4)	0.2± 0.009	11.4± 0.456	88.2± 3.528	16790±671.6	17.4± 0.696
	SP ₅ (4-5)	0.2± 0.009	10± 0.400	134.4±5.376	14620±584.8	16± 0.640
	SP ₆ (5-6)	0.5± 0.020	7.3± 0.292	65.5± 2.620	12890±515.6	14.2± 0.568
	SP ₇ (6-7)	0.2± 0.009	9.1± 0.364	70.3± 2.812	13620±544.8	19.6± 0.784
	SP ₈ (7-8)	0± 0.00	10.1± 0.404	138.8±5.552	15070±602.8	16± 0.640
	SP ₉ (8-9)	0.2± 0.009	12.8± 0.512	87.5± 3.500	15790±631.6	17.6± 0.704
	SP ₁₀ (9-10)	0.4± 0.016	8.9± 0.356	131.2±5.248	13750± 550	15.6± 0.624
	SP ₁₁ (10-11)	0.3± 0.012	8.9± 0.356	110.6±4.424	13520±540.8	15± 0.600
	SP ₁₂ (11-12)	0.4± 0.016	15.4± 0.616	147.6±5.904	16500± 660	21.1± 0.844
Kapar	SP ₁ (0-1)	0.3± 0.012	8.8± 0.352	125.4±5.016	16540±661.6	18.2± 0.728
	SP ₂ (1-2)	9.8± 0.392	9.8± 0.392	158.3±6.332	18210±728.4	19.3± 0.302
	SP ₃ (2-3)	0.1± 0.005	9±0.360	82.7± 3.308	19640±785.6	19.1± 0.772
	SP ₄ (3-4)	0.3± 0.012	8.8± 0.352	134.9±5.396	19650± 786	21.4± 0.764
	SP ₅ (4-5)	0.3± 0.012	9.5± 0.380	143.7±5.748	16970±678.8	22.7± 0.856
	SP ₆ (5-6)	0.1± 0.005	9.2± 0.368	92± 3.680	20670±826.8	22.7± 0.908
	SP ₈ (7-8)	0.1± 0.005	8.6± 0.344	81± 3.240	17470±832.6	20.9± 0.900
	SP ₉ (8-9)	0.3± 0.012	3.1± 0.124	36.2± 1.448	9325± 698.8	9.9± 0.836
	SP ₁₀ (9-10)	0.1± 0.005	9.3± 0.372	87.8± 3.512	18560± 373	22.8± 0.396
	SP ₁₁ (10-11)	0.3± 0.012	8.5± 0.340	130.1±5.204	17950±724.4	18.7± 0.912
	North Port	SP ₁ (0-1)	0.2± 0.009	3.2± 0.128	92.5± 3.700	7905± 316.2
SP ₂ (1-2)		0.2± 0.009	2.7± 0.108	81.1± 3.244	7731± 309.2	7.5± 0.300
SP ₃ (2-3)		0.3± 0.012	2.6± 0.104	34.9± 1.396	9523± 380.9	8.6± 0.344
SP ₄ (3-4)		0.2± 0.009	3.3± 0.132	36.8± 1.472	10980±439.2	10.3± 0.412
SP ₅ (4-5)		0.3± 0.012	2.6± 0.104	32.6± 1.304	8939± 357.6	9.3± 0.372
SP ₆ (5-6)		0.3± 0.012	3.5± 0.140	83.6± 3.344	10630±425.2	10.3± 0.412
SP ₇ (6-7)		0.2± 0.009	3.3± 0.132	102.6±4.104	8819± 352.7	7.7± 0.308
SP ₈ (7-8)		0.2± 0.009	3±0.120	36.9± 1.476	8550± 342.0	8.1± 0.324
SP ₉ (8-9)		0.3± 0.012	9.9± 0.396	91.5± 3.660	17730±709.2	22.4± 0.896
SP ₁₀ (9-10)		1.1± 0.044	3.6± 0.144	34.7± 1.388	9239± 369.6	7.8± 0.312
SP ₁₁ (10-11)		0.2± 0.009	2.5± 0.100	78.2± 3.128	7989± 319.6	7.7± 0.308
SP ₁₂ (11-12)		0.2± 0.009	2.4± 0.096	80± 3.200	7745± 309.8	7.5± 0.300
SP ₁₃ (12-13)		0.2± 0.009	3.8± 0.152	111.4±4.456	8239± 329.6	7.6± 0.304
Sementa	SP ₁ (0-1)	0.3± 0.012	3.6± 0.144	109.8±4.392	9841± 393.6	8.9± 0.356
	SP ₂ (1-2)	0.4± 0.016	4.3± 0.172	153± 6.120	8785± 351.4	10± 0.400
	SP ₃ (2-3)	1.8± 0.072	6.1± 0.244	95.2± 3.808	14290±571.6	15.5± 0.620
	SP ₄ (3-4)	0.4± 0.016	5.2± 0.208	254± 10.16	11410±456.4	11.7± 0.468

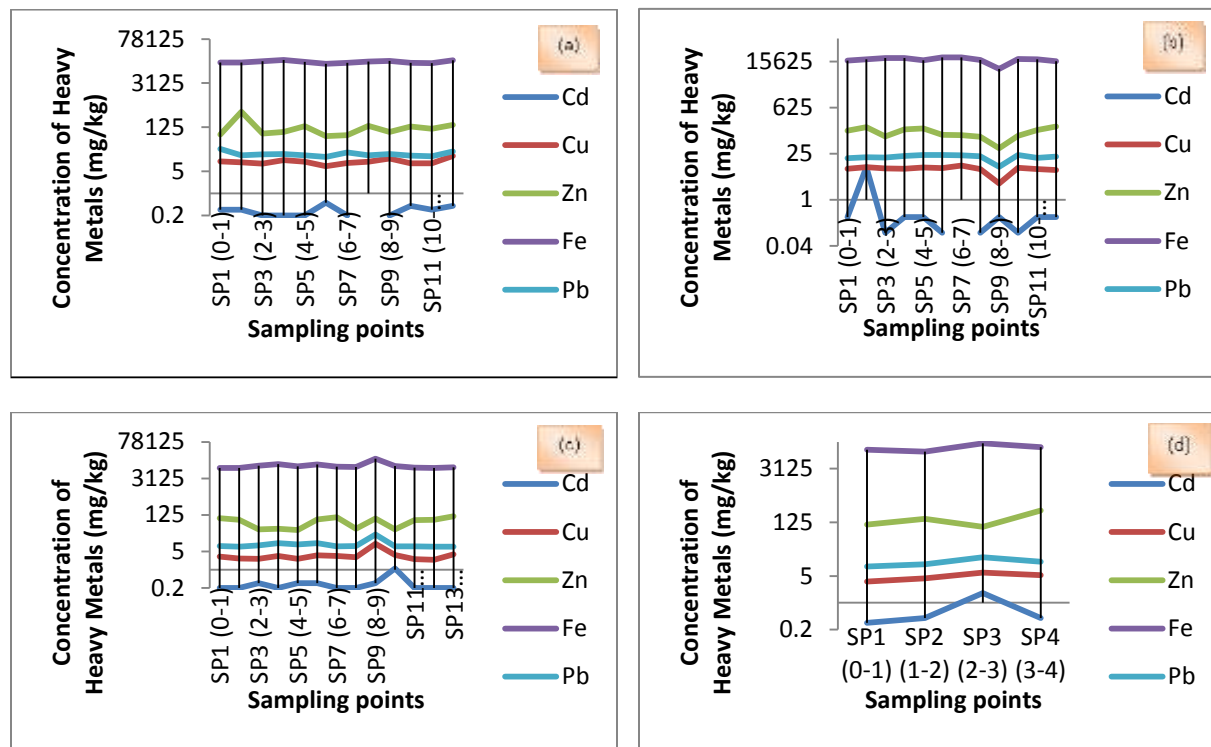


Figure 3. (a)Sungai Puloh (b) Kapar (c) North Port (d) Sementa: The concentration of selected heavy metal in each sediment profile layers.

From the Table 2, the sequence of the concentration heavy metal in sediment profile layers was $Fe > Zn > Pb > Cu > Cd$. Fe reveals high concentration may be due to the release of this metal from agricultural, industrial and shipping that present around there. The activities such as the use of pesticides that flow into sea and discharge of chemicals waste are the major factor in the increasing of the heavy metal concentration in sediment. Fe also was reported in the highest concentration (compared to other heavy metals at sediment samples by Bentum et al. [9]. In order to investigate whether depth had any influence on concentration within the sample, the sediment sample was sliced into 1 cm and analyzed. In general, the concentration of heavy metal will be decreased when the depth of sediment increases [4]. Based on the Figure 3, SP₁ point indicates the bottom of sediment and the SP₁₂ indicates the upper layer of sediment. The concentration of the heavy metals were varies in each layer of samples as a result of the turbulence of sediment as effect of the heavily movement of shipping machine activity and waves as the tides. At the layer SP₉ to SP₁₀, the all types of heavy metal was decreases dramatically this is may be due to the turbulence of water and affect the accumulation of heavy metal in sediment.

Sungai Puloh is the first area of sediment samples. Sediment samples were taken at the estuary part of the Sungai Puloh. Based on the observation made, the study area is close to a variety of human activities such as industrial, shipping and agriculture. The concentration of the heavy metals were varies in each layer of samples as a result of the turbulence of sediment as effect of the heavily movement of shipping machine activity and waves as the tides. Kapar is the second places of sediment sampling collection for the analysis purposes. The heavy metals Fe shows high concentrations due to the release of heavy metals from agricultural, industrial and shipping that present around there. The third location of sediment sampling was at North Port. The main activities at the sampling area were shipping for the import and export of the goods. Table 2 shows the results of sediment samples analysis from North

Port. From the table, the highest concentration of heavy metals is Fe followed by Zn and the lowest concentration of heavy metals is Cd. The activities such as discharge of waste chemicals are the major factor in the increasing of the heavy metal concentration in sediment. The fourth location of the sediment was at Sementa. The main activities at the sampling area are shipping for the import and export of the goods. The activities such as the use of pesticides that flow into the sea and discharge of waste chemicals are the major factor in the increasing of the heavy metal concentration in sediment.

The determination of concentration heavy metal in each layer profile was important for the purpose of identification the continuous accumulation of heavy metal in the sediment and the concentration value of heavy metal accumulated in sediment by year. From the analysis, it can compare the accumulation of heavy metal at four different locations still happen and due to the factor of turbulence of water and the depth of core sampling was short, the concentration of heavy metal in each layer profile was not fully comply to the concept of the decreasing concentration of heavy metals with the increasing of the sediment core depth. In order to identify the level of pollutant present at the sediment sample, the concentration of heavy metal obtained was compare with the permitted level proposed by EPA Region V. In comparison, the location of Kapar was slightly polluted by Fe at the concentration 17612.92 mg/kg whereas the other places was not polluted by Fe. The heavy metal Zn also was polluted the all locations of sampling except North Port whereas the concentration of Zn was 67.03 mg/kg. Based on the comparison of the standard, the heavy metal Cd, Cu, Ni and Pb were not polluted the sediment sample at all locations and indicated their concentration under control.

Correlation Coefficient Analysis

Table 3 shows the relationship between heavy metals concentrations that were analyzed and show significant positive correlation as $P < 0.01$.

For correlation of seawater, the result shows that the correlation coefficient between the heavy metal was not strong. The result only show strong positive correlation between Zn and Fe where the value was $p < 0.01$, $r = 0.921$. Hence, it can be concluded that the concentration of Fe was increases as the concentration of Zn also increases. For sediment, it shows a little different correlation results. From the results, it show three strong correlation coefficient with Fe-Cu with the value $r = 0.841$, Pb-Cu, $r = 0.868$ and lastly Pb-Fe, $r = 0.922$. Therefore, the concentration of the heavy metal with strong correlation will increases and vice versa. After data were analysed, it indicates that the anthropogenic source was the main cause that contributed to the source of the heavy metal such as industries activities, power station, ship activities, dumping waste from residential and agriculture activities.

Table 3. Linear correlation coefficient matrix for heavy metals in (a) Seawater, (b) Sediment

(a) Seawater	Cd	Cu	Zn	Fe	Pb
Cd	1				
Cu	0.320	1			
Zn	0.244	0.555	1		
Fe	0.187	0.607	0.921**	1	
Pb	0.238	0.299	0.322	0.138	1
(b) Sediment	Cd	Cu	Zn	Fe	Pb
Cd	1				
Cu	0.096	1			
Zn	0.127	0.326	1		
Fe	0.152	0.841**	0.215	1	
Pb	0.091	0.868**	0.215	0.922**	1

**Levels of significant are indicated as $p < 0.01$

Enrichment Factor (EF)

Enrichment factor was determined in each sample to indicate how the contaminants migrate into bivalve sample. Table 4 shows the degree of contaminant and contamination factors in earth crust. The EF range was shown in the following:

EF < 2	:	depletion to minimal enrichment;
EF 2–5	:	moderate enrichment;
EF 5–20	:	significant enrichment;
EF 20–40	:	very high enrichment;
EF > 40	:	extremely high enrichment

Enrichment factor for sediment (Table 4) explains the values for enrichment factor of heavy metal in sediment at Klang Coastal area are in order of Cd > Zn > Pb > Ni > Cu. From the result obtained, the element of Cu and Ni are come from natural resources since the values of EF is less than 1 compare the others that come from anthropogenic sources more than 1 values of EF.

Table 4. The value of Enrichment Factor in sediment samples

Sampling locations	Enrichment Factor			
	Cd	Cu	Zn	Pb
Sungai Puloh	6.89	0.65	6.90	4.82
Kapar	21.3	0.46	5.05	4.54
North Port	11.9	0.34	5.57	3.97
Sementa	18.3	0.37	9.78	4.04

Conclusion

The concentration of heavy metals in seawater samples obtained from Klang Coastal area varies by layers. Most of the bottom seawater gave high concentration of heavy metals compare to the surface seawater. However, some of the sampling points showed the high concentration in the surface seawater. Basically, it is common if the bottom of the seawater contained high concentration of heavy metals than the surface as the sediment in the bottom of the seawater will mix together and contribute to the high concentration. The determination of concentration heavy metals in each layer profile was important for the purpose of identification the continuous accumulation of heavy metal in the sediment and the concentration value of heavy metal accumulated in sediment by year. From the analysis, it can compare the accumulation of heavy metal at four different locations still happen and due to the factor of turbulence of water and the depth of core sampling was short, the concentration of heavy metal in each layer profile was not fully comply to the concept of the decreasing concentration of heavy metals with the increasing of the sediment core depth.

Acknowledgement

We would like to thank Universiti Teknologi MARA (UiTM), Shah Alam, Selangor and RIF grant for giving the opportunity and cooperation to successfully perform this study. We also would like to thank fellow colleagues and laboratory staffs of the Faculty of Applied Science as well as the ex-research students for their endless support, assistance, courage and dedication in carrying out this work.

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