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Vertical Distributions of Zn, Cd, Pb and Cu at Tropical Coastal Sediments: In Case of West Coast of Peninsular Malaysia

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ABSTRACT

The level and pollution status of Zn, Cd, Pb, Cu in sediment cores of Bagan Pasir estuary, Sungai Buloh estuary, and the coastline of Port Dickson was assessed. Based on the vertical profiles of metals concentrations, the order of metals' concentration in decreasing manner was Zn>Pb>Cu>Cd at Bagan Pasir and Sungai Buloh stations, while Zn>Cu>Pb>Cd at Port Dickson station. Most of the analyzed metals were below the Interim Sediment Quality Guidelines and the effect range-low (ERL) at all sampling stations. The results of geo-accumulation index, contamination factor and pollution load index classified the sediments quality as unpolluted with studied metals with the exception of the element Pb at certain depths of the sediment cores as well as historical pollution at bottom sediment at Sungai Buloh station. Therefore, metal concentrations in the sediments of these stations were not at an alarming stage, however, requires regular monitoring from the authorities to maintain sustainable management of these areas especially at Sungai Buloh due to anthropogenic activities.

Keywords: Sediment core, Heavy metals, Estuary, Pollution index, Contamination factor.

INTRODUCTION

Contaminants are defined as inputs of foreign and potentially toxic compounds into the environment where not all contaminants cause pollution as they may exist in trace amounts. Whereas, pollutants such as heavy metals are described as substances that pose harmful effects which resulted from anthropic activities[1]. Heavy metals are found naturally but their concentrations in the environment keeps increasing due to human activities[2]. Inevitably, they became the worldwide environmental concerns with the ever-increasing urbanization and industrialization, especially in developing countries, such as Malaysia[3]. Researchers focused more on the coastal environment not only due to the intensified human activities in these areas but because all domestic wastewater were carried by the rivers ended up in coastal environment[4]. The rapid coastal development, urbanization, and agricultural practice on the west part of Peninsular Malaysia are threatening the aquatic environment with anthropogenic activities such as loading and offloading of fishes, cleaning and maintenance of boats, antifouling paint applications, leaded automotive gasoline, diesel fuel, leaded aviation gasoline as well as mining activities and fertilizers and pesticide usage in oil palm estates[5].

These are the sources of heavy metals that are discharged to rivers, carried to estuaries, and eventually incorporated to sediment through times. When resuspension occurs at surface sediment due to water mixing, the heavy metals are remobilized, taken up by filter feeding organism such as blood cockles, and move up the food chain through seafood consumption[6]. This could lead to health problems if metals were to be consumed in the long run[6]. Therefore, it is crucial to have a regular monitoring of heavy metal pollution status in sediments with economic importance to mitigate heavy metals pollution and indirectly ensure suitable habitat of aquatic organisms such as cockles[7].

For the past decades, numerous contamination-oriented studies had been performed with the aim to describe, evaluate as well as to estimate the heavy metals distribution and their potential anthropogenic sources, their correlation with bioavailability of metals in aquatic organisms, the consumption risks, and their ecological risks[8]. However, these continuous studies on heavy metals contamination are crucial to keep updating the level of heavy metals concentration in marine environment not just because of the economic importance of these areas but most importantly for assessing impacts it has on humans and to provide scientific references for better management of the environment as a whole[9].

Furthermore, the study of sediment cores has shown to be an excellent tool for establishing the effects of anthropogenic and natural processes on depositional environment[10]. The present study analyzed core sediments as they provide valuable historical information on heavy metal content through the vertical profile[11]. For the assessment of pollution status, Sediment Quality Guidelines (SQGs) represent an informal tool to evaluate and categorize the relative quality of sediments[12]. Despite its important function, Malaysia has yet to establish its own specific sediment quality guideline to be followed[13]. Therefore, researchers commonly employed internationally established guidelines such as Interim Sediment Quality Guidelines, ISQG invented by Chapman *et al.,*[14] and Sediment Quality Guidelines (SQG) of effect range-low (ERL) and effect range-median (ERM) from Long *et al.,*[15] to asses Malaysia sediment. The determination of heavy metals on the surface horizons of the soil does not allow the distinction between natural background and anthropogenic enrichment, hence, indices are employed with the aim of evaluating the natural content of heavy metal in soils, related to parental materials and possible enrichment due to human activities[16]. It was pointed out that the determination of background levels of the analysed heavy metals is very important regarding the choice of the appropriate assessment metrics which is why it is the key issue in the final result of assessment[17].

Therefore, this study aimed to evaluate the historical elevation of metals from the vertical profiles of Zn, Cd, Pb, and Cu from three selected stations along the west coast of Peninsular Malaysia through the Sediment Quality Guidelines comparison as well as assessment by pollution indices.

EXPERIMENTAL

Sample Collection

Three locations on the west coast of Peninsular Malaysia were chosen as our study areas (Table 1). These areas are considered as the sites receiving anthropogenic inputs from urban areas and port activities, and agricultural areas[8].

Table 1: Locations of sediment cores sampling in three selected sites along the West Coast of Peninsular Malaysia

Sampling Stations	Coordinates	Site Description
Bagan Pasir Perak	N 03°50.598' E 100°47.648'	Agriculture activities
Sungai Buloh, Selangor	N03°15.358’ E101°18.044’	Residential and agriculture area
Port Dickson, Negeri Sembilan	N 02°28.3595' E 101°50.9958'	Jetty, boat ramp, buildings such as hotels and condominiums

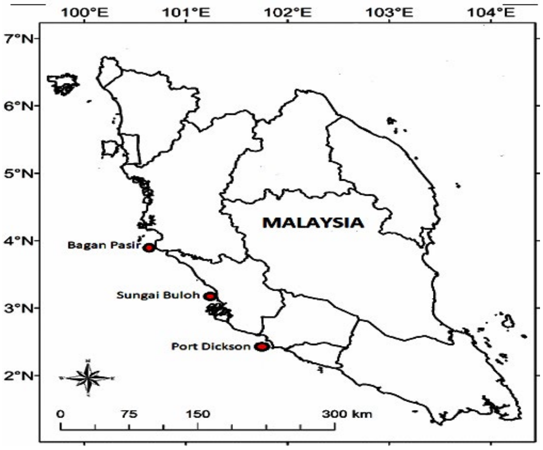

Fig. 1. Sampling sites at Bagan Pasir estuary, Perak; Sungai Buloh estuary, Selangor and Kampung Baharu, Port Dickson, Negeri Sembilan.

Sediment sampling and sample preparation

A sediment core with 30 cm long were collected at each station by using sediment core sampler, sliced in 3 cm interval[18] and kept in tight-sealed plastics. The pH value of each subsample was recorded using Milwaukee MW102 pH meter. The samples were then dried in an air-circulating oven at 60°C until constant dry mass was obtained. The dried sediments were then grinded with pestle and mortar, and sieved through 63 μm sieve to minimize the concentration variability due to grain sizes and because finer sediment particles are more likely to retain heavy metals[19,20].

Chemical preparation

Ultrapure water, Milli-Q, (18.2 Millipore, ELGA Maxima) was used in every chemical solution preparation. The aqueous stock solutions of Zn, Cd, Pb and Cu were prepared from 1000 mg/L Standards (Certified Single Element Standard, TraceCERT®). Acids used were from high purity grade such as 69% nitric acid (J. T. Baker), 37% hydrochloric acid (J. T. Baker) and 49% hydrofluoric acid (J. T. Baker).

Digestion method

The extractions of Zn, Cd, Pb, and Cu in sediments were carried out using the optimized method. One gram of 63 μm dried sediment was weighed in Teflon beaker and heated in 6 mL of 37% HCl for one hour with lid on followed by addition of 10 mL 69% HNO_3. After 15 min 6 mL of 49% HF was added slowly and sample was heated for another 15 minutes. The lid was then removed, and the sample heated to incipient dryness. After cooling, the sample was rinsed with 10 mL diluted HNO_3 (2%) and heated for another 2 minutes. The sample solution was filtered through 0.45 μm nylon syringe filter and kept in centrifuge tube until further analysis. For every batch of sample digested, potential contamination was monitored by reagent blanks which passed through the same procedures but without the sediment sample.

Heavy metal analysis

The analysis of metals concentrations in sediment cores were carried out by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) from Perkin Elmer, Elan DR-e that consists of Autosampler, Peltier oven, LG pump, Vacuum Degasser (Series 200). Performance check was carried out daily by pre-calibration of instrument with standard solution before sample analysis. Aliquot of the extract was diluted 50 times and placed in 15.0 ml centrifuge tubes prior to the ICP-MS analysis.

Methods in this study were validated with Certified Reference Material (CRM), BCR®-667, SRM of estuarine sediment which has been certified by Community Bureau of Reference (BCR) and revised under the responsibility of Institute for Reference Materials and Measurements (IRMM). ICP-MS was selected as the detector because it measured all the metals of interest (Zn, Cd, Pb and Cu) in the real sediment sample simultaneously.

Table 2: Validation of methods by the Certified Reference Material, BCR®-667

Element	Certified value ($mg.kg^{-1}$)	Recovery values(%)
Zinc	175±13	85.28
Cadmium	0.67±0.11	83.37
Lead	31.9±1.1	87.35
Copper	60±9	90.13

Pollution status assessment

To achieve better comprehension on heavy metals pollution in our study area, evaluation was carried out based on the calculation of geo-accumulation index, contamination factor, and pollution load index, and comparison with sediment quality guidelines. These indices are established and widely used in assessing heavy metal pollution in environment[21,22,23]. The overall heavy metals contamination level sediment core was evaluated by the comparison of metal contents with Sediment Quality Guidelines and regional studies[24]. This study applied the Interim Sediment Quality guidelines (ISQGs)[14] and the Effect Range Low, ERL as well as the Effect Range Medium, ERM[15] to assess ecotoxicology of heavy metals in sediment cores. Several ways to infer anthropogenic input from natural input of heavy metals in sediment other than sediment quality guideline were employed in the study which is through the classification by quantitative pollution indices such as geo-accumulation index, contamination factor and pollution load index. The statistical analysis was performed using XLSTAT 2016. One-way ANOVA was used to compare means between stations. To test the possible relationship between metals, the Pearson correlation test was adopted.

RESULTS AND DISCUSSION

Distribution of Zn, Cd, Pb, and Cu

The concentration of Zn, Cd, Pb and Cu throughout the sediment core at each station during this study was presented in Table 3 below. The data was represented the mean concentration along with standard deviation of the metals (mg/kg). The results are expressed as milligrams of metal extracted per kilogram of dry sediment and the mean value of three replicates.

At Bagan Pasir, the distribution of every metal throughout the sediment core was slightly similar. Their concentrations were generally decreased from bottom to the top layer of the sediment core (Fig. 2). The lowest concentration of the metals was determined at 6-9 cm depth of the sediment core. The concentration of Zn, Pb, Cu and Cd was 37.96±0.0022 mg/kg, 12.75±0.0008 mg/kg, 5.68±0.0004 mg/kg and 0.0256±0.0000 mg/kg (Table 3, Fig. 2), respectively at this layer. Moreover, all of the highest concentration of the metals were determined at deeper layer of the sediment core (Fig. 2). The highest concentration of Zn(79.84±0.0011 mg/kg), Pb(27.26±0.0002 mg/kg), Cu(13.52±0.0003 mg/kg) and Cd(0.0607±0.0000 mg/L) was determined at 15-18 cm depth of the core sediment (Table 3, Fig. 2). The fact that metals enriched at the bottom sediment in this area indicates historical extra input in previous years and could have originated from fertilizers application in agricultural areas a few years back when agricultural practices such as palm oil estate, pineapples, rubber estate, and coconut were actively developing in the area[25]. Zinc is essential for metabolic processes in aquatic organisms and also in human body but long-term exposures of high Zn amount could lead to toxicity on cellular level such as cell apoptosis as well as having distinctive role in neuronal deaths[26].

Generally, the concentration of the metals was increased from the bottom to the top layer of the sediment core at Sungai Buloh station (Fig. 2). The lowest concentration was found at 18-21 cm depth of the sediment. At this layer, the concentration of Zn, Cd, Pb and Cu was 40.99±0.00187 mg/kg, 0.0538±0.00001 mg/kg, 12.76±0.00052 mg/kg and 7.13±0.00054 mg/kg, respectively (Table 3). Besides, the highest concentration of Zn (80.19±0.00210 mg/kg), Pb(23.24±0.00063 mg/kg) and Cu (13.09±0.00033 mg/kg) was determined at 9-12 cm depth (Table 3). For Cd, the highest concentration (0.1906±0.00001 mg/kg) was determined at top of the sediment (0-3 m) (Table 3). The vicinity of this station was estuary and inclusive of human settlements resulting in continuous input of metals in these areas which explains the higher metal concentrations at the top sediments. This is in agreement with other studies that had reported gradually increasing metal concentrations as depth decreases throughout sediment cores retrieved from neighbouring anthropogenic activities[27,28].

A slightly high concentration of Cd at Sungai Buloh station could suggest a common behaviour for the metal as it could come from the source that might be attributed to the non-point sources from the historical agriculture and industrial development as well as growing urbanization located along the upstream of Sungai Buloh river[25]. A previous study also reported building of service industry such as car wash, car workshop as well as food stalls along the main road entered the drainage system and ended up entering Sungai Buloh river and through time, it contributed to the high Cd concentration variabilities throughout the sediment cores in the river[25]. Furthermore, the opening and closing of sluice gates located at middle stream of the river could be influencing metal deposition into the surface sediment[29].

At Port Dickson station, all metals concentrations fluctuated at the same layer of depths at 6-9, 15-18 and 24-27cm throughout the sediment core (Fig. 3). Zn and Pb showed decreasing patterns with the highest concentrations at 24-27 cm depth; 112.53±0.0013 mg/kg for Zn and 30.17±0.0003 mg/kg for Pb (Table 3). Cd had the highest concentration at 6-9cm depth (0.1455±0.0000 mg/kg). Cu had the highest concentration at 15-18cm depth (33.83±0.0004 mg/kg). This similar trend could suggest that the metals might had been derived from similar input sources[30,31].

Table 3: The concentration (mg/kg) of Zn, Cd, Pb and Cu throughout the sediment cores at Bagan Pasir, Sungai Buloh and Port Dickson during this present study

Depth.(m)	Bagan Pasir					Sungai Buloh					Port Dickson				
	Zn	Cd	Pb	Cu	pH	Zn	Cd	Pb	Cu	pH	Zn	Cd	Pb	Cu	pH
0-3	56.00± 0.0002	0.0609± 0.0000	22.65± 0.0004	11.49± 0.0004	7.36	77.69± 0.00387	0.1906± 0.00001	17.33± 0.00060	11.85± 0.00080	6.31	44.21± 0.0009	0.0844± 0.0000	9.71± 0.0001	18.09± 0.0000	7.22
3-6	61.76± 0.0005	0.0540± 0.0000	20.29± 0.0004	10.47± 0.0001	7.59	76.98± 0.00137	0.1647± 0.00000	14.73± 0.00009	11.49± 0.00038	6.13	50.82± 0.0013	0.0918± 0.0000	14.16± 0.0001	15.78± 0.0002	7.13
6-9	37.96± 0.0022	0.0256± 0.0000	12.75± 0.0008	5.68± 0.0004	7.58	61.55± 0.00185	0.1189± 0.00001	12.53± 0.00060	9.66± 0.00066	7.09	97.12± 0.0012	0.1455± 0.0000	25.25± 0.0001	33.49± 0.0000	7.29
9-12	51.58± 0.0008	0.0467± 0.0000	19.65± 0.0006	10.46± 0.0003	7.93	80.19± 0.00210	0.1397± 0.00000	23.24± 0.00063	13.09± 0.00033	7.13	77.50± 0.0006	0.0731± 0.0000	18.93± 0.0004	27.39± 0.0002	7.35
12-15	67.47± 0.0016	0.0552± 0.0000	20.94± 0.0003	12.04± 0.0002	7.61	48.56± 0.00177	0.0769± 0.00001	15.07± 0.00056	8.71± 0.00057	7.3	66.67± 0.0008	0.0734± 0.0000	20.35± 0.0001	19.07± 0.0003	7.29
15-18	79.84± 0.0011	0.0607± 0.0000	27.26± 0.0002	13.52± 0.0003	7.48	52.63± 0.00215	0.0611± 0.00000	16.32± 0.00059	8.94± 0.00045	7.37	109.51± 0.0008	0.0976± 0.0000	27.13± 0.0007	33.83± 0.0004	7.77
18-21	51.27± 0.0012	0.0377± 0.0000	17.43± 0.0005	9.18± 0.0001	7.74	40.99± 0.00187	0.0538± 0.00001	12.76± 0.00052	7.13± 0.00054	7.48	78.55± 0.0020	0.0762± 0.0000	20.57± 0.0004	17.79± 0.0005	7.74
21-24	77.49± 0.0001	0.0542± 0.0000	25.78± 0.0003	12.47± 0.0002	7.26	52.98± 0.00257	0.0806± 0.00001	13.11± 0.00068	9.34± 0.00050	7.47	83.90± 0.0027	0.0833± 0.0000	21.53± 0.0001	24.74± 0.0002	7.70
24-27	63.40± 0.0002	0.0584± 0.0000	24.13± 0.0004	14.41± 0.0001	7.80						112.53± 0.0013	0.1011± 0.0000	30.17± 0.0003	27.61± 0.0008	7.80
27-30	70.76± 0.0008	0.0526± 0.0000	22.95± 0.0001	11.77± 0.0002	7.55						110.19± 0.0011	0.0855± 0.0000	27.78± 0.0007	19.57± 0.0002	7.73

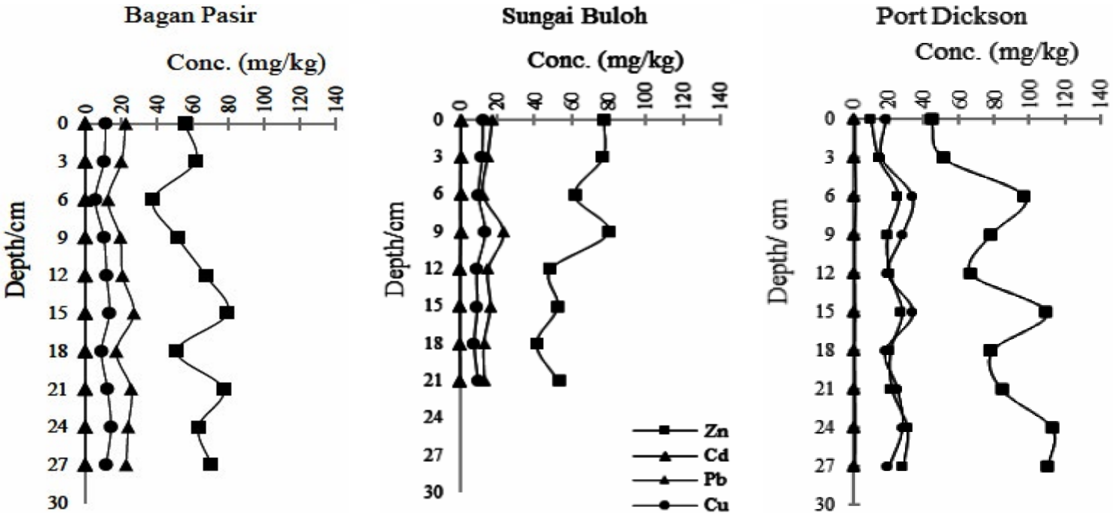

Fig. 2. Summaries of depth profiles of heavy metals in selected stations (Bagan Pasir estuary, Sungai Buloh estuary and of Port Dickson coastline) along the west coast of Peninsular Malaysia

In comparison, the ranged of metal concentrations at Bagan Pasir was slightly similar to the concentration of metals at Sungai Buloh station (Fig. 2). The concentration of Zn, Cd, Pb and Cu at Bagan Pasir were ranged between 37.96-79.84 mg/kg, 0.0256-0.0609 mg/kg, 12.75-27.26 mg/kg and 5.68-14.41 mg/kg throughout the sediment core (Table 3), respectively. In addition, the ranged of metal concentrations at Sungai Buloh was ranged between 40.99-80.19 mg/kg, 0.0538-0.1906 mg/

kg, 12.53-23.24 mg/kg and 7.13-13.09 mg/kg for Zn, Cd, Pb and Cu throughout the sediment core at Sungai Buloh (Table 3). However, at Port Dickson station, the ranged concentration of Zn, Cd, Pb and Cu was between 44.21-112.53 mg/kg, 0.0731-0.1455 mg/kg, 9.71-30.17 mg/kg and 15.78-33.83 mg/kg (Table 3), respectively. This indicated that the concentration of Cu throughout the sediment core at Port Dickson showed the highest concentration, compared to its concentration at others stations (Fig. 2). Its concentration was almost two times higher compared to other stations during this study. A variability in Cu concentrations with stations indicated potentially extra external input rather than natural input, mainly from anthropogenic activities in the surrounding area[28].

Furthermore, we have found that all the stations showed the highest concentration of Zn compared to other metals throughout the sediment core (Fig. 2). On the other hand, Cd was the lowest metal concentration at all stations. In generally, the concentration of Zn in the sediment core was higher at Port Dickson compare other stations. Its concentration was ranged between 44.21-112.53 mg/kg, compared to 37.96-79.84 mg/kg and 40.99-80.19 mg/kg at Bagan Pasir and Sungai Buloh stations (Table 3), respectively. Pb and Cu also showed the highest concentration at Port Dickson compared to Bagan Pasir and Sungai Buloh stations. The ranged concentration of Pb and Cu at Port Dickson was between 9.71-30.17 mg/kg and 15.78-33.83 mg/kg (Table 3), respectively. The difference metals concentration between stations might have been caused by the surrounding natural process and a variety of anthropogenic activities[32]. On the other hand, a slightly similar range concentration of Cd in sediment core was determined at all of our stations.

Sampling station at Port Dickson is also prominent in urbanization compared to the other two sampling locations particularly accommodation. Area surrounding of Port Dickson coastline was developed with hotels, resorts, apartments, condominiums, homestays, as well as other related services such as transportation, recreational facilities, and foods to meet he needs of tourism industry[33]. This active coastal development and port activities in these areas might have contributed to the fluctuating trend of heavy metals in the sediment cores through time.

A different distribution pattern for Cu and Pb throughout the core sediment was found between our stations. At Port Dickson station, we found that the metal concentration was decreased in the following order Zn>Cu>Pb>Cd, where at Bagan Pasir and Sungai Buloh stations, it was Zn>Pb>Cu>Cd order (Fig. 2). This might be due to the types of activities in the vicinities of sampling stations. The Pb input in the vicinities of Bagan Pasir and Sungai Buloh estuaries could possibly be input from a fertilizer application in agricultural activities[34], whereas Cu might be attributed to the coastal development to meet the needs of tourism industry in Port Dickson[33].

Metal concentrations in this study were also compared to the previous reports of heavy metal studies in Malaysia. Data in this study fall within most of the concentration ranges reported in the previous studies in Western part of Peninsular Malaysia (Table 4). For example, present data of Cu, Zn, and Pb estimated were within the concentration range of metals determined in Port Klang[20] and Western part of Johor Strait[34] (Table 4). Conversely, Cd concentration range obtained in Bagan Pasir (0.0256±0.0000 to 0.0609±0.0000 mg/kg) and Sungai Buloh (0.0538±0.0001 to 0.1906±0.0001 mg/kg) stations (Table 4), found to be lower than other reported data. This suggested that Cd enrichments at Bagan Pasir and Sungai Buloh stations occurred naturally. This comparison also showed that there are no extraordinary enrichments of the metals in the present studied areas, from the other sites that had been previously reported in the previous studies.

However, the effects of Zn, Cd, Pb, and Cu on the environment and biota at our study areas can be confirmed by comparing their concentration with the Sediment Quality Guideline (SQG). The numerical sediment quality guidelines revealed that metal contents at our study areas were below ISQG-low values (Table 4). This could indicate that the adverse biological effects are unlikely to occur where studied metals do not implicate sediment of Sungai Buloh and Bagan Pasir stations. Furthermore, other numerical SQGs revealed that Cu, Zn, Cd, and Pb contents were lower than its respective ERM and ERL values, indicating rare effects on the environment and biota are likely to occur.

Table 4: Comparisons of metals (mg.kg^{-1}) in sediment data reported from previous studies done in Malaysia

	Location	Cu	Zn	Cd	Pb	References
Port, Klang	North Port	10.34-30.40	23.45-83.00	0.22-1.40	31.30-98.90	Sany *et al.,*[20]
	West Port	8.60-28.90	17.00-73.60	0.14-1.90	35.70-104.87	
	South Port	11.23-57.01	22.67-192.90	0.40-2.10	36.23-98.56	
Sungai Puloh		16.45-132.91	291.96-2584.34	0.60-1.55	35.51-167.38	Udechukwu *et al.,*[29]
Johor Strait (western part)		12.0-64.5	56.9-307.9	Not analyzed	13.3-62.3	Zulkifli *et al.,*[34]
Sengantang Garam, Kedah		34.79	60.83	1.25	27.78	Buhari and Ismail[36]
Kuala Juru, Penang		65.39	442.19	1.24	29.97	
Sungai Puluh, Klang		35.48	256.5	1.37	34.22	
Bagan Lalang, Selangor		12.79	75.38	0.6	8.46	
Minyak Beku, Johor		37.64	241.87	1.65	53.73	
Sungai Tiga, Johor		13.9	117.38	1.4	28.28	
Bayan Lepas area, Penang		1.922-386.534	8.858-103.207	0.49-2.903	7.743-63.167	Khodami *et al.,*[37]
Bagan Pasir estuary, Perak		5.68-14.41	37.96-79.84	0.0256-0.0609	12.75-27.26	Present study (2019)
Sungai Buloh, Selangor		7.13-13.09	40.99-80.19	0.0538-0.1906	12.53-23.24	
Kampung Baharu, Port Dickson, Negeri Sembilan		15.78-33.83	44.21-112.53	0.0731-0.1455	9.71-30.17	
Average shale		45	95	0.3	20	Turekian and Wedepohl[38]
ERL		34	150	1.2	46.7	Long *et al.,*[15]
ERM		270	410	9.6	218	
ISQG-low		65	200	1.5	75	Chapman *et al.,*[14]
ISGQ-high		270	410	9.6	218	

Conversely, high concentration of Cu throughout the sediment core at Port Dickson station indicated pollution of recent years as contaminants from the sediment-water interface are always incorporated into the top sediment first before sinking into deeper layer[39]. Cu enrichments might probably be due to the boat maintenance and cleaning, application of antifouling paints and craft fuelling 5. Antifouling agents were applied to kill and remove sessile animals and plants attached to boats and ships as they need regular expensive removals, decreases speed and causes drag leading to an increase in fuel consumption 1. Moreover, the extensive hotels and condominiums development back in the 1990s might have attributed to the degradation of sediment in the area[40]. The beach was also reported to be polluted from intense beach activities, while the clear sea became a turbid mess of brown water[40]. Similar as Zn, Cu is vital for metabolic processes[26] but high amount of long-term exposure could lead to diarrhoea, dizziness, headache and vomiting and this is likely to happen if humans were to consume contaminated seafood harvested from polluted breeding grounds[8].

Pollution status assessment

An average shale values from Turekian and Wedepohl[38] were applied in Igeo determination in order to determine and define metal contamination in our sediment cores by comparing current concentrations with preindustrial levels. Most of our stations have negative values of Igeo indicating that the core sediments were unpolluted (Figure 3).

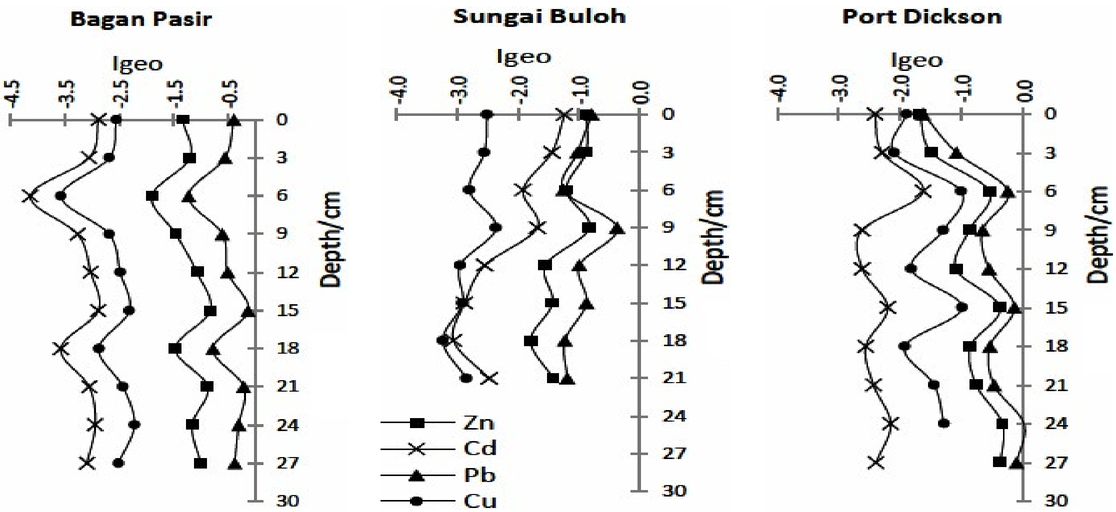

Fig. 3. Geo-accumulation index, Igeo of Zn, Cd, Pb, and Cu in core sediment of Bagan Pasir, Sungai Buloh and Port Dickson stations

The determination of the Contamination Factor (CF) is an important aspect to know the degree of heavy metals risk to the environment in relation to its retention period[36]. The result of Igeo on Pb was further supported by CF output which classified sediments as moderately contaminated with the metal at certain depths in all stations instead of several stations. While the CF of Zn, Cd, and Cu were observed to have mostly less than one indicating low contamination factor (Fig. 4). Overall, the CF values in these stations posed a low to medium potential ecological risk in the sediment.

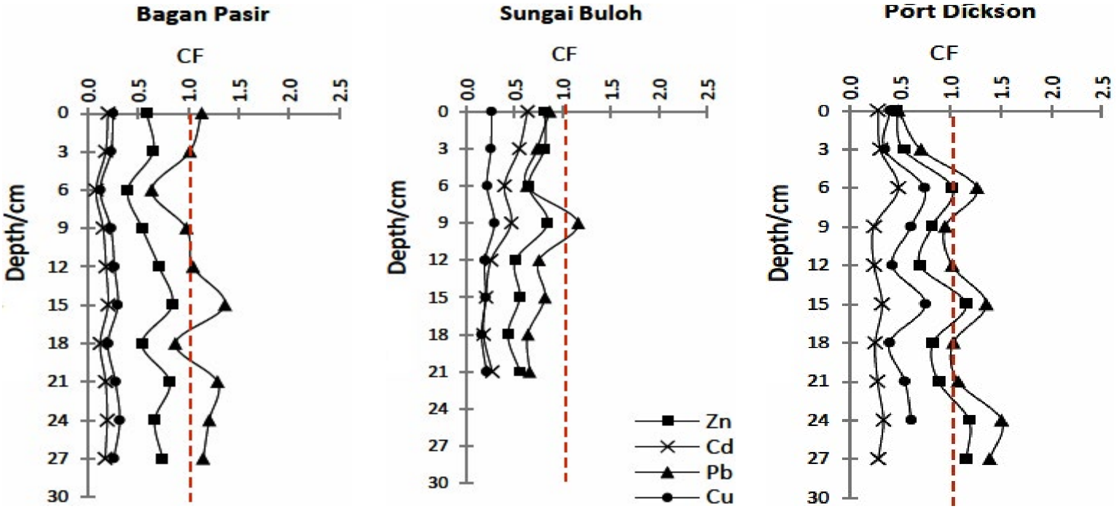

Fig. 4. Graph of Contamination Factors of Zn, Cd, Pb, and Cu against depth of core sediment of Bagan Pasir, Sungai Buloh and Port Dickson stations

According to Tomlinson *et al.,*[41] PLI>1 represent the starting point of sediment quality deterioration. The PLI values of less than one confirmed Igeo and CF output by classifying the sediment cores in all locations as not polluted (Table 5).

Table 5: Depths with its respective Pollution Load Index, PLI of core sediment of Bagan pasir, Sungai buloh and Port dickson stations

Depth, cm	Bagan pasir	Sungai buloh	Port dickson
0-3	0.43	0.59	0.40
3-6	0.41	0.54	0.45
6-9	0.23	0.43	0.83
9-12	0.37	0.60	0.58
12-15	0.44	0.37	0.52
15-18	0.51	0.37	0.79
18-21	0.33	0.30	0.54
21-24	0.48	0.38	0.62
24-27	0.47		0.78
27-30	0.44		0.67

Statistical analysis

The One-way ANOVA tested the concentrations of metals between stations with 95% confidence interval. Table 6 showed the Fisher's F test where the probability corresponding to the F value is 0.0001 for Zn, Cd, Pb, and Cu. This means we would take 0.01% risk to conclude the null hypothesis (no different of heavy metals concentration in all stations) is wrong. Consequently, we could suggest that the concentrations of Zn, Cd, Pb, and Cu in all stations during this study were significantly different.

At Bagan Pasir station, the pH value of the sediment core was ranged from 7.36 to 7.93, while at Sungai Buloh station, the pH value of sediment core ranged from 6.13 to 7.48 and at Port Dickson the pH value of the sediment core ranged from 7.13 to 7.80 (Table 3). It was reported that metal distributions in sediments can directly be changed by the sediment pH[42]. The correlation between metals and pH values in the present study showed a negative to weak correlation at Bagan Pasir station (Table 6). We found that the negative correlation between all metals to the sediment pH were significant. The moderate correlation between Zn-pH and Pb-pH of sediment at Port Dickson was also significant (Table 6).

Table 6: ANOVA table according to elements determined in sediment.

ANOVA	Source	DF	Sum of squares	Mean squares	F	Pr>F
Zn	Model	14	51413.097	3672.364	10.178	<0.0001
	Error	122	44017.633	360.800		
	Corrected Total	136	95430.731			
Cd	Model	14	0.284	0.020	8.982	<0.0001
	Error	122	0.276	0.002		
	Corrected Total	136	0.560			
Pb	Model	14	3101.068	221.505	10.400	<0.0001
	Error	122	2598.433	21.299		
	Corrected Total	136	5699.502			
Cu	Model	14	6211.988	443.713	21.511	<0.0001
	Error	122	2516.514	20.627		
	Corrected Total	136	8728.502			

At Bagan Pasir station, a strong correlation found to be significant ($p<0.05$) between most of the metals. The strong correlation between metals except for Zn-Cd (moderate) suggesting a similar source of metals from fertilizer and pesticide application in the agricultural activities (palm oil estate) and leaded fuel from boat activities surrounding the area[43,44,45]. As for Sungai Buloh, metal was strongly (Zn-Cd, Zn-Cu, Cd-Cu) and moderately (Pb-Zn, Pb-Cu) correlated (Table 6) and all correlations were significant ($p<0.05$). This correlation probably means that the metals input at Sungai Buloh station from slightly similar sources, mobility mechanisms as well as accumulation processes in the sediments[8]. Meanwhile at Port Dickson station, moderately (Cu-Zn, Cu-Cd, Cu-Pb) and weak (Cd-Zn, Cd-Pb) correlated metals was mostly found and all the correlation between metals were significant ($p<0.05$). This moderate and weak correlation indicated the metals could be input from different sources either natural or anthropogenic input. This makes sense as the Port Dickson coastline development is continuously growing, hence, keep on enriching the coastline with contaminants. The strongest correlation between Zn-Pb was the same as in Bagan Pasir and Port Dickson stations might be due to the input of Zn from agricultural practices at Bagan Pasir and could be attributed to domestic wastewaters, cement production, and atmospheric emissions from nonferrous metals from the active urbanization along the Port Dickson coastline[8].

Table 7: Correlation of metals (Zn, Cd, Pb and Cu) according to our location of sampling. Values in bold are significant with significance level alpha=0.05

Location	Elements	Zn	Cd	Pb	Cu	pH
Bagan Pasir	Zn	1				
	Cd	0.7741	1			
	Pb	0.9148	0.8970	1		
	Cu	0.8264	0.9146	0.9319	1	
	pH	-0.4547	-0.3003	-0.3935	-0.1301	1
Sungai Buloh	Zn	1				
	Cd	0.9306	1			
	Pb	0.6390	0.4061	1		
	Cu	0.9760	0.8576	0.7533	1	
	pH	-0.7805	-0.9011	-0.1669	-0.6513	1
Port Dickson	Zn	1				
	Cd	0.3768	1			
	Pb	0.9750	0.3663	1		
	Cu	0.6616	0.6186	0.6004	1	
	pH	0.7754	-0.0989	0.7364	0.2898	1

CONCLUSION

The vertical profiles concentration of Zn, Cd, Pb, and Cu in sediment cores at a few selected stations along the west coast of Peninsular Malaysia (Bagan Pasir, Sungai Buloh, and Port Dickson stations) was studied. The range of metal concentrations were slightly similar at all stations except for Cu, which found higher at the Port Dickson station. A pollution status assessment has revealed that all these sediments were not polluted and rarely give an adverse effect on the environment and biota. However, an increase of metal distributions throughout the sediment core at Sungai Buloh station is needed to be concerned due to the increasing input of man activities along the river of Sungai Buloh in recent a few years.

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