E3S Web of Conferences **34**, 02018 (2018) https://doi.org/10.1051/e3sconf/20183402018
CENVIRON 2017

The Study of Heavy Metals on Sediment Quality of Kuala Perlis Coastal Area

A.A. Ahmad Zubir[1], *F.N.* Mohd Saad[1*], and *F.A.* Dahalan[1]

[1]School of Environmental Engineering, Universiti Malaysia Perlis, 02600 Arau, Perlis, Malaysia

Abstract. The contamination of heavy metals gives bad implications to the aquatic environment. Thus, a study was conducted to assess the sediment quality by using different contamination indices such as Enrichment Factor (EF), Geo-accumulation Index (I_{geo}), and Pollution Load Index (PLI). Each sediment sample was collected at the surface (0-15cm) at 5 locations based on the land use activity; jetty port (A), seaside restaurant (B), roadside area (C), power plant (D) and residential area (E). All samples were undergoes acid digestion and analyzed with AAS. Four elements identified from the sediment samples which are Cr, Cu, Pb and Zn were used to calculate the respective indices. Results show that, the highest EF value of Pb which categorized as very severe enrichment was at point E. Meanwhile minor enrichment was detected at point B for Cu while Cr and Zn at point A. Based on I_{geo} value the sediment quality along Kuala Perlis was in the unpolluted-moderately polluted condition (class 1). As for PLI it shows that the sediment of the coastal area is unpolluted (PLI<1). Therefore, this study revealed that, the main contributor of heavy metals in this area is Pb while the sediment quality of Kuala Perlis was in minor pollution condition.

1 Introduction

The increasing of industrialization and urbanization activities in Kuala Perlis, more waste waters that containing various types of toxic contaminants such as heavy metals were release to the rivers, surface runoff and finally reach the coastal waters [1]. The transportation of the toxic contaminants to the coastal water ways finally deposited in the marine sediment over the time exposure [2].The heavy metals contaminated the aquatic environment, through the bioaccumulation in the sediments thus toxicity of the metals that altered the environmental background conditions. This resulting the long term bad implications to the marine habitat and human health along the food chain in the ecosystem[3]. In order to overcome this problem, a pollution study must be conducted to assess the sediment quality in the coastal area. This assessment is very significance to give an understanding the degree of sediment pollution as well as basic information for future supervision such as monitoring and the mitigation of pollution control. Therefore, this study is aimed to identify the type of heavy metals that polluting the sediment of coastal area

* Corresponding author: farahnaemah@unimap.edu.my

based on the land use activities as well as to assess the pollution degree by using different contamination indices such as Enrichment Factor (EF), Geo-accumulation Index (I_{geo}), and Pollution Load Index (PLI). The enrichment factor (EF) of metals is an indicator reflecting the status and degree of environmental contamination of that metal while Geo-accumulation Index (I_{geo}) shows the various degree of enrichment above the background value ranging from unpolluted to very polluted sediment quality [4]. Pollution Load Index (PLI) is the n^{th} root of the product of n contamination factors (CF) values and also one of the indices to assess the pollution in the sediment [4].

2 Materials and methods

2.1 Sampling location

Five sediment samples pointed as A, B, C, D and E were taken along the coastal area of Kuala Perlis as shown in Fig. 1. The distances between each point approximately 1 km-3 km and these 5 locations were selected based on different land use activity. The sample on each location was collected at the subsurface (0-15cm) by using hand mud auger before taken to laboratory for analysis.

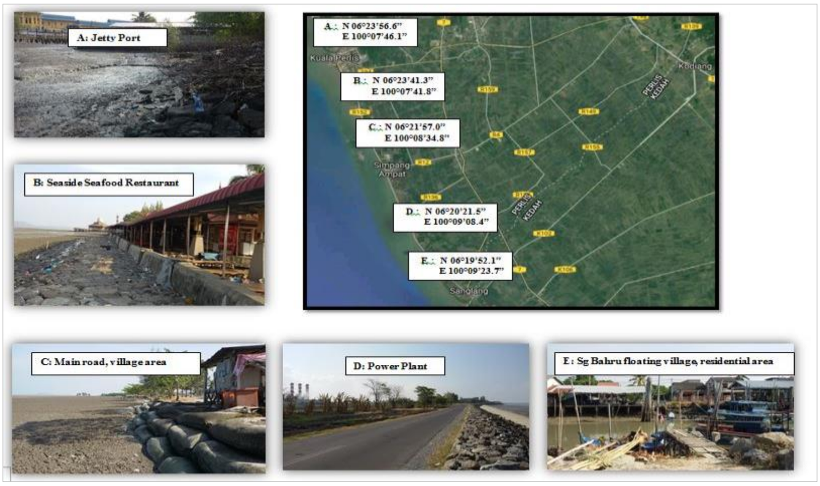

Fig. 1. Location of each sampling point based on land use activity.

2.2 Experimental methods

The sediment samples were oven dried at 110°C for 24 hours. The moisture content of the sediment was measured and the pH value was determined by pH meter. Then, the dried samples were sieved to obtain the particle size distribution of the sediment (ASTM D422-63). Some of the dried samples were also sieved into 60 µm to identify the types of heavy metal by using XRF (X-Ray Fluorescence) analyser [1]. Then, by following aqua regia method [5], 2g of sample was diluted with 25ml deionized water (wetting), and digested with H_2O_2, HNO_3, $HClO_4$, and H_2SO_4. The digested samples were filtered into 50ml of volumetric flask [5,6] and analysed by AAS (Atomic Absorption Spectrometer) to determine the element's concentration.

The quality of sediments in this study was assessed through three ways which are EF, I_{geo} and PLI. In this study, Fe is used as a reference element [10] while average shale concentrations given by Wedepold and Turekian [11] are used as the background concentration for the element tested. Therefore, the equation 1, 2 and 3 are used to calculate EF, I_{geo} and PLI.

$$EF = \frac{\left(\frac{Cn}{Cref}\right)sample}{\left(\frac{Bn}{Bref}\right)} \tag{1}$$

where *Cn* (sample) is concentration of the examined element in examined environment, *Cref* (sample) is the concentration of the examined element in reference environment, *Bn* is the concentration of the reference element in examined environment and *Bref* is the concentration of the reference element in reference environment.

$$I\text{geo}=\text{Log2}\left(\frac{\text{C}n}{1.5\text{B}n}\right) \tag{2}$$

where C*n* is the concentration of metal in examined environment, and B*n* is the concentration of metal in reference/background environment.

$$PLI = (CF1 \times CF2 \times CF3 \times \dots \times CFn)^{\frac{1}{N}} \tag{3}$$

where CF is the contamination factor ($C_{sample}/C_{background}$) of the element while N is the number of metals.

3 Results and discussions

3.1 Sediment characteristics

Sediment moisture content, sediment pH and sediment classification of each sample collected at 5 locations are determined in this study. Table 1 shows the moisture content of each sediment collected at different location. It shows that Point A and B recorded high moisture content with more than 60%. This condition is due to the watery sediment condition. On the other hand, sediment sample taken from Point C, D and E have lower percentage of moisture content ranging from 46% to 51%. Based on the observation, it was found that the sediment in Point C,D and E was a little bit dry thus the water content is lesser than sample in Point A and B.

Table 1. Moisture content and pH value of sediment sample.

Parameter	Point A	Point B	Point C	Point D	Point E
Moisture content (%)	65.7	63.5	46.1	47.5	50.9
pH	7.48	7.51	7.99	8.17	8.01

As stated in Table 1, the sediment pH value in point A, B, C, D and E are 7.48, 7.51, 7.99, 8.17 and 8.01 respectively. Normally, the pH value of marine water is closely to 8.2 since most of the water has some capacity to resists the changes of pH value due to the effects of carbonate-buffer system [7]. Bicarbonate ions which are the main component in the system, were produce from the weathering of silicate or carbonate minerals as rainwater passes through the soil zone [7]. During the hydrolysis of bicarbonate ion, hydroxyl ions are produce to neutralise hydrogen ions thus maintain the pH near the constant level [7].

However, the presence of contaminants carried by the contaminated waterways altering the normal pH conditions. In this study, pH value in point A and B are in the range of 7.1-

7.5 which shows the environment is in slightly alkaline condition. The pH condition was quite similar to the study done by Idris and Ahmad [8] which shows that Juru river sediment condition were also in slightly acidic to slightly alkaline condition which are due to the presence of heavy metals (nickel and chromium) in the sediment. Meanwhile, point C, D and E were exists in moderately alkaline environment since the pH range between 7.6-8.3 which the pH where not mainly altered by the waterways contaminants. According to Singare et al.[9] the sediment can be considered as acidic and hazardous if the pH<6, while it can be also harm the aquatic life if the pH>10 which contaminated with strong base such as NaOH and $Ca(OH)_2$[9]. Therefore, in this study, since the pH is in the range of 7.4 to 8.1 thus, the sediment in each location can be considered as not in hazardous condition.

Particle size distribution is also studied in this study to classify the sediment. Table 2 shows the sieve analysis of the sediment in each point along Kuala Perlis coastal area. According to Unified Soil Classification System (USCS)[10], point A, B, C, D and E gives a similar soil type which is silt and clay. Silt and clay is the smallest grain in soil classification. According to Seyedeh Belin [11] the concentration of heavy metal enriched more in fine sediment particle compared to sand particle. This is due to the adsorption of metal from water to deposit at the bottom sediment are more significant. Besides, the capacity of fine grained particles are high to retain the heavy metals within the sediment compared to other sand fraction types[11-13].

Table 2. Sieve analysis.

Soil type (%)	Sampling Point				
	A	B	C	D	E
Sand	38.5	41.7	24.5	36.9	32.9
Silt & Clay	61.5	58.3	75.5	63.1	67.1

3.2 Pollution assessment

3.2.1 Sediment Quality Guidelines (SQG)

Sediment Quality Guidelines (SQG) has been developed by MacDonald[14] in order to predict the adverse effects in polluted sediment [15]. In this study, the concentration of metals were compared with SQG of PEL: Probable Effect Level, SEL: Severe Effect Level, and TET: Toxic Effect Threshold [14].

Table 3 shows the metal concentration in subsurface sediment of this study area. The results reveal that, the concentration of Cu, Cr, Pb and Zn contain in the sediment sample does not exceed the probable effect level, severe effect level, and toxic effect threshold of the sediment quality guidelines. Thus, this indicates that, the sediment of Kuala Perlis coastal area can be considered as a good quality and will not give the harmful effect to the marine environment.

3.2.2 Contamination Indices : Enrichment Factor (EF), Geo-accumulation Index (I_{geo}), Contamination Factor (CF) and Pollution Load Index (PLI)

Table 4 shows the types of contamination indices and the terminologies[16]. The assessment of sediment contamination in this study was carried out by using the Enrichment Factor (EF), Geo-accumulation Index (I_{geo}), Contamination Factor (CF) and Pollution Load Index (PLI). Enrichment factor (EF) of metals (Cu, Cr, Pb and Zn) on each study point were tabulated in Table 5.

Table 3. Comparison of metals concentration and Sediment Quality Guidelines (SQG).

Point	Heavy metals concentration (mg/kg)			
	Cu	Cr	Pb	Zn
A	0.538	1.182	5.119	1.469
B	0.315	0.367	3.088	0.687
C	0.165	0.588	3.722	0.514
D	0.266	0.414	4.218	0.655
E	0.314	0.058	4.428	0.545
	USEPA : Dry weight (mg/kg)			
PEL	197	90	91.3	315
SEL	110	110	250	820
TET	86	100	170	540

Among the metals studied, Pb gives the highest enrichment in the sediment collected at Point A and E since the EF values are ranging between 25 to 50 which categorized as very severe enrichment. Meanwhile, point C shows that Pb is in the severe enrichment since EF value is in the range of 10-25. The minor enrichment of Zn ($1<EF<3$) was shown in point A,B,D and E while there are no Zn enrichment in point C. There is also minor enrichment of Cr in point A and no enrichment on the other points. For Cu, there are minor enrichment detected at point A, B, E and no enrichment in point C and D. Therefore, it can be seen that there is enrichment of elements in Point A, B, and E which are the Jetty Port, Seaside restaurant and Sg. Bahru Estuary respectively.

Since Pb gives the highest enrichment factor so, it can be considered as the possible contamination from these land use. The shipping and ferries activities that operates daily may incidentally expelled the discharged of fuel and oil spillage directly to the coastal waters [2]. This is because in the marine environment there are two main factors of metal leaching into the waters such as from the anthropogenic activities and the earth natural processes from minerals and the physical characteristics of the sediments [17].

Previous studies proved that, the combustion of fuels by the vehicles and boat activities resulted in the high enrichment of Pb in the sediment [18]. Besides, Ong and Kamaruzzaman[19] also reported that the sediment of eastern coast of Johor resulted from high Pb enrichment due to the natural erosion of earth's surface.

Table 6 shows the results of Geo-accumulation Index (I_{geo}), Contamination Factor (CF) and Pollution Load Index (PLI) of the sediment in 5 locations. For I_{geo} assessment, it shows that Point A gives the highest I_{geo} value followed by Point E, D, C and B. According to the mean of I_{geo} value, all the sediment samples in the study area are in unpolluted- moderately polluted condition and categorized as class 1. As for CF assessment, the result reveals that Point A gives the highest CF value while the lowest of CF value is identified at point B. Overall, it can be concluded that low elements contaminations were detected in the sediments of study area since the CF value are less than 1. As the overall assessment, the Pollution Load Index (PLI) shows the highest value in point A while the lowest was in point D. Since the PLI values in all the sampling points were <1, this has shown that the sediments of Kuala Perlis coastal area are in unpolluted condition.

Table 4. Contamination indices categories and terminologies.

EF		I_{geo}			CF		PLI	
Value	Enrichment condition	Value	Class	I_{geo} condition	Value	Condition	Value	Condition
EF<1	No enrichment	≥0	0	Unpolluted	CF<1	Low CF	>1	Polluted
EF=1-3	Minor enrichment	0-1	1	Unpolluted-moderately polluted	1≤CF<3	Moderate CF		
EF=3-5	Moderate enrichment	1-2	2	Moderately polluted	3≤CF<6	Considerable CF		
EF=5-10	Moderately severe enrichment	2-3	3	Moderately-strongly polluted	CF≥6	Very high CF		
EF=10-25	Severe enrichment	3-4	4	Strongly polluted			<1	Unpolluted
EF=25-50	Very severe enrichment	4-5	5	Strongly-extremely polluted				
EF>50	Extremely severe enrichment	>5	6	Extremely polluted				

Table 5. Enrichment Factor (EF) of metals.

Point	EF value of each metal			
	Cu	Cr	Pb	Zn
A	1.56	1.71	33.31	2.01
B	1.58	0.92	34.79	1.63
C	0.41	0.72	20.56	0.6
D	0.9	0.7	32.06	1.05
E	1.22	0.11	38.86	1.01

Through observation it is believed that the source of pollution in point A and point E are mainly form the shipping and boat activities. Since the boat are operates daily, the coastal water are contaminated with the effluent from the boats such as the oil, fuel and other toxic agent for boat antifouling paints[20]. Point A gives the highest sediment moisture content so, the overlying waters carries the pollutants [21] and finally deposited and settled on the bottom of the sediment. Besides, both point A and E are located at nearby estuary which all the municipal and domestic wastes created by the residents in the area are flown in the waterway before ended up to the sea. On the other hand, the existence of metals in point C are from the surface runoff of the road or the effect of paddy field activities which surrounding the area.

As mentioned by Wahidatul [1]the present of Pb is mainly from the using fertilizers and pesticides in the paddy fields. In point D, the present of Cr, Cu, Zn and Pb might be from the power plant that release the vapour effluent containing metals contaminants to the air. Thus, the metal contains in the air will cause the acid rain at nearby area. These acid rain will effects the costal water quality and finally deposited in the sediment [22].

Table 6. Geo-accumulation Index (Igeo), Contamination Factor (CF) and Pollution Load Index (PLI) of sediments taken from 5 locations.

Point	I_{geo} value of each metal					Cf value of each metal					PLI
	Cu	Cr	Pb	Zn	mean	Cu	Cr	Pb	Zn	mean	
A	0.0023	0.0026	0.0514	0.0031	0.015	0.012	0.013	0.256	0.015	0.074	0.028
B	0.0014	0.0008	0.031	0.0014	0.008	0.007	0.004	0.154	0.007	0.043	0.013
C	0.0007	0.0013	0.0373	0.0011	0.010	0.003	0.006	0.186	0.005	0.050	0.012
D	0.0012	0.0009	0.0423	0.0013	0.011	0.006	0.004	0.211	0.006	0.056	0.011
E	0.0014	0.0001	0.0444	0.0012	0.012	0.007	0.001	0.221	0.005	0.058	0.014

4 Conclusions

This study has shown that the sediment of Kuala Perlis coastal area is currently contain with four elements which are copper (Cu), chromium (Cr), zinc (Zn) and lead (Pb). The result reveal that the highest enrichment of element in the sediment is Pb, thus indicating it as the most contributors of heavy metals in the sediment of Kuala Perlis. The high enrichment of Pb is effected by the land use resulting from the anthropogenic activities that are operates daily in the area. Point A and E were identified to have high metals enrichment since each location has lots of activities that contribute to the release of these metals to the environment. However, according to SQG, the sediments are in good quality since the metal concentration does not exceed the Probable Effect Level (PEL), Severe Effect Level (SEL), and Toxic Effect Threshold (TET). Based on the geo-accumulation index the sediment were consider as class 1 which is unpolluted- moderately polluted condition. While PLI assessment shows that the coastal area is unpolluted sediment.

The author's gratitude goes to the support of School of Environmental Engineering and School of Material Engineering Universiti Malaysia Perlis (UniMAP) for providing the laboratory facilities in conducting this research. In addition, we are also thankful to the Kuala Perlis Maritim Department for providing the schedule and useful knowledge regarding the sea water tidal in Kuala Perlis which are related to the sampling activities.

References

1. N. Wahidatul, A. Zainon, S. A. Mohammed, S. H. Ismail, W. Amiza, Int. J. Civ. Environ. Eng. **12**(6), 28–33 (2012)
2. K. Lias, T. Jamil, S. N. Aliaa, J. Appl. Chem. **4**(1), 48–54 (2013)
3. P. Saikia, S. Das, R. K. Shah, S. Islam, Int. J. Adv. Biol. Res. **5**(2), 150–154 (2015)
4. S. M. Praveena, M. Radojevic, M. H. Abdullah, Int. J. Environ. Sci. Educ. **2**(3), 60–68 (2007)
5. Z. Y. Hseu, Z. S. Chen, C. C. Tsai, C. C. Tsui, S. F. Cheng, C. I. Liu, H. L. Ta, N, Water Air Soil Pollut. **141**,189–205 (2002)
6. E. Geana, A. M. Iordache, C.Voica, M.Culea, R.Ionete, Asian J. Chem. **23**(12), 5213–5216 (2011)
7. L. Radke, http://www.ozcoasts.gov.au/indicators/ph_coastal_waterways.jsp. (2015)
8. A. A. Idriss, A.K. Ahmad, J. Environ. Prot. **4**, 1245–1250 (2013)
9. P. U. Singare, M. P. Trivedi, R. M. Mishra, Mar. Sci. **1**(1), 22–29 (2011)
10. U. Lowell, http://www.dphu.org/uploads/attachements/books/books_2789_0.pdf. (2008)

11. S. Belin, T. Sany, A. Salleh, W. Port, N. Port, S. Port, Water Soil Pollut. **224**, 1476, 2–18 (2013)
12. G. M. S. Abrahim , R. J. Parker, Environ. Monit. Assess. **136**, 227–238 (2008)
13. E. P. Nobi, E. Dilipan, T. Thangaradjou, K. Sivakumar, L. Kannan, Estuar. Coast. Shelf Sci. **87**(2), 253–264 (2010)
14. D. D. MacDonald, C. G. Ingersoll, T. A. Berge, T. A. Berger, Arch. Environ. Contam. Toxicol. **39**(1), 20–31(2000)
15. A. Naji , A. Ismali, Environ. Asia **4**(1), 30–38 (2011)
16. A. S. Likuku, K. B. Mmolawa, G. K. Gaboutloeloe, Environ. Ecol. Res. **1**, 2, 32–402 (2013)
17. B. M. Mwashote, West. Indian Ocean J. Mar. Sci. **2**, 1 25–34 (2003)
18. S. Sabri, M. I. M. Said, S. Azman, Malaysian J. Anal. Sci. **18**(1), 37–42 (2014)
19. M. C. Ong, B.Y. Kamaruzzaman, Am. J. Appl. Sci. **6**(7), 1418–1423 (2009)
20. E. J.A.McCoy, L. T. Johnson, http://ucanr.edu/sites/coast/files/59476.pdf. (2010)
21. M. E. Goher, H. I. Farhat, M. H. Abdo, S. G. Salem, Egypt. J. Aquat. Res. **40**(3), 213–224 (2014)
22. A. Singh, M. Agrawal, J. Environ. Biol. **29**(1), 15–24 (2008)