Heavy metals level in the surficial sediment from Perai River of Penang, Malaysia

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Abstract. Perai river is one of the important rivers to Penang and Kedah states. Many industries are located along the river that flows to the Strait of Malacca. In order to gather the status of pollution along the river, a total of 47 stations were established to measure the heavy metals content and the sediment characteristics. Findings show that finer sediments had dominated all sampling sites as samples are mostly muddy sediment. The heavy metal concentration in the surficial sediment was analyzed using the Inductively Coupled Plasma Mass Spectrometer after the Teflon Bomb digestion method. The average concentration for Zn, Cr, Cu, Cd, Pb were 74.7±33.3, 66.0±28.1, 21.8±9.05, 0.42±0.32, and 28.6±6.84 μg/g dry weights, respectively. Generally, the concentration of metals studied seemed to be controlled by natural processes. This is proved by the enrichment factor, categorized as a deficiency to minimal enrichment, and can be concluded to be the main source from the lithogenous in origin. The sources of the heavy metals in some of the stations in the Perai river are speculated from the nearby urban runoff, industry activities along with the river, fishing and shipping activities, and land transportation emission may also accumulate for the pollution in the river.

Keywords: enrichment factors, heavy metals, ICP-MS, pollution, Straits of Malacca

1. Introduction
The river is the main communication and transportation where trade and social meetings happen [1]. Many major cities were evolved from small settlements situated at the river mouth and along the riverbanks [2]. Nowadays, the rivers are not just for transportation purposes but also other purposes such as tourism, water supply, and agriculture activities. The river is a major pathway for delivering terrestrial materials [3] from the inland to the coastal residential area. The coarse-grained riverbed sediments and fine-grained suspended sediments act as a useful medium to determine the erosion and weathering in the source area to understand supergene geological processes [4]. Pollution is one of the biggest threats to the river. The pollutants can come from natural and anthropogenic sources. Pollutants such as heavy metals can severely affect aquatic organisms and human being health [5].

Sediment is one of the major components of the river. The sediment is formed from the precipitation of the sand, organic and inorganic particles through weathering processes and biological activities. Hence, it resulted in a loose and unconsolidated form. In general, these particles were derived naturally...
through the weathering and erosion of the rocks. Pollutants can always be detected through the sediment due the sediment is a good geomarker. Sediment can be categorized as the ultimate sink for heavy metals, but it is not permanent [6].

Heavy metals are classified among the most dangerous and toxic groups of anthropogenic environmental pollutants due to their toxicity, persistence and bioaccumulation in the environment [7]. Heavy metals are elements that have free electrons. In sediment, the heavy metals present in different chemical forms and generally exhibit different physical and chemical behaviours in chemical interaction, mobility, biological availability, and potential toxicity [8]. Currently, heavy metals contamination has become an environmental problem in terrestrial areas throughout the world.

Therefore, this study aims to examine the concentration of the Zn, Cr, Cu, Cd, Pb concentrations in the Perai river sediment and further calculate the pollution status using the Enrichment Factor (EF) approach.

2. Materials and Methods

2.1. Study area
Sampling was conducted at the Perai river, Penang, northern Peninsular Malaysia (Figure 1). A total of 47 sampling stations were deployed in the Perai River. The position of each sampling station was taken by using the Global Positioning System (GPS). Station R40 to R47 is classified as the upstream of the river while station R1 to R10 is classified as the downstream area of the river.

![Figure 1. Sampling sites for sediments in the Perai river, Penang.](image)

2.2. Sample collection
The sampling station location was recorded using the Global Positional System (GPS) during the sampling period. The surface sediment samples were collected using the Ponar Grab Sampler. The top of the sediment was removed with the plastic spoon to minimize or prevent any contamination. The outer part of the sediment was removed and the inner sediment was taken for further analysis. After the collection, the sediment was immediately put in the polyethylene bags and preserved at low temperature until further analysis.
2.3. Sample preparation
All the frozen samples were taken out and defrosted at room temperature for few hours. The samples were transferred into the petri dish and dried using the oven at 60°C until a constant weight was achieved. The dried samples were kept in a clean plastic container and store in dry condition before further analysis.

2.4. Sample digestion
The samples were digested for the total heavy metals content using the published methodologies with some modifications on the techniques [9-11]. A total of 50mg of samples were transferred into the Teflon beaker. The samples were heated in the sealed Teflon vessel with a mixture of acids (HF, HCl and HNO₃). The Teflon vessel was kept in an oven using 100°C for eight hours. Then the samples were left for cooling to room temperature. After that, the samples were transferred to a polypropylene test tube and added to 10 mL in volume using the deionized water. The measurement was carried using an inductively coupled plasma spectrometer, ICP-MS model Perkin Elmer Elan 9000 to obtain the precise results of the heavy metals concentration. This procedure was also applied to Standard Reference Material (SRM1646a) Estuarine Sediment to determine the accuracy and precision of the results.

2.5. Data analysis
The Enrichment Factor (EF) is a popular evaluation as it identifies and quantifies human interference to the element cycle [12]. The EF differentiates between the metals originating from anthropogenic sources and the natural process based on the degree of anthropogenic influence [13]. The EF of the heavy metals can be calculated using the formula below:

\[
\text{Enrichment Factors (EF)} = \frac{(\text{Element concentration} / \text{background concentration})_{\text{sample}}}{(\text{Element concentration} / \text{background concentration})_{\text{background}}}
\]

There is a total of five categories based on the EF calculation (Table 1) [13] as follows:

| EF Range | Contamination category                      |
|----------|--------------------------------------------|
| EF < 2   | Deficiency to minimal enrichment           |
| 2 < EF < 5 | Moderate enrichment                        |
| 5 < EF < 20 | Significant enrichment                     |
| 20 < EF < 40 | Very high enrichment                      |
| EF > 40  | Extremely high enrichment                 |

Further to evaluate the relationship between heavy metals and sediment characteristics, a matrix of Pearson correlation [14] was used and shown in Table 2. The correlation values given in \( r \) were calculated by SPSS statistic software.

| Correlation coefficient (\( r \)) | Strength of relationship                  |
|-----------------------------------|-------------------------------------------|
| < 0.20                            | Very negligible relationship              |
| 0.20 – 0.40                       | Low correlation; definite but weak related |
| 0.40 – 0.70                       | Moderate correlation; substantial related |
| 0.70 – 0.90                       | Moderate correlation; substantial related |
| > 0.90                            | Very high correlation; very reliable relationship |
3. Results and Discussion
The distribution of the heavy metals studied is shown in Figure 2. As for Zn, station R29 had the highest concentration while station R3 had the lowest concentration of Zn. The high concentration of Zn in R29 may be due to the port activities such as the loading and unloading materials from the fishing boat and antifouling applications in the river [15]. Other anthropogenic sources such as mining activities, urban and agricultural runoff [16-17]. This can be supported by the environmental setting of station R29, located near the urban area. There is the possibility where waste containing Zn is being emitted into the river. The lowest concentration is observed in the estuary and coastal area because the estuary is where the freshwater output and seawater input are happening in that area. Dilution of the chemical content in that area may be occurred due to this phenomenon [18]. The mining process of the Zn can also produce waste materials such as gangue, where the gangue minerals can be the silica (SiO₂) as the quartz, aluminium oxide (Al₂O₃), calcite (CaCO₃) can also be harmful to human beings [19].

Figure 2. The spatial distribution maps of heavy metals concentration in Perai river, Penang.
The sources of the Cr in the aquatic environment can come from the mineral weathering process and also the river and atmospheric input [20-21]. The river input represents the terrestrial origin due to the high affinity of the silicates. Station R41 had the lowest concentration while station R33 had the highest concentration of Cr. From the results, lower concentrations of Cr are normally in places less or not present in any urban and industrial areas. The main sources of the Cr can originate from industrial activities and laundry activities [22]. The higher concentration of Cr in the Perai river might be due to factories along the river. Waste that contains the Cr substances is emitted from the factory to the river. Other possible sources of the Cr to be higher can be the painting activities such as the boat painting and the use of anti-rust paint consisting of Cr as the components [23].

The highest concentration of Cu is recorded in station R6 while the lowest concentration of Cu is in station R3. The increased concentration of Cu in the Perai river may be due to the port activities such as loading and unloading the materials from the boat, cleaning the boat process, antifouling painting applications, and other related activities [24]. The runoff from urban areas can also influence the concentration of Cu in the environment. Copper is usually associated with industrial sectors and the waste is discharged to the river nearby [25]. Station R6 has the highest concentration of Cu compared to other stations due to factories located in the area. The lower concentration of Cu in the coastal area might be due to seawater dilution after the pollutants are discharged from the river [18].

The lowest concentration of Cd is located in station R42 while the highest is located in station R6. Similar to other metals, the possible sources for increasing the concentration in the Perai River are industrial activities and urban runoff. It can be proven from the experiment results, the higher concentration of Cd is located in the urban area and factory activities. Waste and runoff from these sources are contributing to the increases in the concentration of Cd in the River [26]. Other anthropogenic activities may also lead to increases in Cd concentration, such as mining activities [27] and shipping activities [28]. This is a concern situation where continuous monitoring should be employed to observe the current state of the environment to minimize the impacts on humans.

The possible sources of Pb in Perai River may be due to the use of leaded gasoline in the ships and boats. Leaded gasoline is commonly used in the industry [29] due to the commonly found and the prices are lower compared to other types of gasoline. Station R17 had the highest concentration of Pb due to a dockyard located in that area that may emit waste such as leaded gasoline and paint into the river. In contrast, station R2 had the lowest concentration due to dilution of the metals by seawater after being discharged from the river. Other sources for the Pb may also be due to the emission from the vehicles on the road [30]. The Perai river is near some of the main road where many vehicles pass through the road each day where the emission of leaded waste to the river may occur.

The suitability of the Li and Al to be the geochemical normalizer was tested in the Perai river surficial sediments. The values of the Pearson’s correlation between Li and Al coefficients versus the heavy metals are shown in Table 3. The stronger positive covariance of all studies of heavy metals with Li over Al shows that Li is a better normalizer for this evaluation in Perai river surficial sediments.

### Table 3. The comparison correlation coefficient of selected heavy metals with Li and Al in surficial sediments from Perai river, Penang.

| Heavy metals | Zn | Cr | Cu | Cd | Pb |
|--------------|----|----|----|----|----|
| Li           | 0.482 | 0.358 | 0.476 | -0.286 | 0.133 |
| Al           | 0.153 | -0.005 | -0.038 | -0.484 | 0.310 |

To be a metals normalizer, stronger correlated to the fine sediments and not dependent on the anthropogenic sources is a must [31]. The concentration of Li in Perai River surficial sediment has a better relation with the sediments grain sizes with the r-value = -0.009 compared to Al, r = -0.189 (Figure 3), which is satisfied with the qualification demand this contamination status assessment in Perai River of Penang.

Lithium also has a higher affinity to be the alternative for Al [32]. Other than that, the Li meets the
basic requirement for use as the normalizing agent for heavy metals because of several factors, namely: 1. It is a lattice component of fine-grained major trace-metal-bearing minerals such as the clay minerals; 2. it also reflects the granular variability of its host mineral component; and 3. it is a conservative element.

Figure 3. Relationships between concentrations of Li and Al with the mean size of sediment in Perai river, Penang.

After all considerations, the Li is used as the reference element in the enrichment factor (EF) calculation to gain more information regarding the level of pollution or contamination in Perai river surficial sediments. From Table 4, based on the average value, all of the five metals are categorized as a deficiency to minimal enrichment. This means that the metals can be considered dominantly from the lithogeneous or terigenous in that area. This EF value indicates that the elements were crustal origin and did not significantly contribute to the anthropogenic sources. Natural sources such as weathering can contribute to the content of metal in the area. However, some sampling locations have higher EF, especially Cd and Pb indicate that anthropogenic input might influence that area.

Table 4. EF value with respect to crustal ratios in surface sediment of Perai river, Penang.

| Element | Min-Max value | EF value | Contamination category          |
|---------|---------------|----------|---------------------------------|
| Zn      | 0.04-0.43     | 0.22±0.09| Deficiency to minimal enrichment|
| Cr      | 0.04-0.65     | 0.22±0.11| Deficiency to minimal enrichment|
| Cu      | 0.05-0.33     | 0.14±0.06| Deficiency to minimal enrichment|
| Cd      | 0.00-4.11     | 0.50±0.68| Deficiency to minimal enrichment|
| Pb      | 0.25-1.52     | 0.43±0.19| Deficiency to minimal enrichment|

4. Conclusion
The level of heavy metal contamination in the Perai river was assessed by measuring the total concentration of the metal in the surficial sediment. The study of enrichment levels throughout most samples demonstrates the low EF value for all the metals selected in this study. It is proven that the selected heavy metals to be deficient to minimal enrichment with the EF values ranging from 0.14 to 0.50. Some of the stations show a relatively high concentration of metals. This might cause by external sources such as the emission from the industry activities and runoff from the nearby urban area.

Acknowledgments
This research was conducted with funding from the Ministry of Higher Education under the Talent and Publication Enhancement Research Grant, TAPE-RG 55188. First of all, the authors wish to acknowledge their gratitude to the anonymous reviewers who gave freely time and effort, constructive recommendations that enhanced the value of this manuscript. The authors also would like to thank Mr. Joseph Bidai for his assistant in detecting heavy metals using ICPMS at the Institute of Oceanography and Environment.
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