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Geostatistical Distribution and Contamination Status of Heavy Metals in the Sediment of Perak River, Malaysia

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Abstract: Heavy metal pollution is one of the major environmental issues in recent decades owing to the rapid increase in urbanisation and industrialisation. Sediments usually act as sinks for heavy metals due to their complex physical and chemical adsorption mechanisms. In this study, heavy metals like lead (Pb), Zinc (Zn), Cadmium (Cd), Copper (Cu) and Iron (Fe) in the surface sediment from 15 location (upstream and downstream) on the Perak River, Malaysia were investigated by means of inductively coupled plasma optical emission spectroscopy (ICP-OES). The geostatistical prediction map showed the range of Pb, Zn, Cd, Cu and Fe concentration in upstream area was 14.56–27.0 µg/g, 20–51.27 µg/g, 1.51–3.0 µg/g, 6.6–19.12 µg/g and 20.24–56.58%, respectively, and in downstream areas was 27.6–60.76 µg/g, 49.04–160.5 µg/g, 2.77–4.02 µg/g, 9.82–59.99 µg/g and 31.34–39.5%, respectively. Based on the enrichment factor and geoaccumulation index, Cd was found to be the most dominant pollutant in the study area. Pollution load index, sediment quality guidelines and sediment environmental toxicity quotient data showed that the downstream sediment was more polluted than the upstream sediment in the Perak River. The multivariate analysis showed that Pb, Zn and Cu mainly originated from natural sources with minor contribution from human activities, whereas Fe and Cd originated from various industrial and agricultural activities along the studied area.

Keywords: heavy metals; sediment; risk assessment; geostatistical distribution; multivariate analysis; Perak river

1. Introduction

The pollution of the aquatic environment by heavy metals is a global problem because these metals are durable and most have toxic effects on living organisms when they are above certain concentrations [1,2]. Heavy metals produced by various activities such as chemical manufacturing, mining, municipal effluents and other anthropogenic activities are ultimately transferred to the aquatic environment [3]. Usually river sediment is a great adsorptive sink for heavy metals and the high concentrations in sediments can be lead to high concentration in living organisms through the food chain because of their nondegradable nature [4,5]. Besides bioaccumulation into the food chain,

heavy metals that seep into sediments and can contaminate drinking water wells, as well as harm the consumers of that water [6]. Heavy metals are unable to be degraded either biologically or chemically hence they may be transported over long distances [2]. Considering their persistence and transferable properties, a distribution analysis of heavy metals in sediment could be performed to analyse the anthropogenic impacts on heavy metal pollution along with a risk assessment. An analysis from upstream to downstream sediments is necessary because downstream regions show much more stable pollutant levels compared to upstream and also water column [7].

Metal concentrations in sediments may not increase with decreasing sediment particle as high concentrations of metals have also been found in larger size fractions of sediment [8]. These exceptions probably demonstrate that metal concentrations in sediment are not controlled exclusively by particle size. There are several other factors such as quality and quantity of organic matter, distribution of different mineral phases and metal loading that may also control metal speciation, distribution, accumulation and bioavailability in coastal sediments [9]. Most contaminants, notably metallic compounds, were found to be accumulated in the sediment through complex physical and chemical adsorption mechanisms [10].

Sungai Perak is the 'River of Life' for the Perak State in Malaysia. It flows over 400 km from a 15,000 km^2 catchment that covers 70% of the state lands and divides the state into two nearly equal halves, and thus forms its natural backbone. This river of life is special in many ways [11]. However, since gaining independence in 1957 and, more recently, driven by Vision 2020, Malaysia is expanding its manufacturing and construction activities which are the main stimuli for the economic growth of the country [12]. Heavy metals produced by various activities around the Perak river, such as chemical manufacturing, municipal effluents and other anthropogenic activities, have contributed to deterioration in the water quality of this water source [13]. Recently, some newspapers reported that there are some problems regarding the Perak River, and news reports also showed that the Perak River is experiencing these problems (Supplementary Materials: Appendix A). Considering the socioeconomic significance of the Perak River as well as the process of sediment acting as a scavenger agent for heavy metals, it is vital to study the distribution and contamination of heavy metals in the surface sediment of the Perak River to understand the natural baseline levels to achieve and monitor the changes that may be affected by anthropogenic activities in the near future.

The present study aimed to find the correlations of heavy metal content in sediment with physicochemical properties such as pH, sediment organic matter content (SOM) and anthropogenic activities, along with geostatistical distribution from upstream to downstream. More specifically, the objectives of this research work were to apply a wide range of extensively used and accurate environmental quality indices like enrichment factors (EF), geoaccumulation index (Igeo), pollution load index (PLI), sediment quality guidelines (SQG), environment toxicity quotient (ETQ) and multivariate statistical analysis to assess the associated ecological risks of the heavy metals and as well as to determine the sediment quality. The present study will help to establish the position of heavy metals present in sediment and their contamination and distribution along the Perak River. Future environmental planning strategies of the Perak River can be made through the understanding the distribution of heavy metals, and the present study can play a significant role in providing this baseline information.

2. Materials and Methods

2.1. Description of the Study Area

Among the 14 states of Malaysia, Perak has the second largest land area (21,006 km^2) and is surrounded by Kedah and Thai state (to the north), the Strait of Malacca (to the west), Kelantan and Pahang (to the east) and Selangor (to the south). Perak has a tropical rainforest climate and there is no dry season. The temperature fluctuates on average from 32 °C to 34 °C during the summer, while

it ranges from 22 °C to 24 °C during the winter [11]. The Perak River is one of the largest raw water sources for the whole state of Perak.

2.2. Sample Collection and Preservation

A total of 45 surface sediments sampled were collected from 15 different sample locations starting from upstream (S1–S7) to downstream (S8–S15) of the Perak River were collected in the year of 2015. Fifteen different stations were selected to show the distribution and contamination of heavy metals in surface sediments of the Perak River. The details of the sampling stations on the Perak River are shown in Figure 1. Samples of approximately 200 g of river bed sediment were taken at depths of 0 to 5 cm using a scoop. Each sediment sample was obtained by randomly collecting three times at each sampling point. The samples were stored in clean polyethylene bags and kept at 4 °C prior to analysis. Sediment samples were freeze-dried to obtain constant weights, homogenised by grinding in an agate mortar, sieved through a 106-µm aperture nylon sieve, and stored in labelled glass bottles until chemical analyses were carried out [14].

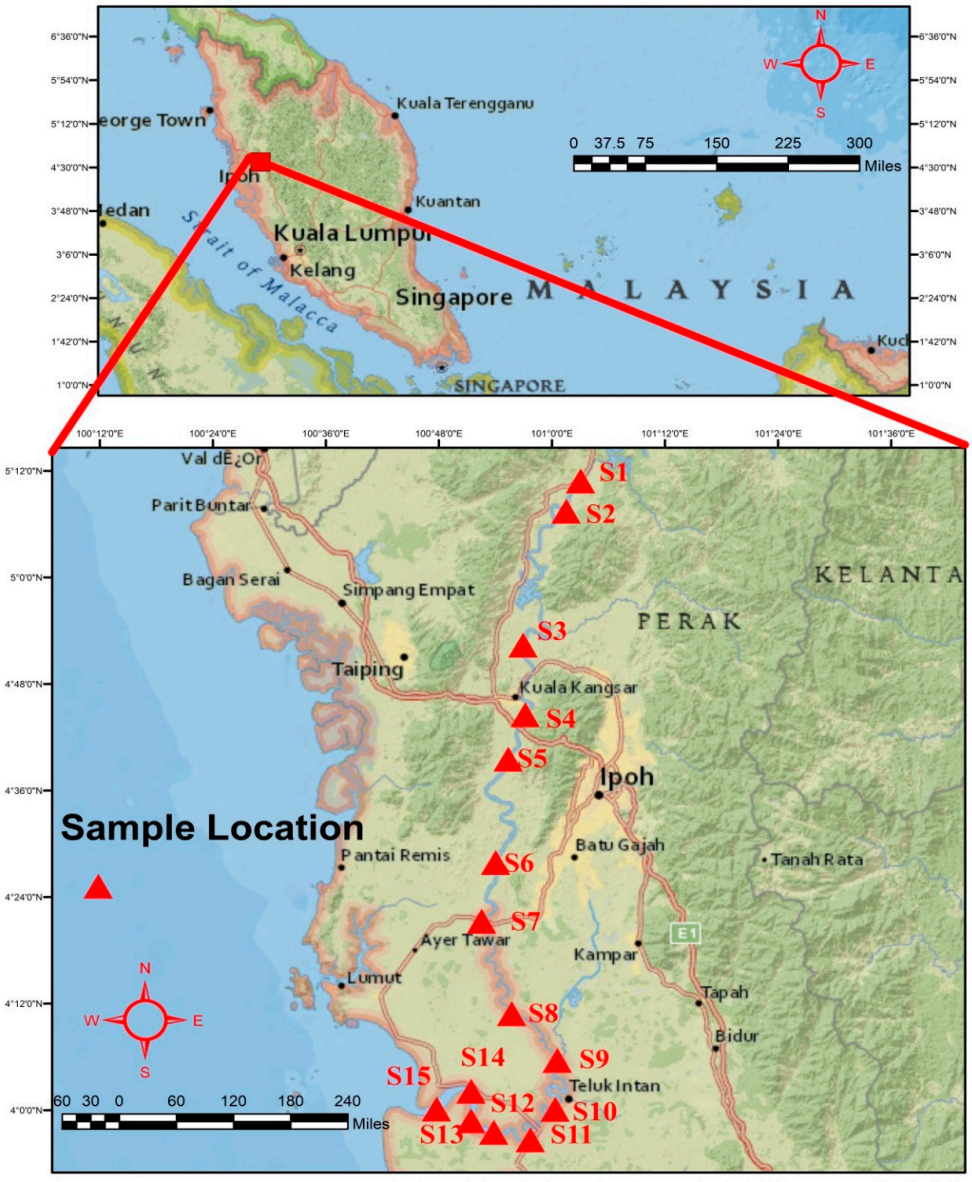

Figure 1. Geographic location of the study area along with the sampling sites in Perak River, Malaysia.

2.3. Analysis of Sediment Physicochemical Parameters

The pH of the sediments samples were measured in a sediment-to-water ratio of 1:5 by means of a pH meter [14]. To determine the organic matter content of the sediment samples, the loss on ignition method was used with Equations (1) and (2) [15,16].

$$LOI(\%) = \frac{\Delta m}{ms} \times 100 \quad (1)$$

where,

$$\Delta\ m = (m_s + m_t) - (m_c + m_t) = m_s - m_c \quad (2)$$

where, Δ m is the loss of mass of the sediment after ignition at 550 °C (g), m_{s-} is the mass of the sediment dried at 105 °C (g), m_{t-} is the mass of the crucibles ignited to 550 °C (g) and m_{c-} is the mass of the sediment ignited to 550 °C (g). The total concentrations of metals in the sediments were determined by means of ICP-OES [17].

Quality assurance (QA) and quality control (QC) made certain that reliable data were produced consistently with minimum error for carrying out the research study. For each set of experiments blanks, certified reference materials (CRMs) and samples were run and corrections applied where necessary. All of the experiments were carried out in three replicates to eliminate any batch-specific errors and only average values were reported [18]. All laboratory equipment used was washed with phosphate-free soap, double-rinsed with distilled water and left in 10% HNO_3 for 24 h to prevent contamination. Calibration, use of blanks, use of spike samples, performance characteristics of the procedure and reporting of outcome were the significant aspects of QA and QC in the study. The recovery of the total digestion procedure i.e., the reliability of the procedure was at a range of 93 to 110%, indicating the reliability of digesting procedure. (Results are shown in Appendix B).

2.4. Assessment of Heavy Metals Pollution in Sediments

2.4.1. Enrichment Factor (EF)

The enrichment factor (EF) is a powerful tool used to elucidate the degree of pollution in sediment with respect to a background value [19]. Several authors have successfully used iron (Fe) to normalise heavy metal contaminants [20]. EF was calculated using the Equation (3).

$$\mathrm{EF} = \frac{\left(\frac{C_M}{C_{Fe}}\right)_{Sample}}{\left(\frac{C_M}{C_{Fe}}\right)_{Background}} \quad (3)$$

where, $(C_M/C_{Fe})_{sample}$ is the ratio of metal and Fe concentration of the sample and $(C_M/C_{Fe})_{background}$ is the geochemical background value of metal to Fe.

2.4.2. Geoaccumulation Index (Igeo)

The I_{geo} index allows the evaluation of contamination by correlating the obtained current concentration of metals with their pre-industrial concentrations. I_{geo} index for the metals was determined using Equation (4) [21]:

$$\mathrm{I}geo = \log 2\left(\frac{\mathrm{C}n}{1.5Bn}\right) \quad (4)$$

where, C_n is the concentration of metals in soil samples and B_n is the geochemical background concentration of the metal (mg/kg) of 0.3 for Cd, 45.0 for Cu, 46,700.0 (4.67%) for Fe, 20.0 for Pb and 95.0 for Zn [22]. The factor (1.5) is the background matrix correction factor due to lithological variations.

2.4.3. Pollution Load Index (PLI)

The PLI is an empirical index that provides a simple and comparative way to evaluate levels of heavy metal pollution [23]. The CF ratio was estimated by dividing the concentration of each metal in the soil by the background value [20] PLI was calculated using Equation (5).

$$PLI = {}^{n}\sqrt{(CF_1 \times CF_2 \times CF_3 \times \ldots \ldots \times CF_n)} \quad (5)$$

where, M_{etal} = metal concentration obtained from sample, $B_{ackground\ value}$ = geochemical background/baseline value of the metal and n = number of metals.

2.4.4. Sediment Quality Guidelines (SQG)

Sediment quality guidelines (SQG) represent the concentration limits of contaminants in sediments [24,25]. The Australian and New Zealand Environment Conservation Council (ANZECC) [26] applies the terminology of sediment quality guideline values (SQGVs) based on the biological effect of contaminants on inhabitants, which was achieved by statistical data evaluation of concentrations and toxicity [27]. Two SQGVs mentioned in the ANZECC guidelines are

$$\text{Effective range median mean quotient ERMQ} = \frac{\sum_{i=1}^{n} M_i / ERM_i}{n} \quad (6)$$

where *Mi* is the concentration of element *i* in sediment and ERM_i is the lower SQGV for element *i*, and

$$\text{Probable effect level mean quotient PELQ} = \frac{\sum_{i=1}^{n} M_i / PEL_i}{n} \quad (7)$$

where *Mi* is the concentration of element *i* in sediment and PEL_i is the upper SQGV for element *i*. The ERMQ values of <0.1, 0.11 to 0.5, 0.51 to 1.5 and >1.5 are related to 12, 30, 46 and 74% toxicity in amphipod survival bioassays, respectively [28]. Similarly, PELQ values of <0.1, 0.11 to 1.5, 1.51 to 2.3 and >2.3 are in accordance with 10, 25, 50 and 76% toxicity, respectively [29]. ANZECC guidelines were followed for determining the ERMQ and PELQ of all the collected sediment samples.

2.4.5. Sediment Environmental Toxicity Quotient (ETQ)

The environmental toxicity quotient (ETQ) was determined to test the sediment quality based on toxicity [30]. It was determined by multiplying the concentration of each contaminant measured in the sediment samples with the corresponding hazard intensity. The hazard intensity of each parameter was determined according to the Priority List of Hazardous Substances prepared by the US Agency for Toxic Substances and Disease Registry (ATSDR) [31]. ETQ was determined by Equation (8).

$$\text{Environmental Toxicity Quotient (ETQ)} = \frac{\sum_{i=1}^{n} TS_i \times C_i / TS_{As}}{n} \quad (8)$$

where C_i is the measured concentration of the element i and n is the number of the analysed elements. TS_i is the total score for each element (T_{As} = 1674, T_{Pb} = 1531, T_{Zn} = 915, T_{Cd} = 1320, and T_{Cu} = 807) and TS_{As} is the total score of arsenic, which has the highest TS published by the Agency for Toxic Substances and Disease Registry (ATSDR). Pollution ranges (toxicity level) were assigned based on the ETQ values, <10 low toxicity, 10–50 moderate toxicity, 50–100 high toxicity, 100–300 very high toxicity and >300 extremely high toxicity [31].

2.5. Analytical Methods

2.5.1. Statistical Method

All statistical analyses were computed by using SPSS version 20. Analysis of variances (ANOVA) was applied to compare the concentrations of five selected heavy metals in sample collected from 15 different stations in the Perak River and the metal–metal correlation values. The graphs were created with Origin (2017) for Windows. Factor analysis based on principal component analysis (PCA) was used to ascertain sources of contamination. Cluster analysis (CA) was applied to identify different geochemical groups, which enabled clustering of the samples with similar metal contents. CA was formulated according to the single linkage technique, and the linkage distance [(Dlink/Dmax) × 100] was used for measuring the distance between clusters of similar metal contents [32].

2.5.2. Geostatistical Methods

The inverse distance weighted (IDW) method was applied to show the spatial distribution of heavy metals in the surface sediment. The IDW interpolation calculated the cell values for the unmeasured site by averaging the sampled data in the target site. More weight is observed when the measured point is close to the centre of the prediction cell. ArcGIS 10.2.2 was used for analysis. The power of two and the number of 30 neighbouring samples were chosen to show both spatial variation and patterns of the heavy metals. Considering the large area of the Perak River, along with its zigzag shape, we have made the distribution an upstream and downstream basis. We created a polygon very similar to Perak River and used this polygon for interpolation. Total root mean square (RMS) error was maintained below 1 (0.001–0.002) to ensure the proper interpolation of data.

3. Results and Discussions

3.1. Physicochemical Parameter of Sediments

The results of the analysed parameters such as pH and SOM are given in Table 1. The pH level at sites S4 to S12 and S14 revealed a low value (pH: 5.56–6.92), i.e., the surface sediments of these stations were in acidic conditions, while sites S13 and S15 revealed alkaline conditions (pH: 7.22–7.33).

Table 1. Heavy metal concentrations (μg/g) in the surface sediments of Perak River (n = 3).

Station	pH	SOM (%)	Pb	Zn	Cd	Cu	Fe (%)
S1	7.05 ± 0.09	4.4	25.4 ± 6.09	33.39 ± 12.80	2.77 ± 0.53	11.68 ± 2.32	20.88 ± 1.53
S2	7.05 ± 0.12	4.4	17.19 ± 3.34	21.31 ± 2.95	1.51 ± 0.50	6.82 ± 6.52	56.58 ± 9.29
S3	7.43 ± 0.10	4.4	22.79 ± 5.13	49.70 ± 10.27	2.07 ± 0.76	10.98 ± 1.50	40.12 ± 28.59
S4	6.92 ± 0.11	4.8	14.56 ± 4.15	26.53 ± 4.23	1.94 ± 0.36	6.60 ± 2.19	42.94 ± 42.49
S5	6.02 ± 0.09	6.2	33.13 ± 12.16	51.78 ± 18.36	3.62 ± 1.22	17.26 ± 6.32	36.40 ± 9.14
S6	6.13 ± 0.08	6.6	19.14 ± 3.67	31.99 ± 6.00	2.21 ± 0.36	8.21 ± 0.93	21.76 ± 44.56
S7	5.56 ± 0.03	7.2	35.06 ± 21.09	58.34 ± 31.80	2.77 ± 0.11	16.44 ± 8.74	38.78 ± 17.65
S8	6.59 ± 0.44	8.2	30.57 ± 2.97	50.03 ± 7.36	3.36 ± 0.71	12.51 ± 1.80	31.34 ± 4.88
S9	6.77 ± 0.24	8.8	27.60 ± 9.42	47.29 ± 8.45	3.63 ± 0.26	13.78 ± 3.16	36.80 ± 2.05
S10	6.74 ± 0.24	9.4	17.75 ± 3.10	37.37 ± 1.03	2.16 ± 0.47	8.55 ± 0.80	20.24 ± 1.38
S11	6.91 ± 0.17	9.4	31.96 ± 9.44	49.03 ± 14.28	3.83 ± 0.61	9.82 ± 2.97	37.51 ± 7.52
S12	6.53 ± 0.07	11	44.80 ± 25.70	95.53 ± 63.24	3.68 ± 0.62	183.52 ± 25.85	40.55 ± 6.82
S13	7.22 ± 0.07	12	60.77 ± 6.65	160.48 ± 16.98	4.02 ± 0.10	50.83 ± 8.33	39.22 ± 4.00
S14	6.36 ± 0.27	12.6	29.69 ± 6.33	77.92 ± 5.54	3.93 ± 0.54	18.13 ± 2.08	39.30 ± 3.85
S15	7.33 ± 0.08	13	22.31 ± 10.78	51.27 ± 17.01	2.62 ± 0.36	19.14 ± 16.30	23.60 ± 1.09
Range	5.56–7.43	4.4–13.00	25.40–60.77	21.31–160.48	1.51–4.02	6.60–183.52	20.24–56.58

The alkaline conditions noted at certain sampling stations (particularly in downstream region) might be explained by the intense influence of the calcareous materials deposition in the downstream region. Again, seawater intrusion by tidal pumping or sea level rising might also be responsible for alkaline condition of sediment of the Perak River (Figure 1). This study revealed S1 had the lowest average SOM percentage (4.40%), while S13 had the highest percentage of SOM (13%), indicating that

the downstream area is rich with SOM content. The studied metal concentrations in the sediment were in the order of Fe> Zn> Pb> Cu> Cd. The Zn concentrations ranged between 21.31 and 160.48 μg/g with an overall average of 55.38μg/g. The highest average concentrations of Zn was found at S13 (160.48 ± 16.98 μg/g) and the lowest was found at S2 (21.31 ± 2.95 μg/g). Again, the highest percentage of Zn distribution was reported at S13 at ~51%, which revealed that half of the heavy metals pollution at S13 came from Zn. Fe concentrations were as low as 20.24% at S10 and as high as 56.58% at S2 with overall average concentration of 35.05%.

The average value of Pb concentrations was 28.86 μg/g and the highest concentration of Pb was at S13 (60.77 ± 6.65 μg/g), while the lowest was at S4 (14.56 ± 4.15 μg/g). In the case of Cu, the most noteworthy concentration was accounted for at S12 (183.52 ± 44.80 μg/g) and the least was at S4 (6.60 ± 2.19 μg/g). Finally, Cd concentrations ranged from 1.51 to 4.02 μg/g with an overall average value of 2.94 μg/g. At some specific sampling areas, high pollution levels of metals were observed which might be because of the local concentration of civil waste, transportation activities, farming exercises and natural weathering. For example the highest concentrations of Cd at S13 (4.02 ± 0.10μg/g) were observed because various metal processing industries, numerous agriculture land and living residents were existed in and around of the Perak River. Again, various shipping construction industries and floating restaurants had contributed to high concentrations of Pb at S13 (60.77 μg/g). The spatial distribution of heavy metals for all stations was compared between upstream and downstream areas of the Perak River by means of a prediction map (Figure 2). The prediction map clearly defines the distribution of heavy metals, where the red colour indicates the highest concentrations and the green colour signifies the lowest concentrations in both upstream and downstream areas. From the maps, it is very clear that the concentrations of Pb, Zn, Cd and Cu were higher in downstream areas than upstream, but Fe showed a different distribution. The distribution of Zn and Pb for both upstream and downstream areas was similar and, as stated earlier, Zn was reported with the highest concentration at S13; Pb also followed the same trend at this station. This indicates that S13 had many intense activities nearby that contributed Zn and Pb to the river. Unlike the pattern of other heavy metals such as Pb, Zn, Cd and Cu, the upstream areas of the river showed high concentrations of Fe. The downstream map also indicates slightly higher concentration (although 1.5 times less than those upstream) of Fe especially at stations 12 and 13, because of the high domestic effluent from the dominant sources of residential areas and construction activities (Appendix C). From the heavy metal distribution pattern in the surface sediment, it is very evident that for most metals the high concentration values were gathered in the downstream region. This may be due to the higher SOM content in downstream areas along with the slower flow rate of the river water near to the Andaman Sea.

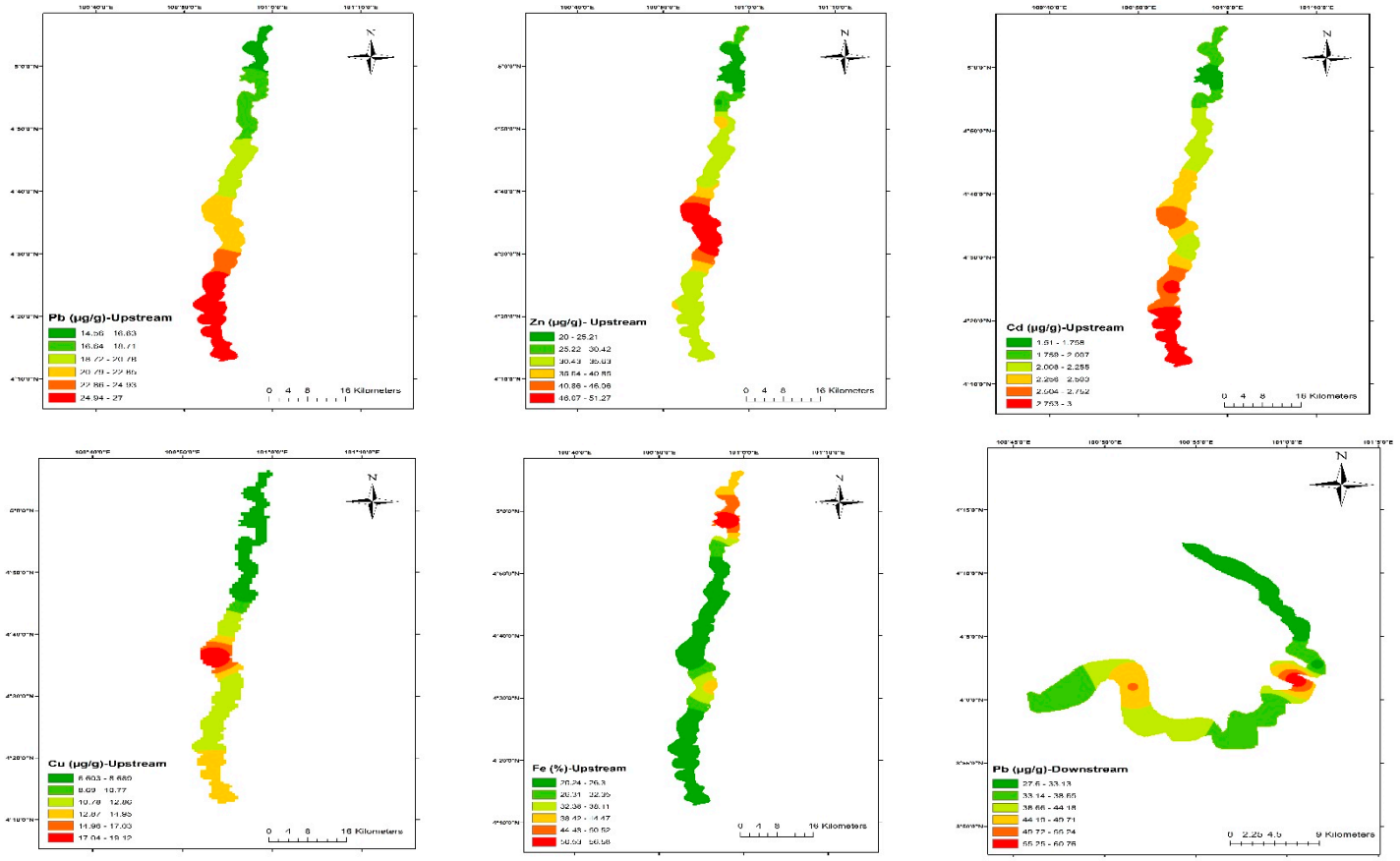

Figure 2. *Cont.*

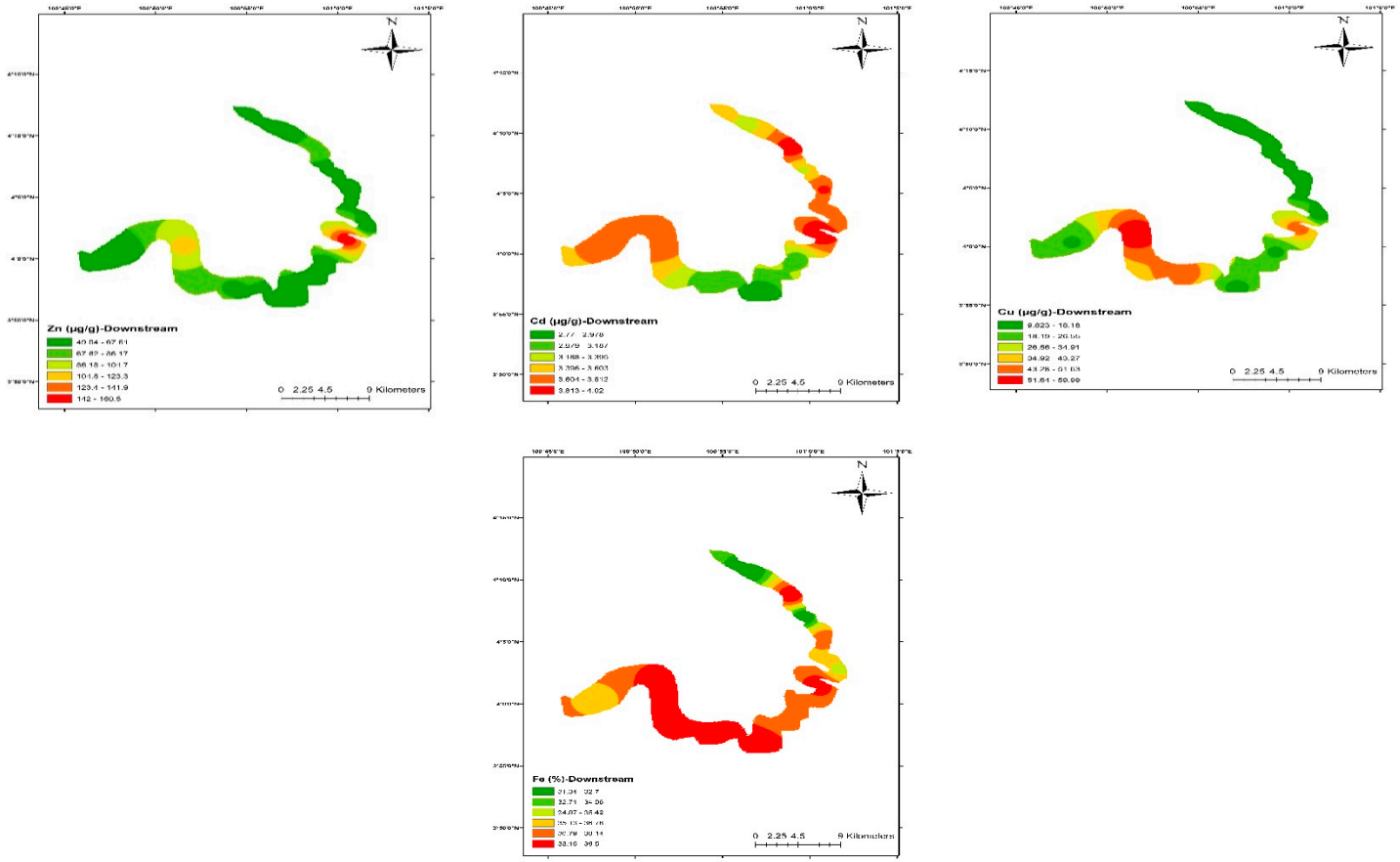

Figure 2. Geostatistical prediction maps of heavy metals in the surface sediment in upstream and downstream areas of the Perak River.

Figure 3 depicts the correlation of pH with the heavy metal content of the sediment. Both Zn and Fe showed a negligible positive correlation, while Cd, Cu and Pb showed a negative correlation with pH values, similar to the results obtained by Idriss et al. [33]. High pH values promote adsorption and precipitation of metal ions in sediment through complex formation, while low pH values can weaken the strength of metal association and impede their retention in sediments, resulting in its release to water [34]. For example, the higher concentration of heavy metals at S13 is due to the higher pH of sediment. This is because a decrease in pH will increase the activity of some ions (H^+, Fe^{3+}, Al^{3+} and hydroxide) and the cations will compete with heavy metals for negative sorption sites in the sediments [35]. Thus, there is a negative correlation of Cd, Cu and Pb, with pH indicating that the pH may potentially be the one of the main factor affecting the distribution of these metals in the surface sediment of the Perak River.

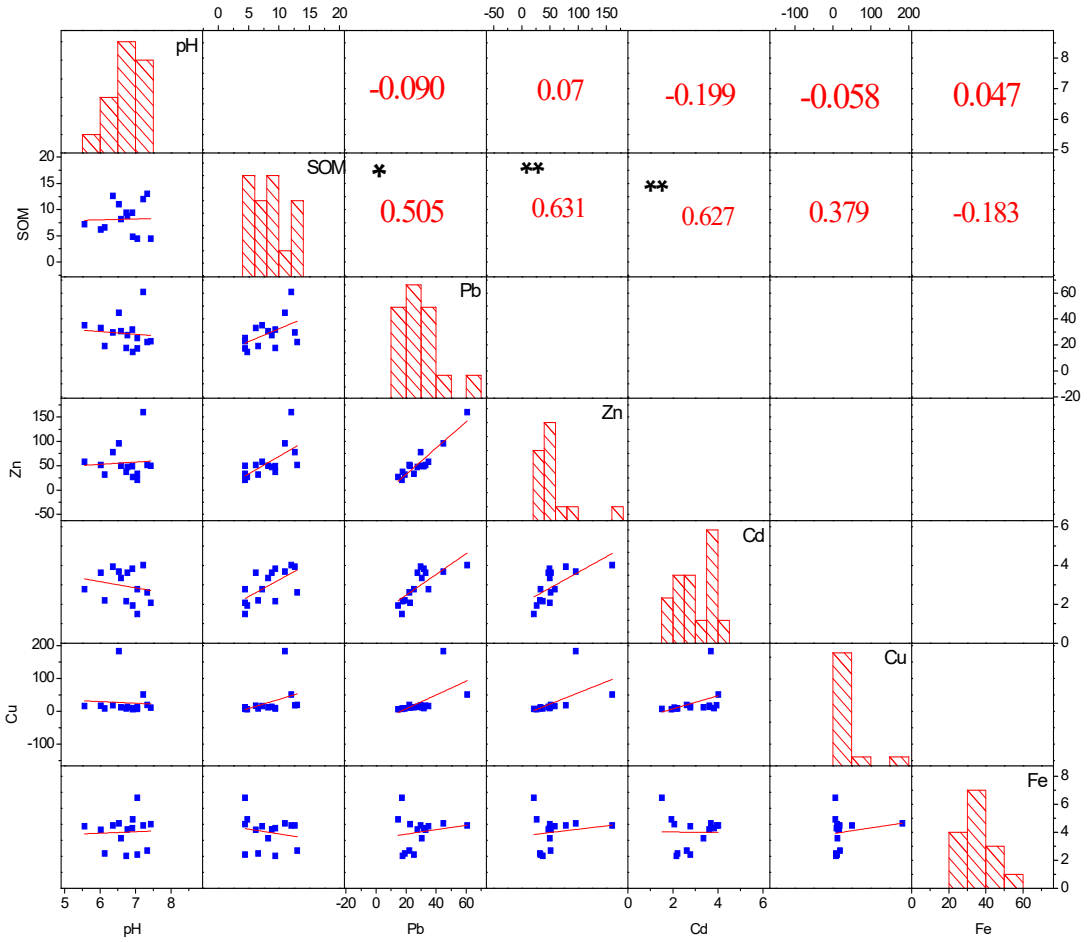

Figure 3. Correlation of heavy metal concentration with pH and sediment organic matter content (SOM) ** Correlation is significant at the 0.01 level (2-tailed) * Correlation is significant at the 0.05 level (2-tailed).

Pb, Zn and Cd were strongly correlated ($p < 0.01$ for Zn and Cd, and $p < 0.05$ for Pb) with the organic matter content in sediment, while Cu was moderately correlated with SOM, indicating that the distribution of Pb, Zn and Cd was strongly controlled by the organic matter content in this area. Significant correlation of Pb, Zn and Cd with organic matter may be due to the high stability constants of the forming organic heavy metal (Pb, Zn and Cd) compounds. Again organic compounds usually play an important role in heavy metal transformation in rivers because of its high sorption properties. The complexation reaction between heavy metals and organic complexants is usually recognised as the most important reaction pathway, and the mobility of trace metals in natural water environment

can be influenced by this reaction [36]. The insignificant correlation of copper with sediment organic matter indicates that it might be less bioavailable in the sediments due to its remobilising tendency in oxidising state. Whereas the negative correlation between SOM and Fe might be due to the highest amount of organic matter content being in the downstream sediment as well as the lower stability constants of organic–iron compounds complexes. This could be because organic matter present in domestic sewage acts as a reducing agent which converts iron mineral into its soluble form (Fe^{3+} to Fe^{2+}), resulting in its abundance in river water rather than in the sediment [37].

3.2. Risk Assessment

The EF is used to estimate the heavy metal sources and the degree of anthropogenic influence based on the use of a normalisation element [38]. The calculated EF results were compared with the assessment criteria as suggested by Birth (2003) and Chen et al. (2007) [39,40]. The EF values for the studied metals were in the order of Cd > Pb > Zn > Cu (Figure 4). In general, the average EF values for all metals were <1.0, suggesting no anthropogenic impact on metal levels in the river sediment.

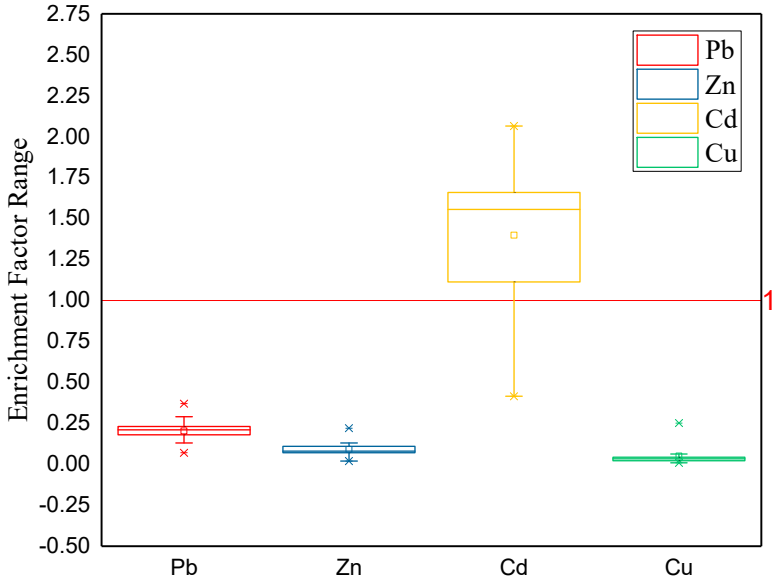

Figure 4. Enrichment factor of surface sediment in the Perak River (straight line at point 1 represents EF index reference line [39,40]; EF < 1, no enrichment; EF 1.0–3.0, minor enrichment; EF 3.0–5.0, moderate enrichment).

The EF values for Cd ranged from 0.415 to 2.07, indicating that 20% of the stations were categorised as having no enrichment and 80% as having minor enrichment. The EF values for Pb ranged from 0.07 to 0.37, Zn ranged from 0.02 to 0.22 and Cu ranged from 0.009 to 0.251, suggesting that 100% of these stations can be categorised as no enrichment for these metals. The EF values of Pb, Zn and Cu were less than 1.5, suggesting that natural sources have a major contribution to their availability, whereas the EF values of Cd were all close to 1.5, indicating an anthropogenic input for Cd concentration.

The pollution intensity based on the calculated Igeo results was in the order of Cd > Fe > Pb > Zn > Cu (Figure 5). Based on Muller's scale, the average Igeo values for all detected metals indicated that only two metals have Igeo > 0. For Cd, approximately 53% of the sampling stations were 'moderately-to-heavily contaminated' (Igeo = 2.11 to 3.16), 40% were 'heavily contaminated', while the remaining stations were 'moderately contaminated'.

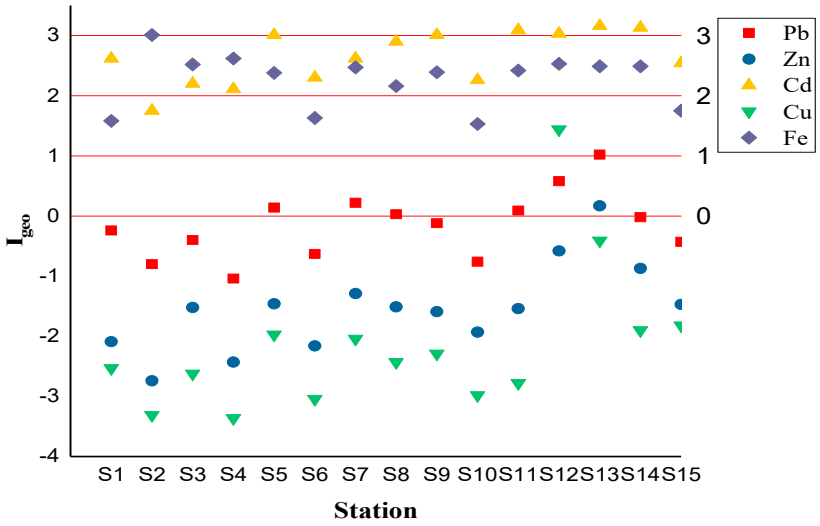

Figure 5. Igeoaccumulation index surface sediment in the Perak River (the reference line at point 0,12,3 represents the different Muller classes). $I_{geo} < 0$, uncontaminated; $0 < I_{geo} < 1$, uncontaminated-to-moderately uncontaminated; $0 < I_{geo} < 2$, moderately contaminated; $2 < I_{geo} < 3$, moderately-to-heavily contaminated; $3 < I_{geo} < 4$, heavily contaminated; $4 < I_{geo} < 5$, heavily-to-extremely contaminated; $I_{geo} > 5$, extremely contaminated.

For Fe, approximately 67% of the sampling stations were 'moderately-to-heavily contaminated' (Igeo = 2.16 to 3.0), 27% were 'uncontaminated-to-moderately contaminated', while the remaining stations were 'heavily contaminated'. For Pb, approximately 60% of the sampling stations were 'uncontaminated' (Igeo = −1.04 to −0.02), 33% were 'uncontaminated-to-moderately contaminated', while the remaining stations were 'moderately contaminated'.

The values of PLI (Figure 6) were found to be generally high (>1) in all the studied stations, indicating that 100% of the sites had metal contamination to some extent. Among them, the contamination factor (Appendix D) of both Cd and Fe went beyond the maximum limit (CF > 6—very high concentration), which specified that these two metal were responsible for major pollution in the Perak river [41]. This confirmed that the Perak River is facing probable environmental pollution especially with dangerous heavy metals (Cd and Fe) resulting from an increased rate of non-treated industrial waste discharged to the Perak River.

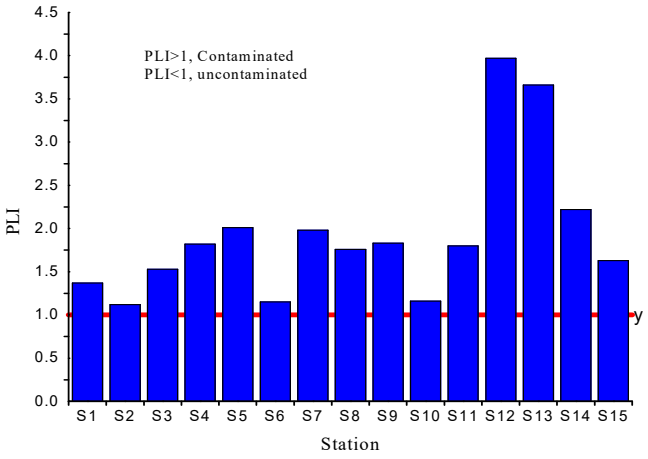

Figure 6. Pollution load index of surface sediment in the Perak River. Straight line at point 1 represents the reference line for pollution indication [42].

The estimated ERMQ values suggest that the sediments from both upstream and downstream sites had an average toxicity of 30%, a similar level of toxicity (25%) was also indicated by the PELQ value (Table 2). The ETQ values confirmed that the sediments of the Perak River are moderately toxic to the inhabitants and that this toxicity level is higher in downstream region as compared to the upstream regions. According to the ETQ based toxicity level, sediments of site S2 had the lowest toxicity which is also shown by the PLI index (Figure 7).

Table 2. Sediment quality guidelines and environment toxicity quotient.

Stations	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15
Stream	Upstream										Downstream				
ERMQ	0.17	0.11	0.16	0.11	0.23	0.14	0.22	0.22	0.22	0.14	0.23	0.411	0.43	0.26	0.18
PELQ	0.31	0.18	0.26	0.21	0.41	0.24	0.36	0.38	0.39	0.24	0.42	0.69	0.64	0.44	0.31
ETQ	12.32	7.96	13.73	8.13	17.44	10.17	18.51	16.0	15.15	10.62	15.95	46.14	42.74	20.40	14.93

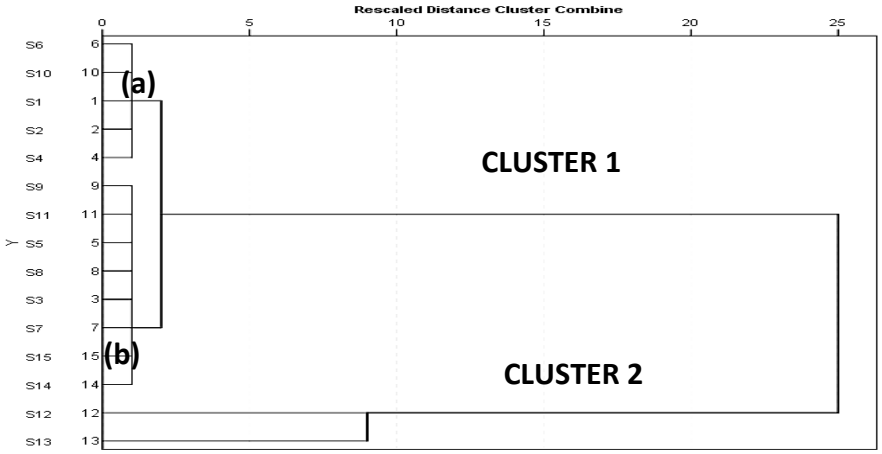

Figure 7. Cluster analysis ("a" and "b" represent sub cluster) of sampling stations in the Perak River.

The differences in the indices results may be due to the differences in sensitivity of these indices towards the sediment pollutants, which means that the basis of the different indices is different [43]. Overall, the heavy metals in the surface sediment of Perak River have a moderate ecological risk. However, on the basis of individual metal contribution Cd and Fe showed the greatest risk and should be considered as major pollutants of the Perak River.

3.3. Heavy Metals Sources

The results of EF, Igeo and CF (Appendix D) indicated that the levels of Pb, Zn and Cu presented a low potential ecological risk, suggesting that this group of elements might originate from natural sources [44]. However, the highest concentration of Pb at S13 may be contributed to by various factories, such as a shipping factory, a match factory and a timber factory. Similarly, apart from natural sources, the highest value of Cu at S12 may be due to the residential area and the fishing port. Additionally, Cu can be retained by sediment through exchange and specific adsorption mechanisms but precipitation may also be an important mechanism of retention in polluted sediments. It is suggested that agrochemicals especially phosphorite fertilisers and residential waste were the major sources of Cu [45]. The highest concentration of Zn at S13 might be due to the influence of prevailing construction and shipping manufacturing activities [13]. The second group of metals (Fe and Cd) had greater concentrations in the sediment than the first group of metals. This indicates that anthropogenic activity was also contributing to the concentrations of Fe and Cd in the sediment. Metal processing industries, large areas of agricultural land and residential areas were existed around of the Perak River were likely to be the sources of Cd in the present sediments. On the other hand, high domestic

effluent from the sources such as residential areas and construction activities contributed to the high Fe concentrations.

Various multivariate techniques such as CA, PCA and intermetal relationships have been shown to be useful for identifying sources of heavy metals and for interpreting their spatial variations. The CA classified the sampling stations into two major clusters (Figure 7). Cluster 1 consists of two subclusters. Cluster 1(a) includes less impacted stations (S1, S2, S4, S6 and S10) that were located further inland from the estuary and Straits of Malacca. Cluster 1(b) includes stations (S3, S5, S7, S8, S9, S11, S14 and S15) that were close to the estuary and Straits of Malacca. Based on the locations and variable concentrations at these stations, this study concluded that seawater intrusion strongly affected the parts of the study area. These stations were characterised by high pH values compared to the other stations. Cluster 2 consists of stations S12 and S13, which are mainly located in the downstream part of the study area. According to Malaysian Department of Environment, the population density of those sites was considerably higher and the land use pattern was predominantly urban activities, agricultural fields and the sampling stations were located in close proximity to the major pollution sources, such as industrial discharge, domestic sewage from treatment plants, construction projects and a shipping port [46].

A clear pattern of strong associations was found among the metal pairs in the sediment sample, which were Pb-Zn, Pb-Cd, Zn-Cd, Pb-Cu, Zn-Cu and Cd-Cu (Table 3). Based on the Pearson correlation coefficients, Zn showed significant strong positive correlation with Pb, Cd and Cu (r = 0.872, 0.649 and 0.591, respectively; $p < 0.05$). These strong correlations among metal-to-metal pairs are an indication of common sources of these metals as well as similar geochemical characteristics. There was a weak negative correlation between Fe and Cu ($r = -0.027$), Fe and Zn ($r = -0.027$) and Fe and Cd ($r = -0.190$) suggesting different origin or dissimilar sedimentological properties of iron.

Table 3. Metal-to-metal correlation coefficient matrix for metals in sediment samples.

	Pb	Zn	Cd	Cu	Fe
Pb	1				
Zn	0.872 **	1			
Cd	0.649 **	0.615 **	1		
Cu	0.591 **	0.600 **	0.346 *	1	
Fe	−0.027	−0.027	−0.190	0.047	1

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed).

The PCA results of the heavy metals concentrations of the sediment surface sediment samples are shown in Figure 8. The PCA yielded two principal components with eigenvalues > 1. The first principal component (PC1) explained 59.41% of the total variation (eigenvalue = 2.97), and was loaded with Pb, Zn, Cd and Cu. PC1 represents moderately strong correlation with four of the variables; it increases with increasing Cu (0.40), Cd (0.47), Pb (0.56) and Zn (0.54). On the other hand, PC2 explained 20.73% (eigenvalue = 1.04) of the total variance and was strongly correlated with Fe (0.93). PCA analysis showed that metal elements assembled in two major groups, where Pb, Zn, Cd and Cu constituted the first group and have similarities in their sources and distribution. Fe is slightly further away from the first group and has contribution from some other sources as well.

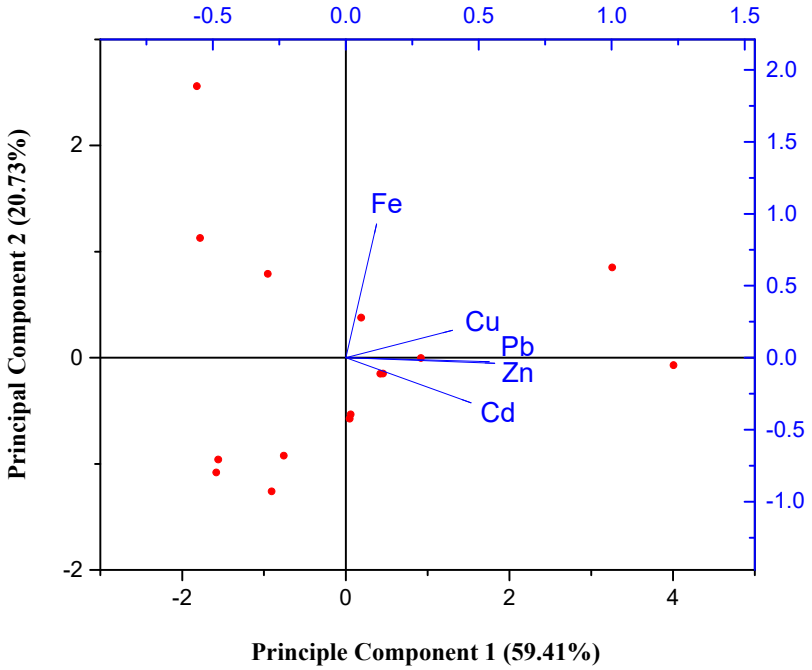

Figure 8. Principal component analysis (PCA) plot showing the loading of two components influencing variation of heavy metals in the sediments.

3.4. Comparison of Observed Result with Sediment Guidelines and Previous Study

Comparison of heavy metal level in sediment from this study with various international guidelines and previous studies provides better perspectives of the state of metal toxicity in the sediment (Table 4). This study revealed that the concentrations of Pb (28.86 µg/g), Zn (55.38 µg/g) and Cu (24.67 µg/g) were below the US EPA guidelines, however Cd (2.94 µg/g) exceeded the guideline's value of 0.99 µg/g [47]. The comparison of elemental concentrations with the ISQGs revealed the absence of pollution for all the stations (Table 4). For Malaysian studies, the concentration ranges of all of the heavy metals in the present study revealed higher concentration than the range of the Langat River, Terengganu River and Kelantan River.

Table 4. Comparison of observed result with sediment guidelines and previous study.

	Average Concentrations (µg/g)					References
	Pb	**Zn**	**Cd**	**Cu**	**Fe (%)**	
Present study (range)	25.40–60.77	21.31–160.48	1.51–4.02	6.60–183.52	20.24–56.58	
Average	28.86	55.38	2.94	24.67	35.07	
Regional studies						
DRS River, China	25.2	72.5	0.29	24.6	3.65	[48]
Red Sea, Egypt	5.0–56	-	0.65–5.75	6.8–190.2	-	[49]
Tamagawa River, Japan	14.4	72.7	0.15	28.77	4.01	[50]
Malaysian studies						
Langat River	5.57–55.71	12.26–74.70	-	2.24–14.84	-	[19]
Terengganu River	-	71.27	-	15.01	2.437	[51]
Kelantan River	20.82	18.67	1.82	-	3.86	[52]
Sediment Guidelines						
Continental crust value	14.8	65	0.098	25	3.49	[53]
USEPA	35.8	121	0.99	31.6	-	[47]
ISQG	35	123	-	35.7	-	[54]

USEPA: US Environment Protection Agency; ISQG: Interim Sediment Quality Guidelines.

This comparative data strongly indicated that among various river of Malaysia the Perak river pollution is most alarming and some of the heavy metal concentrations have already exceeded and some of them are very close to the standard maximum limit.

4. Conclusions

Geostatistical analysis of heavy metals (Pb, Cd, Cu, Zn and Fe) in sediments from 15 sampling stations showed that concentration of target heavy metals varied in the order of Fe> Zn> Pb> Cu> Cd. The enrichment value for the studied metals was in the order of Cd > Pb > Zn > Cu, whereas the geoaccumulation index (Igeo) results were in the order of Cd > Fe > Pb > Zn > Cu. The values of PLI were found to be generally high (>1) in all the studied stations. Both the SQG and ETQ indicated that the downstream region is more polluted than the upstream region. From the source analysis it is clear that Pb, Zn and Cu concentrations are mainly due to natural sources whereas anthropogenic activities contribute to the higher concentration of Fe and Cd. Based on the findings of this study, we suggest that the urban wastewater and the effluents emerging from industries must be monitored periodically for maintaining the standards prescribed by the pollution control board for various industries in the region. Furthermore, treatment of industrial effluents, particularly from textile mills, electroplating/galvanising, lead reprocessing, tanning and chemical industries, before discharging in the upper catchment is a prerequisite for controlling the level of pollution in the river. The limitation of this study was that the sample was collected at summer season only and for clear understanding of the river pollution status a seasonal variation could have maintained.

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