

Assessment of Metals Contamination in Klang River Surface Sediments by using Different Indexes

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Abstract

Surface sediments (0-5 cm) from 21 stations throughout Klang River were sampled for metal concentration as well as sediment's pH, total organic carbon (TOC) and particles sizes to obtain an overall classification of metal contaminations in the area. The concentration of metals ($\mu\text{g/g}$, Fe%, dw) were as follows: 0.57- 2.19 Cd; 31.89-272.33 Zn; 5.96-24.47 Ni; 10.57- 52.87 Cu; 24.23-64.11 Pb and 1.56-3.03 Fe. The degree of sediment contaminations were computed using an enrichment factor (EF) and geoaccumulation index (I_{geo}). The results suggested that enrichment factor and geoaccumulation values of Cd were greatest among the studied metals. Pearson's correlation indicated that effectiveness of TOC in controlling the distribution and enrichment of metals was a more important factor than that of the grain size ($<63\mu\text{m}$). The study revealed that on the basis of computed indexes, Klang River is classified as moderately polluted river.

Keywords: Klang River; heavy metals; indexes; surface sediment; contamination

1. Introduction

Due to rapid industrialization and uncontrolled urbanization around many cities and coastal areas, an alarming level of pollutants has contaminated these aquatic environments (Naji *et al.*, 2010). Out of these pollutants, heavy metals are major concern because of their persistent and bio-accumulative nature (Kaushik *et al.*, 2009). Heavy metals can be introduced into the aquatic environment and accumulate in sediments through disposal of liquid effluents, chemical leachates and runoff originating from domestic, industrial and agricultural activities, as well as atmospheric deposition (Mucha *et al.*, 2003). These metals can be released from the sediments to the overlying water via natural or anthropogenic processes, consequently causing potential danger to the ecosystems (McCready *et al.*, 2006; Chen *et al.*, 2007). Sediments have a high storage capacity for pollutants that in any part of the hydrological cycle far less than 1% of these are actually dissolved in the water and more than 99% are stored in the sediments (Salomons and Stigliani, 1995), hence, producing remarkable metals enrichment. Due to these characteristics, sediments play an important role in the assessment of metal contamination in natural waters (Wardas *et al.*, 1996). Moreover, accumulation or release of metals in sediments is largely controlled by their geochemistry, in particular, type and quantities of organic matter, grain size and cation exchange capacity (Vertacnik *et al.*, 1995). And since they can act as point sources of contamination during anthropogenic activities, sediments are suitable tool for measuring the

extent of metal enrichment using the enrichment factor (EF) and geoaccumulation index (I_{geo}).

This study therefore aimed to determine the distribution and concentration of trace metals in surface sediments with different sediment characteristics from 21 stations in the Klang River; to identify the quality assessment of surface sediments using enrichment factor (EF), geoaccumulation index (I_{geo}) and to appraise their lithogenic inputs; and to determine the relationships between elements and total organic carbon (TOC).

2. Materials and Methods

2.1. Study area

Klang River is one of the most important rivers in Malaysia ($3^{\circ} 13' 01.33'' \text{N}$ $101^{\circ} 40' 54.92'' \text{E}$) (Fig. 1). It has an approximate distance of 120 km and catchment area of about 1288 km^2 . The Klang River discharges throughout the year at an average annual discharge of 17.2 m^3/sec (Balamurugan, 1991). It flows through Kuala Lumpur and Klang Valley and eventually drains into the Straits of Malacca. This area was chosen for the present study because of it is situated in the most urbanized and heavily populated area of more than 4.4 million people (16% of the national population) living around this area. In addition, it drains into the one of the busiest international shipping lanes. Furthermore, most of the industrial growth in Selangor state has taken place on the banks of Klang River. The main sources of heavy metal inputs into Klang River are manufacturing industries, agriculture and animal husbandry,

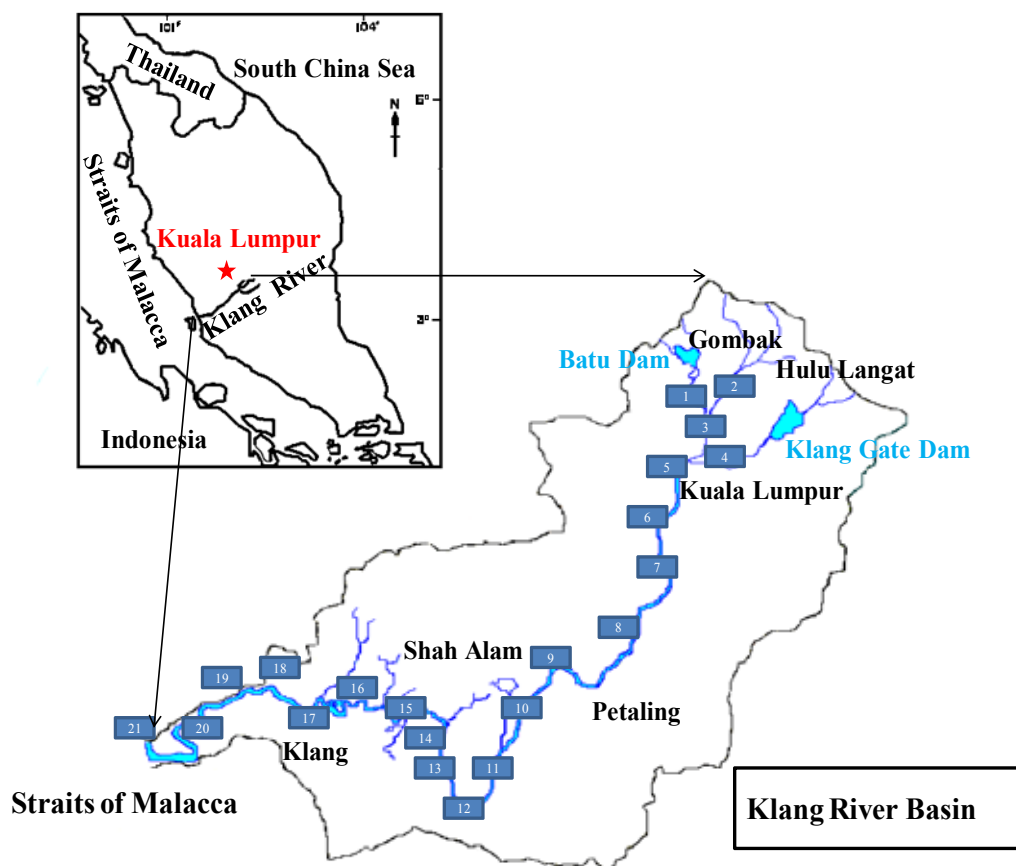


Figure 1. Study area and Geographical location of 21 stations in Klang River.

agro-based industries and urbanization activities (DOE, 1998). However, there is no sufficient information of atmospheric inputs on the Klang River. The land use in the basin is diverse, ranging from tropical forests in the headwater region to urban and the other related activities such as towns, housing and industrial estate, infrastructures in the upper, middle and lower parts of the basin (Balamurugan, 1991). The longitudes and latitudes of sampling stations were measured by using global positioning system (GPS) (Table 1).

2.2. Field and laboratory methods

Surface sediment (0-5) samples were collected from 21 stations between January and February 2009 along Klang River (Fig 1). At each station, three surface sediment samples were collected by scraping the surface layer using a clean plastic spoon. The surface sediments of each sample were placed in polyethylene plastic bags and they were then kept in an ice box. As soon as the field work was finished, samples were brought to the ecotoxicology laboratory at University Putra Malaysia and stored at -10°C freezer for future analysis. The samples for assessment were dried using an air-circulating oven at 80°C , and sieved through $63\mu\text{m}$ mesh size and kept in an acid-washed container

for future use. For metal (Cd, Zn, Ni, Cu, Pb and Fe) analyses, about 0.5 to 1g dried sediments were digested in 10 ml solution of mixed HNO_3 (AnalaR grade, R&M 65%) and HClO_4 (AnalaR grade, R&M 70%) in the ratio of 4:1, starting at low temperature (40°C) for 1 h and then at 140°C for 3 h (Ismail, 1993). The digested samples were then diluted to 40 ml with double-distilled water (DDW) and filtered through Whatman No.1 filter paper into pre-cleaned 50 ml volumetric flasks. The samples were measured for trace metal concentration using an air-acetylene flame Atomic Absorption Spectrophotometer (Perkin-Elmer Model AAnalyst 800).

2.3. TOC, Fine grain-size distribution and pH analysis

Concentration of total organic carbon was measured in surface sediment following the method of Nelson and Sommers (1996). The grain size distribution in surface sediments was determined by pipette method (Gee and Bauder, 1986). And the pH of surface sediments were determined in distilled water with a 1: 2.5 sediment: water ratio (Madejon *et al.*, 2002). All sediment samples for each trace metal were measured in triplicate.

2.4. Quality control

Table 1. The locations of the sampling sites along the Kang River

| Stations | Designation | Sites | Latitude (N) | Longitude (E) | TOC% | Fine grains (%) |
|----------|-----------------|------------------------|---------------|---------------|------|-----------------|
| 1 | Semi-urban | Taman Beringin | 3°13' 01" | 101°40' 54" | 0.19 | 17.92 |
| 2 | Urban | Taman Gombak Jaya | 3°11' 20" | 101°42' 03" | 0.58 | 22.65 |
| 3 | Urban | Ulu Klang | 3°10' 04" | 101°41' 35" | 0.43 | 8.09 |
| 4 | Urban | PWTC | 3° 09' 48" | 101°45' 03" | 0.22 | 1.71 |
| 5 | Urban | Mesjid Jamik | 3° 08' 49" | 101°41' 42" | 0.32 | 0.74 |
| 6 | Semi-urban | Seputeh | 3° 08' 49" | 101°40' 31" | 0.37 | 3.50 |
| 7 | Semi urban | Taman Sri Sentosa | 3° 06' 48" | 101°39' 41" | 1.25 | 30.60 |
| 8 | Semi urban | Bandar Puchong Jaya | 3° 04' 37" | 101°36' 53" | 0.76 | 42.45 |
| 9 | Industrial | Penaga Industrial park | 3° 03' 27" | 101°36' 24" | 2.31 | 24.70 |
| 10 | Rural | Puchong Tengah | 3° 02' 44" | 101°35' 49" | 1.91 | 33.57 |
| 11 | Industrial | Kampung Seri Aman | 3° 01' 05" | 101°34' 47" | 3.40 | 55.65 |
| 12 | Industrial | Kota Permai | 2° 58' 54" | 101°33' 03" | 1.83 | 42.60 |
| 13 | Industrial | Alam Indah | 2° 59' 29" | 101°32' 48" | 2.11 | 75.65 |
| 14 | Industrial | Kampung Baru Hicom | 3° 00' 48" | 101°32' 59" | 1.78 | 27.14 |
| Hicom | | | 3° 01' 49" | 101°30' 42" | 1.34 | 69.06 |
| 15 | Urban | Seksyen 24 | 3° 02' 29" | 101°28' 20" | 2.26 | 94.23 |
| 16 | Urban+ | Kampung Seri | | | | |
| | Industrial | Kenangan | 3° 02' 43" | 101°26' 49" | 2.57 | 87.73 |
| 17 | Urban | Klang Town | 3° 03' 11" | 101°25' 31" | 1.83 | 82.01 |
| 18 | Semi-urban | Sangai Udang | 3° 02' 23" | 101°23' 36" | 2.41 | 95.94 |
| 19 | Local fishing | Sungai Sirih | 3° 01' 07" | 101°22' 28" | 4.50 | 94.54 |
| 20 | Local fishing + | Bandar Sultan | | | | |
| Sulaiman | | | 3° 00' 13.29" | 101°23' 19" | 1.45 | 84.16 |
| | Urban area | | | | | |
| 21 | Near Port | Bagan Hailam | | | | |

To preclude uncertain contaminations, all laboratory equipments used were washed with phosphate-free soap, double rinsed with distilled water (DDW) and left in 10% HNO₃ for 24 hr and all equipments were then rinsed two times with double distilled water and left semi-closed to dry at room temperature. Certified Reference Material (CRM) (International Atomic Energy Agency, Soil-5, and Vienna, Austria) was

determined as a precision check. Recovery and accuracy for certified and measured concentration of the metals were tabulated in Table 2. Calibration curves for each trace element were determined with 1,000 mg/L (BDH Spectrosol®) stock solution. The reagent and procedural blanks were monitored after five samples during the analysis as part of the quality accuracy program.

Table 2. Measured and certified concentration, and percentages of recovery of International Atomic Energy Agency, Soil-5, Vienna, Austria. (Mean± standard deviations; n=5)

| Element | Measured concentration (µg/g) | Certified concentration (µg/g) | Percentage of recovery (%) |
|---------|-------------------------------|--------------------------------|----------------------------|
| Cd | 1.62± 0.05 | 1.5±0.06 | 108.0 |
| Zn | 359.9±2.10 | 368.0±3.20 | 98.0 |
| Ni | 11.53±0.7 | 13±0.0 | 88.7 |
| Cu | 80.0±5.0 | 77.1±4.7 | 103.8 |
| Pb | 123.8±10.0 | 129.0±26.0 | 96.0 |
| Fe | (3.80±0.86)×104 | (4.45±0.19)×104 | 85.6 |

2.5. Statistical analysis

All statistical analyses were computed using Statistical Package for Social Science (SPSS) version 16. Pearson's correlation was applied to determine correlation matrix between metal concentrations, TOC and fine grain-size in surface sediments of Klang River.

3. Results and Discussion

3.1. General sediments characteristics

Some characteristics of the surface sediments at different stations are summarized in Table 1. Some of physico-chemical parameters of sediment as pH, grain size and TOC influence the adsorption process. The results showed that sand was the principal surface sediment type in the upstream stations. Middle parts were clogged with well-sorted silts and sands, and also downstream stations were choked with fine-grained clays and silts. The pH of sediments from 21 stations ranged from 6.1 to 7.1, and most stations were slightly acidic except Stations 6 and 9 that were slightly alkaline. According to Liao (1990), the acidic pH could be due to decomposition of microbial activity of litter and also from oxidation of FeS₂ and FeS to H₂SO₄. The TOC in the sediment ranged between 0.19% and 4.5%. The percentages of TOC in the fine-grained size of the samples were higher than that in sand-grained size. The organic carbon in polluted surface sediments ranged from 1.5 to 2.4 times greater than those in less polluted surface sediments. The fine-grained fraction (≤63μm) has a high specific surface area per unit quantity of material and, because of surface coatings of iron and manganese oxides and natural organic matter, it is more likely to adsorb organic and trace contaminations (Maher *et al.*, 1999). According to Haque and Subramanian (1982) metal absorption capacity is in the order of sand<silt<clay. Due to increases in surface areas, mineral and organic matter content as particle size decreased from sand to clay. However, the trend found in this study, on which more metals were accumulated in the fine-grained fraction of the sediments might not be universal for all metals, and might be varied between metal species (Tam and Wong, 2000).

3.2. The concentration and distribution of trace metals

Metal concentrations (μg/g, Fe %, dw) in the surface sediments from 21 stations varied from 0.57 to 2.19 μg/g for Cd, 31.89 to 272.33 μg/g for Zn, 5.96 to 24.47 μg/g for Ni, 10.57 to 63.03 μg/g for Cu, 24.23 to 64.11 μg/g for Pb and 1.56% to 3.03% for Fe (Table 3). The highest concentration of metals was found in those

stations along the vicinity of industrial parks (e.g., Shah Alam industrial area) and highly populated centers (e.g., Klang Valley and Kuala Lumpur). Surface sediments in these areas have high contents of clay and organic carbon. Conversely, metal concentrations were lowest in those stations with low anthropogenic flux, clay and organic carbon. Mean concentrations of Cd, Zn and Pb in the surface sediments in the study area were higher than the average shale (Turekian and Wedepohl, 1961). Whereas, the average concentration of Ni and Cu were less than average shale. (Table 3)

3.3. Enrichment Factor (EF)

Improved interpretations are obtained by normalizing metal concentration in sediments to percentage of a given grain size, or Al, Fe or organic carbon concentrations (Luoma and Rainbow, 2008). Enrichment factor (EF) is a good tool to differentiate the metal source between lithogenic and naturally occurring (Zhang *et al.*, 2009; Chen *et al.*, 2007; Amin *et al.*, 2009). Enrichment factor is usually distinguished by aluminum because of its high natural concentration, minimal anthropogenic contamination, it is a structural element of clays, and the metals to Al proportions in the crust are relatively constant (Schrop *et al.*, 1990; Summers *et al.*, 1996). However, in the present study we used Fe to compute EF because it is the fourth major element in the earth's crust and most often has no contamination concern. In addition, according to Daskalakis and O'Connor (1995) the main advantages of using Fe as a normalizer are: (1) Fe is associated with fine solid surface; (2) its geochemistry is close to that of many trace metals; and (3) its natural sediment concentration tends to be uniform. Iron (Fe) has been used successfully by several researchers to normalize metals contamination in river and coastal sediments (Baptista-Neto *et al.*, 2000; Zhang *et al.*, 2007; Amin *et al.*, 2009; Cevik *et al.*, 2009). The EF for Fe-normalised data is defined by:

$$EF_{\text{metal}} = \frac{(M_x / Fe_x)_{\text{sample}}}{(M_c / Fe_c)_{\text{shale}}}$$

Where M_x is the concentration of metal in the examined sample, Fe_x is the concentration of Fe in the examined sample, M_c is the concentration of metal in the average shale or undisturbed sediment and Fe_c is the concentration of Fe in the average shale or undisturbed sediment. In the present study, average shale (Turekian and Wedepohl, 1961) was used as background or undisturbed value for those metals because no such data was available for the study area. The undisturbed sediment values utilized were (Turekian and Wedepohl, 1961) in μg/g: 0.30 for Cd, 95 for Zn, 68 for Ni, 45 for

Table 3. Metal concentrations ($\mu\text{g/g}$, Fe %, dw) in surface sediments of the Klang River

| Stations No. | Cd | Zn | Ni | Cu | Pb | Fe |
|--------------------------|------|--------|-------|-------|-------|------|
| 1 | 0.57 | 31.89 | 5.96 | 10.57 | 26.57 | 1.60 |
| 2 | 1.02 | 130.10 | 11.27 | 18.87 | 42.15 | 1.73 |
| 3 | 1.19 | 146.77 | 14.27 | 37.59 | 56.95 | 2.15 |
| 4 | 1.12 | 87.30 | 11.12 | 30.8 | 50.11 | 1.97 |
| 5 | 1.31 | 176.59 | 17.33 | 51.81 | 64.11 | 1.66 |
| 6 | 0.98 | 103.90 | 11.17 | 25.17 | 36.78 | 2.33 |
| 7 | 1.13 | 138.70 | 15.84 | 30.42 | 41.05 | 2.53 |
| 8 | 1.04 | 174.17 | 15.2 | 43.89 | 57.53 | 3.03 |
| 9 | 2.19 | 179.33 | 18.00 | 33.83 | 59.82 | 2.08 |
| 10 | 1.78 | 97.20 | 15.18 | 19.69 | 36.05 | 1.56 |
| 11 | 2.13 | 251.40 | 24.47 | 63.03 | 51.23 | 1.74 |
| 12 | 2.06 | 257.90 | 19.13 | 35.13 | 49.23 | 1.81 |
| 13 | 1.76 | 272.33 | 19.09 | 39.87 | 52.06 | 2.07 |
| 14 | 1.61 | 252.59 | 20.68 | 52.87 | 45.64 | 1.77 |
| 15 | 1.16 | 152.21 | 16.27 | 31.98 | 41.65 | 1.66 |
| 16 | 2.11 | 261.16 | 22.53 | 53.34 | 59.66 | 2.20 |
| 17 | 1.91 | 219.23 | 20.07 | 39.24 | 55.87 | 1.88 |
| 18 | 2.13 | 160.35 | 21.7 | 52.55 | 57.49 | 2.35 |
| 19 | 2.16 | 151.38 | 19.13 | 49.44 | 53.43 | 2.54 |
| 20 | 1.91 | 120.30 | 14.89 | 43.20 | 51.78 | 1.71 |
| 21 | 1.40 | 86.71 | 11.31 | 17.33 | 24.73 | 1.80 |
| Max | 2.19 | 272.33 | 24.47 | 63.03 | 64.11 | 3.03 |
| Min | 0.57 | 31.89 | 5.96 | 10.57 | 24.23 | 1.56 |
| Mean | 1.54 | 163.30 | 16.30 | 37.14 | 47.94 | 2.03 |
| SD | 0.49 | 66.07 | 4.47 | 13.46 | 10.26 | 0.37 |
| Aver. Shale ^a | 0.30 | 95 | 68 | 45 | 20 | 4.7 |
| *TEL ^b **(FW) | 0.60 | 123 | 18 | 36 | 35 | - |
| *TET ^b **(FW) | 3 | 540 | 61 | 86 | 170 | - |

^a Turekian and Wedenphol (1961); ^b MacDonald *et al.* (2000).

* ^b TEL: Threshold effect level, TET: Toxic effect threshold. **FW means fresh water

Cu, 20 for Pb, and 4.7 for Fe (Table 3). The EF values were interpreted as described by Chen *et al.* (2007) where $EF < 1$ indicates no enrichment, $EF < 3$ is minor enrichment, $EF = 3-5$ is moderate enrichment, $EF = 5-10$ is moderately severe enrichment, $EF = 10-25$ is severe enrichment, $EF = 25-50$ is very severe enrichment and $EF > 50$ is extremely severe enrichment.

The result from the present investigation showed that EF of Cd ranged from 5.38 to 19.18, EF from 0.99 to 7.15 for Zn, from 0.26 to 0.97 for Ni, from 0.69 to 3.78 for Cu and from 3.23 to 9.08 for Pb (Table 4). The EF values of Ni in all the stations were found to be less than 1 ($EF < 1$) which indicated that this metal had no enrichment. The lowest EF values were determined in Ni (average value 0.58 ± 0.18) which probably originated

from natural weathering process. The average EF of Cu (1.98 ± 0.79) indicated that this metal was caused by minor enrichment, whereas, the average EF value of Zn (average value 4.13 ± 1.83) suggested moderate enrichment. However in some stations Zn values could be classified as moderately severe enrichment which indicated high anthropogenic discharge. In contrast, Cd EF values were greater than the other four metals studied. The average EF of Cd (average value 13.08 ± 5.24) was determined to be higher than 10 ($EF > 10$) in the Klang River surface sediments (Table 4), suggesting that Cd contamination was caused by severe enrichment and should be of major concern. The average EF value for Pb (average value 5.78 ± 1.38) was $EF > 5$ suggesting that Pb contamination was caused by moderate to severe

enrichment. Lead had the second highest EF values (e.g., 3.23 to 9.08) among the metals studied. The high contamination of these heavy metals could be related to the local point sources. For example, Station 5 and 17 are near the large sewage outlet area while Stations 9 to 16 are near industrial parks. Overall, EF of these metals was higher in the industry-affected area than urban-affected (mostly from domestic source) area.

3.4. Geoaccumulation Index (I_{geo})

The Geoaccumulation Index (I_{geo}) was calculated to determine metals contamination in sediments of Klang River. This expression was proposed by Müller (1979) in order to calculate metals concentration in sediments by comparing current concentrations with undisturbed or crustal sediment (control) levels. Müller (1981) has classified I_{geo} in relation to contamination levels into seven classes, Unpolluted (Class 0, $I_{geo} < 0$), unpolluted to moderately polluted (Class 1, $0 < I_{geo} < 1$), moderately polluted (Class 2, $1 < I_{geo} < 2$), moderately to strongly polluted (Class 3, $2 < I_{geo} < 3$), strongly polluted (Class 4, $3 < I_{geo} < 4$), strongly to very strongly polluted (Class 5, $4 < I_{geo} < 5$) and very strongly polluted (Class 6, $I_{geo} > 5$), the highest grade reflecting a 100-fold enrichment above baseline values.

The geoaccumulation (I_{geo}) is expressed by the following pattern:

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 B_n} \right)$$

Where C_n is the measured concentration of the sediment for metal (n), B_n is the geochemical background value of metal (n) and factor 1.5 is the possible variations of background data due to lithogenic impacts. The background values of the heavy metals were the same as applied in the enrichment factor calculation.

The geoaccumulation index (I_{geo}) of heavy metals in this study revealed that 83.33% of the elements belonged to I_{geo} classes 0 and 1 (unpolluted and unpolluted to moderately polluted), 9.52% belonged to I_{geo} class 2 (moderately polluted) and only 7.14% is classified at I_{geo} class 3 (moderately to strongly polluted) (Table 4). Cadmium had the highest I_{geo} values and in most stations it was classified as moderately polluted (Class 2, $1 < I_{geo} < 2$) and moderately to strongly polluted (Class 3, $2 < I_{geo} < 3$). Moreover, the average geoaccumulation index of Cd (1.71 ± 5.24) suggested that surface sediments of Klang River were moderately polluted by this metal, whereas the average geoaccumulation index of 0.058 ± 1.83 and 0.64 ± 1.38 suggested that surface sediments of Klang River were unpolluted to moderately polluted (Class 1, $0 < I_{geo} < 1$) by Zn and Pb, respectively.

In contrast, the I_{geo} of Ni, Cu and Fe in all stations were of classified to class 0 ($I_{geo} < 0$) suggesting unpolluted state from these metals. None of the trace metals in this investigation belonged in the last three classes that is strongly polluted (Classes 4, 5 and 6).

3.5. Correlation Matrix

Pearson's correlation matrix was used to determine the relationships between Cd, Zn, Ni, Cu, Pb, Fe, TOC and grain-size of surface sediments (Table 5). The result indicated that most metals (Cd, Zn, Ni, Pb and Cu) have a positive significant association within metals ($r = 0.50 - 0.84$; $p < 0.01$) (Table 5). The correlation coefficient between Cd ($r = 0.0$), Zn ($r = 0.09$), Ni ($r = 0.01$), Cu ($r = 0.24$), Pb ($r = 0.33$), fine grain-size (0.01) and Fe were positive, but none of these relationships were significant (at the 5% significance level) (Table 5). On the other hand, there was a negative correlation between Fe ($r = -0.13$) and TOC. The result suggested that concentrations of these metals were not controlled by natural weathering processes (Zhang *et al.*, 2007). Similarly, there was a significant positive correlation between Cd ($r = 0.79$; $p < 0.01$), Zn ($r = 0.42$; $p < 0.05$), Ni ($r = 0.60$; $p < 0.01$), Cu ($r = 0.47$; $p < 0.05$), fine grain-size ($r = 0.72$; $p < 0.01$) and TOC (Table 5). Low positive correlations indicated by Pb suggested that this metal has low association with organic carbon. The number and intensity of binding sites are variable among types of organic matter. Some types of organic material have few sites per unit surface (e.g. lignins) and others have many (fulvic materials) (Luoma and Rainbow, 2008). Although, metal availability is influenced by organic matter content, some characteristics of the sediment such as pH, redox reactions and the metal binding capacity, which control the solubility, availability and mobility of metals, are also important (Naji *et al.*, 2010). Significant correlations between most of these metals were probably due to influxes of some non-lithogenic and natural sources into the surface sediments.

3.6. Sediment quality guidelines (SQGs)

In order to predict adverse biological effects in contaminated sediments, numerous sediment quality guidelines (SQGs) have been developed over the past decade (MacDonald *et al.*, 2000). In this investigation, we compared our total concentration with SQG of threshold effect level (TEL), which includes threshold effect concentrations, and toxic effect threshold (TET), which includes probable effect concentrations (PEC) as described by MacDonald *et al.* (2000) to assess the possible biological consequences of the metal concentrations in the surface sediments (Table 3).

Table 4. Metal Enrichment Factor (EF) and Geoaccumulation Index (I_{geo}) values in surface sediments of Klang River

| Station | Cd | | Zn | | Ni | | Cu | | Pb | | Fe | |
|---------|-------|-----------|------|-----------|------|-----------|------|-----------|------|-----------|----|-----------|
| | EF | I_{geo} | EF | I_{geo} | EF | I_{geo} | EF | I_{geo} | EF | I_{geo} | EF | I_{geo} |
| 1 | 5.58 | 0.34 | 0.99 | -2.16 | 0.26 | -4.11 | 0.69 | -2.68 | 3.90 | -0.18 | - | -2.16 |
| 2 | 9.24 | 1.18 | 3.72 | -0.13 | 0.45 | -3.18 | 1.14 | -1.84 | 5.73 | 0.49 | - | -2.03 |
| 3 | 8.67 | 1.40 | 3.38 | 0.04 | 0.46 | -2.84 | 1.83 | -0.84 | 6.22 | 0.92 | - | -1.72 |
| 4 | 8.91 | 1.32 | 2.19 | -0.71 | 0.39 | -3.20 | 1.63 | -1.13 | 5.98 | 0.74 | - | -1.84 |
| 5 | 12.36 | 1.54 | 5.26 | 0.31 | 0.72 | -2.56 | 3.26 | -0.38 | 9.08 | 1.10 | - | -2.09 |
| 6 | 6.59 | 1.12 | 2.21 | -0.46 | 0.33 | -3.19 | 1.13 | -1.42 | 3.71 | 0.29 | - | -1.66 |
| 7 | 7.00 | 1.33 | 2.71 | -0.04 | 0.43 | -2.69 | 1.26 | -1.15 | 3.81 | 0.45 | - | -1.48 |
| 8 | 5.38 | 1.21 | 2.84 | 0.29 | 0.35 | -2.75 | 1.51 | -0.62 | 4.46 | 0.94 | - | -1.22 |
| 9 | 16.50 | 2.28 | 4.27 | 0.33 | 0.60 | -2.51 | 1.70 | -1.00 | 6.76 | 1.00 | - | -1.76 |
| 10 | 17.88 | 1.98 | 3.08 | -0.56 | 0.67 | -2.75 | 1.32 | -1.78 | 5.43 | 0.26 | - | -2.18 |
| 11 | 19.18 | 2.24 | 7.15 | 0.82 | 0.97 | -2.06 | 3.78 | -0.10 | 6.92 | 0.77 | - | -2.02 |
| 12 | 17.83 | 2.19 | 7.05 | 0.86 | 0.73 | -2.42 | 2.03 | -0.94 | 6.39 | 0.71 | - | -1.96 |
| 13 | 13.32 | 1.97 | 6.50 | 0.93 | 0.64 | -2.42 | 2.01 | -0.76 | 5.91 | 0.79 | - | -1.77 |
| 14 | 14.25 | 1.84 | 7.07 | 0.82 | 0.81 | -2.30 | 3.12 | -0.36 | 6.06 | 0.60 | - | -1.99 |
| 15 | 10.95 | 1.37 | 4.54 | 0.09 | 0.68 | -2.65 | 2.01 | -1.08 | 5.90 | 0.47 | - | -2.09 |
| 16 | 15.03 | 2.23 | 5.87 | 0.87 | 0.71 | -2.18 | 2.53 | -0.34 | 6.37 | 0.99 | - | -1.68 |
| 17 | 15.92 | 2.09 | 5.77 | 0.61 | 0.74 | -2.35 | 2.18 | -0.79 | 6.98 | 0.90 | - | -1.91 |
| 18 | 14.07 | 2.24 | 3.38 | 0.17 | 0.64 | -2.24 | 2.34 | -0.36 | 5.75 | 0.94 | - | -1.59 |
| 19 | 13.32 | 2.26 | 2.95 | 0.09 | 0.52 | -2.42 | 2.03 | -0.45 | .94 | 0.83 | - | -1.47 |
| 20 | 17.50 | 2.09 | 3.48 | -0.24 | 0.60 | -2.78 | 2.64 | -0.64 | 7.12 | 0.79 | - | -2.05 |
| 21 | 12.19 | 1.64 | 2.38 | -0.72 | 0.43 | -3.17 | 1.01 | -1.97 | 3.23 | -0.28 | - | -1.97 |
| Max | 19.18 | 2.28 | 7.15 | 0.93 | 0.97 | -2.06 | 3.78 | -0.34 | 9.08 | 1.10 | - | -1.22 |
| Min | 5.38 | 0.34 | 0.99 | -2.16 | 0.26 | -4.11 | 0.69 | -2.68 | 3.23 | -0.27 | - | -2.18 |
| Mean | 13.08 | 1.71 | 4.13 | 0.06 | 0.58 | -2.70 | 1.98 | -0.98 | 5.78 | 0.64 | - | -1.84 |
| SD | 5.24 | 0.52 | 1.83 | 0.72 | 0.18 | 0.47 | 0.79 | 0.64 | 1.38 | 0.37 | - | 0.26 |

Threshold effect concentrations should be used to identify sediments that are unlikely to be adversely affected by sediment-associated contaminants, while the PECs should be used to identify sediments that are likely to be toxic to sediment-dwelling organisms (MacDonald *et al.*, 2000).

The result of this study showed that Cd concentration of surface sediments in almost all the stations were above the TEL value of $0.6\mu\text{g/g}$ (except for Stations 1) and below the TET value of $3\mu\text{g/g}$. On the other hand, Zn concentrations in all of stations were much lower than TET value ($540\mu\text{g/g}$) and were most stations (except Stations 1, 4, 6, 10, 20, 21) were above TEL ($123\mu\text{g/g}$). Concentration of Ni in surface sediments at all stations were still well below TET ($61\mu\text{g/g}$) value. Likewise, Cu and Pb concentrations in all the stations were below the TET value of $86\mu\text{g/g}$ and $170\mu\text{g/g}$, respectively. In general, the distributions of Cd, Zn, Cu, Ni and Pb in the \leq TEL range were 4.7, 28.57, 38.09, 47.61 and 9.52%, respectively. None of metal

concentrations in the sediments was as high as TET values. However, some metal concentrations exceeded the values for TEL.

4. Conclusions

The influence of anthropogenic metals pollution in surface sediments of Klang River were determined using enrichment factor (EF) and geoaccumulation index (I_{geo}) for Cd, Zn, Ni, Cu, Pb and Fe in fine-grained fraction. Likewise, some other characteristics of surface sediments such as pH, clay, silt, sand and TOC were analyzed from 21 stations along the river. The organic carbons in polluted surface sediments were 1.5 to 2.4 times greater than those in less polluted surface sediments and had close relationship between metal accumulation and fined-grain size. The EF values suggested that Cd had the highest average whereas, Pb, Zn, Cu, and Ni had the lowest average. The geoaccumulation index (I_{geo}) suggested that individual metal contamination in

Table 5. Pearson's correlation coefficient between metals, TOC and Fine grain-size

| | Cd | Zn | Ni | Cu | Pb | Fe | TOC% | Fine grain-size |
|-----------------|--------|--------|--------|--------|------|-------|--------|-----------------|
| Cd | 1 | | | | | | | |
| Zn | 0.61** | 1 | | | | | | |
| Ni | 0.82** | 0.84** | 1 | | | | | |
| Cu | 0.60** | 0.71** | 0.80** | 1 | | | | |
| Pb | 0.50** | 0.58** | 0.59** | 0.76** | 1 | | | |
| Fe | 0.00 | 0.09 | 0.01 | 0.24 | 0.33 | 1 | | |
| TOC% | 0.79** | 0.42* | 0.60** | 0.47* | 0.25 | -0.13 | 1 | |
| Fine grain-size | 0.61** | 0.31 | 0.47* | 0.33 | 0.11 | 0.01 | 0.72** | 1 |

Note: * significant at $p < 0.05$; ** significant at $p < 0.01$; ($n = 63$).

the surface sediments could be classified as “unpolluted to moderately polluted to strongly polluted”. According to SQG of threshold effect level, and toxic effect threshold, none of the metals in the sediments of Klang River was equal or higher than the TET values, however, some metal concentrations exceeded the TEL values. These indexes revealed that stations close to industrial and urban areas were more metal-enriched than other areas. This investigation showed that risk of metal concentrations can be evaluated using some indexes and not only by testing of total metal concentrations. Although the levels of most trace metals in the surface sediments did not show extreme enrichment and did not present any serious threat to the local fauna and flora, it is still highly recommended that further investigations and monitoring be conducted to assess long term effects of anthropogenic inputs into the Klang River ecosystems.

References

- Amin B, Ismail A, Arshad A, Yap CK, Kamarudin MS. Anthropogenic Impacts on heavy metal concentrations in the coastal sediments of Dumai, Indonesia. *Environmental Monitoring and Assessment* 2009; 148: 291-305.
- Balamurugan G. Sediment balance and delivery in a humid tropical urban river basin: the Klang River, Malaysia. *Catena* 1991; 18: 271-87.
- Baptista-Neto JA, Smith BJ, McAllister JJ. Heavy metal concentrations in surface sediments in a nearshore environment, Jurujuba Sound, Southeast Brazil. *Environment Pollution* 2000; 109: 1-9.
- Cevik F, Goksu M, Derici O, Findik O. An assessment of metal in surface sediments of Seyhan dam by using enrichment factor, geoaccumulation index and statistical analyses. *Environmental Monitoring and Assessment* 2009; 148: 291-305.
- Chen CW, Kao CM, Chen CF, Dong CD. Distribution and accumulation of heavy metals in sediments of Kaohsiung Harbor, Taiwan. *Chemosphere* 2007; 66(8): 1431-40.
- Daskalakis KD, O'Connor TP. Normalization and elemental sediment contamination in the coastal United States. *Environmental Science and Technology* 1995; 29:470-77.
- DOE. Environmental quality report, Department of Environment. Ministry of Science Technology and the Environment (Malaysia). Maskha Sdn Bhd, Ampang, Kuala Lumpur. 1998.
- Gee GW, Bauder JW. Particle-size analysis. In: *Methods of soil Analysis. Part 1. Physical and Mineralogical Methods*, Agronomy Monograph No. 9. 2nd ed. ASA-SSSA. Madison, USA. 1986; 383-411.
- Haque MA, Subramanian V. Cu, Pb and Zn pollution of soil environment. *The CRC Critical Review in Environment Control* 1982; 12: 13-90.
- Ismail A. Heavy metal concentration in sediments of Bintulu, Malaysia. *Marine Pollution Bulletin* 1993; 26: 706-07.
- Kaushik A, Kansal A, Santosh, Meena, Kumari S, Kaushik CP. Heavy metal contamination of river Yamuna, Haryana, India: Assessment by Metal Enrichment Factor of the Sediment. *Journal of Hazardous Materials*. 2009; 164: 265-70
- Liao JF. The chemical properties of the mangrove Solonchak in the northeast part of Hainan Island. *The Acta. Scientiarum Naturalium Universitatis Sunyatseni* 1990; (4): 67-72.
- Luoma SN, Rainbow PS. *Metal Concentration in Aquatic Environments*. New York: Cambridge University Press, New York, USA. 2008; 101-16.
- MacDonald DD, Ingersoll CG, Berger TA. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology* 2000; 39: 20-31.
- Madejon P, Murillo JM, Maranon T, Cabrera TF, Lopez F. Bioaccumulation of As, Cd, Fe and Pb in wild grasses affected by the Aznalcollar mine spill (SW Spain). *Science of the Total Environment* 2002; 209: 105-20.
- Maher W, Batkey GE, Lawrence I. Assessing the health of sediment ecosystems: Use of chemical measurements. *Freshwater Biology* 1999; 41: 361-72.

- McCready S, Brich GF, Long ER. Metallic and organic contaminations in sediments of Sydney Harbour. Australia and Vicinity. A chemical dataset for evaluating sediment quality guidelines. *Environment International* 2006; 32: 455-65.
- Mucha AP, Vasconcelos MTSD, Bordalo AA. Macrobenthic community in the Douro estuary: relations with trace metals and natural sediment characteristics. *Environmental Pollution* 2003; 121: 169 - 80.
- Müller G. Schwermetalle in den sedimenten des Rheins-Veränderungen seit 1971. *Umschau* 1979; 79: 778–83.
- Müller G. Die Schwermetallbelastung der sedimente des Neckars und seiner Nebenflüsse: eine Bestandsaufnahme. *Chemical Zeitung* 1981; 105: 157–64.
- Naji A, Ismail A, Ismail AR. Chemical speciation and contamination assessment of Zn and Cd by sequential extraction in surface sediment of Klang River, Malaysia, *Microchemical Journal* 2010; 95: 285-92.
- Nelson DW, Sommers LE. Total carbon, organic carbon, and organic matter. In: *Methods of Soil Analysis, Part 3. Chemical methods*, American Society of Agronomy, Madison, USA. 1996: 961-1010.
- Salomons W, Stigliani W. Biogeochemical dynamics of pollutants in soils and sediments. Heidelberg: Springer-Verlag, Germany. 1995; 352.
- Schrop SJ, Lewis FG, Windom HL, Ryan JD, Calder FD, Burney LC. Interpretation of metal concentration of metal in estuarine sediments of Florida using aluminum as a reference element. *Estuaries* 1990; 13: 227- 35.
- Summers JK, Wade TL, Engle VD, Malaeb ZA. Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. *Estuaries* 1996; 19: 581- 94.
- Tam N FY, Wong YS. Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution* 2000; 110 : 195- 205.
- Turekian KK, Wedepohl KH. Distribution of the elements in some major units of the earth's crust. *Bulletin of Geological Society of America* 1961; 72: 175–92.
- Vertacnik A, Prohic E, Kozar S, Juracic M. Behavior of some trace elements in alluvial sediments, Zagreb water-well field area, Croatia. *Water Research* 1995; 29: 237-46.
- Wardas M, Budek L, Rybicka EH. Variability of heavy metals content in bottom sediments of the Wilga River, a tributary of the Vistula River (Krakow area, Poland). *Applied Geochemistry* 1996; 11: 197-202.
- Zhang L, Ye X, Feng H, Jing Y, Ouyang T, Yu X, Liang R, Chen W. Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Marine Pollution Bulletin* 2007; 54: 974- 82.
- Zhang W, Feng H, Chang J, Qu J, Xie H, Yu L. Heavy metal contamination in surface sediments of Yangtze River intertidal zone: An assessment from different indexes. *Environmental Pollution* 2009; 157; 1533-43.

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