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Metals Fractionation and Evaluation of their Risk Connected with Urban and Industrial Influx in the Klang River Surface Sediments, Malaysia

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Abstract

In the present study, concentration, distribution and speciation of trace metals were conducted to assess the overall classification of Ni, Cu and Pb as well as their risk status in the surface sediments of Klang River. Sequential extraction technique (SET) was used to evaluate the four (exchangeable, acid-reducible, oxidisable-organic and residual) fractions of the surface sediments. The total concentrations of metals ranged from 5.26 µg/g d.w. to 22.93µg/g d.w for Ni; 9.47-66.74 µg/g d.w. for Cu; and 24.78-62.35 µg/g d.w. for Pb. The fractionation of studied metals (except Cu) in most stations were in the order of residual > acid-reducible > oxidisable-organic > exchangeable. The degree of surface sediments contamination was computed for Risk Assessment Code (RAC), Individual Contamination Factors (ICF) and Global contamination factor (GCF). The result of this study showed that none of the metals studied had potential risk to fauna and flora of the Klang River systems.

Keywords: heavy metals; fractionation; surface sediment; risk assessment code

1. Introduction

Since industrial revolution started in the mid-1800s, the bio-geochemical cycle of inorganic contamination present in the environment has been greatly accelerated by human activities (Ahmed and Ishiga, 2006; Davydova, 2005).

Heavy metal contamination of sediments can critically degrade aquatic systems (Charkhabi *et al*., 2005). In sediments, metals can be present in a number of chemical forms, exhibiting different physical and chemical behaviors with respect to chemical interactions, mobility, biological availability, and potential toxicity (Arnason and Fletcher, 2003; Singh *et al*., 2005). In the present study, sediment samples were collected and analyzed. Sediments have several advantages including (1) sediment plays a major role in the transport and storage of metals (Salomons *et al*., 1987); (2) sediment is frequently used to identify sources of pollutants, spatially and temporally (Birch *et al*., 2001); And (3) metals in oxic sediments are mainly distributed in different operationally defined geochemical phases, such as carbonates, total organic carbon (TOC), and Fe-Mn oxides, which have diverse binding abilities with various metals and have contrasting influences on the metal bioavailability (Coquery and Welbourn, 1995; Tessier and Campbell, 1987). The toxicity of the metals particularly depend on their chemical forms rather than on their total contents, and therefore, speciation studies increasingly gain importance (Liu *et al*., 2007). Fractionation is the process of classification of an analyte or a group of analytes into a certain matrix according to physical (size, solubility) or chemical (bonding, reactivity) properties (Weisz *et al*., 2000). In order to assay the fractionation of heavy metals from sediments, various sequential extraction procedures have been applied. Sequential extraction analysis is a technique applied to study the geochemical partitioning of heavy metals amongst solid mineral and organic phases in sediment or other earth material (Badri and Aston, 1983; Howard and Shu, 1996; Tessier *et al*., 1979).

In this investigation, the sequential extraction technique (SET) was used to fractionate resistant fraction (lithogenous) from nonresistant (non-lithogenous) fractions. The procedure of SET consists of four (exchangeable, acid-reducible, oxidisable organic and residual) fractions. The mathematical summation of exchangeable, acid-reducible, and oxidisable-organic fractions constitutes the nonresistant phase (Badri and Aston, 1983). Even though there are two disadvantage of using sequential extraction technique, e.g. non-specificity of extractants and metal re-absorption, it is still widely reported in the literature (Howard and Shu, 1996).

In Malaysia, metal fractionations were reported in river sediments (Ismail and Ramli, 1997; Lim and

Kiu, 1995; Mushrifah *et al*., 1995). But there is no information on the basis of metals in the Klang River. Hence, the study described in this paper would be of great value in this area. The main objectives of this study were: (1) to investigate the fractionation of Ni, Cu and Pb in surface sediments of the Klang River, (2) to assay their mobility and bioavailability in order to provide preliminary baseline data to control pollution, and (3) to determine possible sources of anthropogenic inputs of trace metals in this river.

2. Materials and Methods

2.1. Study area

Klang River is one of the most important rivers in Malaysia (Fig. 1). It flows through Kuala Lumpur and Klang Valley and eventually flows into the Straits of Malacca. The Klang River consisted of 11 main tributaries including Sungai Batu, Sungai Gombak, Sungai Ampang, Sungai Penchala which received sewage discharges from industrial area (e.g. breweries, soft drink, food processing, chemical manufacturing, semiconductor and electrical, rubber processing and palm oil processing discharges) and urban area (e.g., road traffic run-off and municipal sewerage), agricultural activities (e.g., fertilizers and other agricultural run-off) as well as atmospheric fallout (however, there is no sufficient information of atmospheric inputs on the Klang River). Klang River systems is a very important area of study due to the fact that: (1) it is situated along the most urbanized and heavily-populated area where more than 4.4 million people (16% of the national population) lives and (2) the most industrial area of Selangor state is located along this river. it flows into the one of the busiest international shipping lanes in the world (Naji and Ismail, 2011).

2.2. Sampling

Surface (0-5cm) sediment samples were collected from 21 different sites along the Klang River (Fig. 1). The longitudes and latitudes of sampling stations were measured by using GPS (Table 1). The surface sediments were transferred in polyethylene plastic bag and labeled. They were then kept in an ice box for transport to the laboratory for processing and analyses. Samples for assessment were dried using an air-circulating oven at 80°C, and sieved through 63µm mesh size, and kept in an acid-washed container for future use.

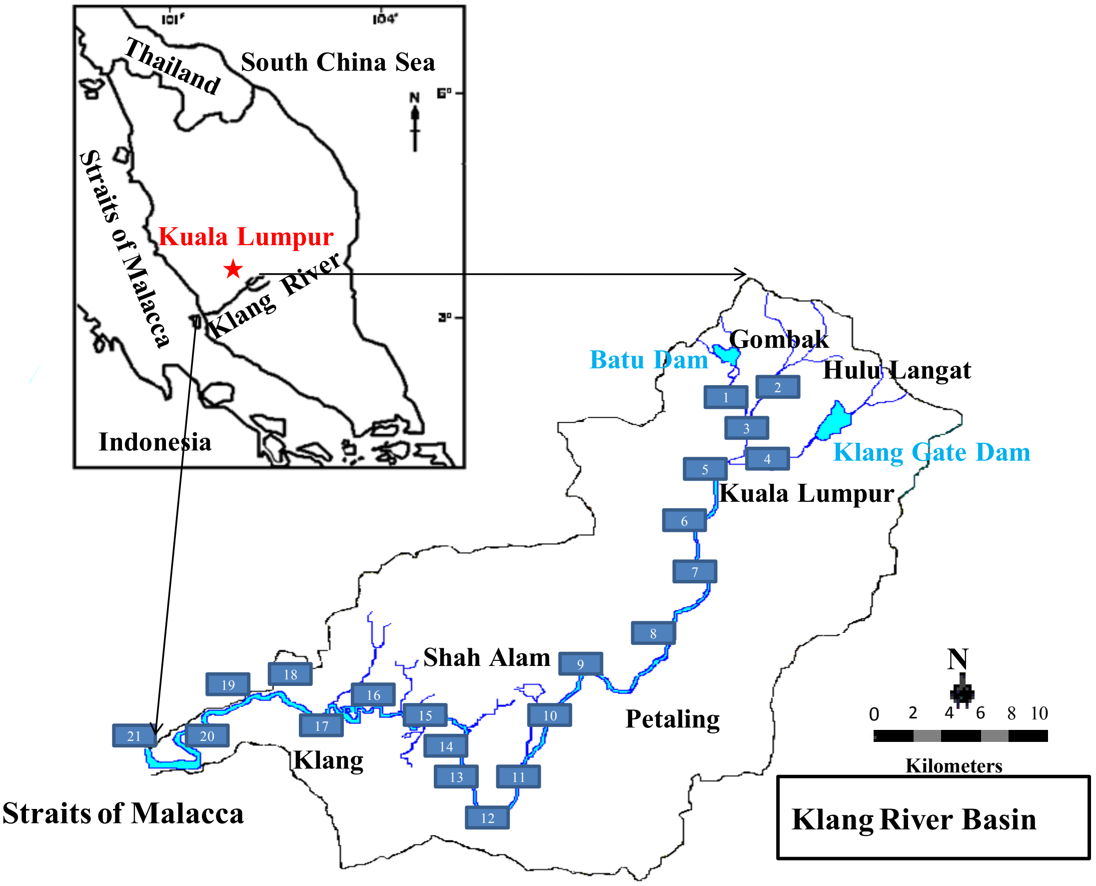

Figure 1. Study area and geographical location of 21 stations in the Klang River

2.3. Sequential extraction

Fractionations of Ni, Cu and Pb in surface sediments were analyzed by using the modified sequential extraction technique (Table 2) (Badri and Aston, 1983; Ismail and Ramli, 1997).

(1) Fraction 1: *Easily, freely or leachable and exchangeable (EFLE)*. About 10 g of sample was continuously shaken for 3 h with 50 ml 1.0M ammonium acetate (NH_4CH_3COO), pH 7.0 at room temperature.

(2) Fraction 2: *Acid-reducible*. The residue form (1) was continuously shaken for 3 h with 50 ml 0.25M hydroxyl-ammonium chloride ($NH_2OH.HCl$) acidified to pH 2 with HCl, at room temperature.

(3) Fraction 3: *Oxidisable-organic*. The residue from (2) was first oxidized with 15ml H_2O_2 (R&M Chemicals 35%) in a water bath at 90˚C. After cooling, the metal released from the organic complexes was continuously shaken for 3 h with 50 ml of 1.0M ammonium acetate (NH_4CH_3COO) acidified to pH 2.0 with HCl, at room temperature.

(4) Fraction 4: *Resistant*. The residue form (3) was digested in a 10 ml combination (ratio of 4:1) of concentrated HNO_3 (AnalaR grade, R&M Chemicals 65%) and $HClO_4$ (AnalaR grade, R&M Chemicals 70%).

The residue of each step was rinsed to 20 ml double-distilled water (DDW) and filtered through Whatman® No.1 filter paper into pre-cleaned 100 ml volumetric flasks. The supernatants liquid of each fractions after filtration were stored for metal determination, excepting for fraction 1 which is sensitive and must be analyzed immediately. The samples were measured for trace metals concentration by using an air-acetylene flame atomic absorption spectrophotometer (Perkin-Elmer Model AAnalyst 800).

2.5. Quality control

To prevent uncertain contaminations, all laboratory glassware used were washed with phosphate-free soap, double rinsed with distilled water and soaked in 10% HNO_3 for 24 h after then 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,Vienna, Austria) was determined as a precision check. Percentage of recoveries (*n*=5 for each metal) for certified and measured concentration of those metals ranged from 95% for Cu to 98% for Ni (Table 3). Calibration curves for each trace metals

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

Station NO.	Designation	Sites	Latitude (N)	Longitude (E)
1	Semi-urban	Beringin	3°13′ 01″	101°40′ 54″
2	Urban	Gombak Jaya	3°11′ 20″	101°42′ 03″
3	Urban	Ulu Klang	3°10′ 04″	101°41′ 35″
4	Urban	PWTC	3° 09′ 48″	101° 45′ 03″
5	Urban	Mesjid Jamek	3° 08′ 49″	101°41′ 42″
6	Urban	Seputeh	3° 08′ 49″	101° 40′ 31″
7	Urban	Sri Sentosa	3° 06′ 48″	101° 39′ 41″
8	Semi-urban	Puchong Jaya	3° 04′ 37″	101° 36′ 53″
9	Industrial	Penaga Industrial park	3° 03′ 27″	101° 36′ 24″
10	Rural	Puchong Tengah	3° 02′ 44″	101° 35′ 49″
11	Industrial	Kampung Seri Aman	3° 01′ 05″	101° 34′ 47″
12	Industrial	Kota Permai	2° 58′ 54″	101° 33′ 03″
13	Industrial	Alam Indah	2° 59′ 29″	101° 32′ 48″
14	Industrial	Kampung Baru Hicom	3° 00′ 48″	101° 32′ 59″
15	Urban	Seksyen 24	3° 01′ 49″	101° 30′ 42″
16	Urban+Industrial	Kampung Seri Kenangan	3° 02′ 29″	101° 28′ 20″
17	Urban	Klang Town	3° 02′ 43″	101°26′ 49″
18	Semi-urban	Sangai Udang	3° 03′ 11″	101°25′ 31″
19	Fishing village+Urban area	Sungai Sirih	3° 02′ 23″	101°23′ 36″
20	Fishing village+Urban area	Bandar Sultan Sulaiman	3° 01′ 07″	101°22′ 28″
21	Near Port	Bagan Hailam	3° 00′ 13″	101°23′ 19″

Table 2. Sequential extraction technique (SET) scheme

Fraction(s)	Extracting reagent(s)	Comment
1-Exchangeable	NH_4CH_3COO 1 mol/L pH=7	Soluble and exchangeable cations
2-Acid-reducible	$NH_2OH.HCl$ 0.25 mol/L pH=2	Easy to mobilize
3-Oxidisable-organic	H_2O_2 (30%), NH_4CH_3COO 1mol/L pH=2	Difficult to mobilize
4-Resistant	HNO_3 (65%), $HClO_4$ (70%)	Strong extracting reagents

were determined with 1,000 mg/L (BDH Spectrosol®) stock solution. The reagent and procedural blanks were monitored for each fraction after five samples during the analysis as part of the quality accuracy program.

2.6. Statistical analysis

All statistical analyses were computed using Statistical Package for Social Science (SPSS) version 16.

3. Results and Discussion

3.1. Ni sequential fractionation

The mean concentrations and percentages of sequential extraction of Ni for each sampling station are shown in Table 4. The total Ni concentration ranged from 5.26 to 22.93 (μg/g d.w.). The exchangeable fraction of Ni ranged from 0.12 to 1.53 μg/g with mean percentage of 3.81%. The acid-reducible fraction ranged from 0.22 to 2.4 (μg/g d.w.) with mean percentage of 6.82%. The oxidisable-organic fraction ranged from 0.63 to 11.16 (μg/g d.w.) with mean percentage of 31.72%. The resistant fraction ranged from 4.31 to 13.18 (μg/g d.w.). In this investigation about 57.66% of Ni in average was computed in the resistant fraction. The fractionation of Ni in the surface sediments of Klang River was in descending order of resistant > oxidisable-organic > acid-reducible > exchangeable. The most Ni ions contained to residual and oxidisable-organic fractions. The mathematical summations of exchangeable, acid-reducible and oxidisable-organic fractions constitute the nonresistant fraction (non-lithogenous) (Badri and Aston, 1983). The nonresistant fraction ranged from 18.37 to 60.3% with mean value of 42.08%. Between the nonresistant fractions, the mean percentages of exchangeable, acid-reducible and oxidisable-organic constituted 8.99, 16.1 and 74.9%, respectively. The Ni concentrations in most of the sampling stations were dominated by the resistant fraction. Exchangeable is most toxic in contrast with the rest of the fractions for aquatic organisms, because it is easily removed and is soluble. In the present study, the small portion of exchangeable fraction showed poor bioavailability of this metal in the surface sediment of the Klang River.

3.2. Cu sequential fractionation

Copper is a micronutrient, essential for most physiological growth for aquatic and terrestrial organisms (Alagarsamy, 2009). Geochemical fractions of Cu in surface sediment of The Klang River are tabulated in the Table 5. The total Cu concentration ranged from 0.28 to1.55 (μg/g d.w.). The exchangeable fraction of Cu range from 0.28 to 1.55 (μg/g d.w.) with mean percentage of 2.28%. The acid-reducible fraction ranged from 0.01 to 0.65 (μg/g d.w.) with mean percentage of 0.7%. The oxidisable-organic fraction ranged from 3.87 to 44.43 (μg/g d.w.) with mean percentage of 53.01%. The resistant fraction ranged from 5.13 to 33.75 (μg/g d.w.) with mean percentage of 44%. The fractionation of Cu in the surface sediments of Klang River was in the order of oxidisable-organic > residual > exchangeable > acid-reducible. This investigation showed that more than 50% of Cu was associated with oxidisable-organic. Organic matter is the most significant sink for Cu in sediments (Chartier *et al*., 2001). The Cu in the Oxidisable fraction is associated with biogenic carriers, which settled through the water column (Callender and Bowser, 1980; Chester *et al*., 1988). Once the particulate material is precipitated at the surface of sediments, the Oxidisable-organic fraction undergoes

Table 3. Total metals concentrations (μg/g dry weight) in certified reference materials (CRM) (Mean±standard deviations; *n*=5).

Element	Measured concentration (μg/g d.w.)	Certified concentration (μg/g d.w.)	Recovery (%)
Ni	12.75±0.09	13.00±0.3	98
Cu	73.09±0.8	77.10±1.20	95
Pb	123.84±22.00	129.00±26.00	96

Table 4. Sequential chemical Concentration of Ni (µg/g d.w.) in surface sediments of Klang River

Station NO.	**Ni**				**Total**
	Exchangeable	**Acid-reducible**	**Oxidisable-organic**	**Resident**	
1	0.12±0.01 (2.3)	0.22±0.00(4.18)	0.63±0.02 (11.89)	4.31±0.05(81.63)	5.26
2	0.15±0.02(1.06)	0.67±0.03 (4.29)	2.53±0.05 (18.49)	10.32±1.5 (75.5)	13.67
3	0.21±0.02(1.73)	0.99±0.01 (8.33)	2.58±0.14 (21.65)	8.15±1.02(68.29)	11.93
4	0.5±0.04(4.21)	0.8±0.02 (6.7)	1.07±0.06 (9)	9.53±0.49 (80.09)	11.90
5	0.73±0.03 (4.54)	0.41±0.04(2.55)	5.43±0.14 (33.93)	9.54±0.34 (58.98)	16.11
6	0.45±0.05 (4.52)	0.34±0.02 (3.41)	1.45±0.11 (14.43)	7.81±0.73 (77.65)	10.05
7	0.53±0.01(2.98)	0.87±0.05 (4.87)	3.23±0.16 (18.15)	13.18±2.31 (74)	17.81
8	0.5±0.05(3.43)	0.7±0.06 (4.82)	4.86±0.21(33.55)	8.44±0.35 (58.2)	14.50
9	0.74±0.07 (3.79)	1.72±0.03 (8.8)	3.59 ±0.15(18.37)	13.7±1.7 (69)	19.75
10	0.78±0.03 (5.68)	0.86±0.06 (6.26)	6.08±0.08(44.2)	6.03± (43.86)	13.75
11	0.97±0.06 (4.25)	1.64±0.03 (7.18)	11.16±1.23(48.87)	9.07± (39.7)	22.84
12	0.9±0.06 (4.42)	1.73±0.1(8.49)	6.39±0.97 (31.36)	11.3±1.03 (55.7)	20.32
13	0.25±0.01(1.45)	1.23±0.06 (6.99)	7.64±0.54 (43.42)	8.47±0.68(48.14)	17.59
14	0.58±0.03 (3)	1.33±0.03 (6.89)	8.57±0.47 (44.48)	8.79±0.70 (45.63)	19.27
15	0.48±0.01 (3.23)	1.1±0.1(7.4)	6.59±0.54(44.44)	6.67±0.46 (44.93)	14.84
16	0.6±0.04 (2.84)	2.17±0.09 (10.24)	8.45±0.30 (39.79)	10.01±0.87 (47.1)	21.23
17	0.97±0.05 (4.53)	1.48±0.06 (6.92)	9.18±0.78(42.92)	9.7±0.32(45.6)	21.33
18	1.03±0.04 (4.5)	2.23±0.01 (9.71)	9.47±0.36(41.21)	10.2±0.56 (44.6)	22.93
19	1.44±0.1(7.19)	2.15±0.08(10.74)	7.67±0.75 (38.21)	8.8±0.32 (43.86)	20.06
20	0.56±0.03 (3.44)	0.79±0.03 (4.78)	5.3±0.38 (33.71)	9.53±0.21 (58.07)	16.18
21	0.79±0.01 (6.8)	1.04±0.02 (8.99)	3.95±0.87 (34)	5.83±0.43 (50.21)	11.61
Range	0.12-1.53	0.22- 2.4	0.63-11.16	4.31-13.18	5.26-22.93

Note: The values in parentheses Shows percentage of elemental concentration

phase transformations as the organic carriers decompose (Alagarsamy, 2009). The present investigation determined that most Cu ion in surface sediments is associated with oxidisable-organic (53.01%) and residual (44%) fractions. The Cu concentrations in the most sampling stations were dominated by the nonresistant fraction. The high level of nonresistant of Cu can be due to industrial activities, dumping and road run-offs in the Klang River. Among the nonresistant fractions, the mean percentages of exchangeable, acid-reducible and oxidisable-organic constituted 4.07, 1.25 and 94.67%, respectively. The high percentage of oxidisable-organic fraction identified that the organically-bound materials such as humic and fulvic can be easily available for biological uptake (Yap *et al*., 2003). The concentration of Cu in the acid-reducible fraction (0.01to 0.65) was low, because of the low affinity of Cu in acid-reducible fraction in surface sediments of Klang River. On the other hand, Iron and manganese-oxides, constituted in acid-reducible fraction have high scavenging efficiencies for trace metals but they are thermodynamically unstable under anoxic circumstances (Tokalioglu *et al*., 2000).

3.3. Pb sequential fractionation

Most often Pb due to its high toxicity entails contamination concern. The geochemical distributions and mean concentrations of Pb are shown in Table 6. The total concentration of Pb ranged from 24.78 to 62.35 (µg/g d.w.). The exchangeable fraction of Pb ranged from 0.59 to 4.07 (µg/g d.w.) with mean percentage of 4.06%. The acid-reducible fraction ranged from 0.38 to 4.16 (µg/g d.w.) with mean percentage of 3.59%. The oxidisable-organic fraction ranged from 2.81 to 28.9 (µg/g d.w.) with mean percentage of 25.09%. The resistant fraction ranged from 14.29 to 49.64 (µg/g d.w.) with mean percentage of 67.26%. The fractionation of Pb in the surface sediments was in descending order of residual > oxidisable-organic > exchangeable > acid-reducible. More than 60% of the total concentration of Pb was dominated by residual fraction in surface sediments of the Klang River. Pb associated largely in the residual fraction and can be less bioavailable except under harsh condition. Since one of the main sources of Pb in the environment is automotive. Our result showed that those stations closed to the intensive main traffic

Table 5. Sequential chemical Concentration of Cu (µg/g d.w.) in surface sediments of Klang River

Station NO.	**Cu**				**Total**
	Exchangeable	**Acid-reducible**	**Oxidisable-organic**	**Resistant**	
1	0.35±0.01 (3.65)	0.11±0.00 (1.21)	3.87±0.24 (40.92)	5.13±0.1 (54.23)	9.46
2	0.62±0.02 (2.98)	0.19±0.01 (0.94)	11.7±0.03 (56.71)	8.12±0.09 (39.37)	0.63
3	1.39±0.09 (3.46)	0.29±0.02 (0.71)	26.1±0.53 (64.57)	12.60±1.11 (31.26)	40.38
4	1.08±0.02 (3.23)	0.38±0.03 (1.13)	21.6±1.02 (64.54)	10.40 ±0.98 (31.1)	33.46
5	1.55±0.04 (2.86)	0.65±0.02 (1.19)	37.3±2.1 (68.8)	14.71±1.24 (27.17)	54.12
6	0.67±0.01 (2.41)	0.39±0.01 (1.41)	15.6±1.02 (56.26)	11.11±0.87 (39.9)	27.77
7	1.02±0.03 (3.1)	0.37±0.03 (1.4)	19.21±1.43 (58.43)	12.28±0.74 (37.3)	32.88
8	0.88±0.03 (1.98)	0.46±0.02 (1.02)	20.68±2.14 (46.22)	22.73±3.45 (50.8)	44.75
9	1.36±0.03 (3.72)	0.59±0.03 (1.62)	15.08±1.21 (41.22)	19.62±2.31 (53.5)	36.65
10	0.38±0.01 (1.73)	0.13±0.00 (0.6)	9.23±1.16 (41.17)	12.43±1.34 (56.0)	22.17
11	0.37±0.00 (0.56)	0.37±0.01 (0.56)	44.43±5.65 (41.6)	21.57±3.41 (32.3)	66.74
12	0.85±0.03 (2.25)	0.18±0.00 (0.47)	15.03±2.1 (66.5)	21.62±1.75 (57.4)	37.68
13	0.81±0.04 (1.92)	0.14±0.00 (0.34)	22.73±3.21 (39.9)	18.83±2.18 (44.2)	42.51
14	1.48±0.07 (2.66)	0.14±0.01 (0.26)	31.39±5.87 (53.52)	22.80±1.67 (40.8)	55.81
15	0.73±0.06 (2.08)	0.13±0.00 (0.37)	18.52±0.45 (56.27)	15.52±0.78 (44.4)	34.9
16	0.96±0.05 (1.73)	0.23±0.01 (0.41)	20.78 ±1.87 (53.2)	33.77±4.53 (60.6)	55.74
17	1.15±0.11 (2.96)	0.22±0.02 (0.52)	23.97±3.10 (37.3)	17.39±1.67 (40.5)	42.73
18	0.80.04 (1.57)	0.12±0.00 (0.21)	36.16±4.32 (56.2)	18.61±0.81 (33.4)	55.76
19	0.42±0.02 (0.82)	0.15±0.00 (0.3)	26.87±2.65 (64.9)	21.93±2.1 (44.4)	49.37
20	0.51±0.01 (1.1)	0.14±0.01 (0.3)	22.27±1.98 (54.5)	23.03±1.89 (50.1)	45.95
21	0.28±0.00 (1.48)	0.01±0.00 (0.06)	8.30±0.76 (43.3)	10.68±0.45 (55.2)	19.27
Range	0.28-1.55	0.01-0.65	3.87-44.43	5.13-33.75	9.47-66.74

Note: The values in parentheses Shows percentage of elemental concentration

had high non-lithogenous percentage of this element such as stations 5, 8, 17, 18, 19 and 20.

Overall, chemical speciation of studied metals in the surface sediments of Klang River from all sampling stations followed the order below:
Ni: residual (57.66%) > Oxidisable-organic (31.72%) > acid-reducible (6.82%)> exchangeable (3.81%); Cu: Oxidisable-organic (53.01%) > residual (44%) > exchangeable (2.28%) > acid-reducible (0.7%); Pb: residual (67.26%) > Oxidisable-organic (25.09%) > exchangeable (4.06%) > acid-reducible (3.59).

3.7. Contamination assessment

3.7.1. Risk assessment code (RAC)

Heavy metals in the sediments can pose hazard to aquatic biota through (1) being released into overlaying water, which may cause acute toxicity; (2) being directly digested by bottom feeders or being transferred through bioaccumulation in food web (Forstner, 1995).

The metals in the sediments are bound with different strengths to the fractions (Singh *et al*., 2005). In the present investigation, the Risk Assessment Code (RAC) has been used to evaluate the risk of heavy metals concentration in surface sediments of the Klang River. The RAC assess the potential release of metals in solution based on the percentage of exchangeable and carbonate fractions in sediments (Tang *et al*. 2010). This classification is tabulated in Table 7 (Singh *et al*., 2005).

The amount of Ni in the exchangeable and carbonate fractions ranged from 5.98% (Station 2) to 17.93% (Station 19), Cu ranged from 1.1 (Station 11) to 5.34% (Station 9) and Pb ranged from 2.25 (Station 19) to 14.60% (Station 4). Based on the classification of the RAC, in all stations the risk associated with Cu in surface sediment was low risk, while Ni was medium risk in most stations. And also, Pb was medium risk in upstream stations (vicinity of intensive main traffic stations), whereas downstream stations can be classified as low risk.

3.5.2. Individual and global contamination factor

The bioavailability and toxicity of trace metals

Table 6. Sequential chemical concentration of Pb (µg/g) in surface sediments of Klang River

Station NO.	**Pb**				**Total**
	Exchangeable	**Acid-reducible**	**Oxidisable-organic**	**Residual**	
1	1.32±0.10 (5.33)	1.71±0.04 (6.91)	3.33±0.06 (13.42)	18.42±1.13 (74.34)	24.78
2	2.39±0.12 (5.45)	3.06±0.05 (6.83)	6.90±0.21 (15.71)	31.63±3.23 (72.01)	43.98
3	2.31±0.14 (4.08)	3.17±0.17 (5.61)	11.13±1.1 (19.7)	39.93±2.43 (70.61)	56.54
4	3.44±0.21 (6.77)	3.98±0.31 (7.83)	8.26±0.16 (16.26)	35.13±1.54 (64.14)	50.81
5	3.02±0.07 (4.9)	4.16±0.10 (6.75)	17.60±0.79 (28.53)	36.91±3.41 (59.81)	61.69
6	2.07±0.04 (5.34)	0.91±0.05 (2.36)	9.59±0.32 (24.77)	26.13±1.98 (67.53)	38.70
7	2.98±0.18 (6.98)	2.78±0.07 (6.5)	8.81±0.51 (26.59)	28.20±0.98 (65.94)	42.77
8	3.67±0.22 (6.28)	1.62±0.02 (2.78)	15.11±0.11 (25.88)	37.96±3.6 (65.05)	58.36
9	4.07±0.32 (6.53)	3.67±0.14 (5.89)	4.96±0.56 (7.95)	49.64±2.5 (79.63)	62.34
10	0.59±0.07 (1.57)	0.77±0.05 (1.92)	10.97±0.67 (29.3)	25.13±1.23 (67.19)	37.46
11	2.39±0.21 (4.45)	0.68±0.06 (1.27)	2.81±0.54 (5.25)	47.73±3.53 (89.03	53.61
12	0.67±0.05 (1.31)	0.67±0.03 (1.3)	12.93±2.87 (25.1)	37.19±2.34 (72.27)	51.46
13	0.71±0.04 (1.31)	0.65±0.02 (1.2)	12.72±1.23 (23.4)	40.31±3.52 (74.1)	54.39
14	0.98±0.02 (2.05)	0.61±0.01 (1.29)	6.73±3.23 (14.15)	39.27±2.13 (82.52)	47.59
15	1.64±0.26 (3.74)	0.56±0.06 (1.27)	9.14±0.34 (20.89)	32.41±3.54 (74.09)	43.75
16	1.19±0.07 (1.93)	1.14±0.09 (1.84)	17.23±1.23 (27.88)	42.23±2.49 (68.35)	61.79
17	2.26±0.18 (3.9)	2.48±0.023 (4.28)	17.01±2.2 (29.3)	36.27±3.45 (62.51)	58.02
18	1.17±0.04 (1.98)	0.54±0.03 (0.9)	23.23±1.32 (39.2)	34.38±2.65 (57.95)	59.32
19	0.87±0.03 (1.57)	0.38±0.01 (0.68)	25.13±3.2 (45.3)	29.12±3.24 (52.45)	55.50
20	3.40±0.17 (6.32)	2.94±0.04(5.47)	28.90±4.1 (53.74)	18.53±1.63 (34.46)	53.77
21	0.94±0.03 (3.53)	0.65±0.02 (2.43)	10.83±0.67 (40.55)	14.29±0.76 (53.49)	26.71
Range	0.59-4.07	0.38-4.16	2.81- 28.9	14.29-49.64	24.78-62.35

Note: The values in parentheses Shows percentage of elemental concentration

depend on its chemical forms. The individual and global contamination factor was calculated to evaluate the metal contamination and their bioavailability in surface sediments of Klang River. The individual contamination factors (ICF) for the various sampling sites were calculated from the result of the fractionation study by dividing the sum of the first three extractions (i.e. exchangeable, acid-reducible and oxidisable organic forms) by the residual fraction for each sampling station. The global contamination factor (GCF) for each sampling station was computed by summing the ICF for Ni, Cu and Pb obtained for a sampling station (Ikem *et al*., 2003).

Table 7. Risk Assessment Code

Risk	Metal in carbonate and exchangeable fraction (%)
No risk	<1
Low risk	1-10
Medium risk	11-30
Very high risk	31-50
High risk	≥75

The ICF and GCF were expressed as in the following expression:

$$\mathbf{ICF}_{\mathbf{metal}} = \frac{C_{nonresistant}}{C_{resistant}} \qquad \textbf{Equation 1}$$

$$\mathbf{GCF} = \sum_{i=1}^{n} CF_i \qquad \textbf{Equation 2}$$

The individual and global contamination factors for Ni, Cu and Pb in the surface sediments are shown in Table 8. The result of ICF showed that contamination degree of Cu was higher than the rest of the metals studied. On the basis of the Ikem (2003), ICF reflects the risk of contamination of a water body by a pollutant. Therefore, Cu had highest risk to water body. However, the bioavailability of metals from sediment into the water column will be influenced by factors such as pH, chemical forms of the heavy metals, and the physicochemical characteristics of the water column (Ikem *et al*., 2003). The mean individual concentration factor in the surface sediments ranged in the descending order of Cu > Ni > Pb.

The global contamination factor analyzed from ICF values showed that Station 3 (confluence of Batu River and Gombak river) and Station 5 (confluence of Klang River and Gombak River) in upstream and most downstream stations were highly impacted by trace metal pollutants. The results obtained were in accordance with Luoma and Rainbow (2008) statement in which the trace metals tend to accumulate in a hotspot near the inputs (Luoma and Rainbow, 2008). GCF is significant because it reflects the overall potential risks posed by the toxic elements (Ikem *et al*., 2003). Since no guidelines for GCF value available, comparison to the results can not be done and therefore, the effects of the combination of metals contamination cannot be assayed comprehensively (Naji *et al*., 2010). The results identified that those stations located near-by municipal and industrial area had high potential risk to the Klang River environment. Notably, determination of the degree of metal contamination is one of the most important aspects to reduce and control pollution in the aquatic environment.

Table 8. Individual and global contamination factors of Ni, Cu and Pb in the surface sediments of Klang River

Station NO.		ICF		GCF
	Ni	Cu	Pb	
1	0.22	0.84	0.35	1.41
2	0.32	1.54	0.39	2.25
3	0.46	2.20	0.42	3.08
4	0.25	2.22	0.45	2.91
5	0.70	2.68	0.67	4.05
6	0.29	1.51	0.48	2.27
7	0.35	1.68	0.52	2.54
8	0.72	0.97	0.54	2.22
9	0.45	0.87	0.26	1.57
10	1.28	0.78	0.49	2.53
11	1.52	2.09	0.12	3.74
12	0.79	0.74	0.38	1.92
13	1.08	1.26	0.35	2.69
14	1.19	1.45	0.21	2.85
15	1.23	1.25	0.35	2.83
16	1.12	0.65	0.46	2.24
17	1.19	1.47	0.60	3.26
18	1.24	2.00	0.73	3.97
19	1.28	1.25	0.91	3.44
20	0.72	0.99	1.90	3.62
21	0.99	0.81	0.87	2.67

4. Conclusion

Rivers in mega cities are more often vulnerable to metals contamination because of widespread point and non-point sources along and near-by them. The chemical fractionation of studied metals (except Cu) in majority of stations were in the order of residual > acid-reducible > oxidisable- organic > exchangeable. The mean percentages of anthropogenic portions of the investigated metals were decreased in the order of Cu (56.01) > Ni (42.08) > Pb (33.22). It showed that Ni and Pb in Klang River surface sediments existed in the resistant fractions (sedimentary matrix), while Cu existed in the non-resistant fractions. Likewise, more than 50% of Cu was associated with oxidisable-organic. The mean exchangeable (EFLE) concentration of Ni, Cu and Pb were less than the rest of the fractions. Since exchangeable fraction is most mobile, the small portion of exchangeable fraction of studied metals indicated the poor bioavailability of these metals in the Klang River. In general based on ICF values many locations along Klang River are low risks except few stations located near-by municipal and industrial area had high potential risk to the Klang River environment This study was the first in accordance with chemical fractionation of metals in surface sediments of the Klang River and provided the baseline information for further study in Klang River systems.

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