



# Journal of Biological Sciences

ISSN 1727-3048

**science**  
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## Heavy Metal Concentrations (Cu, Cd and Pb) in Sediments in the Juru River, Penang, Malaysia

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**Abstract:** The purpose of this study were to determine the concentration of heavy metals namely copper (Cu), cadmium (Cd) and lead (Pb) in sediment and to investigate the effect of sediment pH and sediment organic matter on concentration of copper, cadmium and lead in sediment at oxidation fraction from Juru River, Penang, Malaysia. The sequential extraction procedure used in this study was based on defined fractions: exchangeable, acid reduction, oxidation and residual. The concentration of Cu, Pb and Cd in residual fraction were higher than the other fractions. Among the non-residual fractions, the concentration of heavy metals in organic matter fraction was much higher than other fractions collected from all sampling sites except for Cd. The pH of the sediment in all sites was acidic. The mean of total concentrations of Cu, Cd and Pb for the two sampling times were 667, 4.135 and Pb 927  $\mu\text{g g}^{-1}$  dry weight, respectively. Results of organic matter analysis showed that the percentage of organic matter present in sediment samples varied throughout the river and all sites of sediments were ranged from 7.10 to 16.20%. Comparison between sampling sites using one-way analysis of variance showed that there were significant differences at exchangeable fraction for cadmium and lead while there was no significant differences for copper. At acid reduction fraction and oxidation fraction there were significant differences for the three metals while there was no significant difference at residual fraction.

**Key words:** Concentration heavy metals, individual contamination factor, sediments, sequential extraction, toxicity, ICP-MS, physicochemical parameters

### INTRODUCTION

The pollution of sediments, soils and organisms by toxic metals is of serious issue, mainly in a lot of developed countries around the world, because when they accumulate and cause diseases when enter the body. It is known that Sediments were found to be transporters of most metals. Biological and chemical reactions play important role to recycle some metals within the water body (Soylak and Yilmaz, 2006; Arain *et al.*, 2008). Numerous chemicals like pesticides and heavy metals finally deposit into bottom sediment. Sediments also show essential part of remobilization of pollutants in water systems under opportune situations (Ikem *et al.*, 2003). Much concern has been focused on the investigation of the total metal contents in sediments. However, it cannot provide sufficient information about mobility, bioavailability and toxicity of metals. The speciation of metals in sediments is therefore a critical factor in assessing the potential environmental impacts (Peng *et al.*, 2004). Chemical speciation can be determined as the process of identification and quantification of diverse species, shapes or stages of chemical existent in

a material. These species can be defined (1) functionally, for instance those species that can be digested by flora, (2) practically, in keeping with the techniques or reagents utilized in their extraction and (3) particularly, as particular components or oxidation states of a metal. To evaluate the relative stage associations of metals in sediment in several aquatic environments, Single leaching and joined sequential extraction procedure was improved (Cieri *et al.*, 2008). The two most widely utilized protocols are the Kersten/Forstner procedure (Kersten and Forstner, 1986) and the Tessier procedure (Tessier *et al.*, 1979). However, as these procedures differ in extraction sequences and in operating conditions, it is quite difficult to compare the data obtained from these two methods. Relying on hydrodynamics, biogeochemical processes and ecological circumstances (redox, pH, salinity and temperature) of rivers, sediments are well known as significant sink of metals in waterways along with a possible non-point source that may immediately affect overlying waters (Pekey, 2006).

In order to manage aquatic system it is important to know the biological status of the system, especially when evaluating the impact of a chemical stressor on the biota.

Understanding the ability of aquatic ecosystems to adapt to changes, fundamental knowledge of the ecosystems situation is required. The objectives of this study were to determine the distribution and concentration of three heavy metals, i.e., copper (Cu), cadmium (Cd) and lead (Pb) in sediments and to investigate the effect of sediment pH and sediment organic matter on concentration of copper, cadmium and lead in Juru River.

**MATERIAL AND METHODS**

**Study area:** Sediment samples were collected 2 times (in December 2009 and August 2010). The date for each sampling site is illustrated in Table 1. Juru River originates from Bukit Mertajan hills located at 05°22' N latitude and 100°28' E longitude, Penang, north-eastern of Malaysia (Fig. 1) and drains approximately 7.95 km long. The Juru river receives water from several small tributaries that flow through urban settings that grossly polluted with industrial, agriculture and domestic wastes that are

discharged directly into these rivers. Besides high levels of organic loadings, these wastes are also contaminated with heavy metals (Lim and Kiu, 1995).

In this study, sequential extraction procedure was used and conducted by adopting the method of Badri (1984). This method was applied to identify the amount of lithogenic metals in contrast with natural origin. Sequential extraction method can prove to separate various chemical forms of heavy metals. Recent studies have utilized sequential extraction to understand the chemical associations with specific sedimentary phases and sources of metals in sediment (Yang *et al.*, 2009; Naji *et al.*, 2010). This procedure consists of four stages. The extraction steps employed in this study are described as follows: Extraction 1: Easily and freely leachable and exchangeable fraction: Fifty milliliter 1 M NH<sub>4</sub>CH<sub>3</sub>COOH

Table 1: The date for each sampling time

Sampling	Date
First sampling	26,27/12/2009
Second sampling	27,28/8/2010



Fig. 1: Map of the Juru River and sampling stations

at pH 7 was added to the weighted sample (5 g) into bottle and the sample was shaken for 1 h at a speed of 3000 rpm at room temperature. Extraction 2: Acid reduction fraction: Fifty milliliter 0.25 M CH<sub>2</sub>OH.HCl at pH 2 (adjusted using HNO<sub>3</sub>) was added to the residue from Fraction 1 and the sample was shaken under the same settings described in Fraction 1. Extraction 3: Organic oxidation fraction: Fifteen milliliter H<sub>2</sub>O<sub>2</sub> 30% was added to the residue from Fraction 2 and the sample was placed in water bath until dry. Then, 50 mL 1 M NH<sub>4</sub>CH<sub>3</sub>COOH at pH 3.5 (adjusted using HCl) was added to it and the sample was shaken under the same settings described in Fraction 1. Extraction 4: Resistance fraction: Residue from Fraction 3 was used for final fraction.

**Sediment pH:** Sediment pH was measured following Duddridge and Wianwright (1981). About 20 g of dried sediment was added to 40 mL of distilled water and mixed. pH was measured using a W-500 Witeg Digital pH meter.

**Organic content:** The organic content in sediment was determined following Walkley and Black (1934). About 0.25 g of dried sediment was added into flask containing 0.17 M potassium dichromate followed by 20 mL of sulfuric acid. The mixture was then heated on the hot plate for 30 min. Two hundred milliliter of deionised water was then added into the mixture followed by 10 mL of concentrated phosphoric acid. Diphenylamine was used as indicator and titration was done using ferrous ammonium sulphate 0.4 N (FAS). All titration including the blank was carried out and the percentage of organic content was calculated as below:

$$\text{Organic carbon (\%)} = \frac{Y}{0.25} \times 100$$

where, Y is 3.96 (10-(N<sub>FAS</sub>)).

**Sediment grain size:** Sediment grain size was measured according to Badri (1984). About 10 gram of dried sediment was sieved through using anti rust laboratory test sieve model BS 410 (63 µm mesh size). Sediment that retained in the sieve was dried repeatedly in oven and final weight was used to calculate the percentage of sediment (<63 µm) using formula as below:

$$>63\mu (\%) = \frac{\text{Initial weight-Final weight}}{\text{Initial weight}} \times 100$$

**Statistical analyses:** Pearson's correlation coefficients (r) were used when calculating correlations between pH, organic matter and concentration of heavy metals at oxidation fraction. To determine the significant differences

at different sampling sites of the four sediment fractions, a one-way analysis of variance (ANOVA), Tukey's honest significant difference test was employed. The results showed that there were significant differences between sampling sites within each fraction and between fractions. There was no significant correlation between concentration of cadmium and copper with pH and organic matter (p>0.05). There was high significant correlation between concentration of lead with organic matter percentage and pH (p<0.01).

**Quality control:** To preclude uncertain contaminations, all laboratory equipments used were washed with phosphate-free soap, double rinsed with distilled water and left in 10% HNO<sub>3</sub> for 24 h and all equipments were then rinsed two times with double-distilled water and left semi-closed to dry at room temperature. A quality control samples were routinely run through during the period of metal analysis. Certified Reference Material (CRM) (National Institute of Standards and Technology, Buffalo River Sediment, USA) was determined as a precision check. Percentage of recoveries (n = 5 for each metal) for certified and measured concentration of those metals was satisfactory, with the recoveries being 74.6-79.2%. In order to check the accuracy of this method, the sum of all extraction steps for each metal was compared with that found by using direct digestion for sequential extraction procedure.

## RESULTS

**pH and organic matter in sediments:** The values of pH and percentage of organic matter in sediments are given in Table 3. The pH of the sediment in all sites was acidic. The highest mean pH was at site 20 with pH value of 6.59, from a range of 6.58 to 6.60. The lowest mean pH was at site 2 at pH 3.96 with values ranging from 3.94 to 3.97. The highest mean percentage of organic matter measured was at sampling site 20 with a value of 16.20%, with readings ranging from 14.50 to 16.30. The lowest mean percentage of organic matter was measured at site 5 at 7.10, with values ranging from 5.90 to 9.40. The mean organic matter in sediments exceeded 10% at all sampling sites. 49.67% of sediment from Juru River has grain size less than 63 µm diameter and majority were located close to the estuary. The estuarine area is recognised as a sink for sedimentation which includes suspended particles (Olausson and Cato, 1980). The very fine particles that drifted from upstream finally will precipitate within the estuarine area. The percentage of organic content in river sediments was somewhat high (2.4 to 5.6%) which is consequent from large grain size. The small grain size

(<63 µm) clearly demonstrates significant influence to the metal absorption in sediments. Literature suggests that metals generally have relative potential for sorption onto clay minerals, hydrous oxides and organic matter surfaces, all of which tend to be found in the smaller grain sizes (Salomons, 1980; Sager, 1992; Schoer, 1985).

**Heavy metal concentration in sediment:** The sequential extraction procedure used in this study was based on defined fractions: exchangeable, acid reduction, oxidation and residual. Concentration of copper, cadmium and lead in sequential extraction of sediments are shown in Table 4-6.

**Copper concentration in sediment:** Concentration of copper in sequential extraction of sediments is shown in Table 2. The concentration of copper at easily and exchangeable phase at site 16 was the highest among the sites with a mean value of 0.400 µg g<sup>-1</sup>; the lowest concentration of copper was at site 19 with a mean value of 0.143 µg g<sup>-1</sup>. The highest mean concentration of copper at acid reduction phase was measured at site 11 at 5.505 µg g<sup>-1</sup>; the lowest mean concentration of copper was measured at site 12 at 0.398 µg g<sup>-1</sup>. The highest mean concentration of copper at organic oxidation phase was measured at site 18 at 17.056 µg g<sup>-1</sup> while the lowest mean concentration of it was measured at site 1 at 3.055 µg g<sup>-1</sup>. The concentration of copper in the residual phase was noticeably high at site 17 relative to the other stations with a mean value of 32.513 µg g<sup>-1</sup>; the lowest copper concentration was at site 20 with a mean value of 5.488 µg g<sup>-1</sup> (Table 4).

Table 2: List of sampling sites and geographical locations along the Juru River

Sampling stations	Latitude (N)	Longitude (E)
1	N 05°19'54.2	E 100°26'41.8
2	N 05°19'59.7	E 100°26'30.6
3	N 05°19'93.2	E 100°26'37.1
4	N 05°19'86.2	E 100°26'25.0
5	N 05°19'49.7	E 100°26'05.9
6	N 05°19'48.2	E 100°26'01.2
7	N 05°19'47.1	E 100°25'55.3
8	N 05°19'52.4	E 100°25'52.1
9	N 05°20'00.9	E 100°25'51.4
10	N 05°20'08.2	E 100°25'46.1
11	N 05°20'08.3	E 100°25'36.5
12	N 05°20'06.6	E 100°25'27.7
13	N 05°20'02.1	E 100°25'18.9
14	N 05°19'49.2	E 100°25'19.2
15	N 05°19'42.4	E 100°25'14.3
16	N 05°19'57.0	E 100°25'02.1
17	N 05°20'35.0	E 100°25'07.7
18	N 05°20'27.0	E 100°24'30.6
19	N 05°20'09.1	E 100°24'04.9
20	N 05°19'49.6	E 100°23'45.1

**Cadmium concentration in sediment:** Concentration of cadmium in sequential extraction of sediments is shown in Table 3. The concentration of cadmium at easily and exchangeable phase at site 5 was the highest among the sites with a mean value of 0.067 µg g<sup>-1</sup>; the lowest cadmium concentration was at site 1 with mean value of 0.020 µg g<sup>-1</sup>. Sampling site 16 recorded high cadmium concentration at acid reduction phase relative to the other sites with values at 0.042 µg g<sup>-1</sup>; the lowest mean concentration of cadmium at acid reduction phase was measured at site 4 at 0.006 µg g<sup>-1</sup>. The concentration of cadmium from the organic oxidation fraction at site 4 was highest among the sites with a mean value of 0.055 µg g<sup>-1</sup> while the lowest concentration was at site 3 with a mean

Table 3: Mean levels of pH and organic matter at 20 sites in Juru River

Site	pH	Organic matter (%)
1	4.18±0.08	9.55±0.21
2	3.96±0.02	8.25±0.78
3	4.43±0.17	8.30±0.00
4	4.82±0.73	8.25±1.63
5	4.19±0.19	7.10±1.27
6	5.01±0.87	10.95±1.20
7	4.43±0.24	11.00±0.71
8	5.37±0.94	10.65±0.78
9	4.43±0.23	10.65±1.20
10	4.80±0.57	10.75±0.21
11	4.57±0.21	9.75±1.20
12	4.24±0.03	11.25±0.78
13	4.13±0.07	10.90±0.85
14	4.91±0.72	10.85±1.63
15	4.30±0.07	11.05±0.78
16	4.49±0.30	13.75±1.48
17	4.78±0.26	13.60±0.42
18	5.05±0.29	14.90±1.27
19	6.56±0.13	15.60±0.99
20	6.59±0.01	16.20±1.27

Values are Mean±SD

Table 4: Copper concentration (µg g<sup>-1</sup>)

Sites	F1	F2	F3	F4
1	0.264±0.062	0.512±0.096	3.055±0.082	10.010±0.792
2	0.311±0.011	0.399±0.039	5.429±1.166	14.589±0.027
3	0.162±0.020	0.800±0.078	4.121±0.409	18.976±0.092
4	0.370±0.017	3.484±0.178	10.545±0.383	21.351±0.401
5	0.384±0.060	4.876±0.575	15.267±0.548	15.742±0.430
6	0.322±0.019	0.511±0.037	10.248±0.155	18.738±0.026
7	0.268±0.030	1.039±0.068	6.140±0.950	12.336±0.059
8	0.313±0.118	5.435±0.573	12.927±0.879	15.684±0.298
9	0.226±0.037	2.836±0.303	4.286±0.363	24.687±0.166
10	0.241±0.008	4.769±0.329	9.198±0.951	12.986±0.560
11	0.348±0.062	5.505±0.242	4.077±0.522	27.282±1.175
12	0.251±0.038	0.398±0.050	3.621±0.968	30.655±0.107
13	0.318±0.046	1.311±3.621	10.160±0.690	19.645±0.310
14	0.362±0.056	0.547±0.122	12.982±0.451	23.551±0.119
15	0.373±0.094	3.689±0.365	4.777±0.986	12.290±0.101
16	0.400±0.108	3.368±0.566	4.982±0.740	25.287±0.191
17	0.253±0.015	1.035±0.148	7.203±0.631	32.513±0.036
18	0.158±0.025	4.804±0.033	17.056±1.436	12.383±0.088
19	0.143±0.024	2.827±0.633	4.846±0.623	47.464±0.257
20	0.301±0.049	3.691±0.309	11.547±0.857	51.488±0.235

Values are Mean±SD, F1: EFLE fraction, F2: Acid reduction fraction, F3: Organic oxidation fraction, F4: Resistant fraction

value of 0.010  $\mu\text{g g}^{-1}$ . The highest mean concentration of cadmium at residual phase was measured at site 13 with a mean value of 0.305  $\mu\text{g g}^{-1}$  while the lowest mean concentration was recorded at site 3 at 0.032  $\mu\text{g g}^{-1}$  (Table 5).

**Lead concentration in sediment:** Concentration of lead in sequential extraction of sediments is shown in Table 4. The concentration of lead at easily and exchangeable phase at site 8 was the highest with a mean value of 4.246  $\mu\text{g g}^{-1}$ ; the lowest lead concentration was at site 14 with a mean value of 0.869  $\mu\text{g g}^{-1}$ . The highest mean concentration of lead at acid reduction phase was measured at site 19 at 2.406  $\mu\text{g g}^{-1}$ ; the lowest mean concentration of lead in similar fraction was noted at site 7 with a mean value at 0.413  $\mu\text{g g}^{-1}$ .

The concentration of lead at organic oxidation phase at site 16 was the greatest among the sites with a mean value of 7.309  $\mu\text{g g}^{-1}$  while the concentration of it at site 14 was the lowest among the sites with a mean value of 1.288  $\mu\text{g g}^{-1}$ . The highest mean concentration of lead at residual phase was measured at site 5 with a mean value of 64.732  $\mu\text{g g}^{-1}$  while the lowest mean concentration of it was measured at site 19 at 25.254  $\mu\text{g g}^{-1}$  (Table 6).

**Individual contamination factor:** The Individual Contamination Factor (ICF) for three heavy metals in this study is shown in Table 5. The individual contamination factor for the various sampling sites were calculated from the results of fractionation by dividing the sum of the first three fractions (i.e., loosely and exchangeable, acid

reduction and organic oxidation forms) by the residual fraction for each site (Ikem. *et al.*, 2003). The highest level of individual contamination factor for copper was calculated at site 20 with a value of 2.831 while the lowest level of it was calculated at site 12 with a value of 0.139. The highest level of individual contamination factor for cadmium was calculated at site 16 with a value of 3.030 while the lowest level of it was calculated at site 12 with a value of 0.264. The highest levels of individual contamination factor for lead were calculated at site 19 with a value of 0.466 while the lowest level of it was calculated at sites 14 with a value 0.065 (Table 7).

**Table 6: Lead concentration ( $\mu\text{g g}^{-1}$ )**

Sites	F1	F2	F3	F4
1	2.289±0.088	1.079±0.273	4.703±1.079	29.221±4.270
2	2.672±0.046	1.132±0.234	3.855±0.473	34.172±1.853
3	1.066±0.147	0.450±0.089	4.096±0.186	33.578±0.305
4	3.844±0.112	1.408±0.340	3.405±0.698	54.254±3.429
5	1.263±0.034	0.974±0.137	2.923±0.621	64.732±4.093
6	1.643±0.054	0.708±0.182	4.011±0.692	40.012±1.250
7	2.244±0.064	0.413±0.074	5.411±0.069	37.575±2.074
8	4.246±0.067	0.905±0.251	5.945±0.548	48.853±1.984
9	2.697±0.023	0.685±0.171	2.415±0.404	32.779±3.791
10	1.279±0.157	0.415±0.091	5.124±0.183	49.295±5.288
11	3.714±0.036	1.093±0.216	3.102±0.422	52.282±1.366
12	3.626±0.173	1.203±0.206	3.014±0.414	38.891±3.203
13	2.286±0.068	0.610±0.057	4.146±0.277	46.572±3.677
14	0.869±0.313	0.450±0.093	1.288±0.183	39.609±2.756
15	2.708±0.184	0.807±0.138	4.417±0.277	47.167±2.320
16	1.257±0.007	0.550±0.149	7.309±0.300	38.370±3.618
17	3.237±0.272	1.233±0.163	3.648±0.317	25.693±1.041
18	0.986±0.224	2.226±0.282	4.644±0.671	33.214±1.164
19	3.267±0.176	2.406±0.577	6.104±1.026	25.254±5.009
20	1.189±0.034	1.941±0.450	4.872±0.902	34.996±2.582

Values are Mean±SD, F1: EFLE fraction, F2: Acid reduction fraction, F3: Organic oxidation fraction, F4: Resistant fraction

**Table 5: Cadmium concentration ( $\mu\text{g g}^{-1}$ )**

Sites	F1	F2	F3	F4
1	0.020±0.001	0.016±0.001	0.036±0.004	0.127±0.013
2	0.021±0.004	0.013±0.002	0.041±0.013	0.068±0.020
3	0.025±0.003	0.016±0.002	0.010±0.001	0.032±0.016
4	0.027±0.009	0.006±0.001	0.055±0.012	0.154±0.012
5	0.067±0.002	0.012±0.002	0.039±0.001	0.092±0.019
6	0.021±0.004	0.018±0.000	0.022±0.004	0.109±0.012
7	0.025±0.008	0.018±0.002	0.033±0.001	0.088±0.010
8	0.028±0.005	0.024±0.000	0.027±0.001	0.127±0.001
9	0.024±0.000	0.030±0.001	0.016±0.002	0.128±0.028
10	0.045±0.001	0.011±0.002	0.054±0.015	0.172±0.009
11	0.040±0.007	0.038±0.011	0.014±0.001	0.132±0.011
12	0.025±0.004	0.011±0.003	0.023±0.003	0.223±0.020
13	0.044±0.003	0.018±0.003	0.044±0.011	0.305±0.022
14	0.044±0.009	0.016±0.001	0.054±0.004	0.066±0.024
15	0.062±0.009	0.030±0.007	0.013±0.002	0.164±0.020
16	0.029±0.001	0.042±0.020	0.029±0.002	0.033±0.011
17	0.026±0.001	0.020±0.006	0.048±0.002	0.069±0.012
18	0.025±0.004	0.019±0.006	0.013±0.002	0.135±0.030
19	0.022±0.001	0.023±0.006	0.020±0.004	0.064±0.022
20	0.015±0.003	0.024±0.000	0.025±0.002	0.190±0.031

Values are Mean±SD, F1: EFLE fraction, F2: Acid reduction fraction, F3: Organic oxidation fraction, F4: Resistant fraction

**Table 7: Individual contamination factors (ICF) of 3 elements**

Sites	ICF (Cu)	ICF (Cd)	ICF (Pb)
1	0.382	0.566	0.276
2	0.420	1.102	0.224
3	0.267	1.593	0.167
4	0.674	0.571	0.159
5	1.303	1.282	0.079
6	0.591	0.559	0.159
7	0.603	0.863	0.214
8	1.190	0.622	0.227
9	0.297	0.546	0.176
10	1.094	0.639	0.138
11	0.363	0.696	0.151
12	0.139	0.264	0.201
13	0.600	0.347	0.151
14	0.589	1.727	0.065
15	0.719	0.640	0.168
16	0.346	3.030	0.237
17	0.261	1.362	0.315
18	1.778	0.422	0.236
19	0.164	1.015	0.466
20	0.301	0.336	0.228

At 20 sites in Juru river

### **Comparison between sampling sites in sediment:**

Comparison between sampling sites using one-way analysis of variance showed that there were significant differences at exchangeable fraction for cadmium and lead while there was no significant difference for copper. At acid reduction fraction and oxidation fraction, comparison between sampling sites showed that there were significant differences for cadmium, copper and leads while there was no significant difference at residual fraction.

## **DISCUSSION**

Sequential extraction results can provide information on possible chemical forms of heavy metals in sediments (Xiangdong *et al.*, 2000). The effects of heavy metals in the environment depend to a large extent on whether they occur in forms that can be taken up by plants or animals. According to Elith and Garwood (2001), lead maybe strongly adsorbed onto sediment particles and therefore, largely unavailable while cadmium ions can be directly absorbed to water and it is known to be most mobile among the other metals (Kabata-Pendias and Pendias, 2000). A wide range of values for heavy metal concentrations was observed for the sediments. On the average, the percentage of cadmium associated with different fractions in the sediment from all sites was in the order of residual (59.9%)>organic matter (14.9%)>easily and exchangeable (15.4%)>acid reduction (9.6%) The percentage of copper from all sites was in the order of residual (67%)>organic matter (24.3%)>acid reduction (7.7%)>easily and exchangeable (0.8%). The percentage of lead was in the order of residual (84.1%)>organic matter (8.8%)>easily and exchangeable (4.8%)>acid reduction (2.1%). Present results are in disagreement with the findings of a previous study conducted in the same river by Yap and Tan (2008). They reported that mean concentration of Cd was in order of residual (76.41%)>organic matter (15.09%)>acid reduction (4.46%)>easily and exchangeable (4.42%). The mean concentration of Cu was in order of residual (52.42%)>organic matter (46.87%)>easily and exchangeable (0.47%)>acid reduction (0.22%). The mean concentration of Pb was in order of residual (69.58%)>organic matter (25.04%)>easily and exchangeable (3.01%)>acid reduction (2.35%). Assuming that bioavailability is related to solubility, then metal bioavailability decreases in the order of exchangeable forms>acid reduction forms>organic forms>residual forms (Ma and Rao, 1997; Xiangdong *et al.*, 2000). The residual forms are not expected to be released under normal conditions in nature (Dean, 2003) and could be considered as an inert phase (Xiangdong *et al.*, 2000). The highest

concentration of residual of all metals in this study was in agreement with other studies in Malaysia such as (Yap and Tan, 2008; Naji *et al.*, 2010; Ebrahimpour and Mushrifah, 2008) but in contrast with to that of Nemati *et al.* (2011) who had reported that Cd and Pb in AR fraction was higher than residual.

Besides metal concentrations, metal availability is also influenced by other characteristics of the soil/sediment system such as pH and organic matter content which control the solubility and therefore, the availability of metals (Vogel-Mikus *et al.*, 2005). Among the non-residual fractions, the organic matter fraction was much higher than other fractions in most sites. The percentage of cadmium in the non-residual fractions was greater than the residual fraction. The results were in agreement with that of Yap and Tan (2008) but were disagreement with the values found by Nemati *et al.* (2011) for Cd and Naji *et al.* (2010) for Cd and Pb. About 32.9% of the cadmium in sediment was associated with the exchangeable, acid reduction and oxidation fractions. This result support by Ebrahimpour and Mushrifah (2008) who reported that cadmium in non-residual fractions was high (87.43) but in contrast to that of Yap and Tan (2008). Forstner (1985) reported that cadmium was characteristically enriched in the more mobile fractions and more mobile than most of other heavy metals (Kong and Liu, 1995). The present results indicate that cadmium at sites 9, 11 and 19 and lead at site 11 have greater potential for mobilization from the sediments than copper because of their higher concentration at the acid reduction fraction.

Results of organic matter analysis showed that the levels of organic matter present in sediment samples varied throughout the river and all sampling sites were relatively low in organic matter. It is assumed that such differences were related to variations in the quantity and sources of organic matter present at each site and the ability of organic matter to move in the sediments. Organic matter has a high specific storage capacity for heavy metals (Elith and Garwood, 2001). Acidic pH condition is known to influence the sorption of lead by organic matter fraction in sediments (Ikem *et al.*, 2003). Analysis of pH and percentage of organic matter present in sediments concluded that there were strong correlations between each of these factors and the concentrations of copper and lead. Results showed that the concentration of heavy metals at oxidation fraction at some sites increased with increasing pH levels and percentage of organic matter present in the sediments.

The presence of organic matter may increase the levels of lead and copper in the organically bounded form (Kong and Liu, 1995). Copper can easily form complexes

with organic matters due to its high formation constants forming organic-copper compounds (Xiangdong *et al.*, 2000; Preda and Cox, 2002; Wang *et al.*, 2004) and these are mainly bound to the organic matter fraction (Fernandes, 1997; Kabata-Pendias and Pendias, 2000; Pagnanelli *et al.*, 2004). Under oxidizing conditions, metals present in both natural organic matter and living organisms (as a result of bioaccumulation of metals) may be remobilized into the aquatic environment (Ikem *et al.*, 2003). In aquatic systems, the distribution of copper is mainly affected by natural organic matter such as humic materials and amino acids (Xiangdong *et al.*, 2000). The first two fractions, i.e., the exchangeable and acid reduction fractions were found to be minor contributors for copper. In the present study low copper content in these two fractions indicates that copper maybe less bioavailable in the sediments. There was a significant relationship between copper bound to the organic fraction and sediment organic contents. Thus, it can be suggested that if a significant amount of organic matter is present, the availability and consequently the toxicity of the element will be drastically reduced (Fernandes, 1997).

Concentration of studied metals in sediment could affect the aquatic fauna in the River particularly *Anadara granosa* (cockle) farming where usually live. Kamaruzzaman *et al.* (2011) reported that contamination of some metals in sediment could affect *Anadara granosa* due to the fact that the habitat of *Anadara granosa* (cockles) that are living at the bottom of sea, nearly to the sediment where various kinds of hazardous and toxic substances are accumulated. According to Boscolo *et al.* (2007), bivalve mollusc species had a high capacity and propensity to concentrate pollutants.

A Pearson correlation was carried out between organic matter percentages, pH and concentration of cadmium, copper and lead at the oxidation fraction. There was no significant correlation between concentration of cadmium with pH ( $p > 0.05$ ) but there was significant correlation between concentration of cadmium with organic matter percentage ( $p < 0.05$ ). Cadmium is most mobile in acid soils/sediments within the range of pH 4.5 to 5.5 and the solubility of it is closely related to the acidity of the soil/sediments solution. The result of Pearson correlation ( $r$ ) for organic matter for cadmium was 1 ( $p < 0.05$ ) which means that there was a strong linear correlation with organic matter.

The ICF reflects the risk of contamination of a water body by a pollutant (Ikem *et al.*, 2003). However, oxidation forms are relatively less mobile than those extracted in exchangeable and acid reduction forms because it bound stronger to the sediment components (Kabala and

Singh, 2001). The remobilization of metals from juru 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). At site 16 cadmium showed higher ICF when compared to other sites. Therefore, the risk of cadmium contamination in this site was higher than the other sites. Generally, the ICF for cadmium was much higher than of lead and copper; therefore, cadmium poses a higher risk to the sediment in Juru River in comparison to copper and lead.

## CONCLUSION

The present results indicate that cadmium have higher potential for mobilization from the sediment than copper and lead because of their higher concentration at the exchangeable fraction. Among the non-residual fractions, the organic matter fraction is much higher than other fractions in all sites. Analysis of pH and percentage of organic matter present in sediments conclude that there is correlation between organic matter and the concentration of Pb at oxidation fraction. Results of this study also showed that with an increase in organic matter and pH in sediment a similar increase in the concentration of copper and lead occurs at the oxidation fraction at some sites. The Individual Contamination Factor (ICF) shows that the risk of cadmium is higher than the risk of copper and lead.

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