

Vertical Profile Of Heavy Metal Concentration In Sediments From Sadong River, Sarawak, Malaysia

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Several sources of heavy metals in the environment include biological, geochemical, geological and anthropogenic sources. A total of eighteen core sediments were taken from Sadong river, Sarawak, Malaysia. These samples were digested by acid extraction and thereafter subjected to atomic absorption spectrometry (AAS). This paper aims to determine the vertical profile of heavy metals in core sediments, infer the accumulation history and assess the possible sources of pollution. The results showed that Fe was the most abundant element while Cd had the lowest concentration. Sediment pollution assessment was carried out for the top layer using geoaccumulation index (Igeo), enrichment factor and contamination factor. EF values showed moderate to significant enrichment of heavy metals.

KEYWORDS

Anthropogenic, Atomic absorption spectrometry (AAS), Core sediments, Geoaccumulation index, Sadong river

1. INTRODUCTION

The study of heavy metal deposition and accumulation is of increasing interest because of the awareness that heavy metals present in sediments may have negative consequences on human health and the environment [1]. The composition of river sediments is influenced by the deposition of terrestrial materials due to erosion caused by the frequent rainfall in the study area. The contamination of sediments by heavy metals is a prevalent issue due to increased human population and agricultural activities [2]. Heavy metals are discharged into rivers by activities, such as sewage discharge, wind-blown dust, eroded soils, flooding, municipal waste, vehicular emissions, ships, leakage of metallic storage tanks, mechanized farming, etc., [3,4]. The main pathways of heavy metals partitioning include adsorption, atmospheric deposition, complexation, precipitation and biological uptake [5,6].

Sediment is defined as layers of relatively finely divided particles found in rivers, streams, lakes, reservoirs, bays, estuaries and oceans. They are generally made up of mixtures containing fine to medium and

coarse-grained particles. These particles are composed of clay, silt and sand mixed with organic matter. Sediment concentration and characteristics are the key physical properties of a water body, others are chemical and biological properties that form the ecosystems. Chemical properties of a river are influenced by the dissolution of materials in the river, the heavy metals of sediments are related to factors, such as bedrock geology, drift cover, landuse, climate, tidal and seasonal currents and topography [7,8]. Weathering processes led to the dissolved and suspended particles in most of the world's major rivers. The chemical weathering of soils and rocks is one of the most important processes in the geochemical cycling of metals in rivers.

Heavy metals originate from both natural processes and anthropogenic activities [9]. All heavy metals occur naturally and human activities can increase their concentrations. Sediments serve as traps and can be used to determine the accumulation history of suspended particles and those bound to metals in rivers [2]. This river is biologically active and receives a considerable amount of heavy metal input from municipal sources and agricultural activities. It is believed that the high concentration of heavy metals can cause damage to aquatic life, human health and natural resources due to their bioaccumulative, non-degradable and toxic

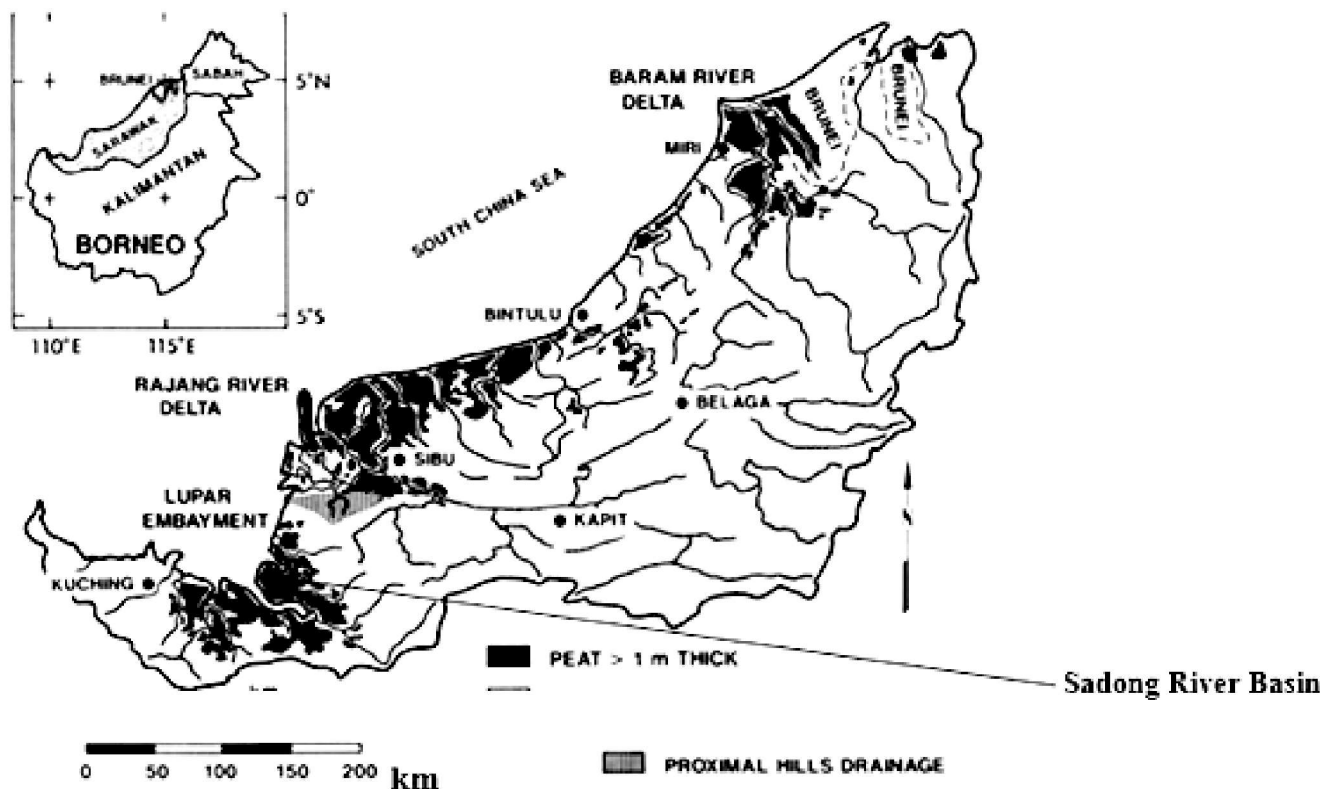


Figure 1. Map showing the Sadong river basin [10]

Table 1. The sampling stations at Batang Sadong, Kota Samarahan, Sarawak

Station	Geographical coordinates	Locality	Major activities
BS1	01°33'03.2"N 110°45'56.4"E	Sebangan	Farming and fishing
BS2	01°30'51.0"N 110°44'24.6"E	Sadong Jaya	Fishing
BS3	01°27'19.4"N 110°41'08.1"E	Sg Buloh	Ferry service
BS4	01°14'49.3"N 110°41'06.6"E	Simunjan	Fishing
BS5	01°14'38.5"N 110°40'42.5"E	Gedong	Residential area (potential tourist attraction)
BS6	01°14'42.1"N 110°38'09.5"E	Seremban	Farming

nature [11]. This study aims to determine the concentration of heavy metals, evaluate the accumulation history by their vertical distribution as well as assess their environmental effect.

2. MATERIAL AND METHOD

2.1 Study area and sample collection

The Sadong river covers an area of 4,000 km² located between longitudes 1° 14' 0.012" and 1° 34' 0.012" north and latitudes 110° 38.09'.5 and 110° 45' 0" east. This river covers a large area from Serian district to the Samarahan- Asajaya district in Sarawak, Malaysia and flows largely through the Sadong basin, southern Sarawak [12]. It receives a major input of

freshwater from upland, transport sediments at several metres then meanders along its path, then flows through the estuary and finally discharges into the South China sea (Figure 1).

The core samples were collected in March 2017 and March 2018 in six sampling stations within the Sadong river, Sarawak, Malaysia (Figure 2). Each core sediments were divided into 2.5 cm based on the depths for detailed analysis. The coordinates were recorded with global positioning system (GPS) (Table 1). The samples were put in a plastic bag and stored at -40°C until further analysis. The topography of this area is generally flat around the floodplain which makes them prone to high flooding and the landmass around the

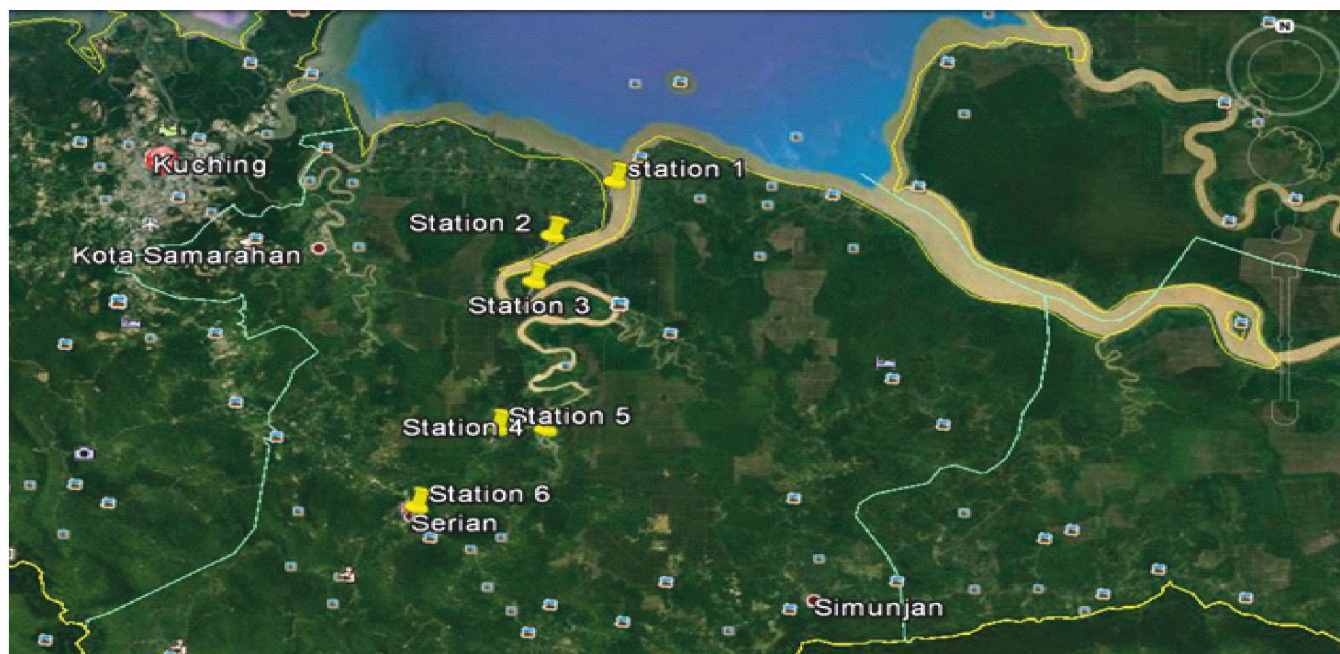


Figure 2. Map showing the sampling stations in the Sadong river basin

Sadong river is endowed with vast vegetation. The major soil type is peat with varied thickness and colour [13]. The environ is overlain by siliciclastic sediments which are tertiary in age and are divided into various stratigraphic provinces [14].

2.2 Sample preparation and digestion

The sediments were air-dried at room temperature for 72 hr and then pulverised into powder form using a mortar and pestle. All geochemical analyses were carried out on the $< 63 \mu\text{m}$ fraction. The total digestion of fine particles of sediments was carried out using a wet digestion method. Approximately 1 g of each sample was placed in a crucible with a solution of concentrated HNO_3 and HCl . 3 mL of HCl was poured into the sample and 9 mL of HNO_3 was thereafter added [15]. The mixture was heated to near dryness using a hot plate and allowed to cool before filtration. The sediment samples were filtered through $0.45 \mu\text{m}$ Whatman filter paper. The filtrate was transferred to a 100 mL volumetric flask and made up to the mark with deionized water. The solution was poured into plastic bottles for heavy analysis using atomic absorption spectrometry (AAS) laboratory in Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, Malaysia. All samples were digested in triplicates and subjected to AAS analysis. The metal contents in sediment are reported in dry weight. The glassware and plastic containers were washed and rinsed with distilled water, then immersed in 10% HNO_3 solution before use.

2.3 Instrumental analysis

The heavy metal analysis was carried out in the Atomic Absorption Spectrometry Laboratory, Faculty of Resource Science and Technology, University of Malaysia Sarawak, Malaysia. The AAS Thermo Fisher Scientific iCE 3500 series model was used, this was validated by evaluating linearity, the limit of detection, the limit of quantification, accuracy and precision. All the chemicals used for atomic absorption spectrometer (AAS) were of analytical grade and certified standards. Three replicates analysis showed a good precision within the results.

2.4 Environmental risk assessment

The environmental risk assessment was carried out for the top layer (0-5 cm). Geoaccumulation index was calculated using the equation given by Muller [16]. The extent of sediment contamination was assessed using the enrichment factor (EF). Fe was the natural reference value [17].

3. RESULT AND DISCUSSION

The vertical distribution was assessed to understand the variation of concentration along the Sadong river. The trend in down core variation of heavy metal is shown in figure 3. The core sediments were collected from the downstream to the upstream of the river. The river bank sediments were visually homogenous and mostly composed of fine-grained sediments. The

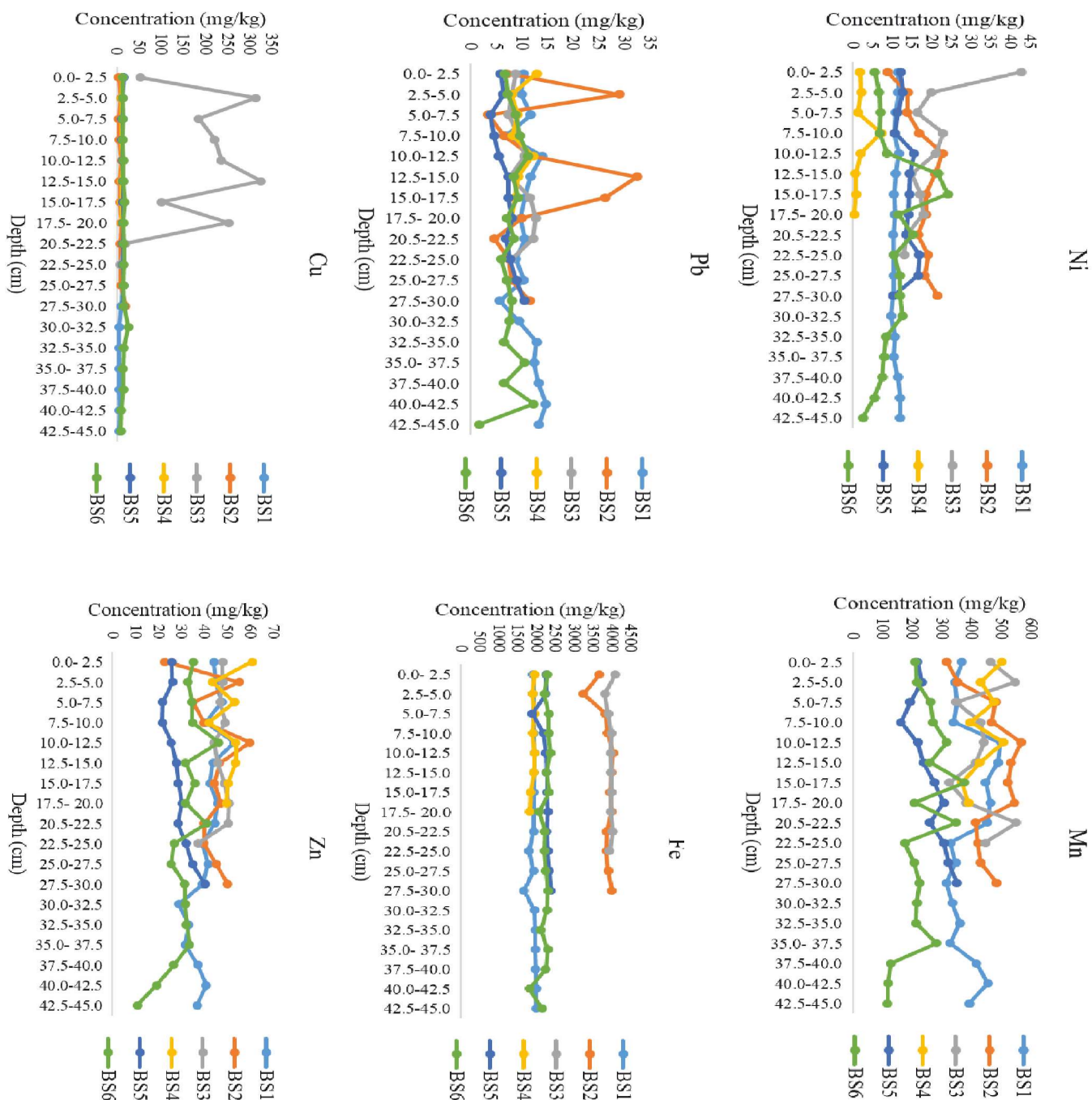


Figure 3. Vertical profile of six heavy metals in sediments from the Sadong river

fate and transport of the heavy metals were governed by sedimentological parameters, such as grain size, sediment composition and organic matter [5]. The factors that affected the grain size variation are sediment transport and sedimentary processes [18]. Fine-grained sediments adsorbed heavy metals from the river and have the capacity to retain heavy metals which is the main parameter that controlled the concentration of the heavy metals in this river [19].

All sampling sites are characterized by atmospheric deposition, movement of river water as well as tidal and seasonal currents. This may have caused the mobility, bioavailability and enrichment of heavy metals in the sediments. The assessment of the core sediments was crucial in the determining anthropogenic input of the heavy metals in the river due to their long residence time hence reflected the history of pollution in the river. The distribution of Cu, Ni, Pb, Zn, Fe and Mn

Table 2. *Igeo values of core sediments from the Sadong river*

Heavy metal	Depth (cm)	Station					
		BS1	BS2	BS3	BS4	BS5	BS6
Cu	0.0-2.5	-2.03	-3.71	0.15	-1.99	-1.64	-1.98
	2.5-5.0	-2.04	-2.50	2.71	-2.23	-1.96	-2.01
Pb	0.0-2.5	-1.23	-1.79	-1.45	-0.90	-2.03	-1.85
	2.5-5.0	-1.28	0.27	-1.59	-1.59	-1.91	-1.74
Ni	0.0-2.5	-2.69	-3.08	-0.78	-5.43	-2.62	-3.73
	2.5-5.0	-2.68	-2.42	-1.89	-5.20	-2.55	-3.48
Zn	0.0-2.5	-2.12	-3.07	-2.00	-1.66	-2.89	-2.44
	2.5-5.0	-2.09	-1.80	-2.00	-2.14	-2.87	-2.54
Fe	0.0-2.5	-4.83	-3.88	-3.72	-4.80	-4.59	-4.56
	2.5-5.0	-4.83	-4.06	-3.82	-4.83	-4.59	-4.61
Mn	0.0-2.5	-1.62	-1.84	-1.28	-1.17	-2.38	-2.43
	2.5-5.0	-1.72	-1.68	-1.05	-1.39	-2.28	-2.39

in the core sediments of the six sampling sites from river Sadong is in figure 3. Three sampling areas (BS2, BS3, BS4) are characterized by a high concentration of heavy metals because of decreased mobility and dilution. The atmospheric deposition may be the main route for metals to accumulate in the sediments because a large number of heavy metals can be transported for hundreds of miles from their place of origin [20]. There is high vehicular movement around the BS2 and BS3 which might have caused the emission of heavy metals into the atmosphere and river. The highest concentration of Cu is found in BS3 with a concentration of 325 mg/kg while the lowest concentration is at BS2 (13 mg/kg). The accumulation of Cu was consistent from top to bottom layer except for BS3 where the concentration of Cu varied considerably from top to bottom. This may be due to the release of the heavy metal from that locality, possibly from human activities at the banks of the river.

The concentrations of Fe in core sediments were noticed to be exceptionally high in all sampling sites compared with other heavy metals studied with concentration ranged between 1818-3953 mg/kg. This was attributed that Fe is the most common metal found in nature and it is relatively abundant on the earth surface. The concentration of Fe is influenced by the presence of dissolved rocks and soils [21]. The concentration of Fe was consistent from top to bottom of cores in the six sampling stations. The concentrations of Cd in core sediments were ranged from -5.20-0.87 mg/kg. Cd was found in BS2 and BS3 but there was a very low concentration of Cd at BS1, BS4, BS5 and BS6. The occurrence of Zn and Mn suggested that these

heavy metals mainly originated from land-based runoff and discharges to Sadong river.

The highest concentration of Cd (0.87 mg/kg) was detected in sediments at BS3. This may be due to the generation of sewage and agricultural activities which is the primary cause of high concentration of Cd in the sediments [22]. The increasing population of the locality has affected the chemical characteristics of the rivers as time passes. The highest concentration of Pb was found in BS2 with a concentration of 32 mg/kg at the upper layer of core while the least concentration is at upper layer of BS5 (4 mg/kg). The highest concentration of Ni is found in BS3 with a concentration of 23 mg/kg while the least concentration is at BS4 (7 mg/kg). The highest concentration of Zn is found in BS4 with a concentration of 60 mg/kg while the lowest concentration is at BS5 (40 mg/kg). The highest concentration of Fe is found in BS3 with a concentration of 4076 mg/kg while the lowest concentration is at BS4 (1934 mg/kg). The highest concentration of Mn is found in BS2 with a concentration of 565 mg/kg while the lowest concentration is at BS5 (349 mg/kg). The predominant process for heavy metals partitioning is adsorption because heavy metals have strong affinities between iron as well as manganese and organic matter but a lesser extent to clay minerals [21].

Weathering and erosion of rocks or unconsolidated deposit caused sediment to be released into this river environment. These sediments were suspended, transported and deposited by water and other forms of sediment transport. The BS2, BS3 and BS6 of river Sadong are characterized by boat docking, ferry service

Table 3. *Enrichment factor values of core sediments from the Sadong river*

Station	Depth (cm)	Heavy metal					
		Cu	Pb	Ni	Zn	Fe	Mn
BS1	0.0-2.5	6.96	12.05	4.39	6.54	1.00	9.21
	2.5-5.0	6.91	11.67	4.42	6.68	1.00	8.64
BS2	0.0-2.5	1.12	4.27	1.74	1.76	1.00	4.11
	2.5-5.0	2.95	20.00	3.12	4.79	1.00	5.20
BS3	0.0-2.5	14.65	4.84	7.68	3.31	1.00	5.44
	2.5-5.0	92.54	4.72	3.81	3.55	1.00	6.86
BS4	0.0-2.5	7.01	14.90	0.65	8.84	1.00	12.41
	2.5-5.0	6.07	9.43	0.77	6.48	1.00	10.84
BS5	0.0-2.5	7.69	5.87	3.92	3.23	1.00	4.61
	2.5-5.0	6.21	6.41	4.13	3.29	1.00	4.95
BS6	0.0-2.5	6.01	6.56	1.79	4.35	1.00	4.40
	2.5-5.0	6.06	7.31	2.19	4.21	1.00	4.66

Table 4. *Contamination factor values of core sediments from the Sadong river*

Station	Depth (cm)	Heavy metal					
		Cu	Pb	Ni	Zn	Fe	Mn
BS1	0.0-2.5	0.37	0.64	0.23	0.35	0.05	0.49
	2.5-5.0	0.37	0.62	0.23	0.35	0.05	0.46
BS2	0.0-2.5	0.11	0.44	0.18	1.76	0.10	0.42
	2.5-5.0	0.27	1.80	0.28	4.79	0.09	0.47
BS3	0.0-2.5	1.66	0.55	0.87	0.38	0.11	0.62
	2.5-5.0	9.80	0.50	0.40	0.38	0.11	0.73
BS4	0.0-2.5	0.38	0.80	0.03	0.48	0.05	0.67
	2.5-5.0	0.32	0.50	0.04	0.34	0.05	0.57
BS5	0.0-2.5	0.48	0.37	0.24	0.20	0.06	0.29
	2.5-5.0	0.39	0.40	0.26	0.20	0.06	0.31
BS6	0.0-2.5	0.38	0.42	0.11	0.28	0.06	0.28
	2.5-5.0	0.37	0.45	0.13	0.26	0.06	0.29

whereby some parts of the ship may have been corroded (Table 4). BS4 has the highest value of total organic matter while BS5 has the lowest value. BS2 and BS4 are characterized by high total organic matter and heavy metals due to the activities around the river banks. There is a high emission of heavy metals from ships and boats. Paddy rice and oil plantation are also found in these two localities, this may account for the high amount of organic matter.

The study area is enriched organic matter, BS4 has the highest value of total organic matter while BS3 has the least value of total organic matter. On-site, BS4 is characterized by low energy and tidal current

and the river was calm with slow sedimentation whereas BS3 has a moderate sedimentation rate. BS1, BS2, BS5 have tides and sediments are gradually transported. Human activities around this area, such as fishing and farming may account for the high total organic matter.

Stations BS4 and BS5 are characterised by low tides and currents, fishing activities are also common at the banks of this locality. The value of the total organic matter in BS1 was observed to be consistent, the area is characterised with ferry service at the banks and high tides and currents. Several factors, such as physico-chemical parameters control the rate of ad-

sorption and desorption of these heavy metals [5]. They occurred as particulates, colloids and dissolved phases which are easily absorbed to silica, clay and organic material. The process adsorption removes the heavy metal from the river water and stores them in the sediment. Other factors, such as alkalinity and acidity (pH) as well as solubility product of each heavy metal are main parameters that the concentration of these dissolved metals. The total concentration of these heavy metals is dependent on their mobility and bioavailability, which should be considered for assessing the potential risk of river sediments accurately [23].

Igeo values showed that BS3 was moderately contaminated with Cu, this may due the anthropogenic activities in the area. BS2 is moderately contaminated with Pb (Table 2). Sadong river is uncontaminated with Ni, Zn, Fe and Mn in all the core sediments because Igeo value is less than 0. Table 3 shows the enrichment factor values for the cores, there is an extremely high enrichment of Cu in BS3 and a significant enrichment of Cu in all other cores. There is a significant enrichment of Pb in BS2 and BS3 with other cores having a moderate enrichment from top to bottom layer. A minimal enrichment of Ni is observed in BS4 with moderate enrichment from top to bottom layer for other cores.

4. CONCLUSION

This study gives an understanding of the heavy metal concentration of river Sadong. Sediments in all sampling sites contained mostly of fine-grained particles except for station 6 (Serian) which is made up of a mixture containing fine and medium-grained particles. The sediment particles are comprised of clay, silt, sand and organic matter. The river sediments were derived mainly from weathered rocks and soils which were transported and deposited by wind and water, from the atmosphere as dust particles and human activities. Fe has the highest concentration and Cd has the least concentrated in the core samples from Sadong river. The presence and concentration of Cd suggest land runoff as a result of the use of fertilizer on farmlands which were transported to the river sediments in two stations. According to the Igeo values, sediments from the Sadong river is uncontaminated except for BS3 which is moderately contaminated with Cu. EF values show significant enrichment of Cu in BS3 as well as Pb in BS2 and BS4. There is a moderate enrichment of Ni, Zn, Fe and Mn in all cores.

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REFERENCES

1. Likuku, A.S., K.B. Mmolawa and G.K. Gaboutloeloe. 2013. Assessment of heavy metal enrichment and degree of contamination around the copper-nickel mine in the Selebi Phikwe region, eastern Botswana. *Env. and Ecology Res.*, 1(2):32-40.
2. Tatone, L.M., *et al.* 2016. Comparative approach for trace metal risk evaluation in settling particles from the Uruguay river, Argentina : Enrichment factors, sediment quality guidelines and metal speciation. *Env. Earth Sci.*, 75(7):1-7.
3. Kara, M., *et al.* 2015. Spatial variation of trace elements in seawater and sediment samples in a heavily industrialized region. *Env. Earth Sci.*, 73:405-421.
4. Sundarajan, M. and S. Srinivasalu. 2010. Geochemistry of core sediments from Gulf of Mannar, India. *Int. J. Env. Resour.*, 4(4):861-876.
5. Sany, S.B.T., *et al.* 2013. Heavy metal contamination in water and sediment of the Port Klang coastal area, Selangor, Malaysia. *Env. Earth Sci.*, 69:2013-2025.
6. Scott, I.M. 1985. The soils of the central Sarawak. Lowlands, east Malaysia. Soil Memoir 2. Department of Agriculture, Soil Division, Sarawak, east Malaysia. 302 pp.
7. Sundararajan, M. and U. Natesan. 2010. Environmental significance in recent sediments along Bay of Bengal and Palk Strati, east coast of India : A geochemical approach. *Int. J. Env. Res.*, 4(1):99-120.
8. Praveena, S.M., *et al.* 2008. Heavy metals in mangrove surface sediments of Mengkabong, Lagoon, Sabah : Multivariate and geoaccumulation index approaches. *Int. J. Env. Res.*, 2(4):139-148.
9. Xin, J., *et al.* 2014. Distribution and pollution assessment of heavy metals in surface sediments in the yellow sea. *Marine Poll. Bullet in.* 83:366-375.
10. Staub, J.R., H.L. Among and R.A. Gastaldo. 2000. Seasonal sediment transport and deposition in the Rajang river delta, Sarawak, east Malaysia. *Sedimentary Geology.* 133:249-264.
11. Sagheer, A.A.A. 2013. Geochemistry in surface sediments of the Kwar Katib. *J. Env. Res. Man-*

- age.*, 4(4):242-248.
12. Bryant, W. 2003. Naturalist in the river : The life and early writings on Alfred Russel Wallace. Universe, Inc., New York. 192 pp.
 13. Zulkifley, M., *et al.* 2015. Development of tropical lowland peat forest phasic community zonations in the Kota Samarahan-Asajaya area, west Sarawak, Malaysia. *Earth Sci. Res. J.*, 20(1):1-10.
 14. Madon, M., K. Cheng and R. Wong. 2013. The structure and stratigraphy of deep water Sarawak, Malaysia : Implications for tectonic evolution. *J. Asian Earth Sci.*, 76:312-333.
 15. Sim, S.F., *et al.* 2016. Baseline trace metals in water and sediment of the Baleh river-A tropical river in Sarawak, Malaysia. *Env. Monitoring Assess.*, 188(9):537.
 16. Muller, G. 1979. Schwermetalle in den Sedimenten des Rheins Veränderungen seit. *Umscha.* 24:778-783.
 17. Abraham, G.M.S. and R.J. Parker. 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki estuary, Auckland, New Zealand. *Env. Monitoring and Assess.*, 136:227-238.
 18. Hakanson, L. 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Resour.*, 14(8):975-1001.
 19. Amune, M., C. Omono and K. Samuel. 2012. Comparison of digestion methods for the determination of metal levels in soils in Itakpe, Kogi State, Nigeria. *Int. J. Pure and Appl. Sci. and Tech.*, 13(2):42-48.
 20. Obaidy, A.H.M.J., A.H. Talib and S.R. Zaki. 2014. Environmental assessment of heavy metal distribution in sediments of Tigris river within Baghdad city. *Int. J. Advanced Res.*, 8(2):947-952.
 21. Nobi, E.P., *et al.* 2010. Geochemical and geostatistical assessment of heavy metal concentration in the sediments of different coastal ecosystems of Andaman Islands, India. *Estuarine, Coastal. and Shelf Sci.*, 87(2):253-264.
 22. Manaf, L.A., M.A.A. Samah and N.I.M. Zukki. 2009. Municipal solid waste management in Malaysi : Practices and challenges. *Waste Manage.*, 29:2902-2906.
 23. Yoo, J.C., *et al.* 2013. Extraction of heavy metals from marine sediments. *Chem. Eng. J.*, 228 : 688-699.