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RESEARCH ARTICLE

Evaluation and assessment of baseline metal contamination in surface sediments from the Bernam River, Malaysia

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Abstract The Bernam River is one of the most important rivers in Malaysia in that it provides water for industries and agriculture located along its banks. The present study was conducted to assess the level of contamination of heavy metals (Cd, Ni, Cr, Sn, and Fe) in surface sediments in the Bernam River. Nine surface sediment samples were collected from the lower, middle, and upper courses of the river. The results indicated that the concentrations of the metals decreased in the order of Sn>Cr>Ni>Fe>Cd (56.35, 14.90, 5.3, 4.6, and 0.62 $\mu g/g^1$ dry weight). Bernam River sediments have moderate to severe enrichment for Sn, moderate for Cd, and no enrichment for Cr, Ni, and Fe. The contamination factor (CF) results demonstrated that Cd and Sn are responsible for the high contamination. The pollution load index (PLI), for all the sampling sites, suggests that the sampling stations were generally unpolluted with the exception of the Bagan Tepi Sungai, Sabak Bernam, and Tanjom Malim stations. Multivariate techniques including Pearson's correlation and hierarchical cluster analysis were used to apportion the various sources of the metals. The results suggested that the sediment samples collected from the upper course of the river had lower metal concentrations, while sediments in the middle and lower courses of the river had higher metal concentrations. Therefore, our results can be useful as a baseline data for government bodies to adopt corrective measure on the issues related to heavy metal pollution in the Bernam River in the future.

Keywords Heavy metals · Geoaccumulation index · Enrichment factor · Contamination factor · Cluster analysis · Sediment quality guideline · Bernam River

Introduction

The Bernam River basin is located in an economic strategic place in Malaysia that is important as an agriculture area and as the largest source of water supply for the state of Selangor and Perak of Malaysia especially for irrigation. However, rapid urbanization within the Bernam River basin due to changes in economy policies by the Malaysian Government involved changes in land use activities which make the river more exposed to different pollution problems such as industrial and domestic sewage, agrochemicals (fertilizers and herbicides) used on agricultural lands, and sand mining. Heavy metals are the most abundant form of pollution in Malaysia either in the form of solid or liquid. With the vast industrialization and economic development in coastal regions, heavy metals are continuing to be introduced to the estuarine and coastal environments which eventually end up into rivers, runoffs, and land-based areas (Yu et al. 2008). The pollution of surface sediments, especially rivers, with toxic metals has been attracting considerable public attention over the past few decades. Additionally, rivers receive anthropogenic sources of metals owing to human activities such as industry, agriculture, mining, domestic sewage, boat activities, and construction

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works for urban development. These can pose serious threats to the food chain system in the aquatic environment (Bartoli et al. 2011). Thus, these wastes are known to contain heavy metals which are known to be toxic, can bioaccumulate, and are persistent in the environment. Sediments are important sinks for different pollutants like pesticides and heavy metals and also play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions (Ikem et al. 2003; Sow et al. 2013). Sediments are considered not only a vital sink of heavy metals proceeding to their discharge into aquatic environments but also an indicator of pollution history (Rodríguez-Barroso et al. 2010). Moreover, elemental concentrations in sediments depend not only on natural and anthropogenic sources but also upon the organic matter content, mineralogical composition, and textural characteristic of the sediment (Filgueiras et al. 2004; Akoto et al. 2008). A successful evaluation for mixed accumulation of heavy metals from natural and anthropogenic sources typically requires normalizing methods for distinguishing the two different sources (Idris 2008). Geochemical normalization approaches such as the enrichment factor (EF) and geoaccumulation index (Igeo) methods have been commonly used for the purpose. Land use may also play crucial roles in the distribution of heavy metals in sediments. Land use is commonly classified into agricultural, forestry, industrial developmental, and urban. However, the types of land use resulting in heavy metal enrichment in sediments are not necessarily the same for different geographical locations. For example, Heikkila (1991) reported that high concentrations of organic matter and heavy metals in sediments were closely related to increased intensity of agriculture, forestry, and peat harvesting in drainage basins. In contrast, Abrahim and Parker (2008) and Horowitz and Stephens (2008) demonstrated that heavy metal concentrations in sediments tend to increase with the degree of industrial development and urbanization of an area. There are no studies assessing anthropogenic influences on sediment chemical composition using such indices in the Bernam River which is one of the major sources of income for fish farmers as well as having great biodiversity in Malaysia. Therefore, the present study was aimed to determine the distribution and source of Cd, Ni, Cr, Sn, and Fe contamination in surface sediments of the Bernam River and to evaluate the degree of anthropogenic pollution using geochemical approaches.

Materials and methods

Study area

The Bernam River is situated in the west of Peninsular Malaysia between the states of Perak and Selangor and covers an area of 3335 km^2. The undulating slopes of the Bernam River converge into an undeveloped peat swamp region, while the downstream of the peat swamp is a densely populated coastal strip along the Bernam River. Rice is cultivated in the lower areas adjacent to peat swamps. Then again, rubber, oil palm, coconuts, and cocoa are cultivated in estates and smallholder schemes. Logging generates pollution through soil erosion, siltation, and sedimentation in the rivers. The Bernam River basin is characterized by high temperatures and relative humidity with small seasonal variations. The mean relative humidity is about 77 % on average, while the minimum and maximum temperatures are 26 and 32 °C, respectively. Rainfall peaks during the Northeast Monsoon (November to January) and Southwest Monsoon (April to September) with a larger peak in October and December, while February, July, and August are inter-seasonal periods and hence recording the lowest rainfall. The mean annual rainfall ranges from 2000 to 3500 mm. The samples were collected from the following locations: Kampung Bagan, Bagan Tepi Sungai, Sabak Bernam, Kampung Tanjung, Ulu Bernam, Selisek, Bandar Behrang, Tanjong Malim, and Slim (Fig. 1).

Sample collection

A total of 27 surface sediment (0–5 cm) samples were collected at nine sites from downstream to upstream of the Bernam River between January and February 2015. Samples were collected using an Ekman grab sampler. The location, designation, description, longitudes, and latitudes of sampling stations are presented in Table 1. The surface sediments of each sample were placed in polyethylene plastic bags, labeled, kept in an ice box, and transported to the laboratory. Upon arrival at the laboratory, samples were further preserved in a −10 °C freezer for future analysis.

Sample digestion and analysis

The dried sediment samples (0.5–1 g) were digested in a 10-ml solution of a mixture of HNO_3 (AnalaR grade, R&M 65 %) and $HClO_4$ (AnalaR grade, R&M 70 %) in the ratio of 4:1 (*v*/*v*), into a pre-heated block digester 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 a Whatman No. 1 filter paper into pre-cleaned 40-ml volumetric flasks. The samples were measured for trace metal concentration using an air-acetylene flame atomic absorption spectrophotometer (Perkin-Elmer Model A Analyst 800). The data are presented on a dry weight basis (μg/g dry weight). In order to avoid contamination, all glassware were soaked in acid wash (10 % HNO_3) for at least 24 h and later rinsed with double-distilled water and air dried

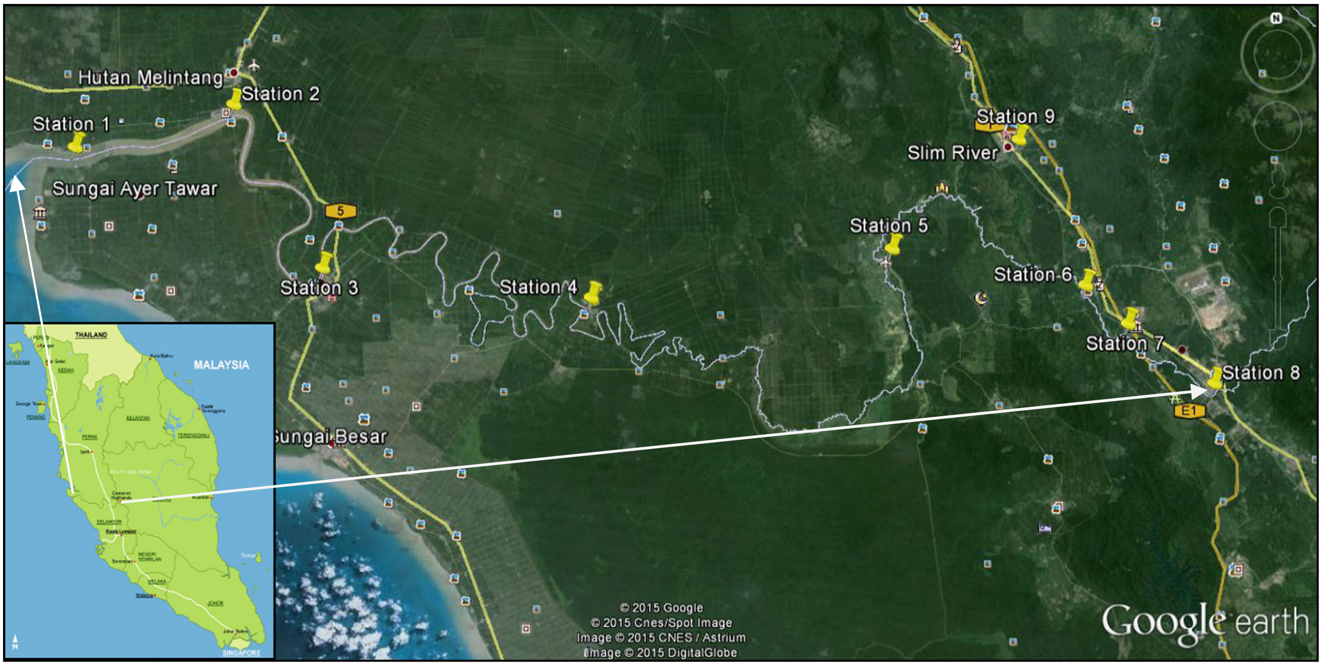


Fig. 1 Map of the Bernam River catchment and sampling stations

before use. To ensure precision and accuracy of the analytical method, quality control calibration curves were generated by analyzing multiple-level calibration standards, and standard solutions of each metal studied were prepared from 1000 mg/l (BDH Spectrosol®) stock solution. PACS-2 (NRCC, Canada) was used to check the quality of this method (Table 2).

The analytical results for the reference material and its certified values showed satisfactory metal recovery percentages being about 104, 81, 97, 107, and 90 % for Cd, Ni, Cr, Sn, and Fe, respectively. A blank was used to zero the instrument and quality control samples were analyzed after every five samples during metal analysis.

Determination of the physical-chemical properties of water

Water quality parameters such as salinity, dissolved oxygen, and pH were measured in situ using YSI (multiprobe system). Water samples were collected only at a single depth, which was 1 m without disturbing the muddy sediment surface.

Sediment pH

Determination of sediment pH was conducted according to McLean (1982) by using distilled water with 1:2.5

Table 1 The coordinates and description for each sampling station

Station	Sampling site	Coordinates	Description
1	Kampung Bagan	N 3° 50′ 46.91″ E 100° 50′ 42.36″	Agricultural area, oil palm, boat harbor
2	Bagan Tepi Sungai	N 3° 52′ 10.56″ E 100° 55′ 57.84″	Residential area, agricultural area, oil palm
3	Sabak Bernam	N 3° 46′ 17.89″ E 100° 59′ 0.05″	Residential area, industry, agricultural area, domestic waste discharge, fisheries
4	Kampung Tanjung	N 3° 44′ 45.37″ E 101° 8′ 41.09″	Industrial, agriculture area, oil palm
5	Ulu Bernam	N 3° 45′ 57.21″ E 101° 19′ 44.19″	Agricultural area, air field
6	Selisek	N 3° 44′ 20.02″ E 101° 26′ 44.06″	Agricultural area, oil palm, fisheries
7	Bandar Behrang	N 3° 42′ 55.09 E 101° 28′ 13.07″	Agriculture area, fisheries
8	Tanjong Malim	N 3° 40′ 40.47″ E 101° 31′ 16.29″	Industrial, domestic waste discharge, car washing, fisheries
9	Slim River	N 3° 49′ 35.46″ E 101° 24′ 32.26″	Residential area, agriculture area

Table 2 Metal concentrations (μg/g, Fe %, dry weight) in certified reference materials (CRM) (mean±standard deviations; *n*=3)

Metal	CRM	Certified value	Measured value	Recovery (%)
Cd	PACS-2	2.11±0.15	2.20±0.16	104
Ni	PACS-2	39.5±2.3	32.10±0.68	81
Cr	PACS-2	90.7±4.6	88.04±0.64	97
Sn	PACS-2	19.8±2.5	21.2±2.16	107
Fe	PACS-2	4.09±0.06	3.68±0.08	90

solid/liquid ratio, that is, 25 ml of distilled water was added to 10 g sediment in a glass beaker, covered with a plastic film and put in an orbital shaker for 4 h at 175 rpm, and then read with a digital electrode pH meter model WTW pH 330.

Determination of total organic matter content

The organic matter was expressed as loss on ignition (LOI) by calculating the difference between the dry weight of sediment samples before and after ashing in a muffle furnace at 550 °C for 5 h (Arain et al. 2008; Kazi et al. 2005).

Pollution indices

Pollution indices, namely pollution load index, contamination factor, geoaccumulation index, and enrichment factor, were used to assess the metal pollution in surface sediments from the Bernam River.

Pollution load index

The pollution load index (PLI) defined by Tomlinson et al. (1980) for sediments based on baseline metal concentrations was used. In the present study, we used average shale (Turekian and Wedepohl 1961) as a background or undisturbed value for those metals in the same way as for the computation of the geoaccumulation index (Igeo) and contamination factor (CF), because no such data was available for the study area. The pollution load index is suggested as a standardized system for detecting pollution which permits a comparison of pollution levels between different locations and at different times (Angulo 1996). The PLI gives an assessment of the overall toxicity status of a sample, and it is the result of the contribution of several heavy metals (Wang and Qin 2005). A PLI value of 0 suggests absence of baseline pollutants, a value of 1 suggests that only baseline levels of pollutants are present, and a value larger than 1 would suggest progressive deterioration of sediment quality (Tomlinson et al. 1980). The PLI was determined for every station using the following equation:

$$\mathrm{PLI} = \sqrt[n]{\mathrm{PLI}\ \ \mathrm{CF}x\mathrm{CF}x\ldots x\mathrm{CF}n} \qquad (1)$$

where $\mathrm{CF}_{\mathrm{metal}}=C_{\mathrm{metal}}/C_{\mathrm{background}}$

Contamination factors

The geochemical and physiochemical characteristics of sediments are an important tool for environmental pollution assessment, as well as for the identification of contamination point sources. The CF is an indicator of sediment contamination which is used to evaluate the pollution of the environment by a given toxic substance. It is expressed as the concentration of each metal with respect to the background value in sediment as follows (Turekian and Wedepohl 1961): $\mathrm{CF}<1$, low degree; $1\leq\mathrm{CF}<3$, moderate degree; $3\leq\mathrm{CF}<6$, considerable degree; and $\mathrm{CF}\geq6$, very high degree. Therefore, the CF values can monitor the enrichment of one given metal in sediments over a period of time.

Geoaccumulation index

The trace metal contamination degree could be assessed by determining the Igeo. The Igeo has often been used in the assessment of soil and sediment contamination (Santos Bermejo et al. 2003). So as to characterize the level of pollution in the sediment, Igeo values were calculated using the equation

$$\mathrm{Igeo} = \log_2\left(\frac{\mathrm{Cn}}{1.5\mathrm{Bn}}\right) \qquad (2)$$

where Cn is the measured concentration of the examined element *n* in the sediment sample and Bn is the geochemical background value of the element *n* of average shale. The seven different classes of geoaccumulation index along with associated sediment pollution extent as proposed by Muller (1981) are given in Table 3.

Enrichment factor

The enrichment factor (EF) is considered as an effective tool to evaluate the magnitude of contaminants in the environment. The EF for each element was calculated to evaluate anthropogenic influences on heavy metals in sediments using the formula proposed by Selvaraj et al. (2004) as stated below:

$$\mathrm{EF}_{\mathrm{metal}} = \frac{\left(\mathrm{Cx}/\mathrm{Fe}\right)\mathrm{sample}}{\left(\mathrm{Cx}/\mathrm{Fe}\right)\mathrm{shale}} \qquad (3)$$

where (Cx/Fe)=sample and (Cx/Fe)=average shale values, respectively, of the metal concentrations' (μg/g) dry weight

Table 3 Muller's classification for the geoaccumulation index (Igeo) (Muller 1981)

Igeo value	Igeo class	Sediment quality
<0	0	Unpolluted
0–1	1	Unpolluted to moderately polluted
1–2	2	Moderately polluted
2–3	3	Moderately polluted to strongly polluted
3–4	4	Strongly polluted
4–5	5	Strongly polluted to extremely polluted
>5	6	Extremely polluted

in relation to Fe levels (dry weight) in sediment samples and average shale values taken from Krauskopf and Bird (1995). EF values were interpreted as suggested by Wang et al. (2008). Thus, if 0.5≤EF≤1.5, then it indicates that the metal could be mainly from natural weathering process, and if EF> 1.5, then it indicates that the metal is from anthropogenic sources or a greater percentage of the metal is from non-natural weathering process. However, the degree of enrichment was interpreted based on the method proposed by Birch (2003). EF<1 indicates no enrichment, 1<EF<3 indicates minor enrichment, 3≤EF≤5 indicates moderate enrichment, and 5≤EF≤10 indicates moderate to severe enrichment.

Results and discussion

Physicochemical characteristics of the sediments and water

The physicochemical characteristics (pH (sediment), total organic matter content (TOM, %), pH (water), dissolved oxygen (DO), and salinity) of the 27 sediments and water samples collected from the Bernam River are presented in supplementary Table 4. The pH value is an important indicator of environmental quality and pollution degree in a water system (Singh Mohan et al. 2005). Sediment pH ranged from 5.91 to 7.50, with an average of 6.52. Water pH varies 6.26 to 8.10 with an average of 6.98. Changes in pH will have profound effects on the speciation of dissolved heavy metals. Decreasing pH reflects increasing hydrogen ion concentrations. Positively charged hydrogen ions protonate ligands in solution, thus replacing metals and causing increased free metal ion activity. The additional H^+ ions at low pH may also compete with metal ions at the membrane binding site and decrease the rate of metal uptake (Luoma and Rainbow 2008). The salinity range in the Bernam River ranged from 9.24 to 29.52 ppt with an average of 16.96 ppt. The mean of DO value was 1.86 to 5.73 mg/l with an average of 3.80 mg/l. The total organic matter ranges from 9.63 to 31.47 %, representing a high content in the downstream when compared to the upstream of the river (Table 4). It has been demonstrated that organic matter levels in sediments provide a good indicator of the metal bioavailability and mobility, since the former tends to form various complexes with trace metals (Arain et al. 2008; Hu et al. 2013).

Heavy metal distribution

Metal concentrations (μg/g, Fe %, dw) in the surface sediments from nine stations varied from 0.30 to 1.43 μg/g for Cd, 1.84 to 10.15 for Ni, 10.27 to 30.45 μg/g for Cr, 9.2 to 106.59 μg/g for Sn, and 2.15 to 4.36 % for Fe (Table 4). It was found that Sn has the highest mean concentration (56.35 μg/g) followed by Cr (14.90 μg/g), Ni (5.3 μg/g), Fe (4.6 %), and Cd (0.62 μg/g) (Table 4). Majority of the heavy metals had their highest concentrations in the Sabak Bernam station, which receives effluents from domestic sewage and urban runoffs from the inner city of Sabak Bernam. Anthropogenic activities resulting from industrial activities, transportation, and agricultural-related activities are most likely the major sources of these metals.

The results of the present study when compared with undisturbed sediment values show that concentrations of Cd and Sn in the surface sediments in the study area were higher than the average shale. Conversely, the average concentrations of Ni, Cr, and Fe were less than that of the average shale (Table 4).

In order to predict the heavy metal pollution, a comparative study was performed using the sediment quality guidelines (SQGs) proposed by USEPA (Luo et al. 2010a, b). The effect range low (ERL) and the effect range median (ERM) (NOAA 1999) are listed in Table 4. The present results showed that Cd concentrations in most of the stations were below the values of ERL (1.2 μg/g) and in all stations were below ERM (9.6 μg/g). Only the value for Sabak Bernam (1.43 μg/g) did exceed the ERL but still well below the ERM value. However, concentrations of Cd in most stations were above the background concentration of non-contaminated sediment (0.17 μg/g) suggested by Salomons and Forstner (1984). Concentrations of Ni in sediments at all stations were below the ERL (20.9 μg/g) and ERM (51.6 μg/g) values. Cr concentrations in all stations were well below the values for ERL (81 μg/g) and ERM (370 μg/g). There were no ERL and ERM for Sn and Fe, and hence, we could not compare our result with SQGs in the area.

Contamination assessment

In the present study, we used the average shale (Turekian and Wedepohl 1961) as background values for Cd, Ni, Cr, Sn, and Fe because there were no background values for these metals in the study area. The enrichment factor is usually evaluated using aluminum (Al) or iron (Fe). In the present study, Fe was

Table 4 Heavy metal concentrations (µg/g, Fe %, dry weight) and physicochemical contents in the surface sediments of the Bernam River

Station no.	pH.sed	TOM (%)	pH.H_2O	DO.H_2O	Salinity	Cd	Ni	Cr	Sn	Fe (%)
1	7.50	24.67	8.1	4.19	29.52	0.53	5.38	16.40	54.49	4.14
2	6.13	31.47	7.66	2.70	23.32	1.05	7.34	11.89	106.59	3.38
3	6.24	29.27	7.47	3.44	21.10	1.43	10.15	30.45	28.54	4.36
4	5.91	20.91	6.90	5.73	18.64	0.66	1.84	10.63	39.2	2.48
5	6.71	11.57	6.63	4.84	10.08	0.59	6.64	10.27	39.4	2.71
6	6.84	9.63	6.72	1.86	15.13	0.28	2.22	14.79	92.94	3.13
7	6.40	14.81	6.26	2.84	11.34	0.24	2.39	12.15	36.63	3.24
8	6.31	14.11	6.67	4.91	13.80	0.55	7.99	14.55	100.2	2.15
9	6.65	10.30	6.44	3.72	9.74	0.30	3.75	13.04	9.2	2.79
Total mean	6.52	18.52	6.98	3.80	16.96	0.62	5.3	14.90	56.35	3.15
Rang	5.91–7.50	9.63–31.47	6.44–8.1	1.86–5.73	9.74–29.52	0.30–1.43	1.84–10.15	10.27–30.45	9.2–106.59	2.15–4.36
Average shale[a]	–	–	–	–	–	0.30	68	90	6	4.6
ERL[b]	–	–	–	–	–	1.2	20.9	81	–	–
ERM[b]	–	–	–	–	–	9.6	51.6	370	–	–
	–	–	–	–	–					

[a] Turekian and Wedepohl 1961

[b] NOAA 1999

used to compute the EF because it is the fourth major element in the Earth's crust and most often has no contamination concern. In addition, the main advantages of using Fe are due to its fine solid surface and its geochemistry which is close to that of many trace metals, which makes its natural sediment concentration to be uniform (Daskalakis and O'Connor 1995; Naji and Ismail 2011). EF was used to assess the degree of anthropogenic pollution in sediments due to problems associated with the evaluation of anthropogenic pollution in sediments compared to their unpolluted references (Christophoridis et al. 2009). EF values for all the metals were highest in station 3 and lowest in station 9 when compared with other stations. A high Cd concentration was recorded in location 3 which had a higher EF value than the other locations, and the average EF value of Cd suggested moderate to severe enrichment (Table 5). The average EF of Cd was determined to be higher than 5 (EF>5) in the surface sediments of the Sabak Bernam River, suggesting that Cd contamination was caused by moderate to severe enrichment and should be a metal of concern in the study area. The high concentration of these heavy metals could be related to the local point sources such as domestic sources and agriculture activities. There was no enrichment (EF<1) for Cr and Ni in all the locations, while Sn showed (5≤EF≤10) moderate to severe enrichment for all the stations except stations 3 and 9 which showed moderate contamination (1≥CF≥3) and hence another source of concern in the study area. The very high CFs for Sn in the Bernam River could arise from agriculture activities such as fertilizers and pesticides that are used for crops (oil palm) within this area and, moreover, from urban runoffs that comprise wastewater discharges (Reimann and de Caritat 1998).

Based on the average shale (Turekian and Wedepohl 1961), the mean CF values of metals studied are shown in Table 5. The highest CFs for Cd, Ni, Cr, and Fe were found in the Sabak Bernam station which is close to residential areas, agricultural activities, and domestic waste discharge. The average contamination factors in surface sediment of the sampling stations were grouped in the order of Sn>Cd>Fe>Cr>Ni. In this investigation, all the stations were found to be contaminated with Sn and most sampling stations had Cd contamination. In contrast, sampling stations were not contaminated with Cr, Ni, and Fe.

The pollution load index (PLI) and the calculated index of geoaccumulation (Igeo) values of the studied metals in the

Table 5 Mean EFs (except Fe) and CF values of heavy metals in all sampled stations in the Bernam River

Station no.	EFs				CF				
	Cd	Ni	Cr	Sn	Cd	Ni	Cr	Sn	Fe
1	2.14	0.089	0.20	10.36	1.77	0.07	0.18	9.08	0.9
2	5.18	0.14	0.18	24.78	3.51	0.10	0.13	17.76	0.73
3	5.47	0.16	0.36	5.14	4.77	0.14	0.33	4.75	0.94
4	4.48	0.05	0.22	12.44	2.22	0.02	0.11	6.53	0.53
5	3.61	0.16	0.19	11.41	1.96	0.09	0.11	6.56	0.59
6	1.50	0.04	0.24	23.38	0.94	0.03	0.16	15.49	0.68
7	1.23	0.05	0.19	8.90	0.8	0.03	0.13	6.10	0.70
8	4.30	0.25	0.35	36.63	1.85	0.11	0.16	16.70	0.46
9	1.80	0.09	0.18	2.59	1.01	0.05	0.11	1.53	0.60
Total mean	3.30	0.11	0.24	15.07	2.09	0.077	0.16	9.39	0.68

Table 6 Mean Igeo, its classes, and PLI of the studied metals in surface sediments for all stations

Station no.	Igeo values based on average shale					Igeo class					PLI
	Cd	Ni	Cr	Sn	Fe	Cd	Ni	Cr	Sn	Fe	
1	0.24	−4.24	−3.04	2.59	−0.15	1	0	0	3	0	0.99
2	1.22	−3.79	−3.50	3.56	−0.44	2	0	0	4	0	1.24
3	1.67	−3.32	−2.14	1.66	−0.07	2	0	0	2	0	1.38
4	0.56	−5.79	−3.66	2.12	−0.89	1	0	0	3	0	0.64
5	0.39	−3.94	−3.71	2.13	−0.75	1	0	0	3	0	0.82
6	−0.66	−5.51	−3.18	3.36	−0.55	0	0	0	4	0	0.75
7	−0.90	−5.41	−3.47	2.02	−0.50	0	0	0	3	0	0.59
8	0.30	−3.67	−3.21	3.47	−1.09	1	0	0	4	0	1.04
9	−0.56	−4.76	−3.74	0.03	−0.71	0	0	0	1	0	0.48
Total mean	0.25	−4.49	−3.29	2.33	−0.57	0.88	0	0	3	0	0.88

Bernam River are presented in Table 6. PLI results in the Bernam River were <1. In addition, the maximum and the minimum PLI were 1.38 and 0.48, respectively. Based on the PLI value, the Bernam River should be classified as no metal contamination, but only Bagan Tepi Sungai, Sabak Bernam, and Tanjom Malim were shown to be polluted (PLI>1). According to the PLI criteria proposed by Tomlinson et al. (1980), this represents the point where progressive deterioration of sediment quality sets in. As a rule, stations located in industrial and agriculture areas as well as residential habitations are more affected. That station therefore needs more attention when planning future developments. Also, stations located close to agriculture activities and municipal areas had the highest values and therefore exhibited the characteristics of baseline pollution. The results of the calculated Igeo values from this study are −0.90 to 1.67 for Cd, −5.79 to −3.32 for Ni, −3.74 to −2.14 for Cr, 0.03 to 3.56 for Sn, and −0.89 to −0.07 for Fe (Table 6). Igeo values for Cd in stations 1, 2, 3, 4, 5, and 8 were high. As a result, they can be classified as moderately contaminated and moderately to strongly contaminated. This may be attributed to increasing human activities from industrial, agricultural, or urban areas. Whereas, the average geoaccumulation index of Sn in all the stations was classified as moderately contaminated and moderately to strongly contaminated. In contrast, the Igeo of Ni, Cr, and Fe in all stations were of class 0 and <0 and hence suggesting that the surface sediments can be considered as uncontaminated for these metals. The total concentrations of Cd, Ni, and Cr in the present study were within the range found when compared with studies from other countries (Table 7). In fact, the values obtained in the present study were lower compared to those in other areas located in large industrialized and densely populated regions such as the Klang River in Malaysia (Naji and Ismail 2011) and the Ergene

Table 7 The concentrations of Cd, Ni, Cr, Sn, and Fe in the surface sediments in the rivers of Malaysia in comparison to those from around the globe

Location	Unit	Cd	Ni	Cr	Sn	Fe (%)	References
Bernam River, Malaysia	μg/g	0.30–1.43	1.84–10.15	10.27–30.45	28.54–106.59	2.15–4.36	This study
Junggat River, Malaysia	μg/g	1.95–2.31	7.49–8.44	–	–	–	Berandah et al. (2010)
Langat River	mg/kg	0.02–0.18	2.33–8.25	4.31–29.04	–	–	Wan et al. (2012)
Sepang Besar River, Malaysia	μg/g	0.1–2.5	–	–	–	–	Ismail and Ramli (1997)
Mamut River, Malaysia	μg/g	0.02	21.13	–	–	1.27	Ali et al. (2004)
Lukut River, Malaysia	μg/g	0.29–2.59	–	–	–	–	Alireza et al. (2007)
Klang River, Malaysia	μg/g	0.57–2.19	5.96–24.47	–	–	1.56–3.03	Naji and Ismail (2011)
Lich River, Vietnam	mg/kg	4.4	64	107.9	–	–	Nguyen et al. (2013)
Sakarya River, Turkey	μg/g	2.6	82.96	37		–	Dundar et al. (2012)
Almendares River, Cuba	μg/g	1.5–3.4	71.6–420.8	–	–	1.7–4.5	Olivares-Rieumont et al. (2005)
Gomti River, India	μg/g	0.34–8.38	6.53–29.7	–	–	–	Singh Mohan et al. (2005)
Ergene River, Turkey	μg/g	1.42–3.53	33.7–126	44.79–800.23	–	–	Ali et al. (2014)
Pearl River, China	mg/kg	0.29–1.55	39.2–76.6	84.1–138	1.7–8	–	Baolin et al. (2011)

Table 8 Pearson's correlation coefficient of heavy metal concentrations and physicochemical parameters

	pH.sed	TOM	Cd	Ni	Cr	Sn	Fe
pH.sed	1						
TOM	−0.203	1					
Cd	−0.354	0.693**	1				
Ni	−0.087	0.495**	0.649**	1			
Cr	−0.073	0.454*	0.514**	0.538**	1		
Sn	−0.049	0.152	0.052	0.169	−0.107	1	
Fe	0.322	0.446*	0.269	0.199	0.338	−0.108	1

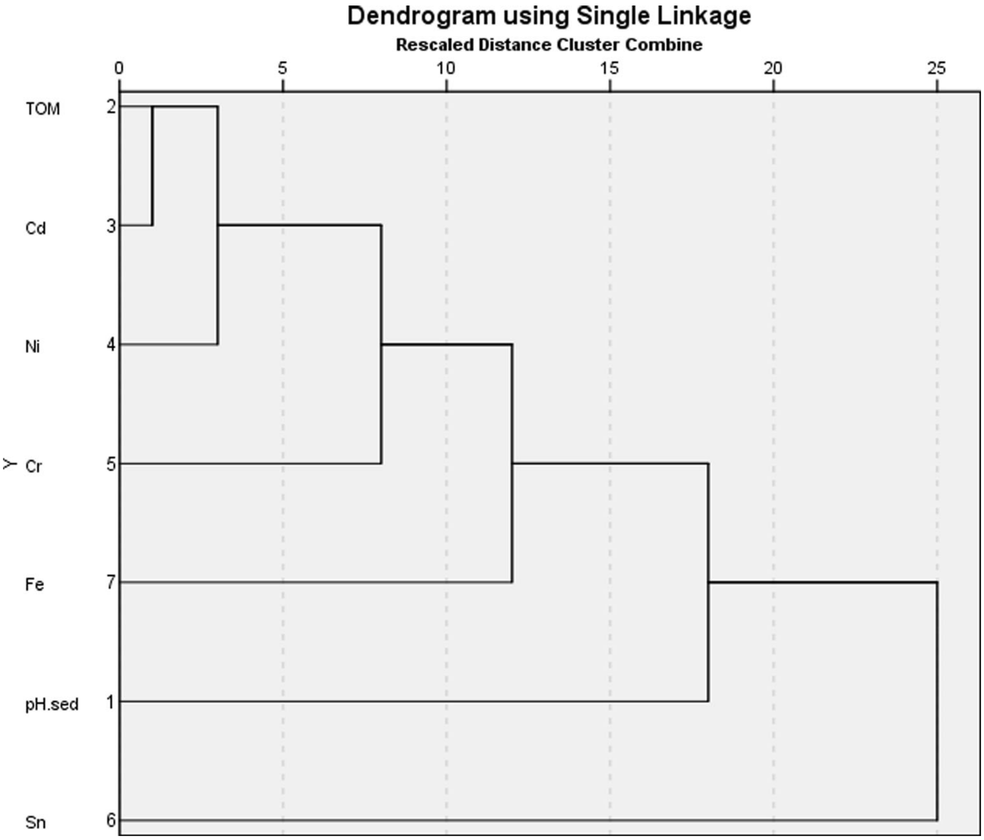
*$p<0.05$; **$p<0.01$

River in Turkey (Ali et al. 2014). Information on the concentrations of heavy metals in the Malaysian riverine system is limited, and in this case, we compared the results of the present study with those of few previous studies. Cd concentrations were higher than those of the Mamut River (Ali et al. 2004). Ni concentrations were higher than those of the Junggat River (Berandah et al. 2010) and the Langat River (Wan et al. 2012). Cr concentration was found to be higher in the Lich River (Nguyen et al. 2013) when compared to that of the current study. Furthermore, Sn concentration was higher than that of the Pearl River, China (Baolin et al. 2011).

Correlation matrix

Physicochemical properties-physicochemical properties, metal-physicochemical properties, and metal-metal relationships were analyzed by Pearson's correlation matrix. The results are shown in Table 8. For the physicochemical properties-physicochemical properties, there were no significant relationships between pH (sediment) and TOM (r=−0.203). For the metal-physicochemical property relationships, Fe and Cr had a strong positive relationship with TOM (r=0.446–0.454; $p<0.01$). Cd and Ni were negatively correlated with TOM (r=0.693–0.495; $p>0.05$). This indicates that these metals are associated with TOM and suggests that TOM content may contribute to increase these metals' concentrations. In the case of the metal-metal relationships, the correlation matrix revealed that Ni and Cr in all the sampled stations were significantly correlated with Cd showing negative relationships (r=0.649–0.514; $p<0.05$), and Cr showed negative relationships with Ni (r=0.538; $p<0.05$). The correlation matrix revealed that Sn in all the sampled stations had no significant relationship with other metals and physicochemical properties: pH (sediment) (r=−0.049), TOM (r=0.152), Cd (r=0.052), Ni (r=0.169), Cr (r=−0.107), and Fe (−0.108). This indicated that Sn was not associated with metals and physicochemical properties and, again, Sn came from different sources than the other metals, such as industry,

Fig. 2 Hierarchical dendrogram for metal elements in sediments of the Bernam River using the nearest neighbour method and Pearson correlation with z standardization



agriculture pesticides, and domestic waste discharge. No correlations were observed between pH (sediment) and heavy metals, suggesting that pH does not exert a significant control on the mobility and distribution of heavy metals in the sediment observed.

Cluster analysis

Cluster analysis (CA) on the physicochemical properties of sediments (TOM and pH (sediment)) and metals was developed in order to further identify similarities in metal content and physicochemical properties of sediments. All the variables were grouped into four distinct clusters, which can be distinguished in the dendrogram shown in Fig. 2, performed with the nearest neighbour method, using Pearson's correlation as a similarity measure. Cluster 1 included Cd, Ni, and TOM, showing relationships between metals and the total organic matter content in the surface sediment of the Bernam River, thus suggesting that these two metals were strongly bound to the TOM. In addition, Cr in cluster 2 was associated with Fe and Ni. Also, Sn in cluster 3 was not associated with any metal, whereas pH (sediment) in cluster 4 was not related to either of the physicochemical properties or the metals. The CA showed stronger relationship existed between Cd and Ni metals and the organic matter content compared to Sn and the organic matter content.

Conclusion

In this study, the status of metal contamination in Bernam River sediments—Cd, Ni, Cr, Sn, and Fe concentrations—was estimated in nine sites. The results of the present study showed that heavy metal concentrations in sediments from the downstream of the river were greater in its upper stream. The tested heavy metals decreased in concentration in the following order: Sn>Cr>Ni>Fe>Cd. This suggested that Cd and Sn are likely to pose greater risks than other metals and hence should be monitored periodically. The correlation matrix of mean concentrations showed that the organic matter content in polluted surface sediments was correlated with heavy metals such as Fe, Cr, Cd, and Ni. The CA classified all the sampling sites into four main groups of similarity sources. The CA further suggested that Cd, Ni, and TOM were related, thus indicating that these metals were strongly sorbed to the TOM fraction.

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