SEASONAL VARIATION AND ASSESSMENT OF HEAVY METALS POLLUTION IN SEDIMENTS FROM SELECTED STATIONS IN TIGRIS AND EUPHRATES RIVERS, CENTRAL IRAQ

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Abstract

In this study, four sampling stations were selected from two locates on the Tigris river (Baghdad region) and others on the Euphrates river (Al-Anbar Governorate) in order to determine concentrations, seasonal variation and pollution intensity assessment of heavy metals (Ni, Cu, Pb, Mn and Cd) in the two rivers sediments. Distribution of studied metals showed that stations in the Tigris river generally had higher concentrations than stations in Euphrates river. Manganese was found at high concentrations in all studied stations and ranged between 200 - 500 ppm, while Cd was found at the lowest concentrations and ranged between not detected to 1.8 ppm during study period. Based on index of geoaccumulation (I-geo) for studied heavy metals indicates that the surface sediments in the studied stations are unpolluted by Ni and Mn, while unpolluted to slightly polluted by Pb and Cd except the Cd at south of Baghdad station (moderately polluted). The I-geo for Cu indicate the sediments were unpolluted to slightly polluted in the Tigris stations, and unpolluted in the Euphrates stations. The calculated enrichment factor (EF) indicate that all stations can be classified as minimal enrichment for Ni, moderate enrichment for Cu and significant enrichment for the elements Pb and Cd.

التغيرات الفصلية وتقييم تلوث المعادن الثقيلة في رواسب محطات مختارة من نهري دجلة والفرات، العراق

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الخلاصة

تم في هذه الدراسة اختيار محطتين في كل من نهر دجلة عند مدينة بغداد هما الراشدية وجنوب بغداد، ونهر الفرات في محافظة الانبار هما هيت والرمادي، وذلك من اجل التعرف على التراكيز والتغيرات الفصلية وتقييم شدة التلوث بالعناصرالثقيلة (النيكل والمنغنيز والرصاص والنحاس والكادميوم) في رواسب النهرين. بينت نتائج دراسة توزيع الفلزات الثقيلة بانها كانت وبصورة عامة اعلى في محطات نهر دجلة مقارنة بنهرالفرات. سجلت اعلى التراكيز لعنصر المنغنيز وفي جميع محطات الدراسة، وتراوحت هذه التراكيز بين 200 – 500 جزء من المليون، بينما سجل الكادميوم اقل التراكيز خلال فترة الدراسة، وتراوحت بين غير محسوس الى 1.8 جزء من المليون. استنادا الى نتائج مؤشر التراكم الارضي (I-geo) المحسوب للفلزات المدروسة

اعتبرت محطات الدراسة غير ملوثة بعنصري النيكل والمنغنيز، ولكنها كانت غير ملوثة الى قليلة التلوث بعنصري الرصاص والكادميوم، ماعدا محطة جنوب بغداد والتي سجلت تلوثا معتدلا بالكادميوم. فضلا عن ذلك فقد بينت قيم المؤشر نفسه بان الرواسب في محطات نهر دجلة غير ملوثة الى ملوثة قليلا بعنصر النحاس، وغير ملوثة في محطات نهر الفرات. وبينت نتائج عامل الاغناء(EF) بأن كل المحطات تصنف على انها ذات حد ادنى من الاغناء بعنصر النيكل، واغناء معتدل بعنصر النحاس واغناء مهم ومؤثر بعنصري الرصاص والكادميوم.

Introduction

*A*mong the various toxic pollutants, heavy metals are particularly severe in their action due to tendency of bio-magnification in the food chain [1]. Sediments are important sinks for heavy metals and also play a significant role in the remobilization of contaminants in aquatic system under favorable conditions and interaction between water and sediments [2]. In a river system, sediments have been widely used as environmental indicators and their chemical analysis can provide significant information on the assessment of anthropogenic activities [3, 4, 5]. The pollution indices evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality [6]. Several numerical sediment quality indices were recently developed to provide interpretative tools for assessing chemical pollution. The most used approaches are Geoaccumulation Index (I-geo) and Enrichment Factor [4]. Several studies were done on heavy metals concentrations in Tigris river, such as Resheed *et al.* [7] study about heavy metals distribution in water, suspended solids, sediments, fish and aquatic plants of this river, Al-Lami *et al.* [8] and Al-Juboury [9] about heavy metals concentrations in the upper – mid region and Northern of Tigris river, while Salih [10] studied the geochemistry of Tigris river from Baghdad to Qurna. Similar work was done by Kassim *et al*. [11] in Euphrates river. The subject of this study involves the sediments collected from selected stations in Tigris and Euphrates rivers to monitor the seasonal variation of heavy metals in the two rivers, and use Geoaccumulation Index and Enrichment Factor to assess the heavy metal contamination in study area.

Study area

Euphrates and Tigris, the twin rivers arise from high plateau near Erzerum in Turkey at an altitude of over 2000 m above sea level.

Tigris is nearly 2000 km long, of which 1360 km runs through Iraq. From north to south, five tributaries drain in to the river: the Khabour, Greater and Lesser Zap, Adheym and the Diyala [12]. The total length of the Euphrates river is 2940 km, from that 1159 km inside Iraq area. It has no tributaries inside Iraq except for few valleys which accumulate water during the rainy season. In this study, four representative sampling stations were selected (Fig 1), two stations locate on Tigris river (Baghdad region), these were station 1 (Al-Rashidia) and station 2 (South of Baghdad), and others on Euphrates River (Al-Anbar governorate), these were, station 3 (Hit) and station 4 (Al-Ramadi).

Material and methods

Sampling and procedure

Forty eight surface sediment samples were collected seasonally from selected stations from Tigris and Euphrates Rivers. Seasonal sampling was carried out from February till November 2008. Sediment samples were collected using clean plastic scoop and stored in polyethylene bags. The concentrations of Ni, Mn, Cu, Pb, and Cd were determined in all samples using Atomic absorption Spectrophotometer (Perkin - Elemer model 5000) with standard solutions in a similar manner to that described by Smith *et a*l .[13] and Abaychi & Douabul [14].

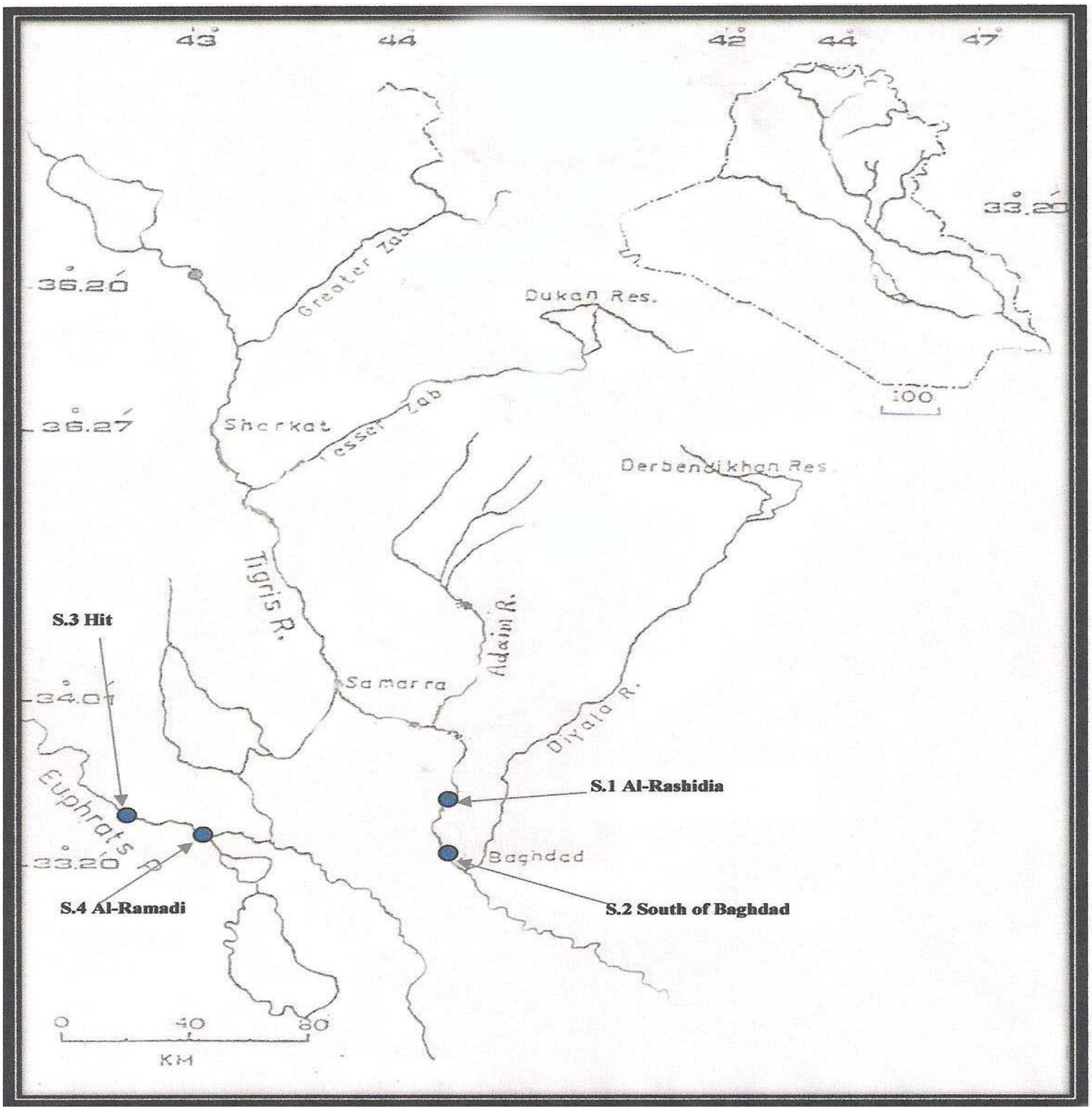

Figure 1: Location map showing sampling stations in Tigris and Euphrates rivers.

The sediments pollution indices

The geo-accumulation index (I-geo) and Enrichment factor were employed to assess the pollution of individual metal in the sediments of studied stations on Tigris and Euphrates rivers.

Index of geoaccumulation (I-geo)

Possible sediment enrichment of metals was evaluated in terms of the I-geo of Muller [15]. The formula used for the calculation of geoaccumulation index is:

$$\textbf{I-geo} = \textbf{Ln}\ (\textbf{Cn} / 1.5\ \textbf{Bn})$$

Where Cn is the measured content of element "n"(ppm), and Bn the element's content in "average shale". In this study, the background concentrations of metals were taken from Turekian and Wedepohl [16] (Table 1). Where 1.5 is the factor used for lithologic variations of trace metals.

Enrichment Factor (EF)

The enrichment factors (EF) were calculated to evaluate the abundance of metals in sediments. Enrichment factor was calculated by a comparison of each tested metal concentration with that of a reference metals [17]. Enrichment factors for mean metal concentration in sediments at all stations were calculated and used for comparison by using the following equation:

$$\mathbf{EF} = \frac{\mathbf{Cn\ (sample)/\ Cref\ (sample)}}{\mathbf{Bn\ (background)/\ Bref\ (background)}}$$

Where:

Cn (sample) = The metals concentration (ppm) in a sample.

Cref (sample) =The reference metals concentration(µg/g).

Bn (Background) = The metals conce-nitration (ppm) in reference (background) environment.

Bref (background) = The reference metals concentration (ppm) in reference background environment .

The commonly used reference metals are Mn ,Al and Fe [17], Thus, Mn was used as the reference metal in this study because it was found most abundant in the sediment and natural in the environment.

Statistical analysis

All statistical analyses were performed using SPSS version 12 for Windows. One-way ANOVA was carried out to assess significant differences between element concentrations in the study area, followed by multiple comparisons using the Duncan's multiple range test. The level of significance was set at $P < 0.01$ and $P < 0.05$.

Results and discussion

The seasonal variation for studied heavy metals

In the present study nickel concentrations in Tigris sediment fluctuated from 40 ppm at station 1 to 66 ppm at station 2 ((Table 1, Fig.2), while it was ranged between 17 – 28 ppm in Euphrates stations (stations 3 and 4). The concentrations for manganese in sediments recorded higher values than other heavy metals. It ranged between 399-500 ppm in Tigris stations and 200 - 450 ppm in Euphrates river (Fig.3). The concentration of Lead showed a less variation where it ranged between 54 – 75 ppm in Tigris river and 35-45 ppm in Euphrates stations (Table1, Fig.4). The concentration of Copper in studied stations sediments fluctuated from 68 -109 ppm in Tigris stations and between 29-63 ppm at Euphrates stations (Fig.5).

Cadmium concentration varied from 0.3 to 1.8 ppm in Tigris stations, while varied between not detected to 1.4 ppm at Euphrates stations (Fig.6). These results were similar to that reported in Tigris and Euphrates rivers in previous studies [9, 10, 11], except for lead which was higher in the present study. The concentration of Mn was the highest among the studied metals at all seasons, and this may be due to high concentration of metal in suspended solids. Gessey et al [18] stated that heavy metals react with suspended particulate matters and through sedimentation processes, accumulate in bottom deposits. Similar results have been reported from several global locations [1, 19].

Table 1: Range, mean ± standard deviation and average shale of heavy metals in monitor stations

Stations	Ni ppm	Mn ppm	Pb ppm	Cu ppm	Cd ppm
Station 1 (Al-Rashidia)	40-60 49±8.4 a	399-500 427.5±38 a	55-60 58.75±2.5 a	70-108 89±15.5 a	0.3-1.5 1.31±0.22 a
Station 2 (South of Baghdad)	46-66 54.2±8.6 a	403-490 457.2±42.4 a	54-75 64.7±8.7 a	68-109 92.2±18 a	0.7-1.8 1.25±0.49 a
Station 3 (Hit)	28-37 31.5±3.8 b	295-450 333±78.9 b	38-45 40.5±3.1 b	31-63 48.5±15 b	ND-1.4 0.95±0.46 b
Station 4 (Al-Ramadi)	17-39 26.7±11.4 b	200-310 272.5±50.2 c	35-44 37.7±4.2 b	29-56 44.7±13 b	ND-1.1 0.52±0.60 c
Average shale ppm	68	900	20	45	0.3

ND= not detected

Different letters refer to significant difference between means of columns.

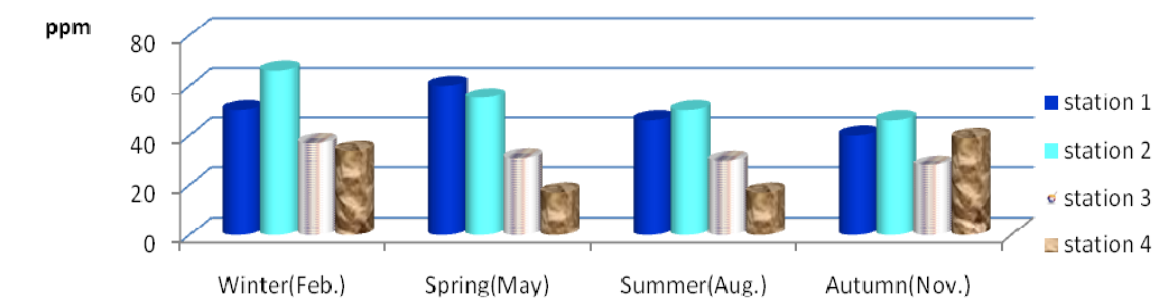

Figure 2: Seasonal variation of average Ni in sediment of studied stations.

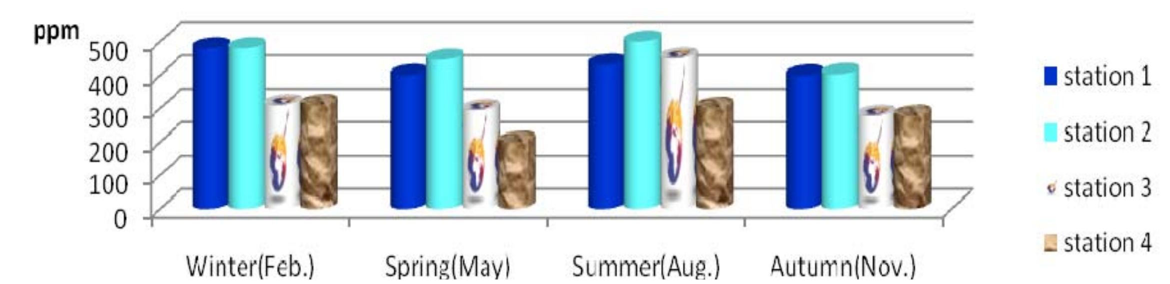

Figure 3: Seasonal variation of average Mn in sediment of studied stations.

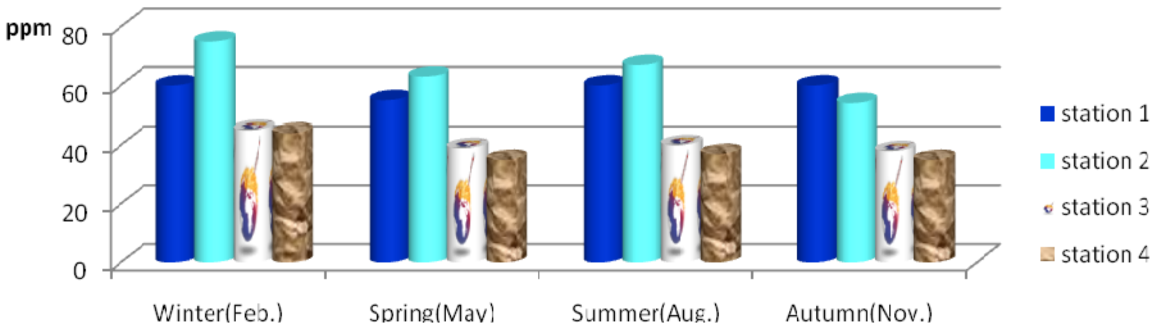

Figure 4: Seasonal variation of average Pb in sediment of studied stations.

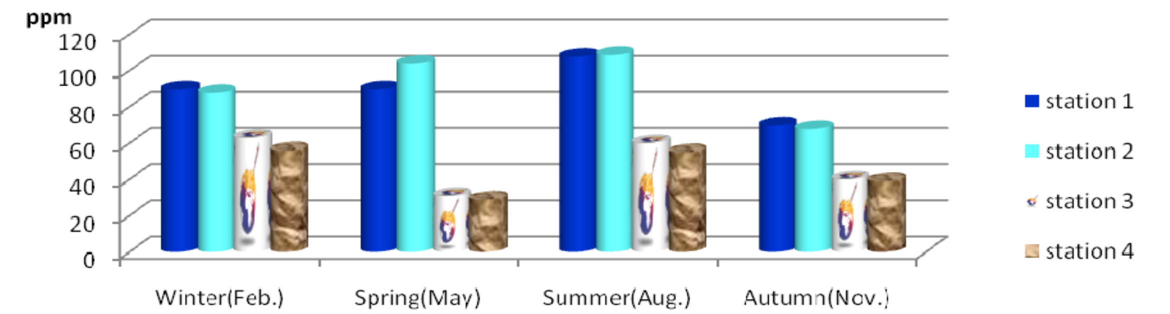

Figure 5: Seasonal variation of average Cu in sediment of studied stations.

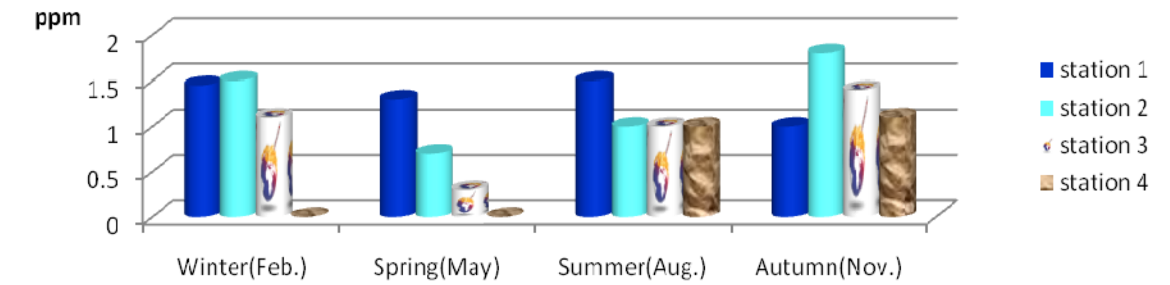

Figure 6: Seasonal variation of average Cd in sediment of studied stations.

From above mentioned results and according to analysis of variance it is clear that the distribution of studied heavy metals showed increased values in the Tigris river stations (Table 1) when comparing with stations of Euphrates river, in addition the spatial distribution of metals in Tigris stations tend to be higher increased in the station 2 than station 1. The higher values obtained for the stations in Tigris sediments may be due to impact of pollution sources in this area which coming from many industrial wastes, agricultural, untreated sewage and other anthropogenic activities in this part of river. Increased metals concentrations in river sediments are a representative of contributions by activities in the sloping side. For instance, some of these metals can be traced from agriculture by the use of fertilizers and others industrial and domestic inputs [20]. In the present study the metals concentration in the sediment showed clear seasonal variations in all metals (although the seasonal variation of this metals were not regular) due to different discharge rate of water in rivers. The concentrations of heavy metals in sediments varied according to the rate of water discharge, the rate of particle sedimentation, the rate of heavy metals deposition, the particle size and the presence or absence of organic matter in the sediments [21]. Almost, lower values of Cd, Mn and Cu were recorded during spring, which may be due to the dilution effect during high water discharge.

Based on inter-element Pearson correlation a very high positive correlation with a very significant probability ($P<0.01$) was observed between Ni and Cd , Ni and Pb, Ni and Cu , Mn and Pb, while high positive correlation ($P<0.05$) was also noticed between Mn and Cu, Pb and Cu. The positive correlation between different elements is an indication of their possible common pollution sources as well as their common sink in sediments. It appears that elements are more associated with solid particles, although sediment metal correlations might indicate the processes and mechanisms influencing the metal associations and behavior, exact bonding and retention mechanisms [20].

Geo-accumulation index (I-geo)

Geo-accumulation index (I-geo) was originally defined by Müller [15] for a quantitative measure of the metal pollution in aquatic sediments [22]. The geo-accumulation index scale consists of seven grades (0 – 6) (Table 2) ranging from unpolluted to very highly polluted.

These seven descriptive classes are as follows: <0 = practically unpolluted; 0 – 1= unpolluted to slightly polluted, 1 – 2 = moderately polluted; 2 – 3= moderately to strongly polluted; 3 – 4= strongly polluted; 4 – 5 = strongly to very strongly polluted and >5 = very strongly polluted [23].

Table (3) presents the geo-accumulation index for the quantification of heavy metal accumulation in the study stations. The I-geo class for the study area sediments varies from metal to metal and station to station . Ni and Mn remains in class 0 (unpolluted) in all stations suggesting that stations sediments are in background value with respect to this metals. The I-geo for Pb and Cd, attain class 1 which indicates that sediments were unpolluted to slightly polluted, except the Cd at station 2 located in class 2 (moderately polluted) . The I-geo for Cu ranged between -0.410 and 0.300 qualifying these sediments as unpolluted to slightly polluted in Tigris stations (1 and 2),while the I-geo for Cu in the Euphrates stations (3 and 4) attain class 0 which expressed that the sediments in the study area were unpolluted.

Enrichment Factor (EF)

The enrichment factor, due to its universal formula, is a relatively simple and easy tool for assessing enrichment degree and comparing the contamination of different environmental media [24].

According to Acevedo-Figueroa *et al.* [25], six contamination categories are recognized on the basis of the enrichment factor: EF<1 indicates no enrichment, EF = 1-2 → minimal enrichment, EF = 2-5 → moderate enrichment, EF = 5-20 → significant enrichment, EF = 20-40 → very high enrichment and EF > 40 → extremely high enrichment .

EF was calculated to determine if levels of metals in sediments of the study area were of anthropogenic origins leading to contamination. The variations of EF for each metal with stations are shown in (Table 4). The EF for Ni, remains in the range 1 - 2 in all stations and indicates a minimal enrichment. The high values for enrichment factor for Pb and Cd (ranged between 5.40 to 8.25) refer to the all studied stations was significant enrichment by these metals. Commonly EF values for Cu qualifying

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Table 4: Enrichment factors (EF) of sediments in the study areas.

	EF Ni	EF Pb	EF Cu	EF Cd
Station 1	1.58	6.12	4.14	8.18
Station 2	1.58	6.41	4.05	8.25
Station 3	1.25	5.40	2.90	8.60
Station 4	1.30	6.20	3.28	5.80

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