International Journal of Environment & Water
ISSN 2052-3408

Identification of sources of heavy metals pollution in Euphrates River sediments (Iraq) using multivariate statistical analysis

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Abstract

The concentration of various heavy metals (Pb, Cd, Zn, Cu, Ni, Co, Fe, Mn and Cr) in sediments from the Euphrates River in Iraq were investigated based on samples collected from 14 sites. The mean concentration of Cd, Cu, Ni, Mn, Fe, and Cr exceeded the USEPA sediment quality guidelines, suggesting that heavy metal contamination of the sediment of the Euphrates River has occurred. Comparison of concentrations of heavy metals with the global average for surface rock suggested an anthropogenic source for Pb, Cd, Ni and Co and a geogenic origin for Zn, Cu, Fe, Mn and Cr. A strong positive correlation was observed among Zn, Cu, Fe and Cr, while a moderate correlation was observed among Cd, Pb, Ni and Co. Principal component analysis (PCA) identified nine heavy metals controlling their variability in sediments, which accounted for 49.494% (factor 1: Zn, Co and Cr) and 22.982% (factor 2: Cd, Cu and Mn) of the total variance. F1 and F2 cover metals having origins in natural and anthropogenic sources. Cluster analysis revealed two groups of metals with close similarities, Pb, Cu, Co, Cd, Zn, Cr, Ni and Mn, which were anthropogenic, and Fe, which was lithogenic.

Keywords: heavy metals; pollution; Euphrates sediments; multivariate analysis

Introduction

Sediments are mixtures of several components of mineral species and organic debris that serve as the ultimate sink for heavy metals discharged into the environment (Abbas *et al*., 2009; Bettinentti *et al.,* 2003). Chemical leaching from bedrock, water drainage basins and runoff from banks are the primary sources of heavy metals in rivers (Venkatesha Raju *et al.,* 2012). Mining operations, disposal of industrial wastes and application of biocides for pest are also anthropogenic sources (Chakravarty and Patgiri, 2009). Heavy metals are serious pollutants because of their toxicity, persistence and nondegradability in the environment (Idris *et al.,* 2007; Morin *et al.,* 2008). Polluted sediments, in turn, can act as sources of heavy metals, imparting them into the water and degrading water quality (Zhong *et al.,* 2006; Atkinson *et al.,* 2007). However, few studies have been conducted to investigate the distribution of heavy metals in sediments of the Euphrates River (Kassim *et al.,* 1997; Rabbe *et al.,* 2009; Hassan *et al.,* 2010; Salah *et al.,* 2012).

Assessments of the anthropogenic release of heavy metals and other pollutants are usually conducted to determine the distribution of pollutants and associated factors, where the contaminants originate, and how each source contributes to the contamination (Yisa *et al.,* 2011). The most rapid and inexpensive tools for assessment of contamination sources are multivariate statistical analyses of data (Kelepersis *et al.,* 2006). Principle component analysis (PCA), factor analysis (FA) and cluster analysis (CA) are multivariate tools commonly applied for pattern recognition, source identification and contribution estimation (Mostert *et al.,* 2010).

Multivariate statistical techniques have been widely applied to investigate heavy metals concentration, accumulation, sources and distributions in sediments (Zhou *et al,.* 2007; Chang *et al.,* 2007; Taghinia *et al.*, 2010; Krishna *et al.,* 2011; Varol, 2011; Wang *et al.*, 2011; Yuan *et al.*, 2012; Singovszka and Balintova, 2012; Venkatesha Raju *et al.*, 2012). Therefore, this study was conducted to identify the pollution sources of heavy metals in Euphrates River sediments by multivariate statistical analyses.

Materials and Methods

Study Area

The Euphrates River is one of most important rivers in the world. Along with the Tigris River, the Euphrates provided much of the water that supported the development of ancient Mesopotamian culture. The Euphrates River originates in the highlands of Turkey and forms the Karasu and Murat tributary rivers. The Euphrates enters Iraq at Al Qaim. During its passage through Iraq, the river crosses more than 1000km. For the present investigation, the study area is bounded by latitudes 33° 26' to 34° 22' N and longitudes 41° 8' to 43° 20' E (Fig.1).

Sample Collection and Analysis

Fourteen sampling sites were selected for collection of sediments along the Euphrates River (Fig. 2), which was conducted in the winter and spring of 2012. Sampling sites were located exactly by GPS (Garmin) and auger tubes were used for sediment sampling. The samples were then placed in polyethylene bags and transported to the laboratory at 4°C. Upon arrival in the laboratory, the samples were dried at 104°C for 48 hours, ground to a fine powder and then sieved through 106-µm stainless steel mesh. The samples were then stored in a polyethylene container until digestion and analysis. Closed vessel microwave assisted acid digestion under high temperature and pressure was conducted (Canadian Counsel of

Ministers of Environment, CCME, 1999) as described by Valeria *et al*. (2003). Briefly, 0.5 grams of sediment sample were put into the reference vessel, after which 25 ml of HCL: H_2SO_4: HNO_3 (3:2:2) were added and the unit was inserted into the microwave unit. The digested solution was then cooled and filtered. Next, the filtrate was diluted to 50 ml with distilled water and stored in a special container unit. AAS (Atomic Absorption Spectrometry) was conducted using a (Phoenix – 986- USA) AAS machine to detect and measure heavy metal content in the sediment samples.

Statistical analysis methods

Principle Component Analysis (PCA)

This technique is the oldest multivariate technique. PCA analyzes a data table representing observations described by several dependent variables, which are generally inter-correlated. The goal of PCA is to extract the important information as a set of uncorrelated (i.e., orthogonal) variables. These variables are called principle components, factors, eigenvectors, singular vectors, or loadings. Each unit is also assigned a set of scores that correspond to its projection onto the components. The results of the analysis are often presented with graphs plotting the projections of the units onto the components, and the loading of the variables. The importance of each component is expressed by the variance (i.e., eigenvalue) of its projection or by the proportion of the variance explained (Abdi, 2003).

Cluster Analysis (CA)

Cluster analysis (CA) is an exploratory method of data analysis for solving classification problems. The objective of CA is to sort cases, data, or objects into groups or clusters. The resulting clusters of objects should exhibit high internal (within cluster) homogeneity and high external (between cluster) heterogeneity (McGarial *et al.*, 2000). Hierarchical CA, the most common approach, starts with each case in a separate cluster and joins clusters together step by step until only one cluster remains (McKenna, 2003). The results of application of cluster analysis are best described using a dendrogram or binary tree.

To study the pollution sources of sediments of the Euphrates river by heavy metals, Pearson's correlation, PCA and CA were conducted using the Statistica 7 software.

Results and Discussion

Heavy metals concentrations in the sediments samples of the Euphrates river are listed in Table 1. USEPA sediment quality guidelines were applied to assess metal contamination in sediments. The mean concentrations of Cd, Cu, Ni, Mn, Fe, and Cr exceeded the USEPA guidelines; however, those of Pb and Zn did not. When compared with the world surface rock average as a background level (Martin and Meybeck, 1979), the concentrations of Pb, Cd, Ni, and Co were higher than the background level, while those of Zn, Cu, Fe, Mn, and Cr were lower. These results suggest an anthropogenic source for Pb, Cd, Ni, and Co and a lithogenic source for Zn, Cu, Fe, Mn and Cr. The interrelationship among heavy metals was examined on the basis of linear correlation between metal pairs in terms of a significant positive correlation coefficient, Table 2. Good positive correlations were observed for Cd-Pb (r=0.436), Cd-Ni (r=0.487), Pb-Ni (r=0.380) and Pb-Co (r=0.472), indicating the existence of a common source (anthropogenic source) of these metals in the sediments. Strong positive correlations were observed for Zn-Cu (r=0.758), Zn-Fe (r=0.595), Zn-Cr (r=0.808), Fe-Cu (r=0.617) and Cu-Cr (r=0.574), suggesting a common origin (lithogenic origin) of these metals.

Table 3 shows the results of principal component analysis (PCA), while Table 4 shows the results after varimax rotation. The first two principal components accounted for 72.47% of total variance, and the variance of F1 and F2 was 49.494 and 22.982%, respectively, Table 4. Factor 1 had strong loadings on Zn, Co and Cr, and moderate positive loading on Pb. Cobalt and Cr are siderophile elements, which are primary rock forming elements. Accordingly, it is easy for them to enter into iron-magnesium silicate minerals because of their similar ionic radius (Krishna *et al.*, 2011). Zinc is geochemically very similar to Pb. The association of Zn, Co, Cr, and Pb in F1 may be attributed to their lithogenic source. Factor 2 comprised Cd, Cu, and Mn with high loadings and Fe and Ni with moderate loadings. As shown in Table 4, Zn, Co, and Cr were the main loadings in F1, while Cd, Cu and Mn were distributed in F2. However, not all heavy metals were distributed in one factor. For example, Zn, Cr and Pb were partially present in F2, while Cu and Mn were partially present in F1. These results suggest that Zn, Cr, Pb, Cu and Mn originate from both natural and anthropogenic sources.

The dendrogram of the hierarchical cluster analysis of metal contents in the study area is shown in Fig. 3. Two distinct clusters were identified. The first cluster (I) contained three subclusters, (a) Pb, Cu, Co and Cd, (b) Zn, Cr, and Ni and (c) Mn. The second cluster (II) included Fe. The elements of cluster I are considered to be anthropogenic in origin, except for Mn, which originates from mixed sources. Cluster II contained lithogenic Fe.

The groupings from hierarchical cluster analysis showed sampling sites ordered in similar clusters (Fig. 4). All 14 sampling sites fall into two statistically significant clusters. Cluster I (sites 1-8 and 10-14) and cluster II (site 9) for the Euphrates River revealed that site 9 was less pollution than the other sites. The spatial distribution of heavy metals concentrations confirmed these results (Fig. 5 and 6). In addition, the sites in cluster I have similar characteristics and were classified into group 1 (S1 and S12), group 2 (S2, S5 and S11), group 3 (S3 and S4), group 4 (S6 and S10), and group 5 (S7 and S13). These findings indicate that members of each group were distributed based on whether the sources of pollution were point or nonpoint (Venkatesha Raju *et al.*, 2012).

Conclusions

The concentrations of various heavy metals (Pb, Cd, Zn, Cu, Ni, Co, Fe, Mn and Cr) in sediments from the Euphrates River in Iraq were investigated. The mean concentration of Cd, Cu, Ni, Mn, Fe, and Cr exceeded the USEPA sediment quality guidelines. These results suggested that heavy metal contamination has occurred in the sediment of the Euphrates River. Comparison of the concentrations of heavy metals in sediments with the world surface rock average as a geochemical background suggested an anthropogenic source for Pb, Cd, Ni and Co and a geogenic origin for Zn, Cu, Fe, Mn and Cr. A strong positive correlation was observed among Zn, Cu, Fe and Cr, while a moderate correlation was observed among Cd, Pb, Ni and Co. Principal component analysis (PCA) identified nine heavy metals controlling the variability in sediments, which account for 49.494% (factor 1: Zn, Co and Cr) and 22.982% (factor 2: Cd, Cu and Mn) of the total variance. F1 and F2 cover metals having origins in both natural and anthropogenic sources. Cluster analysis revealed two groups of metals with close similarities, Pb, Cu, Co, Cd, Zn, Cr, Ni and Mn, which were classified as anthropogenic and Fe, which was lithogenic.

Fig. 1 Study area location map.

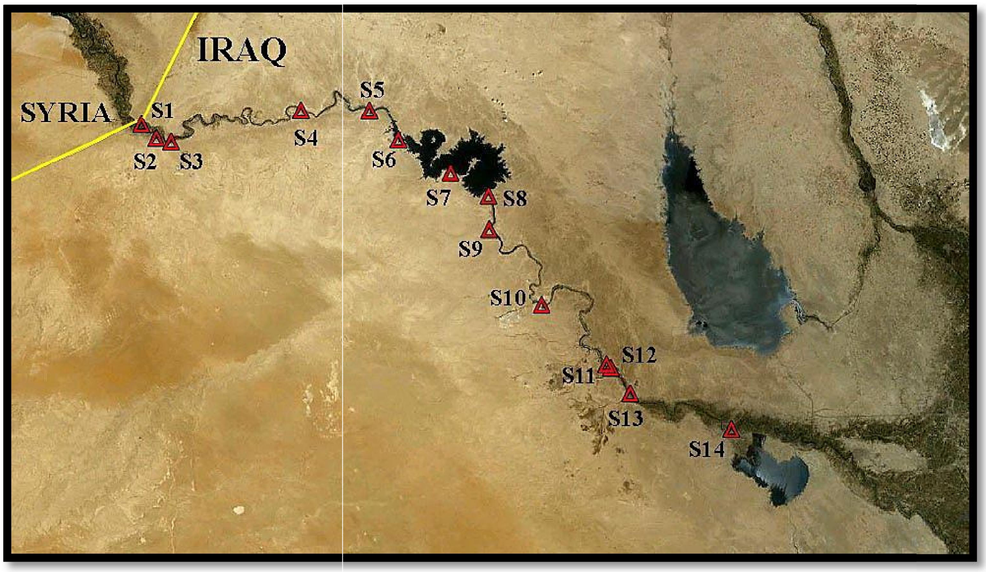

Fig. 2 Sampling sites map.

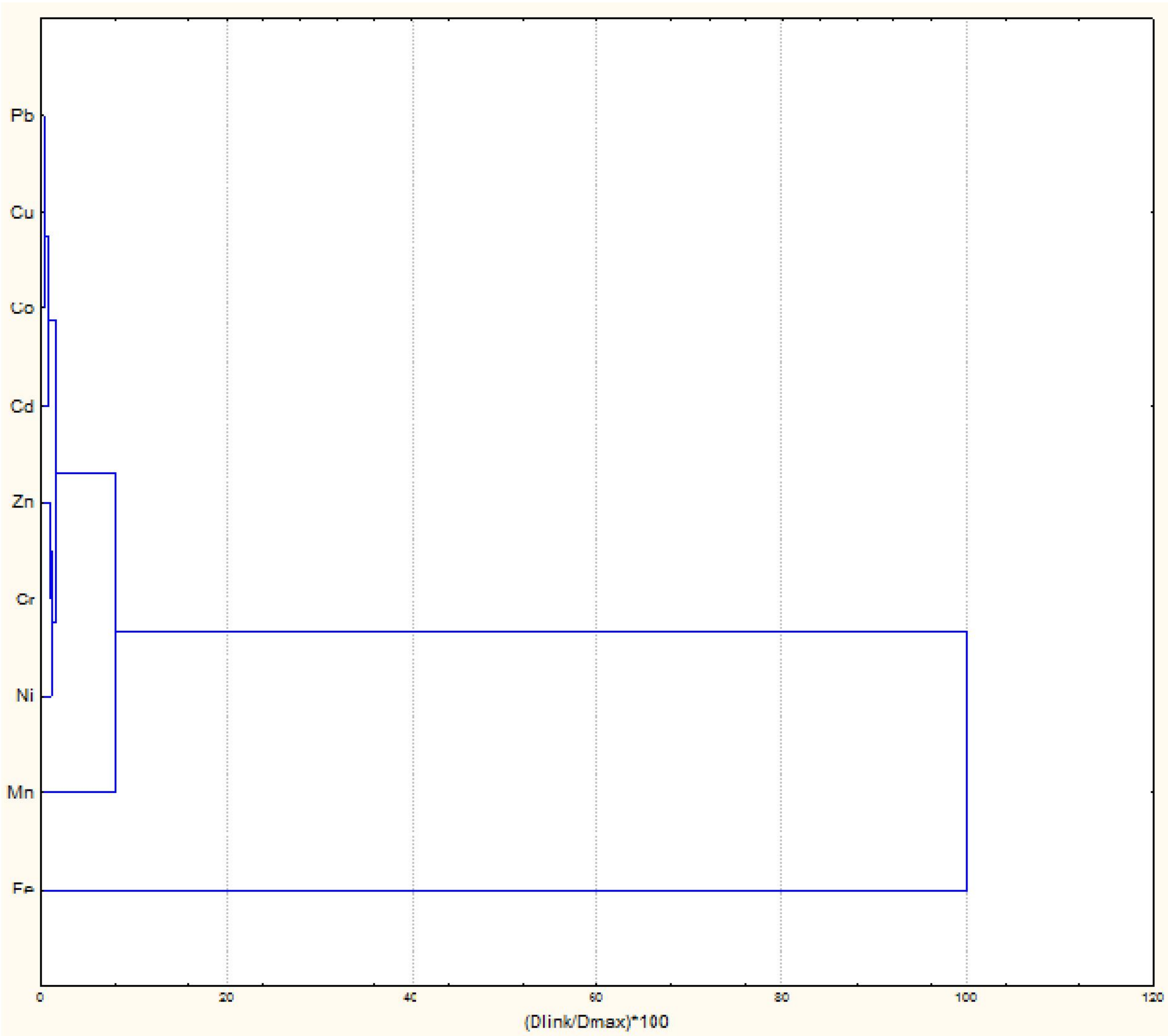

Fig. 3 Dendrogram derived from hierarchical cluster analysis of heavy metal content in Euphrates river sediments samples.

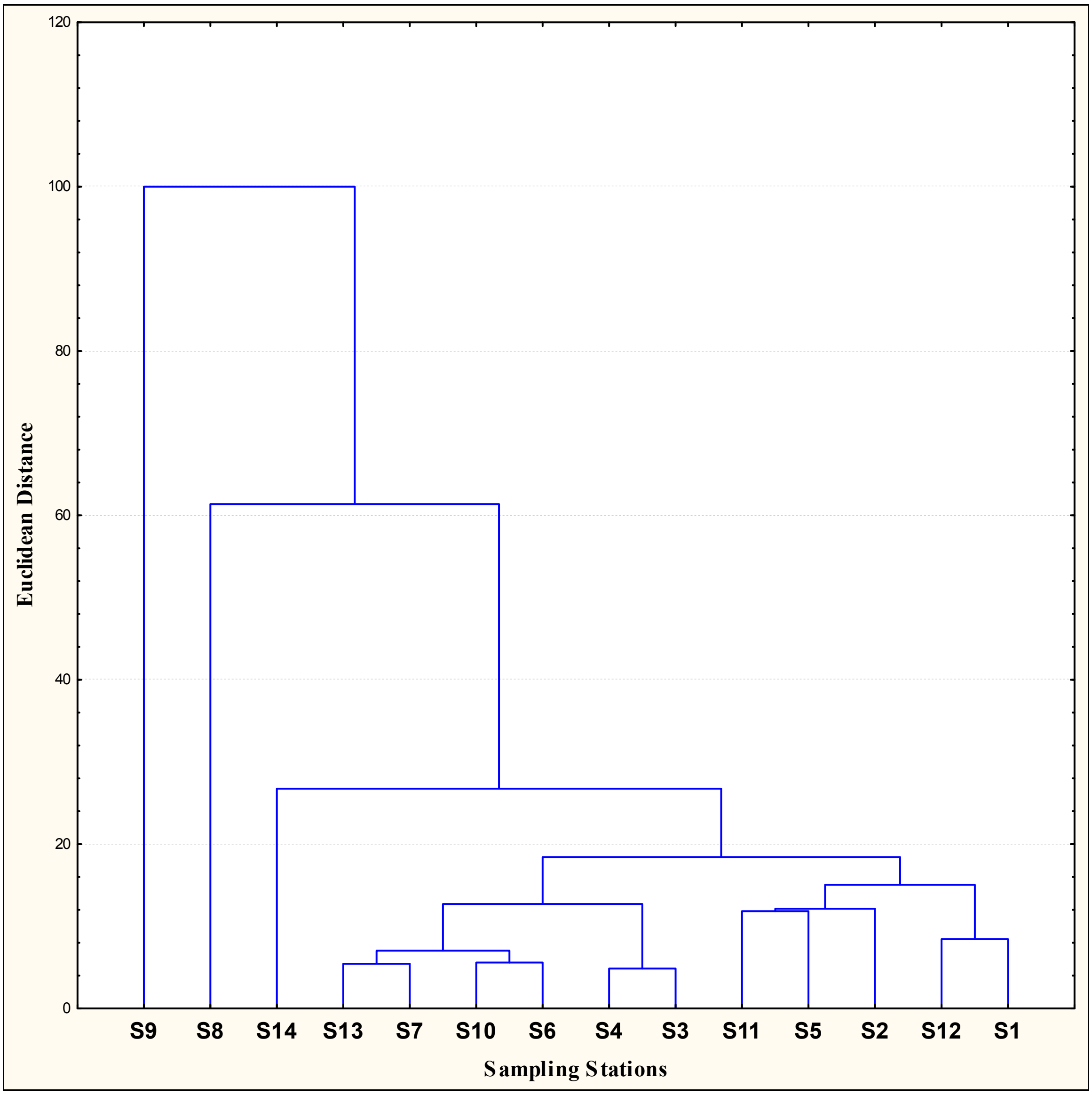

Fig. 4 Cluster analysis of the sampling sites based on their heavy metal concentrations in Euphrates river sediments samples.

International Journal of Environment & Water
ISSN 2052-3408

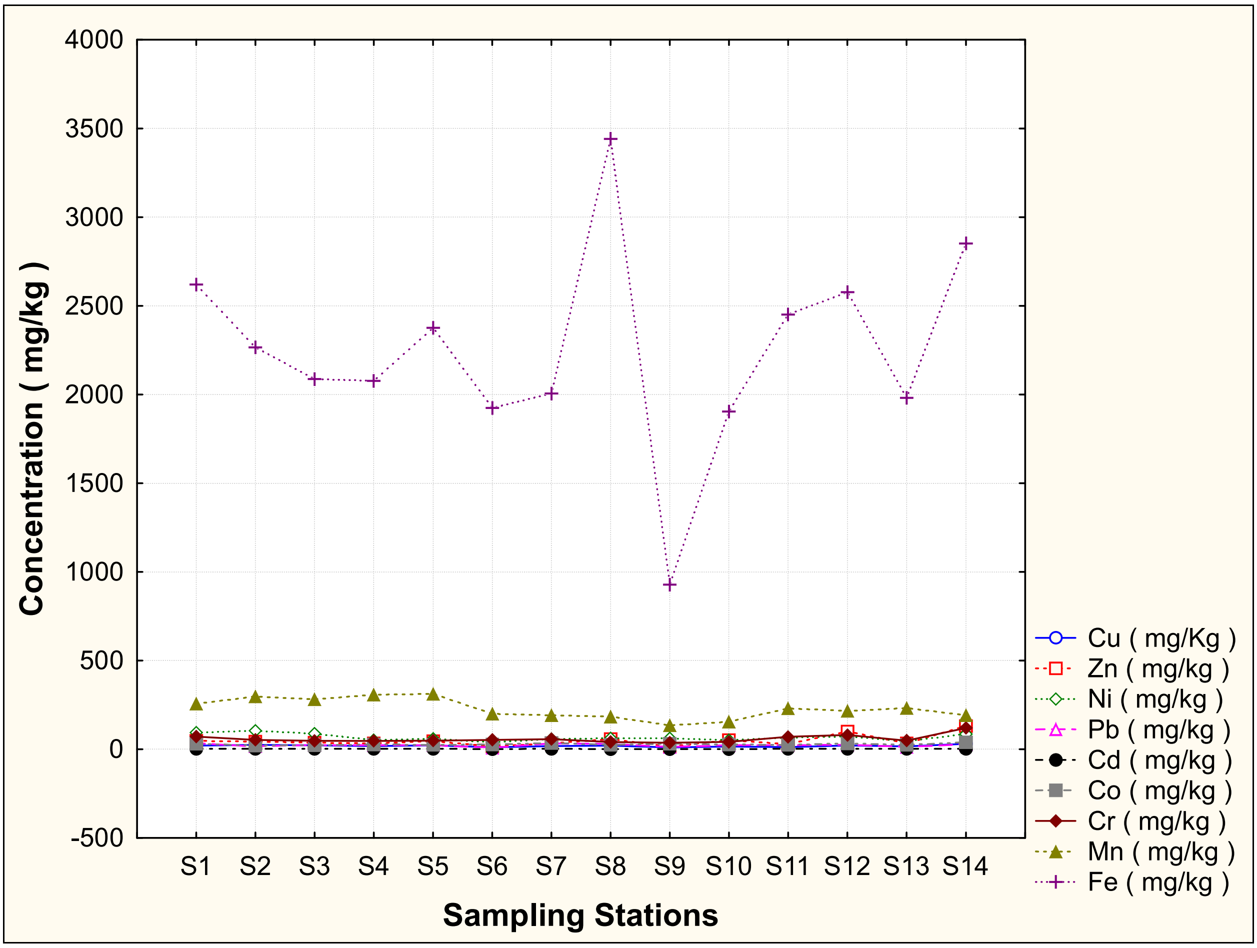

Fig. 5 Spatial variation of heavy metals content in Euphrates river sediments.

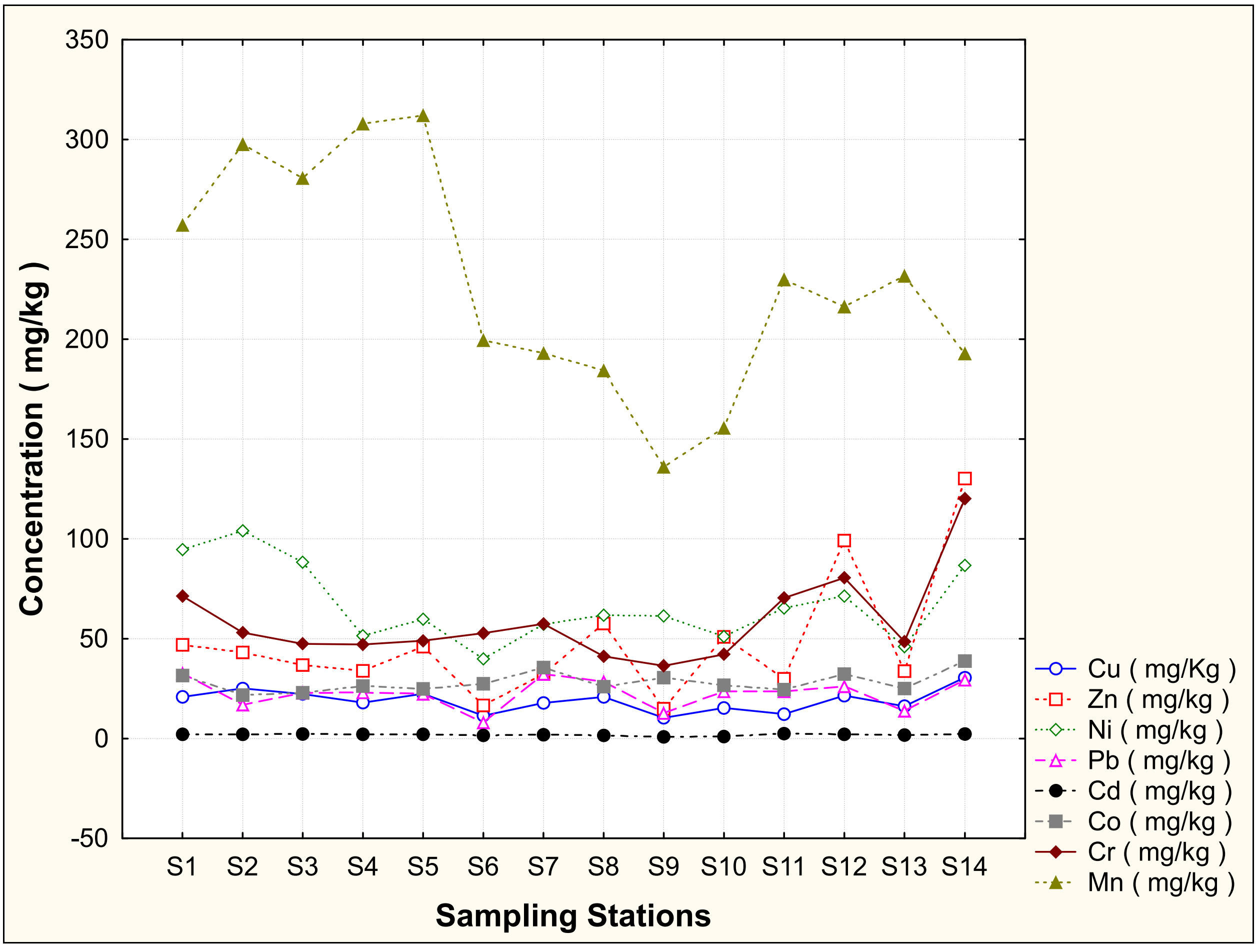

Fig. 6 Spatial variation of heavy metals content in Euphrates river sediments, except iron .

Table 1 Concentration of heavy metals in the sediments samples of Euphrates river during the study period (modified after Salah et al. 2012).

Metal	Minimum	Maximum	Mean	Standard Deviation	World surface[1] rock average	USEPA[2] sediment quality guidelines
Pb	8.02	32.69	22.56	7.37	16	40
Cd	0.87	2.35	1.87	0.45	0.2	0.6
Zn	14.96	130.25	48.00	31.25	127	110
Cu	10.35	30.52	18.91	5.59	32	16
Ni	39.98	103.98	67.08	19.36	49	16
Co	21.88	38.73	28.16	4.91	13	-
Fe	928.7	3441.05	2249.47	571.18	35900	30
Mn	136.05	312.11	228.18	56.13	750	30
Cr	36.45	120.11	58.40	21.73	71	25

Values are in milligram per Kilogram (mg/kg); (1)Martin and Meybeck (1979);) (2) USEPA (1999).

Table 2 Pearson's of correlation coefficient of heavy metals in Euphrates river sediments.

	Pb	Cd	Zn	Cu	Ni	Co	Fe	Mn	Cr
Pb	1.000								
Cd	0.436	1.000							
Zn	0.515	0.374	1.000						
Cu	0.519	***0.598***	***0.758***	1.000					
Ni	0.380	0.487	0.387	***0.683***	1.000				
Co	0.472	0.032	***0.557***	0.234	0.053	1.000			
Fe	***0.610***	0.522	***0.595***	***0.617***	0.318	0.084	1.000		
Mn	0.047	***0.699***	-0.086	0.401	0.342	-0.485	0.208	1.000	
Cr	0.441	***0.580***	***0.808***	***0.574***	0.421	***0.668***	0.451	-0.035	1.000

Table 3 Principal component analysis of Euphrates river sediment samples.

Component	Eigenvalue	%Total Variance	Cumulative Eigenvalue	Cumulative Variance %
1	4.454	49.494	4.454	49.494
2	2.068	22.982	6.522	72.477
3	0.778	8.650	7.301	81.128
4	0.648	7.204	7.949	88.333
5	0.565	6.282	8.515	94.615
6	0.303	3.373	8.818	97.988
7	0.111	1.240	8.930	99.229
8	0.050	0.565	8.981	99.795
9	0.0184	0.204	9.000	100.000

Table 4 Factor loadings (Varimax rotation) on heavy metals in Euphrates river sediment samples.

Element	Factor 1	Factor 2
Pb	*0.629*	0.389
Cd	0.185	**0.861**
Zn	**0.843**	0.336
Cu	0.500	**0.746**
Mn	-0.430	**0.834**
Fe	0.446	*0.595*
Ni	0.255	*0.672*
Co	**0.876**	-0.252
Cr	**0.818**	0.334
Eigenvalue	4.454	2.068
Variance explained %	49.494	22.982
Cumulative variance %	49.494	72.477

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