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Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques

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ABSTRACT

Heavy metal concentrations in sediment samples from the Tigris River were determined to evaluate the level of contamination. The highest concentrations of metals were found at the first site due to metallic wastewater discharges from copper mine plant. Sediment pollution assessment was carried out using contamination factor (CF), pollution load index (PLI), geoaccumulation index (*Igeo*) and enrichment factor (EF). The CF values for Co, Cu and Zn were >6 in sediments of the first site, which denotes a very high contamination by these metals. The PLIs indicated that all sites except the first site were moderately polluted. Cu, Co, Zn and Pb had the highest *Igeo* values, respectively. The mean EF values for all metals studied except Cr and Mn were >1.5 in the sediments of the Tigris River, suggesting anthropogenic impact on the metal levels in the river. The concentrations of Cr, Cu, Ni and Pb are likely to result in harmful effects on sediment-dwelling organisms which are expected to occur frequently based on the comparison with sediment quality guidelines. PCA/FA and cluster analysis suggest that As, Cd, Co, Cr, Cu, Mn, Ni and Zn are derived from the anthropogenic sources, particularly metallic discharges of the copper mine plant.

1. Introduction

Metal contamination in aquatic environments has received huge concern due to its toxicity, abundance and persistence in the environment, and subsequent accumulation in aquatic habitats. Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora and fauna, which, in turn, may enter into the human food chain and result in health problems [1,2]. Heavy metals discharged into a river system by natural or anthropogenic sources during their transport are distributed between the aqueous phase and bed sediments [3]. Because of adsorption, hydrolysis and co-precipitation only a small portion of free metal ions stay dissolved in water and a large quantity of them get deposited in the sediment [4].

Sediments are ecologically important components of the aquatic habitat and are also a reservoir of contaminants, which play a significant role in maintaining the trophic status of any water body [5]. The measurements of pollutants in the water only are not conclusive due to water discharge fluctuations and low resident time. The same holds true for the suspended material [6]. The study of sediment plays an important role as they have a long residence time. River sediments, therefore, are important sources for the assessment of man-made contamination in rivers. Sediments, not only act as the carrier of contaminants, but also the potential secondary sources of contaminants in aquatic system [7,8]. Therefore, the analysis of river sediments is a useful method to study the metal pollution in an area [9].

The Tigris River is one of the most important rivers in Turkey. Some reports have been published on the heavy metal levels in sediment samples from the upper regions of the Tigris River [10,11]. In this paper, we report the first comprehensive study on distribution of heavy metals in sediments of the Tigris River that was accomplished through regular monitoring of the river during a period of one year at seven different sites spread over the river stretch of about 500 km.

The objectives of this study were (i) to determine the spatial and temporal distributions of heavy metals in surface sediments of the Tigris River, (ii) to define the natural and/or anthropogenic sources of these metals using multivariate statistical techniques, (iii) to explore the degree of heavy metal contamination in the river using contamination indices, (iv) to assess environmental risks of these metals in the study area by comparison with sediment quality guidelines (SQGs).

2. Materials and methods

2.1. Study area

The Tigris has been an important river throughout history and was one of the main water sources of the ancient Mesopotamian

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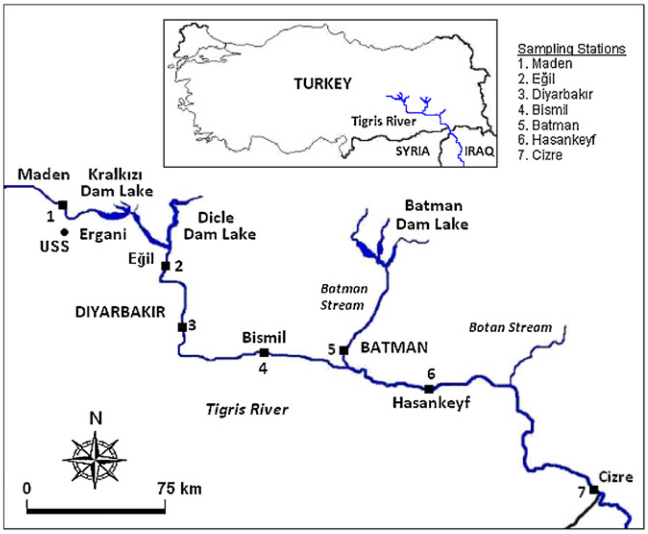

Fig. 1. Map showing sampling sites on the Tigris River.

civilizations. The Tigris River originates in the Toros mountains of the Eastern Anatolia region of Turkey and follows a southeastern route to Cizre, where it forms the border between Turkey and Syria for 32 km before entering Iraq. The total length of the river is approximately 1900 km, of which 523 km is within Turkey. It drains a catchment area of about 57,614 km^2 [12]. Currently, there are two major dams in operation on the Tigris River in Turkey: the Kralkızı and Dicle.

Maximum flows occur from February through April, whereas minimum flows occur from August through October. The annual mean flow of the river in Diyarbakır (upstream) and Cizre (downstream) was calculated to be 28.3 m^3/sn and 211.8 m^3/sn, respectively [13].

The continental climate of the Tigris Basin is a subtropical plateau climate. The annual mean air temperature varied between 14.6 °C (Maden) and 21.8 °C (Cizre) with the highest and the lowest temperature of 35.9 °C and 0 °C, respectively. Annual total precipitation ranged from 294.1 mm Cizre (downstream) to 611.1 mm in Maden (upstream), of which 82% concentrated during the time period of October to April [14].

2.2. Sampling sites

Fig. 1 shows the locations of the sampling sites. Surface sediment samples were collected from seven sites, namely Maden (Site-1), Eğil (Site-2), Diyarbakır (Site-3), Bismil (Site-4), Batman (Site-5), Hasankeyf (Site-6) and Cizre (Site-7), along the Tigris River. Uncontaminated sediment samples (USS) were also collected from a mountain stream in the study area for background studies. The brief description of sampling sites selected for this study is recorded in Table 1.

2.3. Sample collection

Surface sediment samples were collected at monthly intervals between February 2008 and January 2009. The samples collected from each site consisted of 4–5 composite samples. Composite sediments (top 2 cm of surface) were taken by using a self-made sediment core sampler with an inner diameter of 6 cm and length of 60 cm. After sampling, the sediment samples were sealed in clean polyethylene bags, placed in a cooler at 4 °C, and transported to the laboratory immediately for further analysis.

2.4. Chemical analysis

2.4.1. Reagents and standards

All reagents were of analytical grade or of Suprapure quality (Merck, Darmstadt, Germany). Double deionized water (Milli-Q System, Millipore) was used for the preparation of all solutions. The element standard solutions used for calibration were prepared by diluting stock solutions of 1000 mg/l of each element. Stock standard solutions were Merck Certificate AA standard (Merck). All glasswares used were cleaned by soaking in dilute acid for at least 24 h and rinsed abundantly in deionized water before use.

2.4.2. Analysis of sediment samples

Sediment samples were air dried; then, stones and plant fragments were removed by passing the dried sample through a 2 mm sieve. The sieved sample was powdered and finally passed through a 500 μm sieve and stored in acid washed and deionized water rinsed glass bottles. For heavy metal content determinations, 0.25 g sediment subsamples were digested in teflon vessels with 12 ml HNO_3 (65%):HCl (37%) (3:1) mixture in a microwave oven (MARSXpress, CEM) [15]. After microwave digestion, the sample solutions

Table 1
Locations and description of sampling sites along the Tigris River.

Sites	Coordinates	Altitude (m)	Description
S-1	38°20'N–39°41'E	860	Site-1 is located about 3 km downstream of copper mine plant in Maden Township. Wastewaters containing heavy metal from plant discharge into the river before this site.
S-2	38°06'N–40°08'E	616	Site-2 is located about 2 km downstream of Dicle Dam in Eğil Township. Agricultural runoff and irrigation return flow are pollution sources at this site.
S-3	37°53'N–40°13'E	576	Site-3 is just near On Gözlü Köprü (Ten-Eyed Bridge) in Diyarbakır Province. Some wastewater drains that collect mixed domestic and industrial wastewater empty into the river before this site.
S-4	37°50'N–40°39'E	538	Site-4 is situated just near Bismil Bridge. Wastewaters from the Diyarbakır wastewater treatment plant discharge into the river between the site-3 and site-4. In addition, domestic wastewaters from Bismil Township discharge into the river just before it reaches site-4. Agricultural runoff and irrigation return flow are other pollution sources at this site.
S-5	37°54 N–41°05'E	540	Site-5 is situated just near Batman Bridge. Agricultural runoff is pollution source at this site.
S-6	37°42'N–41°24'E	471	Site-6 is located near Hasankeyf Bridge. Animal manure wastes and municipal wastewater discharges from Hasankeyf Township are pollution source at this site.
S-7	37°19'N–42°11'E	371	Site-7 is located just near Cizre Bridge. Wastewater drains from Cizre Township empty into the river directly before this site. Additional pollution sources at this site are the sand pits near the river.

were filtered, adjusted to a suitable volume with double deionized water. The sediment extracts were analyzed for Co, Cr, Cu, Fe, Mn, Ni and Zn by a flame atomic absorption spectrometry (FAAS) equipped with deuterium background correction (AA240FS, Varian). As, Cd and Pb in extracts were measured by using a graphite furnace atomic absorption spectrometry (GFAAS) with Zeeman background correction (AA240Z, Varian).

2.4.3. Quality control

The analytical data quality was guaranteed through the implementation of laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards, analysis of reagent blanks, recovery of spiked samples and analysis of replicates. The accuracy and precision of the analytical procedures were tested by recovery measurements on spiked sediment samples. The sediment samples collected as uncontaminated sediment samples were spiked with metals and digested with the same procedure as the samples. The percentage recoveries of the metals in the spiked samples ranged from 91.4% (Fe) to 105.2% (Pb). The precision of the analytical procedures, expressed as the relative standard deviation (RSD), ranged from 5 to 10%. The precision for the analysis of standard solution was better than 5%. All analyses were carried out in duplicate, and the results were expressed as the mean.

2.5. Assessment of sediment contamination

In the interpretation of geochemical data, choice of background values plays an important role. Many authors have used the average shale values or the average crustal abundance data as reference baselines. The best alternative is to compare concentrations between contaminated and mineralogically and texturally comparable, uncontaminated sediments [16–18]. Since there were no data on background concentrations for the investigated Tigris sediment and soils of close areas, the background values in this paper were calculated from the mean concentrations of heavy metals in uncontaminated sediments of the study area. In this study, four different indices were used to assess the degree of heavy metal contamination in sediments of the Tigris River.

2.5.1. Contamination factor (CF)

The CF is the ratio obtained by dividing the concentration of each metal in the sediment by baseline or background value (concentration in uncontaminated sediment):

$$\mathrm{CF} = \frac{C_{\text{heavy metal}}}{C_{\text{background}}}$$

CF values were interpreted as suggested by Hakanson [19], where: $\mathrm{CF} < 1$ indicates low contamination; $1 < \mathrm{CF} < 3$ is moderate contamination; $3 < \mathrm{CF} < 6$ is considerable contamination; and $\mathrm{CF} > 6$ is very high contamination.

2.5.2. Pollution load index (PLI)

For the entire sampling site, PLI has been determined as the nth root of the product of the n CF:

$$\mathrm{PLI} = (\mathrm{CF}_1 \times \mathrm{CF}_2 \times \mathrm{CF}_3 \times \cdots \times \mathrm{CF}_n)^{1/n}$$

This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. When $\mathrm{PLI} > 1$, it means that a pollution exists; otherwise, if $\mathrm{PLI} < 1$, there is no metal pollution [20].

2.5.3. Geoaccumulation index (Igeo)

The geoaccumulation index (*Igeo*) is defined by the following equation:

$$Igeo = \frac{\mathrm{Log}_2(C_n)}{1.5(B_n)}$$

where C_n is the concentration of metals examined in sediment samples and B_n is the geochemical background concentration of the metal (n). Factor 1.5 is the background matrix correction factor due to lithospheric effects. The geoaccumulation index consists of seven classes [21]. Class 0 (practically unpolluted): $Igeo \le 0$; Class 1 (unpolluted to moderately polluted): $0 < Igeo < 1$; Class 2 (moderately polluted): $1 < Igeo < 2$; Class 3 (moderately to heavily polluted): $2 < Igeo < 3$; Class 4 (heavily polluted): $3 < Igeo < 4$; Class 5 (heavily to extremely polluted): $4 < Igeo < 5$; Class 6 (extremely polluted): $5 > Igeo$ [22].

2.5.4. Enrichment factor (EF)

Enrichment factor (EF) is a useful tool in determining the degree of anthropogenic heavy metal pollution [16]. The EF is computed using the relationship below:

$$\mathrm{EF} = \frac{(\mathrm{Metal/Fe})\,\mathrm{Sample}}{(\mathrm{Metal/Fe})\,\mathrm{Background}}$$

In this study, iron (Fe) was used as the reference element for geochemical normalization because of the following reasons: (1) Fe is associated with fine solid surfaces; (2) its geochemistry is similar to that of many trace metals and (3) its natural concentration tends to be uniform [22]. EF values were interpreted as suggested by Sakan et al. [16], where: $\mathrm{EF} < 1$ indicates no enrichment; <3 is minor enrichment; 3–5 is moderate enrichment; 5–10 is moderately severe enrichment; 10–25 is severe enrichment; 25–50 is very severe enrichment; and >50 is extremely severe enrichment.

2.6. Sediment quality guidelines

Sediment quality assessment guidelines (SQGs) are very useful to screen sediment contamination by comparing sediment contaminant concentration with the corresponding quality guideline [23]. These guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist in the interpretation of sediment quality. Such SQGs have been used in numerous applications, including designing monitoring programs, interpreting historical data, evaluating the need for detailed sediment quality assessments, assessing the quality of prospective dredged materials, conducting remedial investigations and ecological risk assessments, and developing sediment quality remediation objectives [23].

The consensus-based sediment-quality guidelines (SQGs) were used in this study to assess possible risk arises from the heavy metal contamination in sediments of the study area. The consensus-based SQGs were developed from the published freshwater sediment-quality guidelines that have been derived from a variety of approaches [23]. These synthesized guidelines consist of a threshold effect concentration (TEC) below which adverse effects are not expected to occur and a probable effect concentration (PEC) above which adverse effects are expected to occur more often than not. An apparent advantage of the consensus-based guidelines is that MacDonald et al. [23] evaluated the reliability of the TECs and PECs for assessing sediment-quality conditions by determining their predictive ability that is, the ability of the guidelines to correctly classify field-collected sediments as nontoxic or toxic to one or more aquatic organisms.

Table 2
Maximum, minimum, mean and standard deviation values of heavy metals in sediments of all sites studied in the Tigris River.

Sites		Metal concentrations (mg/kg)								
		As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Maden	Max	18.0	4.9	389.8	151.7	5075.6	1657.0	288.0	566.6	2396.6
	Min	5.0	1.4	55.6	76.4	673.1	822.0	151.9	144.4	191.3
	Mean	8.9	2.4	155.9	119.0	1941.9	1233.3	216.8	393.9	530.4
	SD	4.0	1.2	107.7	21.8	1592.3	268.5	44.9	121.7	597.9
Eğil	Max	4.9	2.4	30.6	96.0	131.6	752.0	144.4	358.1	190.6
	Min	2.0	1.4	20.9	56.4	91.6	540.5	113.4	89.1	134.0
	Mean	3.3	1.8	25.7	76.4	117.0	629.8	132.0	255.5	165.2
	SD	0.9	0.3	2.9	11.3	12.4	63.9	9.1	104.0	14.5
Diyarbakır	Max	6.6	3.0	39.7	163.4	297.2	787.5	174.5	387.7	247.0
	Min	3.5	1.4	23.2	98.1	117.5	556.3	153.3	89.0	136.0
	Mean	4.8	1.8	30.3	115.4	189.7	663.2	162.3	250.3	178.2
	SD	1.0	0.4	4.9	16.9	53.4	70.7	5.9	102.7	27.6
Bismil	Max	5.2	2.6	25.6	113.2	136.3	1228.0	172.8	392.4	220.8
	Min	2.4	1.0	12.3	67.7	50.8	528.7	137.0	185.5	107.3
	Mean	3.5	1.6	15.9	83.8	73.9	641.3	149.6	274.3	146.1
	SD	0.8	0.5	3.7	13.6	25.9	189.8	10.1	59.0	31.7
Batman	Max	6.0	1.6	12.2	65.9	36.4	590.8	109.7	299.2	183.1
	Min	2.3	0.7	5.4	35.8	17.2	282.2	79.3	62.3	84.8
	Mean	3.6	1.2	9.0	50.5	24.1	420.2	93.9	163.7	129.6
	SD	1.0	0.3	1.8	9.5	5.7	92.2	8.9	95.6	30.3
Hasankeyf	Max	3.6	2.5	16.1	90.2	64.2	791.0	125.7	344.6	189.0
	Min	2.2	0.8	5.4	28.4	11.2	329.5	74.0	73.9	60.1
	Mean	2.9	1.6	10.0	54.6	28.5	489.7	91.0	221.8	120.5
	SD	0.5	0.5	2.6	15.7	15.5	130.6	15.9	86.9	30.6
Cizre	Max	8.5	2.7	19.0	124.4	59.2	982.9	244.7	387.6	191.2
	Min	2.9	1.8	11.1	65.7	27.7	529.8	135.5	93.7	123.1
	Mean	5.4	2.2	14.1	93.6	37.3	702.5	173.7	297.3	152.1
	SD	1.8	0.3	2.7	20.2	10.4	124.4	35.9	79.8	21.0

2.7. Statistical analyses

Analysis of variance (ANOVA) was performed to analyze the significant spatial and temporal differences ($p < 0.05$). Relationships among the considered variables were tested using Pearson's coefficient with statistical significance set at $p < 0.05$.

Multivariate analysis of the river data set was performed using cluster analysis (CA) and principal component analysis/factor analysis (PCA/FA) techniques. The above statistical analyses were applied to experimental data standardized through *z*-scale transformation to avoid misclassification due to wide differences in data dimensionality. Kaiser–Meyer–Olkin (KMO) and Bartlett's sphericity tests were performed to examine the suitability of the data for PCA/FA [24]. KMO is a measure of sampling adequacy that indicates the proportion of variance that is common, i.e., variance that may be caused by underlying factors. A high value (close to 1) generally indicates that principal component/factor analysis may be useful, as was the case in this study, where KMO = 0.76. Bartlett's test of sphericity indicates whether a correlation matrix is an identity matrix, which would indicate that variables are unrelated. The significance level of 0 in this study (less than 0.05) indicated that there were significant relationships among the variables.

Hierarchical agglomerative cluster analysis (CA) was performed on the normalized data set using Ward's method with squared Euclidean distances as a measure of similarity. Factor analysis (FA) was conducted after principal component analysis (PCA). PCA of the normalized variables (data set) was performed to extract significant principal components (PCs) and to further reduce the contribution of variables with minor significance; these PCs were then subjected to varimax rotation (raw) to generate varifactors (VFs).

3. Results and discussion

3.1. Heavy metals in sediments of the Tigris River

The basic statistics for all of the metal parameters measured during the sampling period of one year at seven different sites are summarized in Table 2.

During the study period, all heavy metals showed significant spatial variations (ANOVA, $p < 0.05$). The ranges of metals

Table 3
Heavy metal concentrations reported for previous studies conducted in the Tigris River.

Sites	Metal concentrations (mg/kg)							References
	Cd	Co	Cu	Mn	Ni	Pb	Zn	
Maden	–	–	3433	–	–	–	891	[27]
Eğil	–	–	1213	–	–	–	456	[27]
Diyarbakır	–	–	904	–	–	–	405	[27]
Bismil	–	–	991	–	–	–	716	[27]
Maden	–	503	3433	–	403	102	891	[10]
Eğil	–	118	1213	–	305	83	456	[10]
Diyarbakır	–	21	904	–	50	31	405	[10]
Bismil	–	4	991	–	41	24	716	[10]
Diyarbakır	–	32.01	728.96	–	66.35	–	369.14	[28]
Diyarbakır	nd	43.13	137	622.9	124.5	nd	30	[11]
Bismil	nd	32.4	92.5	497.7	99.51	nd	42.7	[11]

in sediments were: 2.0–18.0 mg/kg for As, 0.7–4.9 mg/kg for Cd, 5.4–389.8 mg/kg for Co, 28.4–163.4 mg/kg for Cr, 11.2–5075.6 mg/kg for Cu, 282.2–1657.0 mg/kg for Mn, 74.0–288.0 mg/kg for Ni, 62.3–566.6 mg/kg for Pb and 60.1–2396.6 mg/kg for Zn. The highest concentrations of heavy metals were found at site-1 (Maden) due to metallic wastewater discharges from copper mine plant in Maden Township. Site-3 (Diyarbakır) which receives untreated domestic and industrial wastewaters from Diyarbakır province, site-4 (Bismil) which receives partially treated domestic wastewater from Diyarbakır wastewater treatment plant, untreated domestic wastewater from Bismil Township and agricultural runoff, and site-7 (Cizre) which receives untreated domestic wastewater from Cizre Township had also high metal concentrations. The lowest mean values of As, Ni and Zn were found at site-6 (Hasankeyf), while the lowest mean values of Cd, Co, Cr, Cu, Fe, Mn and Pb were calculated at site-5 (Batman). In this study, total metal concentrations followed the order of site-1 > site-7 > site-4 > site-3 > site > 2 > site > 6 > site-5. During the study, all metals studied did not show significant temporal differences (ANOVA, $p > 0.05$).

In this study, heavy metal concentrations in assessed sediment samples from the Tigris River were compared with previous studies (Table 3). The mean values of Co, Cu, Ni and Zn except Pb at site-1 (Maden) were lower when compared with an earlier study conducted in 1990 [10] due to reduction of the activity of the copper mine plant. The mean values of Co, Cu, Ni and Zn at site-2 (Eğil) were found significantly lower than those at the same site reported for the Tigris River owing to the construction of two dams on the river over the last 10 years: Kralkızı and Dicle. It is well known that concentrations of suspended solids and heavy metals in the reservoir water will be decreased significantly due to sediment deposition. The water leaving the reservoir can be clearer, and this could affect the river downstream of the dam. However, the mean values of Co, Ni and Pb except Cu and Zn at site-3 (Diyarbakır) and site-4 (Bismil) were higher than those reported by Gümgüm et al. [10]. In this study, the mean values of Cd, Cu, Mn, Ni, Pb and Zn except Co at site-3 were found higher, while the mean values of Cd, Mn, Ni, Pb and Zn except Co and Cu at site-4 were higher when compared with a previous study conducted in 2000 [11]. The increase in some metal concentrations at site-3 (Diyarbakır) and site-4 (Bismil) may be due to increased anthropogenic activities in the Diyarbakır province which has the largest urban settlement in Tigris Basin. It may have contributed large amounts of heavy metals into the river.

Total heavy metal concentrations in the sediment samples from the Tigris River followed the order: Fe > Mn > Cu > Pb > Zn > Ni > Cr > Co > As > Cd. The results were not compatible with previous studies [10,11] conducted in the Tigris River. Karadede-Akin and Ünlü [11] found that Fe was the most abundant in the sediment, followed by Mn, Cu and Co, and the least was Zn, while Cd and Pb were not recorded. Gümgüm et al. [10] reported that the accumulation order of heavy metals in the sediment samples was Cu > Zn > Ni > Co > Pb.

Comparison of metal contamination data of the Tigris River with the published data of other rivers (Table 4) reveals that the sediments of site-1 are severely polluted with heavy metals, while sediments of the rest of sites are slightly polluted. The extent of metal pollution in the Tigris River was not much more serious than that in the Tinto River, Danube River and Rimac River, and much worse than the Yeşilırmak River, River Po, Luan River, Nile River and Axios River (Table 4).

3.2. Indices of sediment contamination

The results of contamination factors (CFs) and pollution load index (PLI) are presented in Table 5. The highest CF values for all metals studied were found at site-1 (Maden), which receives

Table 4
Heavy metal concentrations in sediment samples from the Tigris River and other selected rivers from the literature.

Locations	Metal concentrations (mg/kg)									References
	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	
Tigris River (site-1), Turkey	5–18	1.4–4.9	55.6–389.8	76.4–151.7	673.1–5075.6	822.0–1657	151.9–288	144.4–566.6	191.3–2396	This study
Tigris River (the rest of sites), Turkey	2–8.5	0.7–3	5.4–39.7	28.4–163.4	11.2–297.2	282.2–1228	74–244.7	62.3–392.4	60.1–247	This study
Shing Mun River, Hong Kong	–	22–47	–	13–66	207–1660	–	–	126–345	32–2200	[3]
Tisza River, Serbia				7–23	32–162	490–2316	17–55	11–123	54–567	[16]
Yeşilırmak River, Turkey	–	0.12–0.55	–	–	13.1–38.7	221–446	15.4–79.2	3.3–17.3	24.7–45.5	[29]
River Po, Italy	–	1.08–3.7	–	–	31.7–90.1	–	52.3–161	32–98.5	178–645	[30]
Gomti River, India	–	0.09–17.83	–	2.4–88.7	3.6–245.33	65.73–834.7	4.75–76.08	4.86–156.2	8.47–343.47	[5]
Almendares River, Cuba	–	1.0–4.3	1.5–23.4	84.4–23.4	71.6–420.8	–	–	39.3–189	86.1–708.8	[31]
Danube River, Europa	8.1–388	1.1–32.9	–	26.5–556.5	31.1–8088	442–1655	17.5–173.3	14.7–541.8	78–2010	[32]
Axios River, Greece	1–40	1–11	–	39–180	14–93	–	19–188	11–140	42–271	[33]
Tinto River, Spain	–	0.13–12	6.8–42	11–151	22–2700	–	1.6–36	17–13400	68–5280	[34]
Nile River, Egypt	–	–	–	8–274	10–81	75–2810	2–112	3.5–23.2	11–221	[35]
South Platte River, USA	2.8–31	0.1–22	–	33–71	18–480	410–6700	–	19–270	82–3700	[36]
Tees River, UK	–	0.95–5.95	–	–	19.5–76.9	936–5240	–	522–6880	404–1920	[37]
Rimac River, Peru	21–1543	0.5–31	13–24	24–71	51–796	750–14000	9–23	62–2281	160–8076	[38]
Sea Scheldt River, Belgium		0.5–24.8		29–240.5	9–1739		6–78	11–681	54–4380	[39]
Luan River, China	2.08–12.90	0.03–0.37	–	28.7–152.73	6.47–178.61	–	–	8.65–38.29	21.09–25.66	[40]

Table 5
Metal contamination factors (CFs) and pollution load indices (PLIs) for sediments of all sites studied in the Tigris River.

Sites	Contamination factors (CFs)										PLI
	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
Site-1	3.42	2.86	8.66	1.86	34.68	1.11	2.37	2.93	5.79	6.80	4.19
Site-2	1.27	2.14	1.43	1.19	2.09	0.99	1.21	1.78	3.76	2.12	1.67
Site-3	1.85	2.14	1.68	1.80	3.39	1.02	1.28	2.19	3.68	2.28	1.99
Site-4	1.35	1.90	0.88	1.31	1.32	1.08	1.23	2.02	4.03	1.87	1.55
Site-5	1.38	1.43	0.50	0.79	0.43	0.88	0.81	1.27	2.41	1.66	1.02
Site-6	1.12	1.90	0.56	0.85	0.51	0.98	0.94	1.23	3.26	1.54	1.11
Site-7	2.08	2.62	0.78	1.46	0.67	1.10	1.35	2.35	4.37	1.95	1.62
Mean	1.78	2.14	2.07	1.32	6.16	1.02	1.31	1.97	3.90	2.60	1.88
Min	1.12	1.43	0.50	0.79	0.43	0.88	0.81	1.23	2.41	1.54	1.02
Max	3.42	2.86	8.66	1.86	34.68	1.11	2.37	2.93	5.79	6.80	4.19

a huge amount of metallic discharge from copper mine plant in Maden Township. The CF values for Co, Cu and Zn were >6 in sediments of site-1, which denotes a "very high contamination" by these metals. The CF values for As and Pb in sediments of site-1 showed a "considerable contamination", while the CF values for Cd, Cr, Fe, Mn and Ni indicated a "moderate contamination". The CF values for metals studied except Pb at other sites showed "moderate contamination". In this study, Cu had the highest and lowest CF values among the ten metals studied. However, Pb had the highest CF values among the ten metals studied at all sites except site-1. Site-3 (Diyarbakır) which receives municipial and industrial wastewater discharges from Diyarbakır and site-7 (Cizre) which receives municipial wastewater discharges from Cizre showed high CF values. Total contamination factors followed the order of site-1 > site-3 > site-7 > site-2 > site-4 > site-6 > site-5.

The pollution load index (PLI) ranged from 1.02 to 4.19 (Table 5). According to the mean PLI value (1.88), the Tigris River was moderately polluted. Site-1 had the highest PLI (4.19) within the study area, indicating that the sediments of site-1 were strongly polluted by investigated heavy metals. Other sites where PLI was between 1 and 2 must be classified as moderately polluted. The PLI followed the order of site-1 > site-3 > site-7 > site-2 > site-4 > site-6 > site-5.

Table 6 presents *Igeo* and EF values of the metals studied. The *Igeo* values of As at sites 2, 4, 5 and 6, Cd at site-5, Co at sites 2, 4, 5, 6 and 7, Cr and Mn at all sites except site-1, Cu at sites 4, 5, 6 and 7, Fe at all sites, and Ni at sites 5 and 6 were less than zero, suggesting that these sites were not polluted by these metals. The *Igeo* values for Cd, Cr, Mn and Ni were under 1 in the sediments of all sites which usually had "unpolluted to moderately polluted" class. Among ten metals studied, Cu, Co, Zn and Pb had the highest *Igeo* values, respectively. The highest *Igeo* values of metals studied were found in the sediments of site-1. The *Igeo* class of Cu was "extremely polluted" for sediments of site-1. The *Igeo* class of As and Pb were "moderately polluted" for sediments of site-1, while the *Igeo* class of Co and Zn were "moderately to heavily polluted". Total *Igeo* values followed the order of site-1 > site-3 > site-2 > site-7 > site-4 > site-6 > site-5.

According to Zhang and Liu [25], EF values between 0.05 and 1.5 indicate that the metal is entirely from crustal materials or natural processes, whereas EF values higher than 1.5 suggest that the sources are more likely to be anthropogenic. In this study, the mean EF values for all metals studied except Cr and Mn were >1.5 in the sediments of the Tigris River, suggesting anthropogenic impact on the metal levels in the river. The highest EF values were found at site-1 (Maden) due to metallic wastewater discharges from the copper mine plant in Maden Township. The EF value for Cu in the sediments of site-1 was 31.34, showing "very severe enrichment", while the EF values for Co, Pb and Zn were between 5 and 10, indicating "moderately severe enrichment". However, the EF values for As, Cd, Cr, Mn and Ni at site-1 indicated "minor enrichment". Cu had the highest and lowest EF values among the ten metals studied. Co had the second highest EF value. Pb at all sites except site-1 had the highest EF values among the ten metals studied. The EF values for metals studied in sediments of other sites showed "minor to moderate enrichment". Total EF values followed the order of site-1 > site-3 > site-2 > site-7 > site-4 > site-6 > site-5.

3.3. Application of sediment quality guidelines

It is important to determine whether the concentrations of heavy metals in sediments pose a threat to aquatic life. In this study, heavy metal concentrations in assessed sediment samples were compared with consensus-based TEC and PEC values (Table 7). As, Cu and Zn were lower than the TEC in 96.4%, 28.6% and 16.7% of samples, respectively. Cd, Cr, Cu and Zn were between the TEC and PEC in 95.2%, 71.4%, 46.4% and 79.7% of samples, respectively. Ni and Pb exceeded the PEC in 100% and 83.3% of samples, respectively. Cr exceeded the PEC in 9 of samples at site-1, 6 of samples at site-3, 1 of samples at site-4 and 3 of samples at site-7. Cu exceeded the PEC

Table 6
Geoaccumulation indices (*Igeo*) and enrichment factors (EF) of heavy metals for sediments of all sites studied in the Tigris River.

Sites	As		Cd		Co		Cr		Cu		Fe		Mn		Ni		Pb		Zn	
	Igeo	EF	*Igeo*	EF	*Igeo*	EF	*Igeo*	EF	*Igeo*	EF	*Igeo*	EF	*Igeo*	EF	*Igeo*	EF	*Igeo*	EF	*Igeo*	EF
Site-1	1.19	3.09	0.93	2.58	2.53	7.83	0.31	1.68	4.53	31.34	−0.44	1	0.66	2.14	0.97	2.65	1.95	5.23	2.18	6.15
Site-2	−0.24	1.29	0.51	2.17	−0.07	1.45	−0.33	1.21	0.48	2.12	−0.60	1	−0.31	1.23	0.25	1.81	1.32	3.81	0.50	2.15
Site-3	0.30	1.81	0.51	2.10	0.17	1.65	0.27	1.77	1.18	3.32	−0.56	1	−0.23	1.25	0.55	2.15	1.30	3.61	0.61	2.24
Site-4	−0.16	1.25	0.34	1.77	−0.76	0.82	−0.20	1.21	−0.18	1.22	−0.48	1	−0.28	1.14	0.43	1.87	1.43	3.74	0.32	1.74
Site-5	−0.12	1.57	−0.07	1.62	−1.58	0.57	−0.93	0.90	−1.80	0.49	−0.77	1	−0.89	0.92	−0.24	1.44	0.68	2.74	0.15	1.89
Site-6	−0.43	1.14	0.34	1.95	−1.43	0.57	−0.81	0.87	−1.56	0.52	−0.62	1	−0.67	0.96	−0.29	1.26	1.12	3.34	0.04	1.58
Site-7	0.47	1.90	0.80	2.39	−0.94	0.72	−0.04	1.34	−1.17	0.61	−0.45	1	−0.15	1.23	0.65	2.14	1.54	3.99	0.38	1.78
Mean	0.14	1.72	0.48	2.08	−0.30	1.94	−0.25	1.28	0.21	5.66	−0.56	1	−0.27	1.27	0.33	1.90	1.33	3.78	0.60	2.50
Min	−0.43	1.14	−0.07	1.62	−1.58	0.57	−0.93	0.87	−1.80	0.49	−0.77	1	−0.89	0.92	−0.29	1.26	0.68	2.74	0.04	1.58
Max	1.19	3.09	0.93	2.58	2.53	7.83	0.31	1.77	4.53	31.34	−0.44	1	0.66	2.14	0.97	2.65	1.95	5.23	2.18	6.15

Table 7
Comparison between sediment quality guidelines (SQGs) with heavy metal concentrations (mg/kg) of all sites studied in the Tigris River.

		As	Cd	Cr	Cu	Ni	Pb	Zn
SQGs	TEC	9.79	0.99	43.4	31.6	22.7	35.8	121
	PEC	33	4.98	111	149	48.6	128	459
Measured values in this study	Minimum	2.0	0.7	28.4	11.2	74.0	62.3	60.1
	Maximum	18.0	4.9	163.4	5075.6	288.0	566.6	2396.6
	Average	4.6	1.8	84.8	344.6	145.6	265.3	203.1
Site-1	Samples < TEC	9	0	0	0	0	0	0
	Samples between TEC and PEC	3	12	3	0	0	0	9
	Samples > PEC	0	0	9	12	12	12	3
Site-2	Samples < TEC	12	0	0	0	0	0	0
	Samples between TEC and PEC	0	12	12	12	0	3	12
	Samples > PEC	0	0	0	0	12	9	0
Site-3	Samples < TEC	12	0	0	0	0	0	0
	Samples between TEC and PEC	0	12	6	3	0	2	12
	Samples > PEC	0	0	6	9	12	10	0
Site-4	Samples < TEC	12	0	0	0	0	0	3
	Samples between TEC and PEC	0	12	11	12	0	0	9
	Samples > PEC	0	0	1	0	12	12	0
Site-5	Samples < TEC	12	2	2	11	0	0	5
	Samples between TEC and PEC	0	10	10	1	0	6	7
	Samples > PEC	0	0	0	0	12	6	0
Site-6	Samples < TEC	12	2	3	9	0	0	6
	Samples between TEC and PEC	0	10	9	3	0	2	6
	Samples > PEC	0	0	0	0	12	10	0
Site-7	Samples < TEC	12	0	0	4	0	0	0
	Samples between TEC and PEC	0	12	9	8	0	1	12
	Samples > PEC	0	0	3	0	12	11	0
Total	Samples < TEC	81 (96.4%)	4 (4.8%)	5 (6%)	24 (28.6%)	0 (0%)	0 (0%)	14 (16.7%)
	Samples between TEC and PEC	3 (3.6%)	80 (95.2%)	60 (71.4%)	39 (46.4%)	0 (0%)	14 (16.7%)	67 (79.7%)
	Samples > PEC	0 (0%)	0 (0%)	19 (22.6%)	21 (25%)	84 (100%)	70 (83.3%)	3 (3.6%)

in all of samples at site-1 and 9 of samples at site-3. Ni exceeded the PEC in all of samples. Pb exceeded the PEC in all of samples at site-1 and site-4, 9 of samples at site-2, 10 of samples at site-3 and site-6, 6 of samples at site-5 and 11 of samples at site-7. Zn exceeded the PEC in 3 of samples at site-1. These results indicate that the concentrations of Cr, Cu, Ni and Pb are likely to result in harmful effects on sediment-dwelling organisms which are expected to occur frequently.

An index of toxicity risk, PEC quotients, was also evaluated in this study. PEC quotients were calculated using the methods of MacDonald et al. [23]. Sediment samples are predicted to be not toxic if PEC quotients are <0.5. In contrast, sediment samples are predicted to be toxic when PEC quotients exceed 1.5 [23]. In this study, PEC quotients varied from 0.09 to 13.03 (Table 8). The lowest value of PEC quotients was calculated at site-6, while the highest value was calculated for the sediments of site-1. The total PEC quotients followed the order of site-1 > site-3 > site-7 > site-4 > site-2 > site-6 > site-5. PEC quotients of Cu at site-1, Ni and Pb at all sites exceeded 1.5, suggesting a potential toxicity of these metals in sediments of the river. Conversely, the toxicity risks were much lower for As and Cd at all sites, Cr and Cu at sites 5 and 6 and Zn at all sites except site-1, with PEC quotients <0.5.

3.4. Multivariate statistical analyses

3.4.1. Principal component analysis/factor analysis

PCA/FA was performed on the normalized data to compare the compositional pattern between the sediment samples and to identify the factors influencing each one. PCA of the entire data set (Table 2) revealed three PCs with eigenvalues >1 that explained about 83.9% of the total variance in the sediment quality data set. The first PC accounting for 54.8% of the total variance was correlated (loading >0.70) with Cd, Co, Cu, Mn and Ni. The second PC accounting for 17.4% of total variance was correlated with Fe. Whereas the third PC accounted for the total variance of 11.7%, it correlated (loading >0.70) with none of the metal parameters.

Three VFs were obtained through FA performed on the PCs. The corresponding VFs, variable loadings and the explained variance are presented in Table 9. The loading plots of the first two VFs are presented in Fig. 2. VF coefficients having a correlation greater than 0.70 were considered significant (strong).

VF1, which explained 56.5% of the total variance, had strong positive loadings (>0.70) on Cd, Co, Cu and Mn, and a moderate positive loading on Ni. This VF represents anthropogenic sources. In Maden Township (upstream), there is a copper mine plant that discharges

Table 8
PEC quotients of heavy metals for sediments of all sites studied in the Tigris River.

	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6	Site-7
As	0.27	0.10	0.14	0.11	0.11	0.09	0.16
Cd	0.48	0.36	0.37	0.33	0.23	0.31	0.44
Cr	1.07	0.69	1.04	0.76	0.45	0.49	0.84
Cu	13.03	0.78	1.27	0.50	0.16	0.19	0.25
Ni	4.46	2.72	3.34	3.08	1.93	1.87	3.57
Pb	3.08	2.00	1.96	2.14	1.28	1.73	2.32
Zn	1.16	0.36	0.39	0.32	0.28	0.26	0.33
Mean	3.36	1.00	1.22	1.03	0.63	0.71	1.13
Min	0.27	0.10	0.14	0.11	0.11	0.09	0.16
Max	13.03	2.72	3.34	3.08	1.93	1.87	3.57

Table 9
Loadings of experimental variables (10) on significant principal components for the Tigris River data set[*].

	VF1	VF2	VF3
As	0.458	−0.096	**0.792**
Cd	**0.726**	0.263	0.165
Co	**0.938**	0.102	0.234
Cr	0.031	0.258	**0.911**
Cu	**0.945**	0.141	0.130
Fe	−0.016	**0.931**	0.090
Mn	**0.732**	0.304	*0.533*
Ni	*0.507*	0.414	*0.669*
Pb	0.342	**0.908**	0.143
Zn	0.561	−0.198	*0.547*
Eigenvalue	5.655	1.707	1.158
% Total variance	56.546	17.065	11.584
Cumulative % variance	56.546	73.611	85.196

[*] Bold and italic values indicate strong and moderate loadings, respectively.

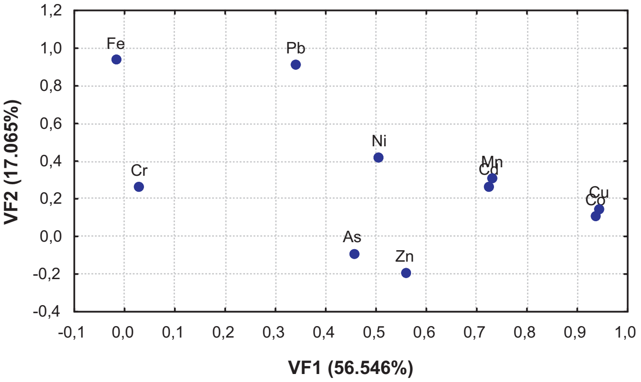

Fig. 2. Loading plots of the first two VFs obtained for the data set.

metallic wastewaters containing high levels of Co, Cu and Ni into the Tigris River [10,26]. VF2, which accounted for 17.0% of the total variance, had strong positive loadings on Fe and Pb. This factor represents lithogenic sources. VF3 (11.5% of total variance) had strong positive loadings on As and Cr, and moderate positive loadings on Mn, Ni and Zn. This VF represents anthropogenic sources. The elements are derived from municipal and industrial wastewaters, and metallic wastewaters of the copper mine plant.

3.4.2. Cluster analysis

Cluster analysis (CA) was applied to the river sediment quality data set to group the similar sampling sites (spatial variability). Spatial CA rendered a dendrogram (Fig. 3) where all seven sampling sites on the river were grouped into three statistically significant clusters at $(D_{\text{link}}/D_{\text{max}}) \times 100 < 40$. Cluster 1 (Maden) site was located in a high pollution region, which receives metallic wastewater discharges from copper mine plant. Cluster 2 (Eğil, Diyarbakır, Bismil, Hasankeyf and Cizre) sites were in a moderate pollution region. Cluster 3 (Batman) site was in a region of relatively low pollution.

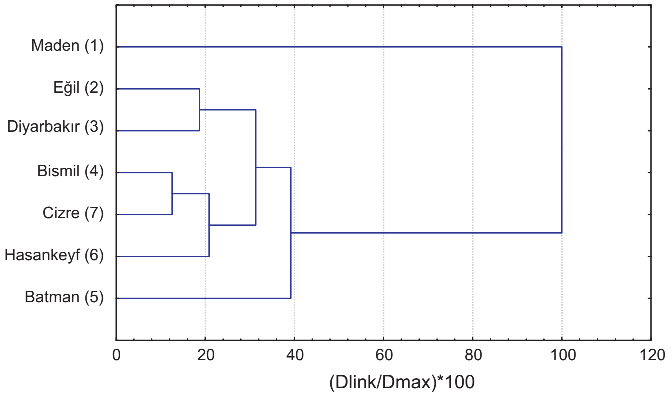

Fig. 3. Dendrogram showing clustering of sampling sites on the Tigris River.

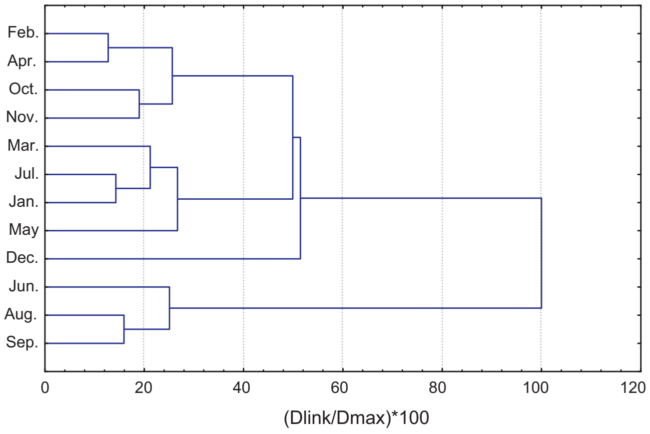

Fig. 4. Dendrogram showing clustering of sampling periods.

Temporal CA generated a dendrogram (Fig. 4) that grouped the 12 months into two clusters at $(D_{\text{link}}/D_{\text{max}}) \times 100 < 60$, and the difference between the clusters was significant. Cluster 1 included February, April, October, November, March, July, January, May and December roughly corresponding to the wet season in Turkey (October to April). In this study, about 82% annual total precipitation was concentrated in the time period from October to April. Cluster 2 included the remaining months (June, August and September), closely corresponding to the dry season (May to September). However, if 12 months had been empirically divided into spring (March to May), summer (June to August), autumn (September to November) and winter (December to February), or into dry/wet seasons, a mistake in grouping could have been made. In fact, Fig. 4 shows that the temporal patterns in water quality were not purely consistent with the four seasons or the dry/wet season.

Similarly, CA was performed to group the analyzed parameters. CA rendered a dendrogram (Fig. 5) where all ten metal parameters were grouped into three statistically significant clusters at $(D_{\text{link}}/D_{\text{max}}) \times 100 < 85$. Cluster 1 includes As and Zn which were identified as contaminants derived from anthropogenic sources (wastewater discharges of copper mine plant). Cluster 2 contains Cd, Mn, Ni, Cr, Co and Cu derived from anthropogenic sources

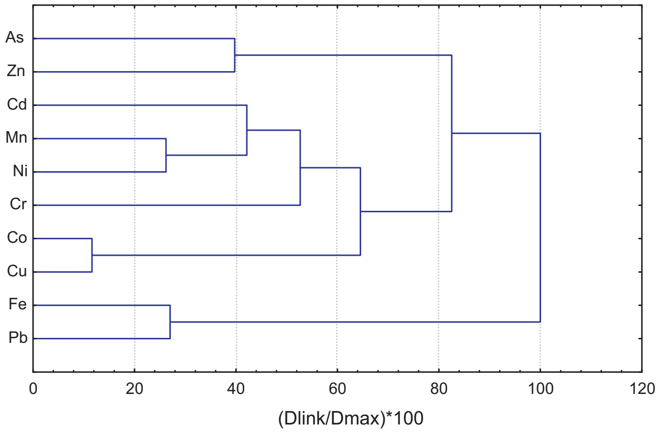

Fig. 5. Dendrogram showing clustering of the analyzed parameters.

Table 10
Pearson correlation matrix of heavy metals in the Tigris River.

	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
As	1									
Cd	**0.277**[b]	1								
Co	**0.404**[a]	**0.660**[a]	1							
Cr	**0.583**[a]	**0.331**[a]	**0.317**[a]	1						
Cu	**0.383**[a]	**0.682**[a]	**0.973**[a]	**0.259**[b]	1					
Fe	−0.013	0.214	**0.219**[b]	**0.267**[b]	0.213	1				
Mn	**0.575**[a]	**0.714**[a]	**0.835**[a]	**0.585**[a]	**0.796**[a]	**0.363**[a]	1			
Ni	**0.473**[a]	**0.699**[a]	**0.717**[a]	**0.732**[a]	**0.673**[a]	**0.425**[a]	**0.862**[a]	1		
Pb	0.120	**0.466**[a]	**0.488**[a]	**0.398**[a]	**0.502**[a]	**0.853**[a]	**0.608**[a]	**0.629**[a]	1	
Zn	**0.681**[a]	**0.260**[b]	**0.393**[a]	**0.316**[a]	**0.389**[a]	−0.068	**0.528**[a]	**0.342**[a]	0.088	1

Bold values represent correlation with significance.

[a] Significance at the 0.01 probability level (2-tailed).

[b] Significance at the 0.05 probability level (2-tailed).

(wastewater discharges of copper mine plant, and industrial and domestic wastewaters). Cluster 3, which contains Fe and Pb, are derived from lithogenic sources.

3.4.3. Correlation matrix

In order to establish relationships among metals and determine the common source of metals in the Tigris River, a correlation matrix was calculated for heavy metals in the sedimens. According to the values of Pearson correlation coefficients (Table 10), a significant positive correlation existed among the metals studied. In this study, Fe did not show significant correlation with As, Cd, Cu and Zn, and Pb did not show significant correlation with Zn. Fe was significantly correlated with Pb ($r = 0.853$, $p < 0.01$), indicating that the elements were derived from lithogenic sources. The significantly positive correlation of As ($r = 0.383$, $p < 0.01$), Cd ($r = 0.682$, $p < 0.01$), Co ($r = 0.973$, $p < 0.01$), Cr ($r = 0.259$, $p < 0.01$), Mn ($r = 0.796$, $p < 0.01$), Ni ($r = 0.673$, $p < 0.01$), and Zn ($r = 0.389$, $p < 0.01$) with Cu showed that the elements were derived from wastewater discharges of copper mine plant and also moving together.

4. Conclusion

Different useful tools, methods, guidelines and indices have been employed for evaluation of sediment pollution in the Tigris River, Turkey. The highest concentrations of heavy metals were found at site-1 (Maden) due to metallic wastewater discharges from copper mine plant in Maden Township. Site-3 (Diyarbakır), site-4 (Bismil) and site-7 (Cizre) had also high metal concentrations due to domestic and industrial wastewaters. Total heavy metal concentrations in the sediment samples from the Tigris River followed the order: Fe > Mn > Cu > Pb > Zn > Ni > Cr > Co > As > Cd. The highest values of contamination factor (CF), pollution load index (PLI), geoaccumulation index (*Igeo*) and enrichment factor (EF) for all metals studied were found at site-1 (Maden), which receives a huge amount of metallic discharge from copper mine plant in Maden Township. Heavy metal concentrations in assessed sediment samples were compared with consensus-based TEC and PEC values. The results have indicated that the concentrations of Cr, Cu, Ni and Pb are likely to result in harmful effects on sediment-dwelling organisms which are expected to occur frequently. Multivariate analysis (PCA/FA, CA) and correlation matrix were used in this study. The PCA/FA applied on the investigated heavy metals identified three varifactors (VFs). VF1 and VF3, which were loaded with As, Cd, Co, Cr, Cu, Mn, Ni and Zn, were related to the anthropogenic sources. The CA classified all the sampling sites into three main groups of spatial similarities. A significant positive correlation is observed among As, Cd, Co, Cr, Cu, Mn, Ni and Zn, indicating that these metals were derived from similar sources and also moving together.

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