

Ecological and health risk assessment of potential toxic elements in surface sediments: Gediz River, Türkiye

Saniye Turk Culha

saniye.turk.culha@ikcu.edu.tr

Izmir Kâtip Çelebi University

Şeyda Fikirdeşici Ergen

Ankara University

Haşim Sömek


Izmir Kâtip Çelebi University

Research Article

Keywords: Potentially toxic elements, Ecological risk assessment, Sediment pollution indices, Gediz River

Posted Date: February 26th, 2024

DOI: <https://doi.org/10.21203/rs.3.rs-3972214/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Additional Declarations: No competing interests reported.

Abstract

The Gediz River, which flows through many cities and connects to the Aegean Sea, has an important economic potential for the Aegean Region. Given this importance, a detailed assessment of potential toxic elements (PTEs) in the river sediment is required. 18 PTEs (Co, Cr, Cu, Mn, Ni, Fe, Al, Se, Mo, Sr, Mg, Ag, Pb, Zn, As, Hg and Cd) were collected from 13 stations along the Gediz River covering three basins to determine the level of pollution and ecological risk. For pollution assessment in sediments, contamination factor (CF), pollution load index (PLI), geographical accumulation index (I_{geo}), enrichment factor (EF) were analyzed. Potential impacts of PTEs in the sediment matrix of the Gediz River on human health (Potential Ecological risk factor (E_{ir}), Potential ecological risk index (PERI), hazard quotient (HQ), hazard index (HI), lifetime cancer risk (LCR) were investigated in detail. The mean concentrations of the majority of the PTEs exceeded the corresponding background values, indicating that the highest pollution load was in the downstream basin. Based on the PTEs spatial distributions and pollution indices, the Gediz River was found to have high accumulation of As, Cu, Cr, Ni and Zn in the sediments. In addition, HQ_{ing} and HI values were greater than 1 for As, Co, Cr, Mn, Ni and Pb in all three basins. It was determined that As and Cr had a high effect in terms of LCR value. Correlation analysis and principal component analysis were also applied to explain the main sources of PTEs formation.

Introduction

The rivers and their basins have been the settlement areas of ancient civilizations in the past and modern urbanization in the recent ages due to the presence of productive agricultural lands along the flow beds and the water supplier of these lands, as well as their deltas containing elevated levels of biological richness. As a result of these phenomena, they have always been under the negative pressure of anthropogenic activities (such as industrial, agricultural, urbanization, mining and others). Point and non-point pollutants from these human activities threaten the ecosystem balance of lotic or lentic surface waters and their biological life (Maguire et al., 2019; Moiseenko & Sharov, 2019; Li et al., 2022). River sediment, which is the accumulation medium of several pollutants such as microplastics, toxic chemicals, and organic or inorganic loads, is the focus of researchers as a helpful indicator in environmental monitoring investigations (Scherer et al., 2020; Köck-Schulmeyer et al., 2021). The most remarkable of these pollutants are potential toxic elements (PTEs), called Heavy Metals, with well-known directional or non-directional negative effects on the ecosystem and human health (Emgwa et al., 2019; Sonone et al., 2020).

Gediz River, which is approximately 401 km long, passes through the lands of four different cities of Türkiye (Kütahya, Uşak, Manisa and İzmir) and flows into the Aegean Sea. The river's source is Murat Mountain (Kütahya Province), which has an altitude of 1400 m. In the upper basin, the Selendi Stream, Deliniş Stream, the Demirci Stream and in the middle basin, the Alaşehir Stream, Gürdük Stream, and Nif Stream join the main branch of the river. The Gediz River provides Salihli and Menemen Plains' irrigation water in the river basin. Adala Regulator (Salihli), Ahmetli Regulator and Emiralem Regulator (Menemen) were built on the main branch for irrigation and flood control. In the river basin, there are also stagnant water structures such as Gölmarmara (almost dry), Gördes Reservoir, Demirköprü Reservoir, and the Avşar Reservoir, which are connected to the river. In the region where it flows into the sea (Menemen-İZMİR), the Gediz River forms a delta with an area of 40,000 ha, 40% of which is wetland and 60% of which is agricultural land (Onmuş et al., 2009). In addition, this delta is home to a wildlife area that is an indispensable shelter for many birds and has international protection status under the Ramsar Convention.

The Gediz River is influenced by domestic, industrial, and agricultural pollution from three major cities, and this pollution load carries to the Gulf of İzmir. Numerous studies have been carried out on the environmental interactions of pollutants in the Gediz River basin, where urbanization, agricultural and industrial activities are forceful, and basin protection action plans have been generated by the relevant authorities (Anonymous, 2013; Şentürk & Yıldız, 2015). According to our literature search, a few investigations on the occurrence of PTEs in surface sediments of Gediz River have been carried out in the past. On the other hand, these studies were limited to the lower basin areas of the river (Kindler & Sevim, 1990; Akçay et al., 2003; Parlak et al., 2006; Kucuksezgin et al., 2008; Şentürk & Yıldız, 2015; Eroğlu & Esenpınar, 2019) or only local areas such as Manisa City province (Minareci et al., 2009). The objectives of the current study were: (1) to determine the distribution and concentration of 18 PTEs in surface sediments sampled from 13 stations located from upper basins to lower basins of the Gediz River; (2) to find out potential sources of PTEs by using multi-variable statistical techniques; (3) to assess comprehensively the ecological and health risks of PTEs. In this context, the level of toxicity and risk of contamination caused by the PTEs in surface sediments of the study area was evaluated based on probable effect level (PEL), threshold effect level (TEL), effects range low (ERL), effects range median (ERM), reported using the Sediment Quality Guidelines (SQGs) degree of contamination (Cd), modified degree of contamination (mCd), contamination factor (CF) and enrichment factor (EF), Geoaccumulation index (I_{geo}), toxic unit (TU), Pollution Load Index (PLI), mean ERM quotients (m-ERM-q), and mean PEL quotients (m-PEL-q). Moreover, indices generated by the USEPA (2004) were used to estimate the probability of carcinogenic risks to public health caused by PTEs.

Material and methods

Study Area

The Gediz River originates from the slopes of the Murat Mountain 26 km east of the Gediz district of Kütahya, and its major tributaries are Nif, Murat, Kum, Medar, Selendi, Alaşehir, Derbent, Gördes, Eliniş and Demrek streams. The Gediz River, which is further enlarged by the addition of streams such as Kurşunlu, Tabak, Sart, Gencer, Yeniköy, Karaçalı, Irlamaz and Keçili, flows into the Aegean Sea near Çamaltı Salt Pan, south of Foça, after crossing Salihli, Manisa and Menemen plains (Anonymous, 1998).

Approximately 80% of the water demand in the Gediz Basin is for agricultural irrigation. Manisa and Kemalpaşa industrial zones are the most important water users in the basin and discharge their wastewater into the Gediz River. Near Menemen, there are mainly leather factories. The Gediz Basin provides water to the municipalities within its borders and drinking water to the city of İzmir outside the basin. On the other hand, in the basin where ceramics, leather, food and metal industries are located, enterprises utilize groundwater by obtaining permission from State Hydraulic Works. The western part of the lower basin, defined as the Lower Gediz Lower basin, is the part where industrialization is the most intense. The food sector takes the first place in the sectoral distribution of the

industry, and agricultural products grown in the fertile lands of the basin are processed. The food sector is followed by textile and leather manufacturing. Almost all of the wastewater discharged to the receiving environment in the Gediz Basin is discharged to the rivers within the basin and reaches the Aegean Sea by connecting to the main Gediz tributary through tributaries (Aydin & Kucuksezgin, 2012; Anonymous, 2013).

Sediment Sampling

Surface sediment samples were collected in the summer of 2023. 13 stations on the Gediz River Basin were chosen following initial field research, considering the primary basin components and sources of pollution. According to this, four of the stations were located upstream, five of the stations were located on the midstream, and four of the stations were located Downstream in Gediz River (Fig. 1). The river sediment was sampled using an Ekman-Birge grab with a 15x15 cm mouth opening. To avoid metallic contamination, samples were taken from the upper 10 cm of the sediment surface with a polyethylene spoon and stored in 1 Liter sterile glass bottles at 4°C until chemical analysis. Location characteristics (Coordinates, explanations, and the locations of selected stations) is given in Table 1.

Analytical procedure

It was aimed to determine the possible pollution loads and ecotoxicological risks of 18 potentially toxic elements [magnesium (Mg), aluminium (Al), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), strontium (Sr), mercury (Hg), cadmium (Cd), silver (Ag), gold (Au), molybdenum (Mo) and lead (Pb)] in the river in sediment samples taken from 3 basins (13 stations) covering the entire Gediz River in July 2023. Elemental analysis inductively coupled plasma mass spectrometry (ICP-MS) using Bureau Veritas Mineral Laboratoires Canada (ACME LAB.) by applying the AQ270 method.

The percentage in each station's sediment of burnable organic matter (%BOM) (Buchanan, 1984) and the percentage of organic carbon amounts were calculated (%TOC) according to the Walkley-Black method (Gaudette et al., 1974). For calibration of the instrument, standards for each metal were generated from analytically pure solutions and all analytical data were validated using Certified Reference Material OREAS 234 and OREAS 262. Recoveries of PTEs in the CRM ranged from 85.2–125%. All chemicals used in the tests were of ultrapure quality (Merck Suprapur). Ultrapure water (Milli-Q System, Millipore) was used for the standard solutions. All glassware was cleaned by soaking in 10% v/v HNO₃ for 24 hours before use and rinsing with Milli-Q water.

Sediment pollution indices

Sediment Quality Values, the reference data of Turekian & Wedepohl (1961), among the most preferred reference values, were preferred as reference values in this study. Contamination factor (C_f^i): It is an index calculated from the ratio of the concentration of the metal (loid) detected in the sediment to the pre-industrial concentration reference value of the same metal (loid) (Hakanson, 1980). Contamination degree (C_d): is obtained from the sum of the contamination factors of all sampled metals (loids) (Hakanson, 1980). If $C_d \geq 24$ it is correct to speak of serious anthropogenic contamination in the sampled area. Modified degree of contamination (mC_d): used to estimate the degree of overall contamination of the sampled area (Abraham & Parker, 2008). Pollution loading index (PLI): It is an index used to understand and quantitatively assess the degree of metal (loid) pollution in various regions (Tomlinson et al., 1980). PLI < 1 indicates that the environment is not contaminated; PLI = 1 indicates the presence of major contaminants in the environment; and PLI > 1 indicates deterioration in the quality of the environment. Enrichment factor (EF): The enrichment factor is an index used to assess the level of enrichment of metal (loids) in the study area. It is also possible to determine the sources of metal (loids) with this index (Looi et al., 2019). The enrichment factor (EF) calculation was performed according to Hasan et al. (2013). Geoaccumulation Index (I_{geo}): It was developed by Muller (1969) to evaluate the current metal (loid) concentration in sediment compared to the pre-industrial concentration. Mean effect range median ratio (m-ERM-Q) and mean probable effect level ratio (m-PEL-Q): These are indices frequently used in environmental studies and SQGs to understand the contaminant in sediment and its effects on sediment quality. However, their information on the potential ecological effects of pollutants is limited. M-ERM-Q (Long et al., 2000) and m-PEL-Q (Carr et al., 1996) are indices used to determine the possible biological effects of combined toxicants based on the fact that metal (loids) are present in sediment in mixtures. Therefore, they are based on calculating the average amount of toxic substances (Gao, 2012). Total toxic units (Σ TU) and proportional toxic units: TU values correspond to their total concentrations and are considered preliminary indicators of the effects of metal (loids) (Niu et al., 2020). By giving percentages of the total toxic effects of the metal (loid) s detected in the sediment, it reveals which metal (loid) has the highest impact on the sediment (Pederson et al., 1998).

Potential human health risk assessment

The calculation of human health risk assessment is based on dermal contact and ingestion routes of exposure. USEPA (2004) and Song et al. (2019) formulas were used to calculate exposure values. Health risks associated with exposure to metal (loid)s in sediments were assessed with hazardous ratios (HQs) according to the USEPA (2004) health risk assessment guidelines (Wang et al., 2015). HQ is the hazardous ratios under the measured exposure concentration through one of the exposure routes, ingestion or dermal contact. The reference value for exposure through skin contact is generally considered to be the same as for the ingestion route (Wang et al., 2015). If the value is less than one (HI < 1), no significant risk of non-carcinogenic effects is expected. However, if the HI is greater than one (HI > 1), non-carcinogenic risk effects may occur, which tend to increase with increasing HI (USEPA, 2004). In addition, As, Cd, Cr, and Pb are metal (loids) with the potential to pose carcinogenic risks. The health risk posed by carcinogenic metals can be calculated by the total lifetime cancer risk (LCR). Cancer slope factor (CSF) values for As, Cd, Cr and Pb are given by USEPA (2012) as 1.5, 6.3, 0.5, 0.0085 and mg/kg/day, respectively. The acceptable LCR range is 1.0×10^{-6} – 1.0×10^{-4} , while the tolerable threshold of cancer risk is 1.0×10^{-4} USEPA (2012). The sediment evaluation scale of all formulations is given in Table 2.

Data analysis

Descriptive statistics of all values according to the measured quantity were listed. Levene's test was used to check the homogeneity of variances. ONEWAY ANOVA Test was used to check whether there was a significant difference between the groups. Statistical significance was set at $\alpha = 0.05$ for all tests. As post-hoc, the Tukey test was used when variances were considered homogeneous, and Dunnett T3 was used when variances were not considered homogeneous. Correlation analysis was used to determine the relationship between metal amounts, and Principal Component Analysis (PCA) and Cluster Analysis (CA) were used to determine whether metal sources were common. Statistical analysis was performed with SPSS 21v.

Results and discussion

Concentrations of PTEs in the Gediz River

The average PTE concentrations (As, Ag, Al, Co, Cu, Cr, Cd, Fe, Hg, Mn, Mo, Mg, Ni, Pb, Se, Sr, Zn) in sediments sampled from 3 basins (13 stations) along the course of the Gediz River, the analyzed %TOC and %BOM values and the average shale values (Turekian & Wedepohl 1961) that can be compared with the natural background values of the sediments are shown in Table 3. In this study, average PTE values in Gediz River sediments were analyzed on the basis of lower, middle and upper basins. The average PTE values determined in Gediz River sediments without being divided into basins are $Fe > Mg > Al > Mn > Sr > Zn > Ni > Cr > As > Cu > Pb > Co > Mo > Se > Cd > Hg > Ag > Au$, respectively. The distribution of maximum PTE values according to the basins is as follows: Mg and Ni concentrations are Upper > Lower > Middle; Cr, Hg, Mo, Sr concentrations are Lower > Upper > Middle; and Fe, Al, Mn, Zn, As, Cu, Pb, Co, Se, Cd, Ag, Au concentrations are Lower > Middle > Upper. The highest concentrations of PTEs were found in the lower basin, and in general, PTEs increased gradually from the upper Gediz to the mouth of the river. According to one-way ANOVA, statistically significant differences were found between the three basins. P values showed significant differences in Cu, Fe, Se, and Zn concentrations and % BOM in the upper and lower basin of the river ($p \leq 0.05$). Observation of the distribution of PTEs in sediments is of great importance for determining the pollution level, as this allows the recognition of areas with higher concentrations of PTEs and the identification of possible sources (Xiao et al., 2021).

Kindler & Sevim (1990), Akçay et al. (2003), Parlak et al. (2006), and Kucuksezgin et al. (2008) mostly studied the lower and middle basin region of the Gediz River (Table 4). In this study, unlike the others, it was determined that As, Cr, Mg and Ni values in the upper basin, which is close to the outlet source of the Gediz River, pose a pollution risk in sediments according to the average shale value values. Average shale values in sediment have been widely used in many studies to compare sediment pollution (Morillo et al., 2002; Kucuksezgin et al., 2008; Fikirdişçi Ergen et al., 2023). When the PTE concentrations on a basin basis are compared with the average shale values, it is observed that the upper basin has a higher abundance of As, Mg, and Ni; the middle basin has a higher abundance of As; and the lower basin has a higher abundance of As, Ag, Cu, Cd, Cr, Zn, Ni and Pb. This may be because the river passes through an agricultural area, an industrial zone and an urban center (i.e. higher urbanization and more anthropogenic activities). Considering that the Gediz River is highly affected by the processing and coating of industrial wastes generated in the river basin, these results seem normal. This is because the Nif Stream, located at the mid-basin point, is one of the tributaries that potentially carry pollutant wastes (Kara et al., 2017).

On the contrary, other PTE values are similar to the average shale values, indicating no significant pollution source for these elements in the Gediz River. This indicates that PTEs in this region are probably of natural geogenic origin. In the Kucuksezgin et al. (2008) study, the average shale values detected in Gediz River sediments were Pb, Cr, Cu, Zn, Mn, and Ni. Accordingly, when the studies are compared, Pb, Cr, Cu, Zn, Mn, and Ni pollution continues in a decreasing direction. In contrast, in the present study, it was determined that there was a significant increase in As in all three basins and Mg in the upper basin. The main sources of As pollution are alluvial and volcanic sediments, high alkalinity, closed basin lakes, thermal springs, mining activities, pesticides and various rocks (Güneş & Güneş, 2012). In addition to natural conditions such as biological activity and volcanic emissions, the burning of fossil fuels, the use of arsenic-containing herbicides and desiccants, and the use of arsenic as an additive in animal feed increase arsenic pollution (Terlecka, 2005). Considering the basin-based status of the stations selected along the area where the Gediz River flows (Fig. 1), the Gediz River is the discharge point of the industries (textile, paint, metal coating, beverage, leather and paper factory) located in Muradiye, Nif stations in the middle basin as well as agricultural and residential areas (Akçay et al., 2003; Kucuksezgin et al., 2008; Aydın & Kucuksezgin, 2012; Şentürk & Yıldız, 2015; Minareci et al., 2009; Parlak et al., 2006). Akçay et al. (2003) stated that high concentrations of Zn, Mn, and Cr are caused by anthropogenic effects, practically by industry and pesticides used in agriculture, which pose a pollution risk. Şentürk & Yıldız (2015) stated that anthropogenic and agricultural activities negatively affect the water quality of the Gediz River according to the results of nutrient analysis in Gediz River water samples.

PTE values determined in Gediz River sediments are considerably higher than the data from the present study. Again, when compared with the studies conducted in the Gediz River in Table 5, Co, Cr, Cu, Cd, Mn, Ni, Fe, Zn, Pb, Al and Hg concentrations measured in this study are lower than the other results Kindler & Sevim (1990); Akçay et al. (2003); Parlak et al. (2006); Kucuksezgin et al. (2008); Minareci et al. (2009); Aydın & Kucuksezgin, (2012). It was observed that the concentrations of PTEs detected in different rivers of Anatolia (Tigris, Meriç, Ergene, Pazarsuyu, Kızılırmak and Munzur) were generally high. Only the As concentrations in Tigris, Pazarsuyu, Kızılırmak and Munzur river sediments are lower than the data of the present study. In the present study, Cd, Al, Hg, Sr, Mg, Ag, Au, Mo and Se concentrations were even lower than all the data in Table 5. When compared with the results of different countries; Co, Cr, Ni, As in Xiao et al. (2021); Cr, Ni, As in Woiitke et al. (2003); Ni, As in Zhuang (2021); Cr, Cu, Cd, Ni, Zn, Pb in Obodai et al. (2022) and Cu, Cd, Mn, Ni, Zn, Pb in Klubi et al. (2018) are lower than the data in this study. The most important factor common to these studies is that anthropogenic pollution has increased over time and that no adequate measures have been taken. The concentrations of As, Sr, Mg, Au, Mo and Se in the Gediz River were determined for the first time in this study.

The %TOC and BOM analysis results in the three basins (Table 4) also support the high level of PTE pollution in the lower basin. This shows that the amount of organic matter and organic carbon is an important factor controlling the distribution of As, Cr, Cd, Zn, Ni, Pb and Mg in sediments (Kucuksezgin et al., 2008). Because organic matter accumulation and organic carbon values determined in watersheds vary depending on human activities (agriculture, domestic and industrial wastes, terrestrial and inputs) and increasing traffic density (Türk Çulha et al., 2016). In the present study, the average BOM value in the Gediz River was 1.23%, which is lower than the BOM values of 0.42–5.6% determined by Aydın & Kucuksezgin (2012) and 1.2–3.6% determined by Kucuksezgin et al. (2008). When the TOC values were analyzed, it was higher than the % TOC value determined by Sarı et al. (2016) in Ergene River. Organic matter helps metals

to accumulate in sediments. In this way, it can increase the toxicity of the metal by reaching organisms living in the sediment to plants and even plays an important role in the distribution of metals to different places through groundwater. In order to understand the processes affecting metal mobility and bioavailability in soil, it is crucial to know the mechanisms of metal binding to organic matter and their long-term behavior under the influence of different natural and anthropogenic factors (Twardowska & Kyzioł, 2003).

Sediment quality guidelines (SQG)(PEL/TEL)

These screening values describe the biological effects of certain elements on reference biotic communities (Klubi et al., 2018). The low-valued limit values used in the study are the low effects range (ERL (Long & Morgan, 1991)) and the threshold effects level (TEL (Smith et al., 1996)). This means that metal (loid) concentrations detected below the ERL and TEL values can rarely affect living organisms. The higher values are the effects range median (ERM (Long & Morgan, 1991)) and probable effects level (PEL (Smith et al., 1996)), and metal(loid) concentrations detected above these values indicate that there is a high probability of observing the toxic effect of that metal(loid) in the region (Ouchir et al., 2016). Metal (loid) concentrations below the ERL are expected to affect less than 10% of the population in the wetland. In comparison, concentrations above the ERM are expected to affect more than 50% of the population (Abraham & Parker, 2008). The values of As, Ni and Cr (Table 5) obtained in the sediments were at higher limits, indicating the possibility of a significant negative impact on biota when using any SQG (Hakanson, 1980). The most important result is that As and Cr concentrations in all three basins exceed the PEL value, while Ni concentrations are above both the PEL and ERM values. Due to the high toxic potential of As, Cr and Ni, it can be said that more than 50% of the organisms living in the sediment are exposed to the negative effects of all three metals (loid). In many studies, it has been reported that concentrations exceed TEL values and are caused by various anthropogenic activities such as the treatment of agricultural lands with chemical fertilizers and the use of arsenic pesticides (Islam et al. (2015); Ustaoglu & Islam, 2020). The largest source of Cr in agricultural soils is inorganic fertilizers, while atmospheric deposition and sewage sludge are other sources (Quinton & Catt, 2007). In the Ergene basin, where agricultural and industrial activities are intense, chromium concentration was recorded as 160 mg/kg, which is well above the values in the present study (Sarı et al., 2016). It was previously reported that very high Ni values were detected in the sediment of the Sakarya River, which is polluted by anthropogenic sources such as industrial facilities (Dundar et al., 2012). Akçay et al. (2003) reported that human activities and wastewater from the leather industry caused Cr and Ni concentrations in the Gediz River.

Pollution assessment of PTEs in the Gediz River

The highest levels of Mn, Fe and Al metals were detected in the sediments of all three basins. The result is not surprising because all three metals are among the most abundant in the Earth's crust. Mn is a transition metal, usually found with Fe, and an essential element for living organisms. As a metal that affects water quality, high concentrations of Mn in drinking water can cause neurotoxic effects, especially in children and adults, impairing mental functioning (Yang et al., 2023; Bouchard et al., 2018). High concentrations of Mn in groundwater are often associated with high concentrations of Fe and As (Jia et al., 2018). Increased Fe exposure can cause cardiovascular diseases, Alzheimer's, Parkinson's, diabetes, respiratory, renal, cognitive and neurological difficulties (Ghosh et al. 2020). Excess Al exposure has also been found to cause Alzheimer's disease (Mold et al., 2020). Although the presence of all three metals in the study is high, it is not at toxic levels. When the proportional toxic units of the metals (loids) that have the potential to show intense toxic effects in the basins are analyzed, it is determined that Ni, As and Cr have the highest risk potential. Previous studies observed similar results (Fikirdeşici-Ergen et al., 2021; Tunca et al., 2016).

When all PTE values are evaluated in terms of C_f^i , As has the highest C_f^i in all three basins with values of 2.87, 2.23, and 2.00 respectively. According to the limit value stated by Hakanson (1980), it is in the range of $1 \leq C_f^i < 3$ and classified as medium pollution. In general, except for Al, Fe and Mg, EF value showed a very high value, and > 50 is severe enrichment according to extreme. This was observed in all three basins (Table 3). All sampling sites were assessed for contamination levels based on C_d and mC_d . It was observed that all three basins were moderately contaminated according to C_d and negligibly contaminated according to mC_d . The lower basin is relatively more polluted when all three basins are compared according to C_d , mC_d and PLI values. However, it is impossible to talk about general pollution in all basins. The calculated Igeo values (Table 3, 6) showed that only As $0 < I_{geo} < 1$ caused moderate pollution in all three basins and the highest value was found in the lower basin. The E_f^i values of the impact value of all metal(loid)s vary between 57.49-100.11 and show an acceptable level. PERI is between 1.32–2.42, which is low. According to the m-ERM-Q value for each basin, there is a 49% probability of toxicity in the lower basin and 21% in the other two basins. M-PEL-Q value shows a moderate level of impact for all three basins (Table 2, 5). Individual (TU) and total (TTU) potential hazards of pollutants in sediments were calculated in toxic units. When toxic unit values were analyzed, the lower basin value was higher than the other basins. For Ni, 34.31% of the total toxic impact is in the lower basin, 34.96% in the middle basin and 54.79% in the upper basin; for As 29.49% of the total impact is in the lower basin, 35.81% in the middle basin and 23.47% in the upper basin and for Cr 16.28% in the lower basin, 13.90% in the middle basin and 13.65% in the upper basin (Table 5). Although the rates seem high, when evaluated within the framework of contamination factors, it was determined that Cu, Pb, Zn, Ni, As, Cd, Cr and Ag in the lower basin, only As in the middle basin, and Ni and As in the upper basin indicate moderate contamination.

Ecological risks of PTEs in Gediz River

PTE contamination levels and calculated ecological risk for each basin of the Gediz River are presented in Tables 7, 8, and 9. HQs and HI values greater than 1 indicate that sediment-derived inputs may cause adverse health impacts. The calculated HQing and HI values are greater than 1 for As, Co, Cr, Mn, Ni and Pb in all three basins. HQderm values were below 1 for all metal(loid)s. These results indicate that dermal exposure to As, Co, Cr, Mn, Ni and Pb does not pose any health risk, but ingestion may pose health risks. Previous studies also show that ingestion exposure is always more likely and dangerous than dermal exposure (ur Rehman et al., 2018; El Fadili et al., 2022; She et al., 2022; Taghavi et al., 2023). This suggests that the ecological risk and pollution posed by PTEs should be a major concern for future management plans and pollution control of the Gediz River. As, Cd, Cr and Pb results were also evaluated for the lifetime cancer risk value LCR. Accordingly, it was observed that the LCR values for As and Cr were very close to each other, higher than Cd and Pb and lowest for Pb. This indicates that As and Cr have a higher carcinogenic risk potential. This suggests that ingestion exposures to As and Cr are particularly risky

(Tables 6,7, 8). In addition, another important result is that As, Cd, Cr and Pb in the study data, which have higher values than the LCR values in the range of $1.00E-06$ $1.00E-04$, which are considered normal by USEPA (2004), pose a great risk to living organisms. In this sense, it is important to determine the important pollutant sources of the Gediz River.

Potential sources of PTEs

Pearson correlation analysis and Principal component analysis have been used in many studies to identify possible sources and relationships of PTEs in various environments (Xiao et al., 2019; Xiao et al., 2021). Correlations between PTEs indicate a common origin, similar migration and geochemical behavior. If no correlation can be found between metals, they are not controlled by any common factor (Song et al., 2019). According to the PTEs profile in the lower basin, correlations between Zn-Cu, Fe-Co, Cd-Pb, Cr-Pb, Cr-Cd, Hg-Mn, Ag-Pb, Ag-Cr, Al-Fe, Mg-Mn, Mg-Hg, Au-Al, Sr-As are significant strong correlations (Table 9). The correlation between Cr-Cd ($r = 1.000^{**}$) shows an increasing linear relationship. Significant high correlations were also found between BOM-Ni ($r = 965^*$) and TOC-BOM ($r = 953^*$). PCA and CA tests also support these strong correlations. PCA analysis showed that Cu, Zn, Pb, Cd, Cr, Ag, Co, Fe, Hg, Al, Mg, Mg and Au were clustered in the 1st component, Co, Fe, Hg, Al, Mg and Au in the 2nd component, and As and Sr in the 3rd component (Table 10, Fig. 2). In the proximity matrix, it was determined that the closest distances, i.e. the strongest relationships, were again between the highly correlated elements and that they were in the same cluster (Table 11, Fig. 3). According to the metal (loid) profile in the middle basin, Pb-Cu, Zn-Cu, Zn-Pb, Ni-Cu, Co-Cu, Co-Ni, Mn-Zn, Fe-Cu, Fe-Pb, Cd-Pb, Cd-Zn, Cd-Mn, Cr-Cu, Cr-Ni, Cr-Co, Cr-Fe, Ag-As, Al-Ni, Al-Co, Al-Cr, Mg-Cu, Mg-Ni, Mg-Co, Mg-Fe, Mg-Cr, Mg-Al, Se-Cu, Se-Zn, Se-Co, Se-Cr, Au-Co, Au-Pb, Au-Ni, Au-Co, Au-Fe, Au-Cr, Au-Mg, Sr-Cu, Sr-Ni, Sr-Co, Sr-Cr, Sr-Al, Sr-Se, Sr-Au, TOC-Co, TOC-Al, TOC-Sr, BOM-Co, BOM-Al, BOM-Au, BOM-TOC are significant strong correlations (Table 12). Cu, Zn, Ni, Co, Fe, Cr, Al, Mg, Se, Au, Sr, TOC and BOM are in Component 1, Pb, Mn, As, Cd, Hg, Ag are in Component 2 and Mo is in Component 3. Mo is inversely related to other metals, and correlation and cluster results confirm this result (Table 13, Fig. 4). In the proximity matrix, it was determined that the closest distances, i.e. the strongest relationships, were again between the highly correlated elements and that they were in the same cluster (Table 14, Fig. 5). When the statistical results for the upper basin were analyzed, it was observed that there were high positive correlations between Co-Pb, Mn-Pb, Mn-Ni, Mn-Co, Cr-Mn, Mg-Ni, Mg-Mn, Mg-Cr, Se-Al, Sr-Hg and high negative correlations between Au-Fe (Table 15). The highest correlation was observed between Mg-Ni ($r = .999^{**}$). PCA and CA test results support these strong correlations. The proximity matrix found the closest distance between Ni and Mg. According to PCA analysis, Pb, Ni, Co, Mn, As, Cd, Cr, Cr, Mg, and Mo are grouped in Component 1, Cu, Zn, Fe, Al, Se, Au, and BOM in Component 2, and Hg, Ag, Sr, and TOC in Component 3 (Table 16, Fig. 6). The negative correlation between Au in Component 2 and Hg and Sr in Component 3 supports that Sr-Hg ($r = .963^*$) do not correlate with other metals(oids) except each other. At the same time, Au shows a high negative correlation with Fe ($r = -.970^*$), also supported by the cluster proximity matrix result. In the proximity matrix, it was determined that the closest distances, i.e. the strongest relationships, are between the highly correlated elements and that they are in the same cluster (Table 17, Fig. 7).

TOC and BOM values in sediments showed strong correlations with PTEs. Especially the correlations between BOM-Ni in the lower basin, TOC-Co, TOC-Al, TOC-Sr, BOM-Co, BOM-Al, BOM-Au, BOM-TOC in the middle basin indicate that these metals are affected by the BOM and TOC content in the environment (Chen et al., 2023). Organic carbon has a high adsorption capacity, which allows it to form organometallic complexes with some metals (Fang et al., 2022). Therefore, it shows significant positive correlations with TOC and BOM in most of the sediment. In this study, Ni, Co, Al, Sr, Au and organic carbon and organic matter are particularly important in the distribution and remineralization of metals. Furthermore, these results show that PTEs with a strong and positive correlation with each other are probably enriched by similar or different sources located near each other. This is evidence that the PTEs in the three basins are affected by similar geochemical events. However, it is also concluded that the industrial zone and volcanic terrain, especially in the middle basin point, greatly affect this metal increase. As stated in many studies, the Gediz River, which is used as a discharge point and passes through many large cities, still creates severe problems due to various anthropogenic activities from many source points, pesticides used in agriculture for high crop yields, and untreated discharge of wastes from increasing industrial activities into the receiving water environment (Akçay et al., 2003; Parlak et al., 2006; Kucuksezgin et al., 2008; Minareci et al., 2009; Aydın & Kucuksezgin, 2012).

Conclusion

The main pollutants of the Gediz River are agriculture, industry and residential areas. In previous studies, it has been stated that anthropogenic pollution is predominant. However, in the present study, ecological risks and the impact on human health were evaluated with different pollution indices, and it is predicted that exposure to As, Co, Cr, Mn, Ni and Pb by ingestion may pose health risks and may even trigger cancer risk in the long term. Another important conclusion is that there is a dominant pollution, especially in the lower basin, and that the pollution in this region, which has an outlet to the sea, can seriously affect the marine ecosystem and ecological balance.

Declarations

Author contribution All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Saniye Türk Çulha, Haşim Sömek and Şeyda Fikirdeşici Ergen. The first draft of the manuscript was written by Saniye Türk Çulha, Seyda Fikirdeşici Ergen and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding The study was carried out by Bureau Veritas Mineral Laboratoires Canada (ACME LAB.) with the authors' own contributions.

Data availability Data will be available on request.

Consent to participate Not applicable.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

References

1. Abraham, G. M.S., & Parker, R. J. (2008). Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand. *Environmental Monitoring and Assessment*, 136 (1-3) 227-238. <https://doi.org/10.1007/s10661-007-9678-2>
2. Akcay, H., Oğuz, A., & Karapire, C. (2003). Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water research*, 37(4), 813-822. [https://doi.org/10.1016/S0043-1354\(02\)00392-5](https://doi.org/10.1016/S0043-1354(02)00392-5)
3. Anonumous (1998). *Manisa City Environmental Status Report*. Manisa City Environmental Directorate., Manisa, (in Turkish) (unpublished data).
4. Anonymous (2013). *Gediz Basin Protection Action Plan (Gediz HKEP)*, TÜBİTAK-MAM, Türkiye, (in Turkish) (unpublished data).
5. Aydin, S., & Küçüksezgin, F. (2012). Distribution and chemical speciation of heavy metals in the surficial sediments of the Bakırçay and Gediz Rivers, Eastern Aegean. *Environmental Earth Sciences*, 65, 789-803. <https://doi.org/10.1007/s12665-011-1124-7>
6. Bouchard, M. F., Surette, C., Cormier, P., & Foucher, D. (2018). Low level exposure to manganese from drinking water and cognition in school-age children. *Neurotoxicology*, 64, 110-117. <https://doi.org/10.1016/j.neuro.2017.07.024>
7. Buchanan, J. B. (1984). Sediment Analysis, In: N.A. Holme and A.D. McInntyre (Eds.), *Methods for the Study of Marine Benthos*. Blackwell Science Publishing, 41-65.
8. Carr, S. R., Chapman, D. C., Long, E. R., Windom, H. L., Thursby, G., Sloane, G. M., & Wolfe, D. A. (1996). Sediment quality assessment studies of Tampa Bay, Florida. *Environmental Toxicology and Chemistry: An International Journal*, 15(7), 1218-1231. <https://doi.org/10.1002/etc.5620150730>
9. Gaudette, H. E., Flight, W. R., Toner, L., & Folger, D. W. (1974). An inexpensive titration method for the determination of organic carbon in recent sediments. *Journal of Sedimentary Research*, 44(1), 249-253. <https://doi.org/10.1306/74D729D7-2B21-11D7-8648000102C1865D>
10. Chen, C. F., Lim, Y. C., Ju, Y. R., Albarico, F. P. J. B., Chen, C. W., & Dong, C. D. (2023). A novel pollution index to assess the metal bioavailability and ecological risks in sediments. *Marine Pollution Bulletin*, 191, 114926. <https://doi.org/10.1016/j.marpolbul.2023.114926>
11. Cüce, H., Kalipci, E., Ustaoglu, F., Baser, V., & Türkmen, M. (2022). Ecotoxicological health risk analysis of potential toxic elements accumulation in the sediments of Kızılırmak River. *International Journal of Environmental Science and Technology*, 19(11), 10759-10772. <https://doi.org/10.1007/s13762-021-03869-z>
12. Dundar, M. S., Altundag, H., Eyupoglu, V., Keskin, S. C., & Tutunoglu, C. (2012). Determination of heavy metals in lower Sakarya river sediments using a BCR-sequential extraction procedure. *Environmental monitoring and assessment*, 184, 33-41. <https://doi.org/10.1007/s10661-011-1944-7>
13. El Fadili, H., Ben Ali, M., Touach, N., El Mahi, M., & Mostapha Lotfi, E. (2021). Ecotoxicological and pre-remedial risk assessment of heavy metals in municipal solid wastes dumpsite impacted soil in morocco. *Environmental Nanotechnology, Monitoring and Management*, 17: 100640 <https://doi.org/10.1016/j.enmm.2021.100640>
14. Engwa GA, Ferdinand PU, Nwalo FN, Unachukwu MN (2019) Mechanism and health effects of heavy metal toxicity in humans. In O. Karcioğlu, & B. Arslan (Eds.), *Poisoning in the Modern World: New tricks for an old dog?* <http://dx.doi.org/10.5772/intechopen.73906>
15. Eroglu, E., & Esenpinar, A. A. (2019). Heavy Metal Analysis of the Gediz River, Turkey. *Fresenius Environmental Bulletin*, 28(12A), 10186-10198.
16. Fang, T. H., Huang, Z. T., & Chang, F. W. (2022). The geochemical and environmental characteristics of trace metals in surface sediments of the river estuarine mouths around the Taiwan Island and the Taiwan Strait. *Marine Pollution Bulletin*, 182, 113967. <https://doi.org/10.1016/j.marpolbul.2022.113967>
17. Fikirdeşici-Ergen, Ş., Tekatli, Ç., Gürbüz, P., Üçüncü-Tunca, E., Türe, H., Biltekin, D., Kurtuluş, B., & Tunca, E. (2021). Elemental accumulation in the surficial sediment of Kesikköprü, Çubuk II and Asartepe Dam Lakes (Ankara) and potential sediment toxicity. *Chemistry and Ecology*, 37(6), 552-572. <https://doi.org/10.1080/02757540.2021.1902509>
18. Fikirdeşici-Ergen, Ş., Tekatli, D., Altındağ, A., Kamaşlı, G., & Tunca, E. (2023). Determination of Metal (loid) s in Mavi Dam Lake Sediment (Ankara) and Evaluation of Health Risks Level. *KSU Journal of Agriculture and Nature*, 26(5), 1010-1020. <https://doi.org/10.18016/ksutarimdogu.vi.1201244>
19. Gao, X., & Li, P. (2012). Concentration and fractionation of trace metals in surface sediments of intertidal Bohai Bay, China. *Marine Pollution Bulletin*, 64(8), 1529-1536. <https://doi.org/10.1016/j.marpolbul.2012.04.026>
20. Ghosh, G. C., Khan, M. J. H., Chakraborty, T. K., Zaman, S., Kabir, A. E., & Tanaka, H. (2020). Human health risk assessment of elevated and variable iron and manganese intake with arsenic-safe groundwater in Jashore, Bangladesh. *Scientific reports*, 10(1), 5206. <https://doi.org/10.1038/s41598-020-62187-5>
21. Güneş, S. T., & Güneş, C. (2012). Geochemical Behaviour of Arsenic from Geothermal Resources in Groundwater and Surface Water: Coprecipitation, Adsorption, pH-Eh. *Dokuz Eylül Üniversitesi Mühendislik Fakültesi Fen ve Mühendislik Dergisi*, 14(2):43-64 (in Turkish).
22. Hakanson, L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. *Water research*, 14(8), 975-1001. [https://doi.org/10.1016/0043-1354\(80\)90143-8](https://doi.org/10.1016/0043-1354(80)90143-8)
23. Hasan, A. B., Kabir, S., Reza, A. S., Zaman, M. N., Ahsan, A., & Rashid, M. (2013). Enrichment factor and geo-accumulation index of trace metals in sediments of the ship breaking area of Sitakund Upazilla (Bhatiyar–Kumira), Chittagong, Bangladesh. *Journal of Geochemical Exploration*, 125, 130-137. <https://doi.org/10.1016/j.gexplo.2012.12.002>
24. Islam, M. S., Ahmed, M. K., Raknuzzaman, M., Habibullah-Al-Mamun, M., & Islam, M. K. (2015). Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. *Ecological indicators*, 48, 282-291. <https://doi.org/10.1016/j.ecolind.2014.08.016>

25. Jia, Y., Xi, B., Jiang, Y., Guo, H., Yang, Y., Lian, X., & Han, S. (2018). Distribution, formation and human-induced evolution of geogenic contaminated groundwater in China: A review. *Science of the total environment*, *643*, 967-993. <https://doi.org/10.1016/j.scitotenv.2018.06.201>
26. Kara, G. T., Kara, M., Bayram, A., & Gündüz, O. (2017). Assessment of seasonal and spatial variations of physicochemical parameters and trace elements along a heavily polluted effluent-dominated stream. *Environmental Monitoring and Assessment*, *189*, 1-16. <https://doi.org/10.1007/s10661-017-6309-4>
27. Klubi, E., Abril, J. M., Nyarko, E., & Delgado, A. (2018). Impact of gold-mining activity on trace elements enrichment in the West African estuaries: The case of Pra and Ankobra rivers with the Volta estuary (Ghana) as the reference. *Journal of Geochemical Exploration*, *190*, 229-244. <https://doi.org/10.1016/j.gexplo.2018.03.014>
28. Kindler, F. M., & Sevim, H. E. (1990). Heavy metals in sediments of Turkish river systems – Natural background and anthropogenic effects. In J.A.C. Broekaert, Ş. Güçer & F. Adams (Eds), *Metal Speciation in the Environment*. NATO ASI Series, 23 Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-642-74206-4_32
29. Köck-Schulmeyer, M., Ginebreda, A., Petrovic, M., Giulivo, M., Aznar-Alemany, Ò., Eljarrat, E., Valle-Sistac, J., Molins-Delgado, D., Diaz-Cruz, M. S., Monllor-Alcaraz, L. S., Guillem-Argiles, N., de Alda Miren, L., Llorca, M., Farré, M., Peña, J. M., Mandaric, L., Pérez, S., Majone, B., Bellin, A., ... & Barceló, D. (2021). Priority and emerging organic microcontaminants in three Mediterranean river basins: Occurrence, spatial distribution, and identification of river basin specific pollutants. *Science of the Total Environment*, *754*, 142344. <https://doi.org/10.1016/j.scitotenv.2020.142344>
30. Kucuksezgin, F., Uluturhan, E. S. İ. N., & Batki, H. (2008). Distribution of heavy metals in water, particulate matter and sediments of Gediz River (Eastern Aegean). *Environmental Monitoring and Assessment*, *141*, 213-225. <https://doi.org/10.1007/s10661-007-9889-6>
31. Kutlu, B. (2023). Contamination and Ecological Risk Assessment of Heavy Metals in Surface Sediments of the Munzur Stream, Turkey. *Polish Journal of Environmental Studies*, *32*(1). <https://doi.org/10.15244/pjoes/154734>
32. Li, W., Chen, W., Bian, J., Xian, J., & Zhan, L. (2022). Impact of Urbanization on Ecosystem Services Balance in the Han River Ecological Economic Belt, China: A Multi-Scale Perspective. *International Journal of Environmental Research and Public Health*, *19*(21), 14304. <https://doi.org/10.3390/ijerph192114304>
33. Looi, L. J., Aris, A. Z., Yusoff, F. M., Isa, N. M., & Haris, H. (2019). Application of enrichment factor, geoaccumulation index, and ecological risk index in assessing the elemental pollution status of surface sediments. *Environmental geochemistry and health*, *41*, 27-42. <https://doi.org/10.1007/s10653-018-0149-1>
34. Long, E. R., MacDonald, D. D., Severn, C. G., & Hong, C. B. (2000). Classifying probabilities of acute toxicity in marine sediments with empirically derived sediment quality guidelines. *Environmental Toxicology and Chemistry: an International Journal*, *19*(10), 2598-2601. <https://doi.org/10.1002/etc.5620191028>
35. Long, E. R. & Morgan, L. G. (1990). *The potential for biological effects of sediment-sorbed contaminants tested in the national status and trends program*. NOAA Technical Memorandum NOS OMA 52. Seattle, WA: NOAA 175
36. Maguire, T. J., Spencer, C., Grgicak-Mannion, A., Drouillard, K., Mayer, B., & Mundle, S. O. (2019). Distinguishing point and non-point sources of dissolved nutrients, metals, and legacy contaminants in the Detroit River. *Science of the Total Environment*, *681*, 1-8. <https://doi.org/10.1016/j.scitotenv.2019.04.311>
37. Minareci, O., Ozturk, M., & Minareci, E. (2009). Determination of some heavy metal concentrations in water and sediment samples taken from Gediz River (Turkey). *Fresenius Environmental Bulletin*, *18*(3), 270-274.
38. Mold, M., Linhart, C., Gómez-Ramírez, J., Villegas-Lanau, A., & Exley, C. (2020). Aluminum and amyloid-β in familial Alzheimer's disease. *Journal of Alzheimer's Disease*, *73*(4), 1627-1635.
39. Morillo, J., Usero, J., & Gracia, I. (2002). Partitioning of metals in sediments from the Odiel River (Spain). *Environment international*, *28*(4), 263-271. [https://doi.org/10.1016/S0160-4120\(02\)00033-8](https://doi.org/10.1016/S0160-4120(02)00033-8)
40. Moiseenko, T., & Sharov, A. (2019). Large Russian lakes Ladoga, Onega, and Imandra under strong pollution and in the period of revitalization: A review. *Geosciences*, *9*(12), 492. <https://doi.org/10.3390/geosciences9120492>
41. Müller, G. (1969). Index of geoaccumulation in sediments of the Rhine River. *GeoJournal*, *2*:108-118
42. Niu, Y., Jiang, X., Wang, K., Xia, J., Jiao, W., Niu, Y., & Yu, H. (2020). Meta analysis of heavy metal pollution and sources in surface sediments of Lake Taihu, China. *Science of the Total Environment*, *700*, 134509. <https://doi.org/10.1016/j.scitotenv.2019.134509>
43. Obodai, J., Amaning Adjei, K., Duncan, A. E., & Nii Odai, S. (2022). Potentially Toxic Elements (PTEs) contamination and ecological risk of sediment in the upper course of the Ankobra River, Ghana. *Environmental Monitoring and Assessment*, *194*(6), 446. <https://doi.org/10.1007/s10661-022-10120-w>
44. Onmuş, O., Durusoy, R., & Eken, G. (2009). Distribution of breeding birds in the Gediz Delta, Western Turkey: (Aves). *Zoology in the Middle East*, *47*(1), 39-48. <https://doi.org/10.1080/09397140.2009.10638345>
45. Ouchir, N., Aissa, L. B., Boughdiri, M., & Aydi, A. (2016). Assessment of heavy metal contamination status in sediments and identification of pollution source in Ichkeul Lake and rivers ecosystem, northern Tunisia. *Arabian Journal of Geosciences*, *9*, 1-12. <https://doi.org/10.1007/s12517-016-2560-1>
46. Quinton, J. N., & Catt, J. A. (2007). Enrichment of heavy metals in sediment resulting from soil erosion on agricultural fields. *Environmental science & technology*, *41*(10), 3495-3500. <https://doi.org/10.1021/es062147h>
47. Parlak, H., ÇAKIR, A., BOYACIOĞLU, M., & Arslan, Ö. Ç. (2006). Heavy Metal Deposition in Sediments from the Delta of the Gediz River (Western Turkey): A Preliminary Study. *Ege Journal of Fisheries and Aquatic Sciences*, *23*(3), 445-448.
48. Pedersen, F., Bjørnstad, E., Andersen, H. V., Kjølholt, J., & Poll, C. (1998). Characterization of sediments from Copenhagen Harbour by use of biotests. *Water Science and Technology*, *37*(6-7), 233-240. [https://doi.org/10.1016/S0273-1223\(98\)00203-0](https://doi.org/10.1016/S0273-1223(98)00203-0)

49. Sari, E., Neven, C., Stanislav, F. B., Ali, K. M., & Mihri, H. (2016). Contamination assessment of ecotoxic metals in recent sediments from the Ergene River, Turkey. *Environmental Earth Sciences*, 75, 1-11. <https://doi.org/10.1007/s12665-016-855-3>
50. Scherer, C., Weber, A., Stock, F., Vurusic, S., Egerci, H., Kochleus, C., Arendt, N., Foeldi, C., Dierkes, G., Wagner, M., Brennholt, N., & Reifferscheid, G. (2020). Comparative assessment of microplastics in water and sediment of a large European river. *Science of the Total Environment*, 738, 139866. <https://doi.org/10.1016/j.scitotenv.2020.139866>
51. She, W., Guo, L., Gao, J., Zhang, C., Wu, S., Jiao, Y., & Zhu, G. (2022). Spatial distribution of soil heavy metals and associated environmental risks near major roads in Southern Tibet, China. *International Journal of Environmental Research and Public Health*, 19(14), 8380. <https://doi.org/10.3390/ijerph19148380>
52. Sonone, S. S., Jadhav, S., Sankhla, M. S., & Kumar, R. (2020). Water contamination by heavy metals and their toxic effect on aquaculture and human health through food chain. *Letters in Applied NanoBioScience*, 10(2), 2148-2166. <https://doi.org/10.33263/LIANBS102.21482166>
53. Song, J., Liu, Q., & Sheng, Y. (2019). Distribution and risk assessment of trace metals in riverine surface sediments in gold mining area. *Environmental Monitoring and Assessment*, 191, 1-13. <https://doi.org/10.1007/s10661-019-7311-9>
54. Smith, S. L., MacDonald, D. D., Keenleyside, K. A., Ingersoll, C. G., & Field, L. J. (1996). A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. *Journal of Great Lakes Research*, 22(3), 624-638. [https://doi.org/10.1016/S0380-1330\(96\)70985-1](https://doi.org/10.1016/S0380-1330(96)70985-1)
55. Şentürk, T., & Yıldız, Ş. (2015). Determination of some physicochemical parameters and inorganic nutrient content of Gediz River (Manisa). *Turkish Journal of Biochemistry*, 40(3), 210-216. <https://doi.org/10.1515/tjb-2015-0003>
56. Taghavi, M., Darvishiyan, M., Momeni, M., Eslami, H., Fallahzadeh, R. A., & Zarei, A. (2023). Ecological risk assessment of trace elements (TEs) pollution and human health risk exposure in agricultural soils used for saffron cultivation. *Scientific Reports*, 13(1), 4556. <https://doi.org/10.1038/s41598-023-31681-x>
57. Terlecka, E. (2005). Arsenic speciation analysis in water samples: A review of the hyphenated techniques. *Environmental Monitoring and Assessment*, 107, 259-284. <https://doi.org/10.1007/s10661-005-3109-z>
58. Tokatli, C., & Baştatlı, Y. (2016). Trace and toxic element levels in river sediments. *Polish Journal of Environmental Studies*, 25(4), 1715-1720. <https://doi.org/10.15244/pjoes/62678>
59. Tomlinson, D. L., Wilson, J. G., Harris, C. R., & Jeffrey, D. W. (1980). Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer meeresuntersuchungen*, 33, 566-575. <https://doi.org/10.1007/BF02414780>
60. Tunca, E., Aydın, M., & Şahin, Ü. (2016). Interactions and accumulation differences of metal (loid) s in three sea cucumber species collected from the Northern Mediterranean Sea. *Environmental Science and Pollution Research*, 23, 21020-21031. <https://doi.org/10.1007/s11356-016-7288-7>
61. Turekian, K. K., & Wedepohl, K. H. (1961). Distribution of the elements in some major units of the earth's crust. *Geological society of America bulletin*, 72(2), 175-192. [https://doi.org/10.1130/0016-7606\(1961\)72\[175:DOTAIS\]2.0.CO;2](https://doi.org/10.1130/0016-7606(1961)72[175:DOTAIS]2.0.CO;2)
62. Turk Culha, S., Dereli, H., Karaduman, F. R., & Culha, M. (2016). Assessment of trace metal contamination in the sea cucumber (*Holothuria tubulosa*) and sediments from the Dardanelles Strait (Turkey). *Environmental Science and Pollution Research*, 23, 11584-11597. <https://doi.org/10.1007/s11356-016-6152-0>
63. Twardowska, I., & Kyzioł, J. (2003). Sorption of metals onto natural organic matter as a function of complexation and adsorbent-adsorbate contact mode. *Environmental International*, 28(8), 783-791. [https://doi.org/10.1016/S0160-4120\(02\)00106-X](https://doi.org/10.1016/S0160-4120(02)00106-X)
64. ur Rehman, I., Ishaq, M., Ali, L., Khan, S., Ahmad, I., Din, I. U., & Ullah, H. (2018). Enrichment, spatial distribution of potential ecological and human health risk assessment via toxic metals in soil and surface water ingestion in the vicinity of Sewakht mines, district Chitral, Northern Pakistan. *Ecotoxicology and environmental safety*, 154, 127-136. <https://doi.org/10.1016/j.ecoenv.2018.02.033>
65. Usman QA, Muhammad S, Ali W, Yousaf S, Jadoon IA (2021) Spatial distribution and provenance of heavy metal contamination in the sediments of the Indus River and its tributaries, North Pakistan: Evaluation of pollution and potential risks. *Environ. Technol. Innovation*, 21:101184, <https://doi.org/10.1016/j.eti.2020.101184>
66. Ustaoglu, F., & Islam, M. S. (2020). Potential toxic elements in sediment of some rivers at Giresun, Northeast Turkey: A preliminary assessment for ecotoxicological status and health risk. *Ecological indicators*, 113, 106237. <https://doi.org/10.1016/j.ecolind.2020.106237>
67. USEPA. (2004). Environmental Protection Agency. Office of Emergency, & Remedial Response. *Risk assessment guidance for superfund (RAGS). Volume I. Human health evaluation manual (HHEM). Part E. Supplemental guidance for dermal risk assessment*, United States Environmental Protection Agency.
68. USEPA (2012) Environmental Protection Agency Integrated Risk Information System of the US Environmental Protection Agency.
69. Xiao, H., Shahab, A., Li, J., Xi, B., Sun, X., He, H., & Yu, G. (2019). Distribution, ecological risk assessment and source identification of heavy metals in surface sediments of Huixian karst wetland, China. *Ecotoxicology and Environmental Safety*, 185, 109700. <https://doi.org/10.1016/j.ecoenv.2019.109700>
70. Xiao, H., Shahab, A., Xi, B., Chang, Q., You, S., Li, J., ... & Li, X. (2021). Heavy metal pollution, ecological risk, spatial distribution, and source identification in sediments of the Lijiang River, China. *Environmental Pollution*, 269, 116189. <https://doi.org/10.1016/j.envpol.2020.116189>
71. Varol, M. (2011). Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *Journal of hazardous materials*, 195, 355-364. <https://doi.org/10.1016/j.jhazmat.2011.08.051>
72. Wang, S., Wang, Y., Zhang, R., Wang, W., Xu, D., Guo, J., Li, P., & Yu, K. (2015). Historical levels of heavy metals reconstructed from sedimentary record in the Hejiang River, located in a typical mining region of Southern China. *Science of the Total Environment*, 532, 645-654. <https://doi.org/10.1016/j.scitotenv.2015.06.035>
73. Voitke, P., Wellmütz, J., Helm, D., Kube, P., Lepom, P., & Litherat, P. (2003). Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube. *Chemosphere*, 51(8), 633-642. [https://doi.org/10.1016/S0045-6535\(03\)00217-0](https://doi.org/10.1016/S0045-6535(03)00217-0)

74. Yang, Y., Deng, Y., Xu, Y., Yan, J., Du, Y., Xie, X., & Wang, Y. (2023). Manganese mobilization from sediment to groundwater in alluvial-lacustrine aquifer system along the lower reaches of Han River. *Journal of Hydrology*, 627, 130400. <https://doi.org/10.1016/j.jhydrol.2023.130400>

75. Zhuang, S., Lu, X., Yu, B., Fan, X., & Yang, Y. (2021). Ascertaining the pollution, ecological risk and source of metal (loid) s in the upstream sediment of Danjiang River, China. *Ecological Indicators*, 125, 107502. <https://doi.org/10.1016/j.ecolind.2021.107502>

Tables

Table 1 Location characteristics of the Gediz River

Stations	Locations	Coordinates	Elavations	Specification Keywords	
Lower basin	G1	Delta (İzmir)	38°35'20.04"N 26°50'17.87"E	Sea level	Fishing Shelters-Agriculture
	G2	Geren around (İzmir)	38°36'43.17"N 26°50'43.46"E	3 m	Agriculture
	G3	Maltepe around (İzmir)	38°37'57.59"N 26°50'43.46"E	3 m	Agriculture-Settlement
	G4	Emiralem Regulators (İzmir)	38°37'41.94"N 27°10'40.58"E	16 m	Agriculture-Settlement
Middle basin	G5	Muradiye around (Manisa)	38°40'52.05"N 27°20'04.76"E	20 m	Agriculture-Settlement
	G6	Nif Stream (Manisa)	38°37'4.35"N 27°29'45.72"E	24 m	Chemical Industry-Livestock-Agriculture-Settlement
	G7	Akhisar stream (Manisa-Şehzadeler)	38°39'51.33"N 27°31'50.47"E	33 m	Agriculture
	G8	Turgutlu around (Manisa)	38°32'47.72"N 27°45'16.66"E	49 m	Agriculture
	G9	Salihli around (Manisa)	38°30'45.60"N 28°05'58.98"E	78 m	Agriculture-Settlement
Upper basin	G10	Adala Regulators (Manisa)	38°34'44.75"N 28°16'18.22"E	117 m	Volcanic Land-Agriculture-Settlement
	G11	Selendi around (Manisa)	38°40'08.92"N 28°36'14.55"E	296 m	Volcanic Land-Soda Water mixture-Agriculture
	G12	Güneli around (Uşak)	38°39'42.96"N 29°05'07.13"E	520 m	Settlement-Agriculture
	G13	Gediz around (Kütahya)	38°56'39.85"N 29°20'15.17"E	670 m	Treatment plant-Furniture Industry-Agriculture-Settlement

Table 2 Sediment assessment scale

Contamination factor (Hakanson 1980)

CF<1	low contamination
1≤CF<3	moderate contamination
3≤CF<6	considerable contamination
CF≥6	high contamination

Degree of contamination (C_d) (Hakanson 1980)

Cd≤8	low degree of contamination
8≤Cd≤16	moderate degree of contamination
16≤Cd≤32	considerable degree of contamination
Cd≥32	very high degree of contaminations

Modified degree of contamination (mCd) (Abraham and Parker 2008)

mCd < 1.5	nil to very low degree of contamination
1.5 ≤ mCd < 2	low degree of contamination
2 ≤ mCd < 4	moderate degree of contamination
4 ≤ mCd < 8	high degree of contamination
8 ≤ mCd < 16	very high degree of contamination
16 ≤ mCd < 32	extremely high degree of contamination
mCd ≥ 32	ultra high degree of contamination

Pollution load index (PLI) (Tomlinson et al. 1980)

PLI <1	no pollution
PLI is >1	deterioration

Enrichment factor (EF) (Hasan et al. 2013)

<1	no enrichment
1 to 3	minor enrichment
3 to 5	moderate enrichment
5 to 10	moderately severe enrichment
10 to 25	severe enrichment
25 to 50	very severe enrichment
>50 extremely	severe enrichment

Geoaccumulation index (I_{geo})

I _{geo} ≤0	practically uncontaminated
0<I _{geo} <1	uncontaminated to moderately contaminated
1<I _{geo} <2	moderately contaminated
2<I _{geo} <3	moderately to strongly contaminated
3<I _{geo} <4	strongly contaminated
4<I _{geo} <5	strongly to extremely contaminated
I _{geo} ≥5	extremely contaminated

Potential Ecological Risk Factor (Eir) (Hakanson 1980)

Eir<40	indicating low
40≤Eir<80	moderate
80≤Eir<160	considerable
160≤Eir<320	high
Eir≥320	very high risks

Potential Ecological Risk Index (PERI) (Hakanson 1980)

PERI<95	indicating low
95≤ PERI<190	moderate
190≤ PERI<380	considerable
PERI≥380	very high ecological risks
Ratio of average effects range median (m-ERM-Q) (Long et al. 2000)	
m-ERM-q<0.1	9%
0.11<m-ERM-q<0.5	21%
0.51 <m-ERM-q <1.5	49%
m-ERM-q>1.50	76% probability of being toxic
Ratio of average probable effect level (m-PEL-Q) (Carr et al. 1996)	
m-PEL-Q<0.1	unimpacted
0.1< m-PEL-Q<1	moderately impacted
m-ERM-Q>1	highly impacted

Table 3 Mean PTEs concentrations in the sediment of Gediz River and TEL, PEL values (in mg/kg dw)

PTEs	Gediz River (n=13)	Lower basin (n=4)	Middle basin (n=5)	Upper basin (n=4)	PEL	ERM	TEL	ERL	PERI-RI	Earth Crust*
As	30.58±9.96	37.28±7.70^a	28.94±10.92^a	25.95±9.24^a	17.00	85.00	5.90	33.00	10	13.0
Al	11415±6398.8	15000±3909.8 ^a	12900±7432.7 ^a	5975±3782.7 ^a						80000
Ag	0.06±0.04	0.09±0.05 ^a	0.04±0.03 ^a	0.04±0.02 ^a						0.07
Au	0.01±0.00	0.01±0.00 ^a	0.01±0.00 ^a	0.003±0.00 ^a						
Cu	27.84±26.06	51.69±32.08^a	23.62±17.89 ^{ab}	9.28±3.62 ^b	197.00	390.00	35.70	70.00	5	45
Cd	0.19±0.15	0.31±0.21 ^a	0.16±0.09 ^a	0.11±0.04 ^a	3.53	9.00	0.60	5.00	30	0.3
Cr	80.97±60.78	108.93±60.71^a	59.46±41.82 ^a	79.90±83.33 ^a	90.00	145.00	37.30	80.00	2	90
Co	11.13±4.55	13.80±3.27 ^a	10.62±5.04 ^a	9.10±4.76 ^a						19
Hg	0.11±0.08	0.17±0.07 ^a	0.07±0.03 ^a	0.12±0.10 ^a	0.49	1.30	0.17	0.15	40	0.4
Fe	18084±6655.3	23225±4630.6 ^a	18580±6379.8 ^{ab}	12325±4646.4 ^b						47200
Mn	395.46±188.31	544.50±222.26 ^a	386.60±165.84 ^a	257.50±25.32 ^a					1	850
Mo	1.03±0.84	1.47±1.15 ^a	0.67±0.27 ^a	1.04±0.97 ^a						2.6
Mg	11576±5780.8	10700±4484.8 ^a	8940±6145.5 ^a	15750±11119.2^a						15000
Ni	90.75±74.92	91.85±31.07^a	59.82±49.90 ^a	128.30±121.1^a	36.00	50.00	18.00	30.00	5	68
Pb	15.79±10.55	25.17±12.77 ^a	12.61±7.77 ^a	10.39±5.38 ^a	91.30	110.00	35.00	35.00	5	20
Se	0.32±0.19	0.50±0.16 ^a	0.32±0.15 ^{ab}	0.15±0.10 ^b						0.6
Sr	104.05±49.38	123.38±53.96 ^a	80.24±59.83 ^a	114.48±21.98 ^a						300
Zn	94.35±79.58	162.25±99.47^a	92.38±51.40 ^{ab}	28.90±7.24 ^b	315.00	270.00	123.00	120.00	1	95
%TOC	1.23±1.23	2.38±1.42 ^a	0.72±0.87 ^a	0.72±0.71 ^a						
%BOM	7.16±6.74	13.56±5.66 ^a	5.35±7.00 ^{ab}	3.02±1.14 ^b						

a,b,c: The fact that the letters are different indicates that the ANOVA single factor p-value is ≤0.05 and there is a statistical difference as a result of comparing the mean values of the groups; *Turekian and Wedepohl (1961).

Table 4 Detected PTEs concentrations in surface sediments in some selected world rivers (mg/kg; dw)

Locations	Co	Cr	Cu	Cd	Mn	Ni	Fe	Zn	Pb	As	Al	Hg	Sr	Mg	A
Gediz River, Türkiye	11.13	80.97	27.84	0.19	395.46	90.75	18084	94.35	15.79	30.58	11415	0.11	104.05	11576	0
Gediz River, Türkiye	28.0	232.0	110.0	0.24	1222.0	222.0	39000	147.0	35.0	-	-	-	-	-	-
Gediz River, Türkiye	38.0	200.0	140.0	-	510.0	106.0	25500	160.0	128.0	-	-	-	-	-	-
Gediz River, Türkiye	14.51-2.95	2565-5.97	25.28-0.23	0.54-0.04	-	66.78-12.08	-	-	79.30-1.04	21.47-3.54	-	-	-	-	-
Gediz River, Türkiye	-	140.0-439.0	32.0-88.0	-	747.0-1371.0	86.0-175.0	35215-72387	55.0-158.0	59.0-93.0	-	-	0.28-0.49	-	-	-
Gediz River, Türkiye	2.44-0.98	356-27.7	735-20.4	0.95-0.26	662.0-145.0	135.0-31.1	5727.0-3072.0	631.0-129.0	53.1-2.6	-	-	-	-	-	-
Gediz River, Türkiye	-	351.0-57.0	113.0-34.0	1.8-0.65	1277.0-673.0	111.0-54.0	52031-40746	152.0-75.0	61.0-32.0	-	78473-36829	-	-	-	-
Tigris River, Türkiye	10.0	54.6	28.5	1.60	489.70	91.0	-	120.5	221.8	2.90	-	-	-	-	-
Meriç River, Türkiye	330.5	2599.9	639.9	24.0	27.78	888.0	13505	3349.2	1034.5	248.4	14.79*	-	2518.4	3654.1	7
Ergene River, Türkiye	11.0	160.0	66.80	1.34	348.0	72.90	28340	183.0	97.60	258.0	73961	2.22	134.0	-	3
Pazarsuyu River, Türkiye	20.63	60.39	114.0	0.71	1137.0	23.33	42024	138.0	72.13	15.83	45060	-	-	-	-
Kızılırmak River, Türkiye	15.5	212.3	18.5	0.86	922.0	121.9	30.1*	52.5	13.6	15.8	22.06*	0.44	-	-	-
Munzur River, Türkiye	-	315.0-3.0	33.25-4.5	3.09-0.9	982.5-133.0	555.0-21.5	179471-22973	77.5-17.5	108.3-9.8	2.8-1.5	-	0.03-0.002	-	-	-
Danube River, Germany	-	64.0	65.7	1.20	819.0	49.6	29700	187.0	46.3	17.6	33300	0.22	-	-	-
İndus River, Pakistan	136.0-24.0	398.0-16.0	151.0-14.0	4.88-0.34	2662.0-271.5	246.0-26.0	65648-10896	-	128.0-12.0	-	-	-	-	-	-
Lijiang River, China	8.62	43.62	31.72	0.97	565.6	22.95	-	129.3	42.8	18.3	-	0.39	-	-	-
Danjiang River, China	25.9	81.6	46.7	-	925.1	37.5	-	139.0	38.9	10.1	-	-	-	-	-
Ankobra River, Ghana	-	9.5	4.2	0.07	179.6	-	3873.6	36.3	0.25	37.5	72.7*	1.01	-	-	-
Ankobra River, Ghana	13.6	123.0	23.8	0.07	261.0	25.0	4.1*	53.0	10.6	50.0	8.1*	0.28	120.0	-	0

Reference: 1. This study; 2. Kindler & Sevim (1990); 3. Akçay et al. (2003); 4. Parlak et al. (2006); 5. Kucuksezgin et al. (2008); 6. Minareci et al. (2009); 7. Aydin & Kucuksezgin (2012); 8. Varol (2011); 9. Tokatli & Başatlı (2016); 10. Sari et al. (2016); 11. Ustaoglu & Islam (2020); 12. Cuce et al. (2022); 13. Kutlu (2023); 14. Woitke et al. (2003); 15. Usman et al. (2021); 16. Xiao et al. (2021); 17. Zhuang et al. (2021); 18. Obodai et al. (2022); 19. Klubi et al. (2018)

Table 5 Interpretation of basins according to sediment quality values, ^a: Lower basin; ^b: Middle basin; ^c: Upper basin

	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Al	Co	Hg	Se	Mo	Sr
CF ^a	1.15	1.26	1.71	1.35	0.64	0.005	2.87	1.04	1.21	0.002	0.73	0.42	0.83	0.57	0.41
CF ^b	0.52	0.63	0.97	0.88	0.45	0.004	2.23	0.53	0.66	0.002	0.56	0.16	0.53	0.26	0.27
CF ^c	0.21	0.52	0.30	1.89	0.30	0.003	2.00	0.37	0.89	0.00	0.48	0.30	0.25	0.40	0.38
Cd ^a	15.49														
Cd ^b	9.29														
Cd ^c	8.92														
Mcd ^a	0.91														
MCd ^b	0.55														
MCd ^c	0.52														
Ef ^a	233.42	255.79	347.09	274.51	130.19	1.00	582.72	211.70	245.96	0.38	147.61	84.47	169.36	115.10	83.5
Ef ^b	133.34	160.17	247.03	223.48	115.54	1.00	565.52	133.79	167.83	0.41	141.99	41.28	135.49	65.27	67.9
Ef ^c	78.98	198.90	116.50	722.56	116.01	1.00	764.45	140.42	339.98	0.29	183.42	113.93	95.74	152.45	146.
Igeo ^a	-0.39	-0.25	0.19	-0.15	-1.23	-8.25	0.93	-0.53	-0.31	-9.64	-1.05	-1.85	-0.85	-1.41	-1.85
Igeo ^b	-1.51	-1.25	-0.63	-0.77	-1.72	-8.57	0.57	-1.51	-1.18	-9.86	-1.42	-3.21	-1.49	-2.55	-2.45
Igeo ^c	-2.86	-1.53	-2.30	0.33	-2.31	-9.17	0.41	-2.03	-0.76	-10.97	-1.65	-2.33	-2.58	-1.91	-1.95
PLI ^a	0.150														
PLI ^b	0.058														
PLI ^c	0.046														
PERI ^a	5.74	6.29	1.71	6.75	0.64		28.67	31.25	2.42			16.63			
PERI ^b	2.62	3.15	0.97	4.40	0.45		22.26	15.80	1.32			6.50			
PERI ^c	1.03	2.60	0.30	9.43	0.30		19.96	11.00	1.78			11.90			
E _r ^{i a}	100.11														
E _r ^{i b}	57.49														
E _r ^{i c}	58.31														
m-ERM-Q ^a	0.61														
m-ERM-Q ^b	0.37														
m-ERM-Q ^c	0.48														
m-PEL-Q ^a	0.93														
m-PEL-Q ^b	0.59														
m-PEL-Q ^c	0.81														
TTU ^a	7.44														
TTU ^b	4.75														

TTU ^c	6.50								
TU ^a	3.53	3.71	6.93	34.31	29.49	1.19	16.28		4.56
TU ^b	2.52	2.91	6.17	34.96	35.81	0.94	13.90		2.79
TU ^c	0.72	1.75	1.41	54.79	23.47	0.48	13.65		3.73

Table 6 Effect of PTEs concentrations obtained from the Lower basin on human health

	Exposure assessment			Non-carcinogenic risk			Carcinogenic risk		
	RfD	Exping	Expderm	HQing	HQderm	HI	CRing	CRderm	LCR
Al	1.00E+00	0.0855	0.0003	8.55E-02	2.99E-04	8.58E-02			
As	3.00E-4	0.0212	0.0001	7.08E+01	2.48E-01	7.11E+01	0.031874	0.000112	0.031986
Ag	5.00E-3	0.0001	0.0000	1.03E-02	3.59E-05	1.03E-02			
Cd	1.00E-3	0.0002	0.0000	1.77E-01	6.18E-04	1.77E-01	0.001113	0.0001	0.001213
Co	3.00E-4	0.0079	0.00003	2.62E+01	9.18E-02	2.63E+01			
Cr	3.00E-3	0.0621	0.0002	2.07E+01	7.24E-02	2.08E+01	0.031045	0.000109	0.031154
Cu	4.00E-2	0.0295	0.0001	7.37E-01	2.58E-03	7.39E-01			
Fe	7.00E-1	0.1324	0.0005	1.89E-01	6.62E-04	1.90E-01			
Hg	1.6E-04	0.0001	0.0000	6.06E-01	2.12E-03	6.08E-01			
Mn	1.40E-1	0.3104	0.0011	2.22E+00	7.76E-03	2.22E+00			
Ni	2.00E-2	0.0524	0.0002	2.62E+00	9.16E-03	2.63E+00			
Pb	3.00E-3	0.0143	0.00005	4.78E+00	1.67E-02	4.80E+00	0.000122	4.27E-07	0.000122
Zn	3.00E-1	0.0925	0.0003	3.08E-01	1.08E-03	3.09E-01			

Table 7 Effect of PTEs concentrations obtained from the Middle basin on human health

	Exposure assessment			Non-carcinogenic risk			Carcinogenic risk		
	RfD	Exping	Expderm	HQing	HQderm	HI	CRing	CRderm	LCR
Al	1.00E+00	0.0510	0.0002	5.10E-02	1.78E-04	5.11E-02			
As	3.00E-4	0.0165	0.0001	5.50E+01	1.92E-01	5.52E+01	0.024744	8.66E-05	0.02483
Ag	5.00E-3	0.0000	0.0000	4.94E-03	1.73E-05	4.96E-03			
Cd	1.00E-3	0.0001	0.0000	9.01E-02	3.15E-04	9.04E-02	0.000567	1.99E-06	0.000569
Co	3.00E-4	0.0061	0.00002	2.02E+01	7.06E-02	2.02E+01			
Cr	3.00E-3	0.0339	0.0001	1.13E+01	3.95E-02	1.13E+01	0.016946	5.93E-05	0.017005
Cu	4.00E-2	0.0135	0.0000	3.37E-01	1.18E-03	3.38E-01			
Fe	7.00E-1	0.1059	0.0004	1.51E-01	5.30E-04	1.52E-01			
Hg	1.6E-04	0.0000	0.0000	2.32E-01	8.10E-04	2.32E-01			
Mn	1.40E-1	0.2204	0.0008	1.57E+00	5.51E-03	1.58E+00			
Ni	2.00E-2	0.0341	0.0001	1.70E+00	5.97E-03	1.71E+00			
Pb	3.00E-3	0.0072	0.00003	2.40E+00	8.39E-03	2.40E+00	6.11E-05	2.14E-07	6.13E-05
Zn	3.00E-1	0.0527	0.0002	1.76E-01	6.14E-04	1.76E-01			

Table 8 Effect of PTEs concentrations obtained from the Upper basin on human health

	Exposure assessment			Non-carcinogenic risk			Carcinogenic risk		
	RfD	Exping	Expderm	HQing	HQderm	HI	CRing	CRderm	LCR
Al	1.00E+00	0.0341	0.0001	3.41E-02	1.19E-04	3.42E-02			
As	3.00E-4	0.0148	0.0001	4.93E+01	1.73E-01	4.95E+01	0.022187	7.77E-05	0.022265
Ag	5.00E-3	0.0000	0.0000	5.04E-03	1.77E-05	5.06E-03			
Cd	1.00E-3	0.0001	0.0000	6.27E-02	2.19E-04	6.29E-02	0.000395	1.38E-06	0.000396
Co	3.00E-4	0.0052	0.00002	1.73E+01	6.05E-02	1.74E+01			
Cr	3.00E-3	0.0455	0.0002	1.52E+01	5.31E-02	1.52E+01	0.022772	7.97E-05	0.022851
Cu	4.00E-2	0.0053	0.0000	1.32E-01	4.63E-04	1.33E-01			
Fe	7.00E-1	0.0703	0.0002	1.00E-01	3.51E-04	1.01E-01			
Hg	1.6E-04	0.0001	0.0000	4.24E-01	1.48E-03	4.25E-01			
Mn	1.40E-1	0.1468	0.0005	1.05E+00	3.67E-03	1.05E+00			
Ni	2.00E-2	0.0731	0.0003	3.66E+00	1.28E-02	3.67E+00			
Pb	3.00E-3	0.0059	0.00002	1.97E+00	6.91E-03	1.98E+00	5.03E-05	1.76E-07	5.05E-05
Zn	3.00E-1	0.0165	0.0001	5.49E-02	1.92E-04	5.51E-02			

Table 9 Correlation of PTEs detected in the Lower basin.

	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr	Hg	Ag	Al	Mg	Se	Mo	Au	Sr
Cu	1																	
Pb	.606	1																
Zn	.971*	.775	1															
Ni	.715	.895	.816	1														
Co	.184	.759	.348	.818	1													
Mn	-.701	-.505	-.732	-.284	.178	1												
Fe	.106	.577	.225	.745	.961*	.395	1											
As	-.330	-.637	-.479	-.255	-.086	.829	.192	1										
Cd	.761	.976*	.892	.906	.648	-.624	.471	-.635	1									
Cr	.756	.978*	.889	.910	.657	-.615	.482	-.629	1.000**	1								
Hg	-.731	-.316	-.698	-.172	.360	.965*	.527	.663	-.477	-.466	1							
Ag	.640	.972*	.803	.795	.590	-.684	.369	-.789	.971*	.970*	-.503	1						
Al	-.119	.467	.016	.591	.929	.527	.974*	.224	.323	.334	.676	.256	1					
Mg	-.630	-.290	-.614	-.084	.401	.972*	.589	.734	-.432	-.421	.989*	-.494	.710	1				
Se	-.021	.003	-.054	.386	.562	.718	.767	.763	-.039	-.030	.682	-.227	.741	.783	1			
Mo	.433	-.428	.207	-.098	-.491	-.042	-.326	.523	-.242	-.247	-.290	-.415	-.460	-.183	.221	1		
Au	-.204	.462	-.051	.532	.917	.525	.941	.159	.298	.310	.695	.262	.991**	.710	.664	-.567	1	
Sr	-.445	-.530	-.541	-.183	.111	.934	.373	.966*	-.581	-.573	.827	-.715	.437	.883	.836	.296	.389	1
TOC	.941	.696	.939	.882	.467	-.463	.429	-.167	.808	.807	-.463	.650	.214	-.344	.284	.344	.118	-.2
BOM	.796	.761	.837	.965*	.703	-.245	.684	-.076	.815	.817	-.199	.654	.501	-.082	.484	.163	.413	-.0

Table 10 CA proximity matrix of PTEs detected in the Lower basin.

Proximity Matrix

Case	Matrix File Input																
	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr	Hg	Ag	Al	Mg	Se	Mo	
Cu	0.000	2.365	.172	1.710	4.899	10.206	5.364	7.980	1.435	1.466	10.386	2.158	6.711	9.780	6.124	3.404	
Pb		0.000	1.349	.630	1.443	9.028	2.536	9.821	.141	.129	7.898	.171	3.197	7.738	5.981	8.566	
Zn			0.000	1.105	3.910	10.390	4.648	8.873	.645	.668	10.189	1.183	5.904	9.686	6.323	4.756	
Ni				0.000	1.089	7.707	1.529	7.533	.564	.542	7.031	1.232	2.452	6.505	3.682	6.585	
Co					0.000	4.934	.233	6.516	2.113	2.058	3.838	2.461	.423	3.595	2.628	8.947	
Mn						0.000	3.629	1.029	9.744	9.688	.210	10.101	2.835	.167	1.691	6.251	
Fe							0.000	4.850	3.172	3.109	2.836	3.789	.157	2.467	1.398	7.959	
As								0.000	9.808	9.777	2.020	10.735	4.655	1.597	1.420	2.861	
Cd									0.000	.000	8.862	.176	4.064	8.593	6.234	7.449	
Cr										0.000	8.797	.180	3.995	8.527	6.178	7.482	
Hg											0.000	9.016	1.944	.069	1.911	7.742	
Ag												0.000	4.466	8.962	7.359	8.491	
Al													0.000	1.738	1.552	8.757	
Mg														0.000	1.303	7.100	
Se															0.000	4.675	
Mo																0.000	
Au																	
Sr																	
TOC																	
BOM																	

Table 11 PCA rotated component matrix in the Lower basin. Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. ^a; Rotation converged in 9 iterations.

Rotated Component Matrix^a

	Component		
	1	2	3
Cu	.953		
Pb	.718		
Zn	.958		
Ni	.880		
Co		.881	
Mn			.645
Fe		.906	
As			.960
Cd	.831		
Cr	.829		
Hg		.739	
Ag	.684		
Al		.977	
Mg		.742	
Se			.737
Mo			.725
Au		.996	
Sr			.871
TOC	.998		
BOM	.942		

Table 12 Correlation of PTEs detected in the Middle basin.

	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr	Hg	Ag	Al	Mg	Se	Mo	Au
Cu	1																
Pb	.928*	1															
Zn	.912*	.946*	1														
Ni	.892*	.665	.716	1													
Co	.915*	.744	.757	.967**	1												
Mn	.849	.875	.978**	.672	.670	1											
Fe	.917*	.936*	.839	.731	.851	.711	1										
As	.504	.702	.512	.106	.152	.468	.554	1									
Cd	.837	.919*	.983**	.594	.626	.986**	.755	.570	1								
Cr	.984**	.860	.835	.942*	.961**	.758	.902*	.404	.733	1							
Hg	.189	.341	.503	-.035	-.115	.647	.000	.378	.643	.033	1						
Ag	.290	.598	.463	-.169	-.084	.445	.399	.907*	.571	.145	.559	1					
Al	.814	.577	.634	.971**	.973**	.565	.709	-.063	.488	.887*	-.194	-.307	1				
Mg	.911*	.765	.749	.935*	.994**	.643	.891*	.194	.615	.957*	-.165	-.037	.950*	1			
Se	.897*	.833	.900*	.851	.922*	.834	.867	.191	.813	.886*	.153	.105	.861	.918*	1		
Mo	.138	.023	-.184	.141	.042	-.211	.049	.439	-.215	.196	-.288	.084	.013	.045	-.280	1	
Au	.995**	.902*	.866	.908*	.928*	.794	.915*	.494	.779	.994**	.105	.246	.834	.926*	.872	.213	1
Sr	.886*	.667	.751	.993**	.958*	.721	.711	.070	.638	.925*	.043	-.169	.966**	.920*	.879*	.045	.891*
TOC	.745	.472	.520	.951*	.938*	.451	.632	-.138	.364	.839	-.298	-.413	.989**	.914*	.778	.088	.776
BOM	.656	.360	.469	.918*	.878*	.432	.501	-.293	.322	.750	-.237	-.528	.965**	.837	.741	-.024	.679

Table 13 CA proximity matrix of PTEs detected in the Middle basin.

Proximity Matrix

Case	Matrix File Input																
	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr	Hg	Ag	Al	Mg	Se	Mo	
Cu	0.000	.576	.705	.865	.682	1.205	.667	3.966	1.306	.125	6.486	5.678	1.488	.711	.825	6.894	
Pb		0.000	.431	2.680	2.051	.998	.508	2.386	.651	1.120	5.270	3.216	3.385	1.879	1.338	7.819	
Zn			0.000	2.268	1.942	.175	1.288	3.902	.137	1.320	3.980	4.292	2.930	2.006	.798	9.469	
Ni				0.000	.263	2.624	2.154	7.150	3.248	.463	8.280	9.349	.232	.517	1.189	6.870	
Co					0.000	2.638	1.191	6.784	2.996	.315	8.920	8.676	.219	.050	.627	7.667	
Mn						0.000	2.315	4.252	.114	1.932	2.823	4.441	3.479	2.859	1.329	9.687	
Fe							0.000	3.569	1.959	.786	7.998	4.810	2.325	.870	1.063	7.611	
As								0.000	3.443	4.767	4.978	.745	8.503	6.448	6.474	4.484	
Cd									0.000	2.140	2.854	3.434	4.093	3.081	1.495	9.719	
Cr										0.000	7.736	6.841	.907	.346	.911	6.433	
Hg											0.000	3.530	9.548	9.319	6.777	10.303	
Ag												0.000	10.457	8.295	7.160	7.325	
Al													0.000	.396	1.115	7.893	
Mg														0.000	.653	7.636	
Se															0.000	10.244	
Mo																0.000	
Au																	
Sr																	
TOC																	
BOM																	

Table 14 PCA rotated component matrix in the Middle basin. Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. ^a; Rotation converged in 5 iterations.

Rotated Component Matrix^a

	Component		
	1	2	3
Cu	.852		
Pb		.761	
Zn	.672		
Ni	.979		
Co	.986		
Mn		.649	
Fe	.755		
As		.941	
Cd		.744	
Cr	.918		
Hg		.622	
Ag		.959	
Al	.997		
Mg	.968		
Se	.878		
Mo			-.902
Au	.871		
Sr	.971		
TOC	.981		
BOM	.944		

Table 15 Correlation of PTEs detected in the Upper basin.

	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr	Hg	Ag	Al	Mg	Se	Mo	Au	Sr
Cu	1																	
Pb	,871	1																
Zn	,823	,503	1															
Ni	,596	,912	,170	1														
Co	,768	,959*	,466	,948	1													
Mn	,709	,951*	,359	,980*	,993**	1												
Fe	,922	,866	,836	,680	,875	,811	1											
As	-,156	,134	-,067	,409	,409	,420	,227	1										
Cd	,766	,927	,267	,851	,809	,832	,641	-,129	1									
Cr	,619	,925	,166	,996**	,937	,970*	,670	,329	,892	1								
Hg	-,794	-,672	-,450	-,394	-,435	-,419	-,506	,644	-,808	-,464	1							
Ag	,442	,456	-,021	,311	,204	,242	,104	-,717	,739	,394	-,882	1						
Al	,613	,177	,935	-,190	,121	,004	,587	-,235	-,029	-,191	-,326	-,112	1					
Mg	,564	,894	,146	,999**	,943	,976*	,664	,448	,827	,992**	-,351	,275	-,215	1				
Se	,505	,047	,883	-,311	0,000	-,118	,484	-,242	-,157	-,315	-,231	-,187	,991**	-,333	1			
Mo	,574	,840	,012	,861	,740	,792	,459	-,070	,966*	,901	-,694	,742	-,287	,844	-,407	1		
Au	-,822	-,732	-,870	-,560	-,792	-,714	-,970*	-,358	-,439	-,531	,306	,135	-,659	-,550	-,578	-,245	1	
Sr	-,710	-,472	-,480	-,136	-,210	-,179	-,383	,798	-,620	-,211	,963*	-,837	-,449	-,090	-,381	-,482	,210	1
TOC	-,475	-,615	-,497	-,670	-,800	-,764	-,775	-,790	-,295	-,610	-,112	,420	-,240	-,685	-,174	-,214	,847	-,28
BOM	,561	,291	,900	,070	,375	,266	,730	,289	-,048	,028	-,022	-,452	,861	,065	,843	-,273	-,860	-,05

Table 16 CA proximity matrix of PTEs detected in the Upper basin.

Proximity Matrix

Case	Matrix File Input																
	Cu	Pb	Zn	Ni	Co	Mn	Fe	As	Cd	Cr	Hg	Ag	Al	Mg	Se	Mo	
Cu	0.000	.776	1.060	2.426	1.394	1.745	.466	6.933	1.406	2.284	10.765	3.347	2.321	2.616	2.973	2.556	
Pb		0.000	2.983	.529	.247	.294	.803	5.195	.438	.448	10.030	3.262	4.936	.637	5.715	.960	
Zn			0.000	4.977	3.205	3.848	.983	6.405	4.399	5.006	8.702	6.128	.392	5.122	.700	5.929	
Ni				0.000	.309	.123	1.919	3.546	.893	.023	8.365	4.133	7.141	.007	7.865	.833	
Co					0.000	.043	.751	3.545	1.145	.376	8.608	4.774	5.273	.343	6.000	1.562	
Mn						0.000	1.132	3.482	1.010	.177	8.515	4.550	5.978	.145	6.711	1.248	
Fe							0.000	4.640	2.155	1.982	9.037	5.377	2.479	2.016	3.095	3.249	
As								0.000	6.776	4.028	2.137	10.300	7.408	3.311	7.450	6.421	
Cd									0.000	.647	10.850	1.567	6.174	1.040	6.943	.205	
Cr										0.000	8.785	3.639	7.149	.050	7.891	.591	
Hg											0.000	11.293	7.953	8.105	7.384	10.163	
Ag												0.000	6.672	4.352	7.122	1.548	
Al													0.000	7.288	.052	7.723	
Mg														0.000	7.997	.936	
Se															0.000	8.444	
Mo																0.000	
Au																	
Sr																	
TOC																	
BOM																	

Table 17 PCA rotated component matrix in the Upper basin. Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. ^a;Rotation converged in 5 iterations.

Rotated Component Matrix^a

	Component		
	1	2	3
Cu		.651	
Pb	.920		
Zn		.967	
Ni	.999		
Co	.959		
Mn	.986		
Fe		.708	
As	.416		
Cd	.848		
Cr	.994		
Hg			-.887
Ag			.926
Al		.971	
Mg	.998		
Se		.951	
Mo	.850		
Au			-.798
Sr			-.939
TOC			.558
BOM		.954	

Figures

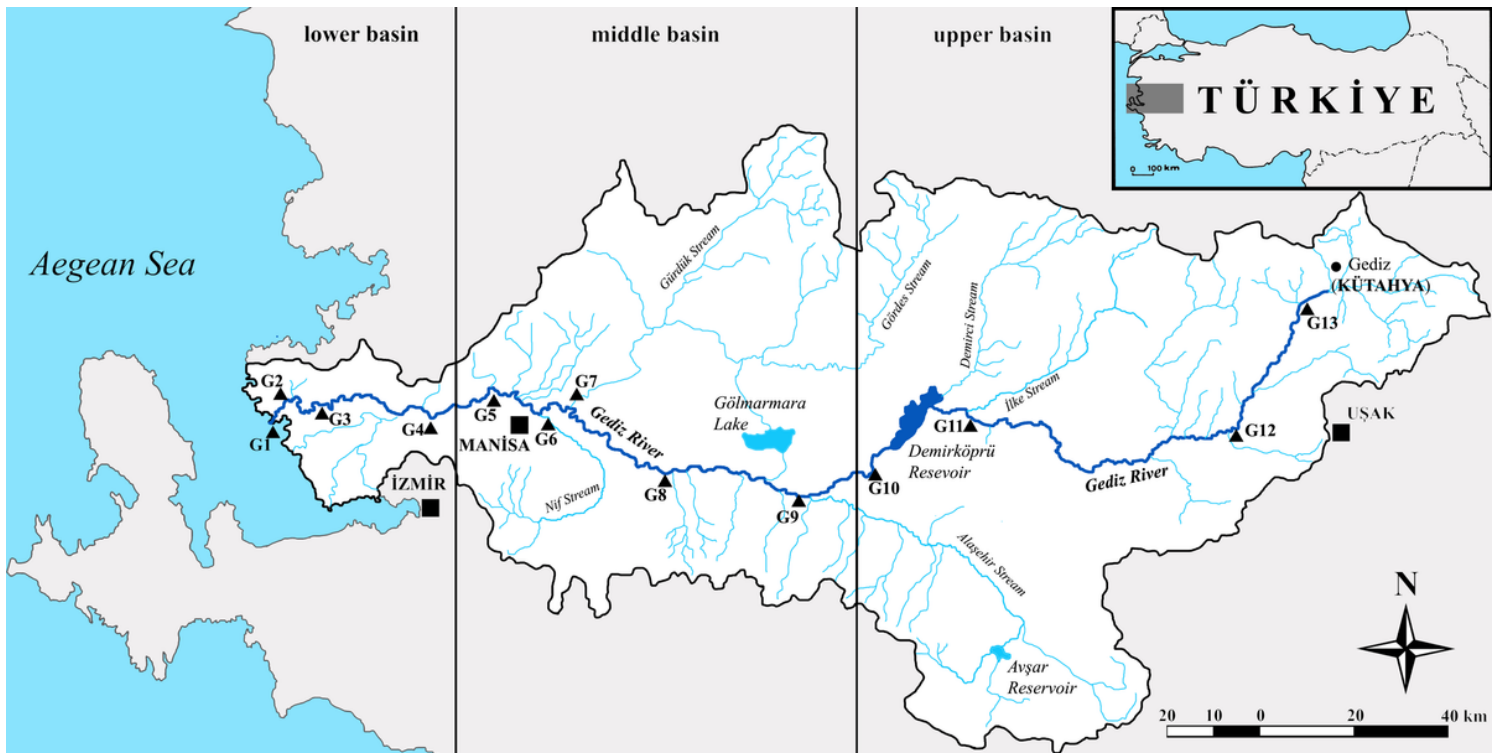


Figure 1

The study area in Gediz River (Aegean region/Türkiye)

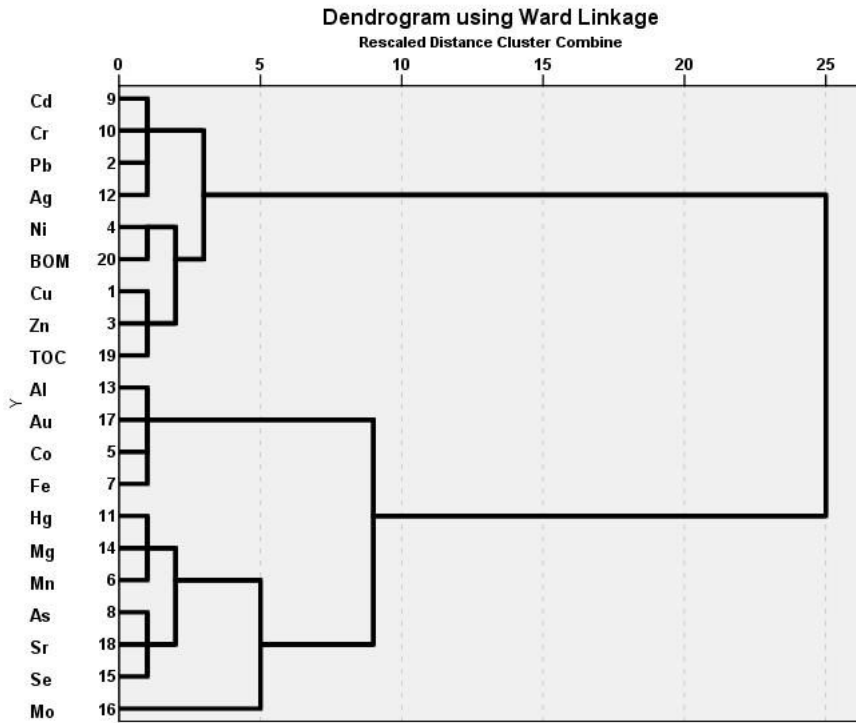


Figure 2

Cluster analysis of Lower basin.

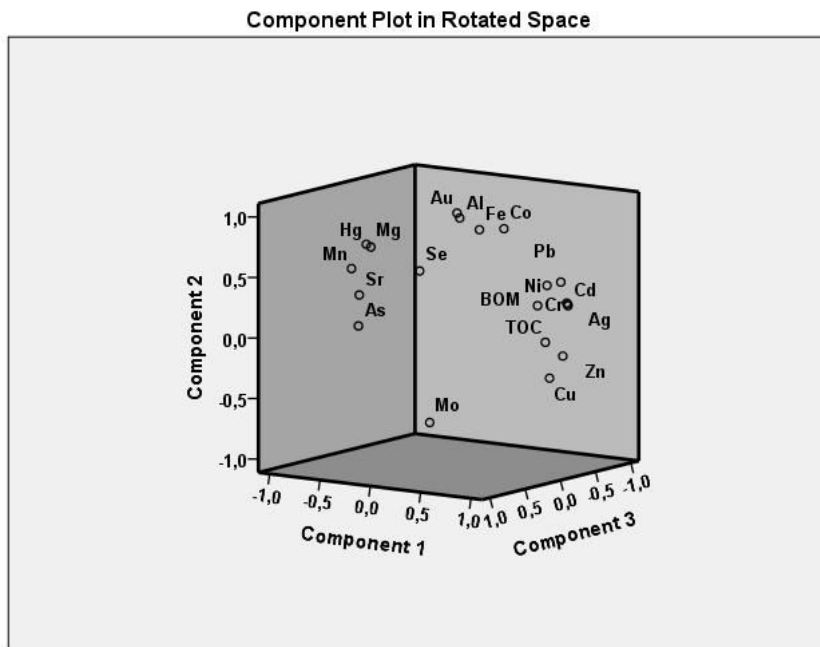


Figure 3

PCA analysis of Lower basin.

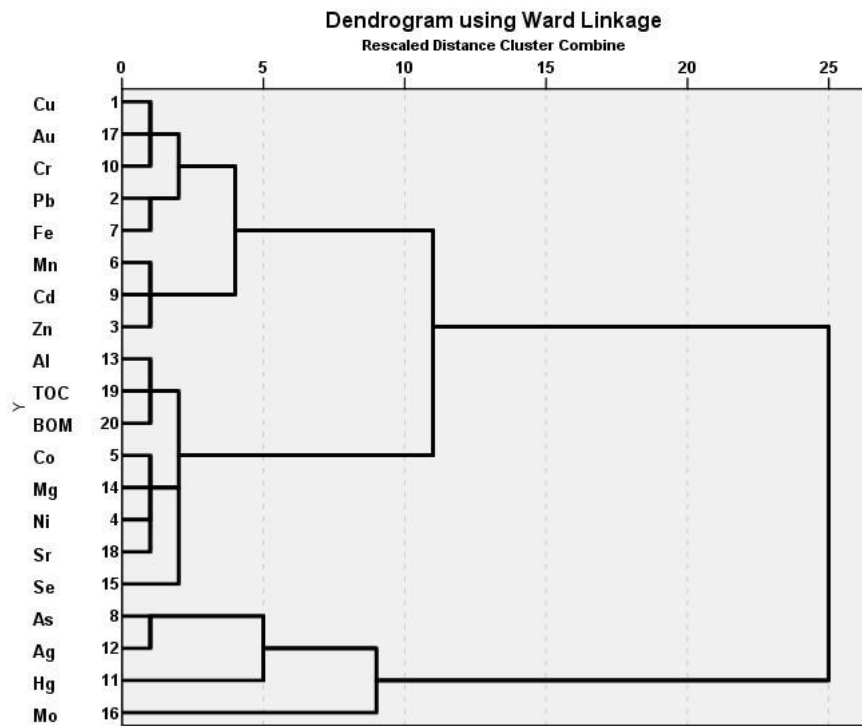


Figure 4
Cluster analysis of Middle basin.

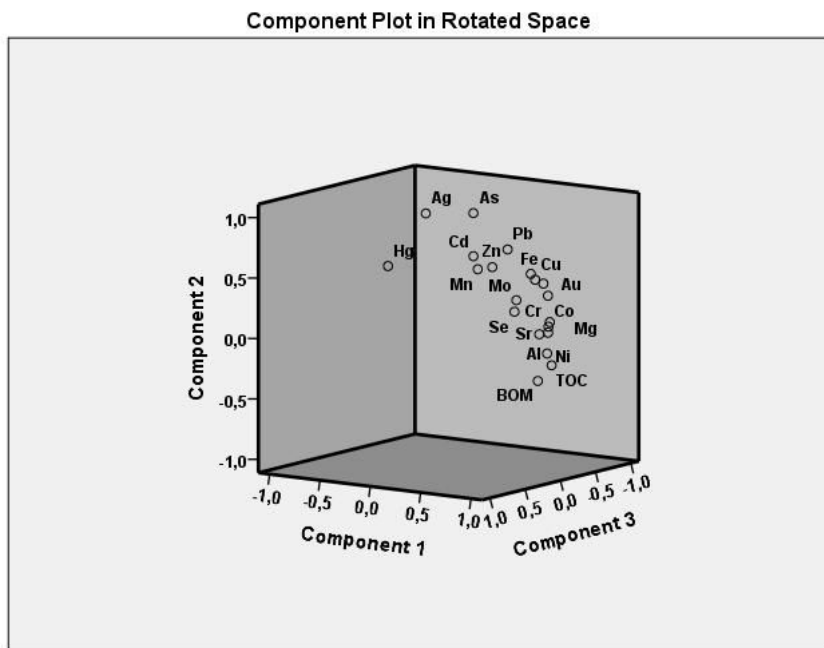


Figure 5
PCA analysis of Middle basin.

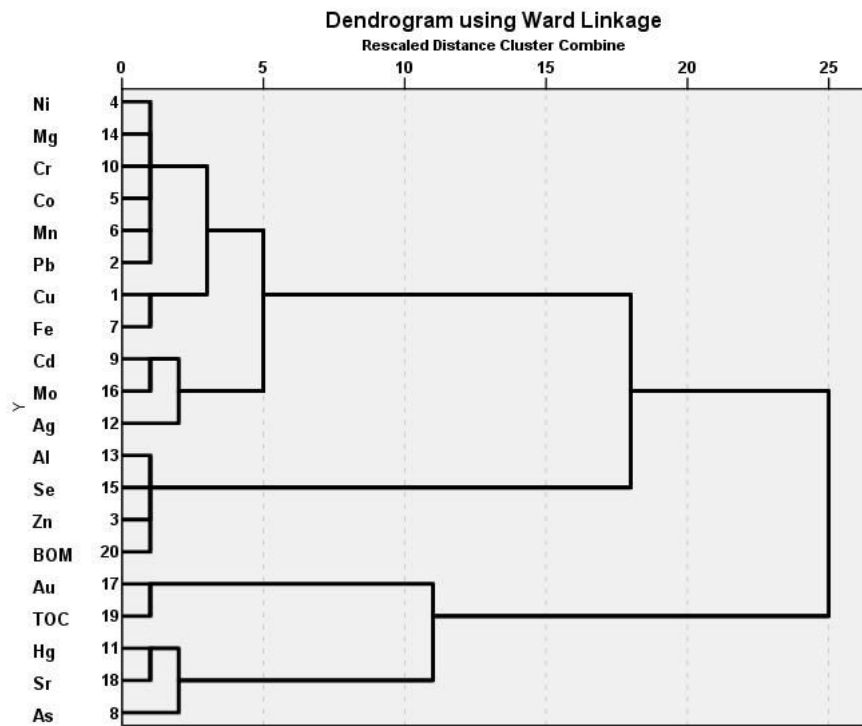


Figure 6

Cluster analysis of Upper basin.

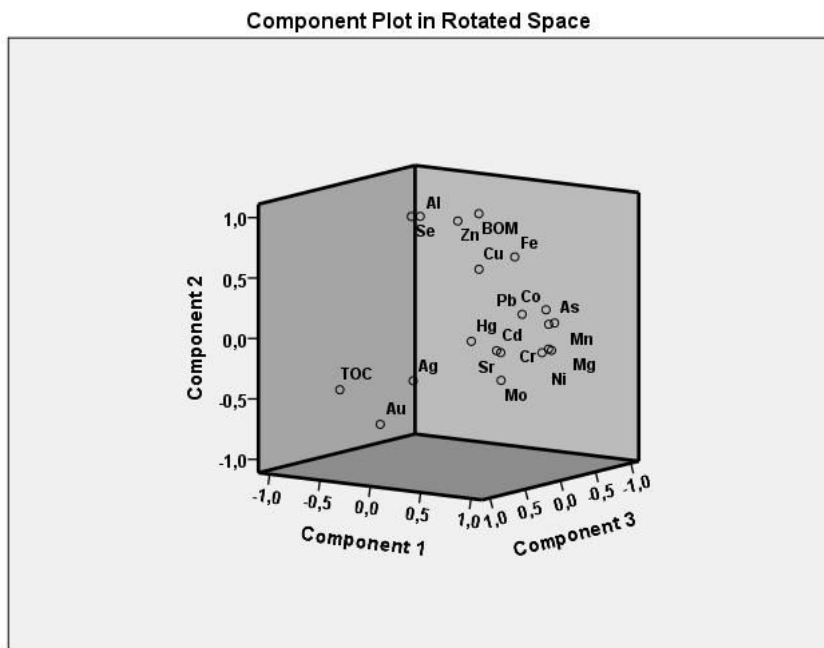


Figure 7

PCA analysis of Upper basin.