Heavy Metals in Water and Surface Sediments of the Fenghe River Basin, China: Assessment and Source Analysis

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Heavy metals in water and surface sediments of the Fenghe River Basin, China: Assessment and Source Analysis

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Abstract

This paper combines environmental science, inorganic chemistry, water quality monitoring and other disciplines, and uses several representative evaluation methods (WQI, Pn, I-geo, RI) for heavy metals in water and sediments. A preliminary assessment and source analysis of heavy metals (Cd, Cr, Fe, Mn, Zn, Cr, Ti, Ni, Cu, As, Pb, Sr) in water and surface sediments of the Fenghe River Basin, Shannxi Province, China was carried out in this study. Results indicate that most of the heavy metals in water are below national water quality standards. Exceptions include Mn, which exceeds national tertiary standards and Cr, which exceeds national drinking water standards. Most heavy metals in the sediments exceed the environmental standard values except Ni. Water quality index (WQI) and Nemero index (Pn) showed the same trend in contamination levels of sampling sites. According to the Geological Accumulation Index method (I-geo) and the Potential Ecological Risk Index method (RI), high concentrations of Cd poses a high ecological risk in some sampling locations. Pearson Correlation Analysis (CA), Hierarchical Clustering Analysis (HCA), Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF) models are used to explore the relationships and sources of heavy metals. In general, upstream sources are similar, and middle and lower reaches are easily clustered into a large category except for some specific sampling points. For example, metals in sampling site FHK mainly come from surrounding residents and farms and heavy metals attributes in sampling site SLQ relate to the fact that municipal sewage is collected and treated. The factors or sources of heavy metals in water and sediment are revealed in detail through PMF models. In the water, the average contribution rate of these four source factors for heavy metals is 36.8%, 11.7%, 9.4% and 42.0%, while the average proportion of these four factors for heavy metals in sediment is 8.0%, 29.2%, 23.9% and 38.9% respectively. Results show that the main sources of pollution in the region are urban construction and transportation, electronics industry, machinery manufacturing, tourism and agriculture. These sectors should therefore be given sufficient attention in the prevention and management of heavy metal pollution.

Keywords: Fenghe River Basin, heavy metal, surface water and sediment, assessment, source pollution

1. Introduction

Heavy metals, as common pollutants in the water environment, are toxic, persistent and bio-accumulative (Pekey et al. 2004). Excessive doses of heavy metals threaten the environment and humans through direct exposure and food chain enrichment (Zhang et al. 2016; Lin et al. 2016). Sediments are sources and sinks of heavy metals. Factors such as temperature, pH, dissolved oxygen, redox potential and electrical conductivity control the release of heavy metals from sediments, causing secondary pollution to water quality (Lin and Chen 1998; Bertin and Bourgm 1995; Li et al. 2014; Ndimele 2012). Heavy metal pollution is caused by natural factors, such as weathering and riverbed erosion, and human activities, especially mining, mechatronic industries, urban construction, urban flood, urban transportation, and agriculture (Mohamed 2007; Mu et al. 2020; Ke et al. 2015; Zhuang and Gao 2015). Comprehensive analysis of status, potential risks and sources of heavy metals in water and sediments is therefore essential for environmental control and management.

Heavy metal pollution in rivers has aroused widespread concern due to the rapid development of society (Li and Zhang 2010). By the mid-19th century, about 40% of Britain's rivers and lakes had been polluted by human behavior (Li et al. 2014). Approximately 85% of heavy metals are ultimately enriched in surface sediments on a global scale (Zahra et al. 2014). In Europe, North America, Africa and Asia, heavy metal pollution has been studied extensively, especially the rivers Rhine and Meuse in Western Europe (Wijnhoven et al. 2006), the Danube River (Sunjog et al. 2012), the Mississippi River in America (Grabowski et al. 2001), the Nile River in Egypt

(Elbouraie et al. 2010)，the Soan in Pakistan (NAZEER et al. 2014), the Subarnarekha River in India (Giri and Singh 2014), the Yellow River (Sun et al. 2016) and the Yangtze Rivers (Guo and Yang 2016) in China. In China, about 6 of the 21 major cities along the Yangtze River (Panzhihua, Yichang, Nanjing, Wuhan, Shanghai, Chongqing) have a pollution rate of heavy metals of 65% (Zhang and Shu 2010).

Faced with such serious heavy metal pollution, a great deal of research has assessed aspects of contamination, such as migration and transformation processes, bioaccumulation, and toxicity (Pandey and Bhattacharya 2016; Ogendi et al. 2010; Simpson and Spadaro 2016). However, such studies require complex laboratory analysis which affect data accuracy and precision, are time intensive, and are inapplicable at large scales. The total concentration of heavy metals can be used to evaluate the status of heavy metal pollution, potential ecological risks and sources (Villanueva and Ibarra 2016). In addition to comparison with national water quality standards, evaluation methods for heavy metals in water are well-established and include the single factor water quality index method (Pi) and multi-factor Water Quality Index method (WQI) (Cheng and Dan 2011; Parparov et al. 1992), and the Nemero index method (Pn) (Tianxiang et al. 2018). Similarly, there are many methods for evaluating heavy metals in sediments, including representative methods such as the Enrichment Factor method (EF) (Ergin et al. 1991), the Geological Accumulation Index method (I-geo) (Muller 1969), the Pollution Load Index method (PLI) (Angulo 1996), the Potential Ecological Risk Index method (RI) (Hakanson 1980) and the Sediment Quality Guidelines (SQG) (Macdonald et al. 2000). The Composite Element

Index has a cooperativity effect and can comprehensively evaluate regional pollution status and potential risks. Thus, WQI, Pn, I-geo, RI were selected for this study.

In the source analysis of heavy metals, Correlation Analysis (CA) is used to determine significant correlations between heavy metals through the correlation coefficient (Zhang et al. 2015). The greater absolute value of the correlation indicates a higher correlation between the two variables. Hierarchical Cluster Analysis (HCA) is based on the degree of similarity between variables, which is classified into categories (Facchinelli et al. 2001). Principal Component Analysis (PCA) reduces dimensionality in data to uncover trends (Kaidao et al. 2012). CA, HCA, and PCA can be used in combination to assess contaminant sources (Comero et al. 2011). However, the data required by software (SPSS) is sensitive and needs to be standardized (Pornsawai et al. 2013). The Positive Matrix Factorization (PMF) model (Anttila et al. 1995) is applied to study the contribution rate of each source more accurately and quantitatively. An advanced statistical method, PMF uses the least square method to estimate each value and analyze the uncertainty of each value. Although this model has been widely used in atmosphere studies (Jaeckels et al. 2007; Saraga et al. 2010; Yuan et al. 2012), application to pollution in water and sediments is rare.

Representative sampling points were selected to systematically study the heavy metal pollution in the Fenghe River Basin (FRB). The main goals of this study are (1) to describe the physical and chemical parameters and the concentration of heavy metals in water and surface sediments, (2) to comprehensively evaluate the pollution status of heavy metals in the water through the comprehensive Water Quality Index

(WQI) and the Nemero Index (Pn), as well as the accumulation status and potential risks of heavy metals in sediments through the Geological accumulation Index (I-geo) and Potential Risk Index (RI) methodology, and (3) to qualitatively and quantitatively analyze the potential sources and contribution rates of heavy metal pollution by multivariate statistical analysis and the Positive Matrix Factorization (PMF) model.

2. Materials and methods

2.1 Study area and sample collection

As the first tributary of the south bank of the Wei River, the largest tributary of the Yellow River, the Fenghe River has a total length of 78km and a watershed area of 1460km (Huaien et al. 2016). Its main tributaries include the Taipingyu, Fengyu, Gaoguanyu and the Yu River. Urban expansion and population growth have led to the implementation of the Hei River Water Diversion Project (Zhang et al. 2018; Wang and Tang 2012). As a result of upstream tourism, the construction of towns in the middle and lower reaches and industrial development have led to deterioration of water quality and ecology in the Fenghe River (Zhang et al. 2014).

Eight monitoring stations were investigated in the FRB: Fengyu (FY), Gaoguanyu (GGY), Taipingyu (TPY), Yurufeng (YRF), Fenghekou (FHK), Qinduzhen (QDZ), Yanjiaqu (YJQ), and Sanliqiao (SLQ). The layout of sampling points in the study area is given in **Fig. 1**. Monitoring stations cover representative control sections of hydrological monitoring stations and major tributary intersections from upstream to downstream. As three stations consist of sand and gravel, sediment samples were collected from five sampling locations of the Fenghe River in August, 2018. Water samples were collected from eight sampling locations in October and December 2018. We use the average concentration of heavy metals in water from two months.

2.2 Sample collection and analysis

In this study, water (USEPA 2013) and sediment (USEPA 2014) methods were used to collect samples. An YSI multi-parameter water quality analyzer (Germany) analyzed the physicochemical properties (temperature (℃), pH, dissolved oxygen (DO), redox potential (ORP), electrical conductivity (EC)) of water. Samples (500 ml) were collected with polyethylene plastic bottles and sealed, and then brought back to the laboratory under 4 ℃. Water samples were filtered through a 0.45um filter membrane and put in a 10 ml centrifuge tube. The water samples were centrifuged using a low-speed centrifuge for 10 min under 3500 r/min, and after 2% HNO_3 was added and refrigerated for preservation under 4 ℃. Surface sediment samples were sealed in polythene bags and returned to the laboratory. Samples were put in an oven at 105 ℃ for 12 h after natural drying, lightly crushed, sieved through 200-mesh nylon sieve and sealed in a polyethylene bag.

Pretreatment of sediment samples: The 50mg samples were weighed and placed in polytetrafluoroethylene tanks. Then, 0.5 ml HNO_3 and 1 ml HF were added into the tanks and the samples were put on an electric heating plate for 145 ℃ to remove silicon until the samples were dry. In addition, 1 ml HNO_3 and 1 ml HF were continuously added into the tanks for 5 h under 145 ℃. The treated samples were cooled to room temperature overnight and then steamed for 40 min. A few drops of H_2O_2 were added to remove the organic matter and 1 ml HNO_3 was added to steam. Finally, 2.5ml 40% HNO_3 were added into the samples for 4h, and then the samples were fixed to 50ml with 40% HNO_3. Total heavy metal content in the treated samples was determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

All reagents used in the experiment were analytical reagents. Calibration curves were determined with correlation coefficients in the range of 0.9997-0.9999. In order to ensure the accuracy and precision of data, the standard solution (GSB04-1767-2004) was provided by the national nonferrous metals and electronic materials analysis and testing center for quality control. Standard recovery rates ranged from 87.53% to 102.29%.

2.3 Evaluation method

Evaluation standards for heavy metals in water refers to the surface water environmental quality standard GB3838-2002. The Water Quality Index method (WQI), Nemero Pollution Index method (Pn), Geological Accumulation Index method (I-geo) and Potential Ecological Risk Index method (RI) were selected to evaluate the heavy metal pollution situation in the FRB.

2.3.1 Water quality index method and Nemero index

The water quality index is divided into "single factor pollution index method" and "comprehensive pollution index method". The former indicates the pollution level of a single heavy metal, while the latter takes into account the synergistic effects of pollutants (Duodu et al. 2016; Yan et al. 2016). The calculation formula was as follows (1) (2):

(1) Single factor pollution index: Pi=$\frac{C_i}{Q_i}$

Where *Ci* is the heavy metal measured concentration; *Qi* the reference value of the element.

(2) Comprehensive pollution index: WQI=$\frac{1}{n}\sum_i^n P_i$

Where *Pi* is the single heavy metal pollution index; *n* types of elements.

The Nemero comprehensive pollution index method can reflect current heavy metal pollution in water and the different contributions of various heavy metals. The calculation formula was as follows (3):

$$(3)\ P_n = \sqrt{\frac{\max(Pi)^2+\text{ave}(Pi)^2}{2}}$$

2.3.2 Geological accumulation index method

Geological accumulation index method (I-geo) (Muller 1969) is widely used to evaluate heavy metal pollution in sediments. It reflects both the natural variation characteristics of heavy metal distributions, but also identifies the impact of human activities on the environment. The equation is described as below:

$$I\text{-}geo= log_2[C_i/(k * B_i)]$$

Where: C_i is the heavy metal measured concentration; B_i is the geochemical background value of the heavy metal; *k* is the diagenetic coefficient, the value is taken to be 1.5 in order to explain the possible changes in the environmental background values; *I-geo* is the geological accumulation index.

2.3.3 Potential ecological risk index method

The index method of potential ecological risk[33] (Hakanson 1980) comprehensively considers the ecological, environmental and toxicological effects of heavy metals and is calculated as follows:

$$E_r^i = T_r^i \times (C^i / C_n^i)$$

$$\mathrm{RI} = \sum_i^n E_r^i$$

Where Ci is the heavy metal measured concentration; C_n^i is the reference value of the element; T_r^i is the toxic reaction coefficient of each element (Cu=Pb=Ni=5, Cd=30, Cr=2, Zn=1, Ti=1, Mn=2) (Hakanson 1980; Sijin et al. 2015; Islam et al. 2015); E_r^i is the single element potential ecological risk factor. Classification standards of WQI, I-geo, and RI are presented in **Table1.**

2.4 Statistical analysis

IBM SPSS Statistic 22.0 was used for statistical analysis. Pearson Correlation Analysis (CA) is used to analyze the correlation between the various elements. Hierarchical Clustering Analysis (HCA) is used to group the sampling points according to the metal concentration of the sampling points. Variables with close distance were clustered first, followed by the variables with far distances until each variable is in an appropriate class. Intergroup link method and square Euclidean distance, recognized as the most stable method of systematic clustering analysis, are used in this study. Principal Component Analysis (PCA) focuses on explaining the total variance of each variable through dimensionality reduction (Shin and Lam 2001; Tetsuro et al. 2009). In this study, Principal Component Analysis (PCA) explores the relationship between elements by extracting a small number of potential factors and analyzes the similarity of distribution sources of heavy metals.

2.5 Positive matrix factorization (PMF)

Positive Matrix Factorization (PMF), a multivariable factor analysis method (Paatero and Tapper 1993), is used to analyze the sources of heavy metals in this study (Peng et al. 2016). As the original sample data matrix $X(x\times j)$ was decomposed into the product of factor contribution matrix $G(i\times k)$ and factor profile matrix $F(k\times j)$ by the PMF model, as well as the sum of residuals matrix $E(i\times j)$. The calculation equation is as follows:

$$\mathrm{X} = \mathrm{G} \times \mathrm{F} + \mathrm{E}$$

$$\mathrm{x}_{ij} = \sum_{k=1}^{p} \mathrm{g}_{ik} \times \mathrm{f}_{kj} + \mathrm{e}_{ij}$$

Where, x_{ij} is the concentration of sample component j at the i sample point (mg/kg); g_{ik} is the source k contribution concentration at i sampling point (mg/kg); f_{kj} represents the contribution of source k to sample component j; e_{ij} represents the residual, and p represents the number of source factors.

PMF model is iterated by the least square method, and the original matrix X is split to obtain the optimal matrix G and F, so that the objective function Q approaches the degree of freedom value, namely $i\times j$. Q is defined as follows:

$$Q = \sum\nolimits_{i=1}^{n} \sum\nolimits_{j=1}^{m} ({}^{\mathrm{e}_{ij}}/_{\mathrm{u}_{ij}})^2$$

Where, u_{ij} represents the uncertainty of sample component j, and e_{ij} represents the residual.

3. Results and discussion

3.1 Water quality parameters

The physical and chemical parameters of water, such as temperature (°C), pH, dissolved oxygen (DO), redox potential (ORP), and electrical conductivity (EC) are presented in **Table 2**. Physical and chemical parameters are important to understand given their role in supporting aquatic life and environmental health. The temperature range (taken in winter) is from 6.55 to 15.05°C. Sampling sites FY and GGY have lower values than other sites due to the upstream location and high altitude. The values of pH ranged from 7.88 to 8.49 (**Table 2**), within limits prescribed by GB3838-2002. The water quality in the Fenghe River is slightly alkaline. The average range for DO is between 5.24 and 11.25 mg/l (**Table 2**). Variability in DO may be due to aerobic and organic decomposition of aquatic organisms. Redox potential is a measurement index of water redox capacity. Higher values indicate higher oxidizability. The redox potential ranged from 138.62 to 176.77mV. The electrical conductivity represents the content of soluble impurities in water, and higher values represent worse water quality. The lowest value of 0.07 (ms /cm) for electrical conductivity is located in sampling site FY, which is in the upstream, while the highest value of 0.95 (ms /cm) appears in sampling site YRF, which may be the result of discharge from surrounding enterprises and residential wastewater.

3.2 Heavy metal concentration in water and sediment

The concentrations of heavy metals in water are shown in **Table 3**. At present, there are some studies on heavy metals in water, possibly because they precipitate quickly and tend to accumulate in sediments (Simpson and Batley 2010). However, once secondary contamination occurs, trace concentrations may endanger aquatic organism, accumulate in the foodweb, and eventually pose a threat to human health (Salem et al. 2014). The average concentration of heavy metals in water decreases according to: Sr >Fe> Mn> Zn> Cr >Ti >Ni >Cu> As> Pb >Cd. The highest concentration of Sr was 322.85 ug/L in sampling site FHK and the lowest concentration of Sr was 54.12 ug/L in sampling stie FY. The average concentration of Fe was observed with the value of 7.29 ug/L for sampling site FY and 269.15 ug/L for sampling site TPY. The highest concentration of Fe is slightly below Class I water quality standards and within the drinking water standard range. The concentration of Mn ranges from 0.8 ug/L to 239.8 ug/L. The concentrations of Mn in sampling sites TPY, FHK and QDZ exceeded the three standards of surface water (GB3838-2002). The average concentration of Zn was between 7.34 and 19.86 ug/L. Zn can be used as a nutrient at low concentrations, but exceeding the threshold can cause toxicity to aquatic organisms. Interestingly, the highest value of Zn was observed at sampling site YRF site, which might be attributed to wastewater discharge from an electronics factory. The concentrations of Cr were uniformly distributed, ranging from 6.13 to 7.56 ug/L, which were lower than the Class I surface water standards (GB3838 2002) but higher than the WHO standard (5 ug/L) (**Table 3**). The highest concentration of Ti, Ni and Pb were 8.54, 3.95, 1.51 ug/L, respectively. They are all observed in sampling site TPY, probably because it is surrounded by residential areas, machinery and equipment companies. The concentration range of Cu (1.54-2.92 ug/L), As (0.2-2.66 ug/L), and Cd (0.03-0.1 ug/L) are lower than Class I water quality standards

(GB3838 2002). The highest concentrations of heavy metals are in the middle reaches of the river, except for Cd. Cd is a highly mobile and toxic element that is easily released into the environment (Li et al. 2012). In general, concentrations of heavy metals in water are not high in the downstream, such as sampling site SLQ, due to pollution source control during recent sponge city development. In general, concentrations of heavy metals in water are lower than in sediment, possibly due to the fluidity and dilution of the water (Mohiuddin et al. 2012).

The concentration of heavy metals in sediment is shown in **Table 4**. The average concentration of heavy metals are between 615.25-736.40 mg/kg for Mn, 221.50-409.00 mg/kg for Sr, 182.20-281.30 mg/kg for As, 74.33-125.10 mg/kg for Zn, 50.66-79.01mg/kg for Cr, 26.56-33.33 mg/kg for Pb, 18.21-48.10 mg/kg for Cu, 21.06-34.01 mg/kg for Ni, 0.18-0.48 mg/kg for Cd. They decreased successively according to: Mn> Sr> As >Zn> Cr >Pb> Cu> Ni >Cd. Average concentration of these elements (Mn, Sr, As, Zn, Cr, Pb, Cu, Cd) exceeds background values of Shaanxi soils. Ni is lower than the soil environmental background value of 28.8 mg/kg in Shannxi province, but higher than the average value 25.6 mg/kg for the Wei River (**Table 4**). The excessive multiples of heavy metal concentration for the maximum point position concentration of Mn, Sr, As, Zn, Cr, Pb, Cu, Cd are 0.32, 1.46, 24.34, 0.80, 0.26, 0.56, 1.25, 4.14. In addition to the proportion exceeding the standard value of heavy metal concentration for sampling points were 40% for Cr, Ni and 60% for Cu, as well as 100% for Mn, Sr, As, Zn, Pb, Cd. Pb and As are above average shale values (**Table 4**). The maximum values of Mn, As, Zn, Cr, Pb, Cu and Ni were found at the sampling site FHK, Ti and Cd in sampling site SLQ, and Sr in sampling site TPY. The FHK sampling site is close to farmland, residential areas and surrounding materials technology companies, which reflect complex sources of heavy metals. There are automobile, printing and titanium companies around the SLQ sampling site, which may also explain high concentrations of Ti and Cd. At the TPY sampling point, the mechanical, petroleum, and metallurgical industries may be sources of Sr contamination.

3.3 Evaluation of heavy metal pollution in water and sediment

Water Quality Index (WQI) evaluation for the FRB is presented in **Fig. 2 a**. The WQI values of each sampling point from upstream to downstream are 0.15, 0.19, 0.56, 1.39, 0.40, 0.39, 0.74, and 0.43 respectively. Among them, WQI value of sampling site YRF is within the range of 1~2, which belongs to low pollution. None of the other sampling sites were contaminated with heavy metals. According to the Pn of each sampling point (**Fig. 2 b**), YRF and YJQ sampling points are highly polluted. The pollution levels of TPY and YJQ sampling points are equivalent with moderate pollution indicators. The Pn of FHK and QDZ sampling points are 0.99 and 0.89, indicating low pollution levels (between 0.7 and 1). Nemero index evaluation is basically consistent with an overall pollution trend of: YRF>YJQ>TPY>SLQ>FHK>QDZ>GGY>FY. The overall pollution trend of the FRB is that the middle reaches are the most seriously polluted, followed by the downstream and the upstream. However, the pollution degree obtained by different evaluation methods is somewhat different. For example, the WQI of YRF site shows low pollution while Pn shows high pollution. The WQI of YJQ, TPY and SLQ sites are no-pollution while Pn shows high-pollution, medium-pollution, and medium-pollution respectively. The WQI of FHK and QDZ sites are no-pollution while Pn shows low pollution. WQI reflects the average pollution level of multiple heavy metals. Pn considers the average pollution level and the influence of high heavy metal concentration.

The calculated Geological Accumulation Index (I-geo) and Potential Ecological Risk Index (RI) of heavy metals in sediment are summarized in **Fig3**. In **Fig3 a**, the I-geo ranged from -0.70 to 3.89. Among the studied metals, the I-geo values decreased as: As >Cd >Sr >Pb> Zn >Cu> Mn> Cr> Ni. Among these sample sites, the range of I-geo values for As was 3.45-4.08, indicating high pollution to very high pollution in this sediment. I-geo values for Cd and Sr were 0.34-1.78 and -0.17-0.72 respectively, which indicating no pollution to moderate pollution. I-geo values of other element indicated no contamination in the basin. The Potential Ecological Risk Index (RI) was also calculated and used to assess the ecological risk of heavy metals in the sediment of the FRB (**Fig3 b**). In these sampling points, the trend showed gradually decreasing pollution as: SLQ> FHK> YJQ> YRF >TPY. The Single factor ecological risk index(E_r^i) is divided into 5 levels in total: E_r^i<40, low potential risk; $40 < E_r^i \leq 80$, moderate potential risk; $80 < E_r^i \leq 160$, considerable potential risk; $160 < E_r^i \leq 320$, high potential risk; E_r^i>320, very high potential risk [62](Maanan et al. 2015). According to the calculation results, the single factor ecological risk index(E_r^i) of Cd ranges from 56.81 to 154.15, which indicats that Cd has high ecological risks in FHK and SLQ sample sites and considerable ecological risks in other sites. The E_r^i of As ranges from 164.14 to 253.42, indicating high ecological risk. From each sampling point, the RI values are in the range from 313.24 to 375.59. This result demonstrates that the study area presents moderate potential risk. According to the calculation results of WQI and RI, the pollution degrees of water and sediment are not always consistent with the ecological risk, which may be related to the complex influencing factors of heavy metal pollution. Therefore, the combination of pollution degree and ecological risk is useful for comprehensive analysis of heavy metal pollution risk.

3.4 Multivariate statistical analysis

The Pearson Correlation Analysis of heavy metals reflects the relationship between heavy metals, so as to determine the source and migration of heavy metals (Yi et al. 2012). If the correlation between elements is low, it indicates that heavy metals are affected by complex factors (Kükrer et al. 2014). Pearson Correlation Analysis (CA) between heavy metals in water and sediment is elucidated in the Pearson Correlation Matrix (**Table 5**). However, significantly positive correlations ($p<0.01$) and positive correlations of $p<0.05$ were found among different elements. Heavy metals with high correlation have similar sources. In water, Fe was found to be significantly positively correlated with Mn, Cr, Ni, Ti, but positively correlated with Sr. Ti also shows significant positive correlatation with Pb. Mn is positively correlated with Pb. Cr-Ni (0.753), Cr-Cu (0.814), Cr-Sr (0.817), Ni-Sr (0.758), Ni-Pb (0.772), Cu-Sr (0.801), As-Sr (0.802) were also positively correlated (**Table 5**). In sediment, there was significant positive correlation between Mn and Pb, Cr and Ni, Cu and Zn. Moreover, Ni and Sr exhibited a significant negative correlation of -0.979. And the Cr-Cu (0.913), Cr-Zn (0.924), Ni-Cu (0.941) and Ni-Zn (0.946) showed positive correlations in sediment. However, Cr and Sr exhibited negative correlations of -0.940 (**Table 5**).

The dendrogram of Hierarchical Cluster Analysis (HCA) are shown in **Figs. 4a** and **4b** for water and sediment respectively. In water, all sample sites can be divided into three main types. Sample sites FY, GGY are grouped into Cluster 1. Cluster 2 includes YJQ, SLQ, YRF, and QDZ. The other sites FHK, TPY fall into Cluster 3. Results show that monitoring points assigned to the same group which have similar pollution sources and backgrounds. Group 1 is mainly from the upstream and is largely uncontaminated. Group 2 is mainly distributed in the middle and lower reaches, where the YRF sampling points may reflect heavy metals from sewage outlets. Group 3 is clustered together, possibly because the rivers in the middle and upper reaches were distributed around residents, farmland and orchards. It indicates that there is a significant difference between the upstream and the middle and downstream, so that the source of heavy metals can be preliminarily determined. In sediment, the YRF, YJQ, and TPY samples in the middle stream are classified into Cluster 1, the SLQ and FHK sample sites were grouped in Cluster 2 and 3 respectively. Heavy metal pollution in the downstream area is serious, followed by the FHK sample sites, which is consistent with the result of the Potential Risk Evaluation Index (RI).

Total interpretation variance and rotation component matrix of the principal components analysis (PCA) in water and sediment are presented in **Table 6**. The extracted eigenvalues of the three principal components (PCs) or factors are all greater than 0.25. PCA reduced the dimensionality of the initial dataset to 3 components in water and 2 components in sediment, which explained 87.97% and 89.90% of the data variance, respectively. Therefore, the three factors and two factors play a very important role in explaining the heavy metal pollution in the study area. In water PC1, Mn, Fe, Ni, Pb, and Ti have the highest loadings and accounts for 42.85% of the total variance of water samples. Fe, Mn, Ti may reflect the natural distribution of the Earth's crust. Ni and Pb may be related to the electronics industry and urban transportation. PC2, Cr, Cu, As, Sr, and Cd have high loadings and account for 33.175% of the variance. As is the single dominant metal for PC3, Zn may come from pigment, plastics and some commercial activities. In sediment samples, PC1, Cr, Ni, Cu, Zn, and Sr have the highest loadings and account for 55.76% of the total variance, while, Cd, As, Ti, Mn, and Pb represent PC2 with loadings that account for 34.14% of the variance. More detailed classification and factor analysis were explored by PMF model.

3.5 Positive matrix factorization

PMF model is run in order to better determine the source of the heavy metals in the FRB in Shannxi province. The source apportionment results and factor contribution percentages of heavy metals in water and sediment are shown in **Figs. 5a** and **5b**. From the diagram, we can see the difference between the concentration of the elements and the percentage contribution. For example, in water for Factor 1, Sr has a high concentration but a low contribution rate of 17.5%. However, in sediment for Factor 1, Cd has a low concentration but a high contribution rate of 76.2%. It does not matter whether a particular metal exhibits a high concentration in a particular factor; what matters is whether the metal accounts for a large proportion in that factor. Although it cannot be denied that there is a direct relationship between concentration and percentage, it means that the percentage of heavy metals under certain factors is more significant than the concentration. As a result, heavy metal concentrations and percentages are shown in the chart through PMF models, which play a significant role in explaining and analyzing the distribution of pollution sources.

In water, Factor 1, which constitutes a moderate 36.8% of the contribution (**Fig. 6 a**), has higher loadings of Mn (60.9%), Fe (46.8%) and Ti (50.9%). The background values of these elements are high, and since they are the dominant elements in the Earth's crust (Pehlivan 2010), the may be partly derived from natural causes (recent loess of parent material) (Yang et al. 2014) and partly from companies such as the chemical machinery. This conclusion is also consistent with the results of PCA and HCA, and there is a strong correlation between these elements. Factor 2, which accounted for a lower portion (11.7%) of the contribution (**Fig. 6 a**), mainly includes As (72.6%), Sr (47.3%) and Ni (33.0%). Ni and As may be associated with some of the electronics companies that are regional distributed. Sr is an alkaline earth metal, usually in the form of $SrSO_4$ and $SrSO_3$ in the Earth's crust[67] (Jie et al. 2014). A large number of digital cathode ray tubes are derived from SR[68] (Hibbins 2000), so the source of Sr may be from YJQ sampling point. Factor 3, which explains only the contribution of 9.4% (**Fig. 6 a**), is correlated quite well with Cd (99.8%), and followed by Cr (37.9%) and Cu (31.3%). Some light industries, such as alloy, components and lubricants, can result in significant copper and chromium emissions (Mirbagheri and Hosseini 2005; Yeung et al. 2003). At the same time, Cd is closely related to fertilizers, pesticides and disinfectants (Mansour et al. 2009). The Fenghe River runs through the city center and suburbs of Xi'an city, and some enterprises, residents, farmland and orchards (vineyards and strawberry fields) are distributed around the sampling site, which may be the main sources of Cu, Cr and Cd pollution. Factor 4, which accounted for a very large percentage 42.0% of the contribution (**Fig. 6 a**), contained Zn (49.1%) and Pb (33.2%). The source of Zn and Pb are mainly from electronics industry and urban transportation. Leaded gasoline can cause water pollution of Pb through atmospheric subsidence (Miguel et al. 1997).

In sediment, the proportion of the last three factors is relatively uniform. Factor 1, which makes up the minimum proportion 8.0% of the contribution (**Fig. 6 b**), is composed essentially of Cd (72.6%). As in the case of Factor 3 in water by PMF analysis, Cd occupies the largest contribution rate. It is obvious that Cd is related to agronomic activity (fertilizer, pesticide, insecticide and disinfectant) [73,74] (Wang et al. 2015; Jian-Long et al. 2014), which is mainly distributed in the middle and lower reaches of the study area. Factor 2, which presented 29.2% of the contribution (**Fig. 6 b**), is constituted by Cu (49.5%), Zn (34.7%) and Ni (33.0%). Factor 3, which accounted for 23.9% of the contribution (**Fig. 6 b**), is made up of Cu (31.0%) and Zn (22.2%). These metals are mainly related to tourism in the upstream of the study area, the construction of towns in the middle reaches and the industry in the downstream. Each element of this factor accounts for a small proportion, indicating that it should be given less attention in future pollution control plans. Factor 4 accounted for 38.9% of the contribution (**Fig. 6 b**), and most elements are included in this factor. For example, it includes Sr (96.8%), As (63.8%), Pb (56.5%), Mn (55.6%), Ti (47.8%) and Cr (31.9%). These metals are primarily derived from human activities and are concentrated in the automobile, printing, metallurgy, materials, and petroleum machinery industries (Yang et al. 2013; Chowdhury and Maiti 2016; Loska and Wiechuła 2003).

4. Conclusion

We present a preliminary assessment and source analysis of heavy metal elements in water and surface sediment in the FRB. The concentration, distribution, enrichment characteristics, potential risks and sources of heavy metals were taken into account comprehensively. The results show that most metals do not meet national water quality standards, except for Mn which exceeds the Class III water quality standard and Cr which is higher than the drinking water standard. However, all the elements in the sediments except Ni were higher than the soil environmental background value in Shaanxi province. The results of WQI and Pn show that the most serious pollution is in sampling site YRF, possibly due to direct emissions from sewage outlets. I-geo indicates that As is highly concentrated in the sediments. E_r^i and

RI show that Cd in sediment has a high ecological risk at sampling sites FHK and SLQ and a moderate ecological risk at other sites. As in sediment has high ecological risk for all sampling stations. Results for CA, HCA, and PCA confirm the results of water and sediment analysis, although there are a few differences due to the government's control for downstream sites and some special pollution sources such as factories, businesses, residents, town building and agricultural activity (fields and orchards) in the middle reaches. The factors or sources of heavy metals in water and sediment are revealed in detail through PMF models. In the water, the average contribution rate of these four source factors for heavy metals is 36.8%, 11.7%, 9.4% and 42.0%, while the average proportion of these four factors for heavy metals in sediment is 8.0%, 29.2%, 23.9% and 38.9% respectively. Most of the river basin is influenced by human activities, mainly town construction and transportation, some light industry, machinery and electronics material companies, tourism, and agronomy. Future control and prevention should focus on these aspects in order to provide better ecological and environmental benefits for the FRB.

5. Declarations

5.1 Ethics approval and consent to participate

All procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional and/or national research committee and with the 1964 Helsinki Declaration and its later amendments or comparable ethical standards. The study was approved by National Key R&D

Program of China.

5.2 Consent for publication

Not applicable for that section.

5.3 Availability of data and materials

The data that support the findings of this study are available from Eight water quality monitoring stations in the Fenghe River Basin but restrictions apply to the availability of these data, which were used under license for the current study, and so are not publicly available. Data are however available from the authors upon reasonable request and with permission of Eight water quality monitoring stations in the Fenghe River Basin.

5.4 Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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5.6 Authors' contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Aidi Huo, Daniel Nover and Shuxin Kang. Table and Figure editing are performed by Meimei Zhou, Jiqiang Lyu and Pingping Luo. The first draft of the manuscript was written by Chengyi Xu and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Table Caption List

Table 1 Classifications of heavy metal degree of WQI, Pn,I-geo and RI.

Table 2 Water quality parameters of Fenghe river basin, Shannxi Province

Table 3 Heavy metal average concentration (ug/L) in water sample of Fenghe river basin and the reference value in water (ug/L).

Table 4 Heavy metal concentration (mg/kg) in sediment sample of Fenghe river basin and the reference background value in water (mg/kg).

Table 5 Pearson Correlation matrix between heavy metal concentrations in water and sediment

Table 6 Total interpretation variance and rotation component matrix of the principal components/factors of the Fenghe river in water and sediment samples

Table 1 Classifications of heavy metal degree of WQI, Pn,I-geo and RI.

	WQI		Pn		I-geo		RI	
classes	**Scope**	**Contamination degree**	**Scope**	**Contamination degree**	**Scope**	**Contamination degree**	**Scope**	**Ecological risk**
0	<1	Unpolluted	≤0.7	Unpolluted	0	Unpolluted	<110	low risk
1	1 ~2	Slightly polluted	0.7~1	Slightly polluted	0~1	Unpolluted to moderately	110~200	Moderate risk
2	2~3	Moderately polluted	1~2	Moderately polluted	1~2	Moderately polluted	200~400	Moderately risk
3	≥3	Heavily polluted	≥2	Heavily polluted	2~3	Moderately to highly polluted	≥400	Very high risk
4					3~4	Highly polluted		
5					4~5	Highly to very highly polluted		
6					>5	Very highly polluted		

Table 2 Water quality parameters of Fenghe river basin, Shannxi Province

Sites	**Temperature(°C)**	**Ph**	**Dissolved oxygen (DO mg/l)**	**Redox potential(ORP mV)**	**Electrical conductivity (ms/cm)**
FY	6.55	8.29	10.88	149.85	0.07
GGY	9.98	8.49	11.25	138.62	0.14
TPY	13.20	7.82	5.24	144.25	0.46
YRF	15.05	7.88	6.22	151.43	0.95
FHK	13.62	7.94	8.40	146.37	0.62
QDZ	12.60	8.06	9.80	145.92	0.67
YJQ	11.85	8.40	9.30	146.72	0.52
SLQ	11.30	8.46	9.89	176.77	0.46
Average	11.77	8.17	8.87	149.99	0.49
±SD	2.44	0.26	2.01	10.73	0.27

Table 3 Heavy metal average concentration (ug/L) in water sample of Fenghe river basin and the reference value in water (ug/L).

Sites	Mn	Fe	Cr	Ni	Cu	Zn	Cd	Pb	As	Ti	Sr
FY	0.80	7.29	6.23	0.75	1.54	10.72	0.10	0.75	0.20	0.98	54.12
GGY	4.41	34.29	6.17	0.78	1.40	11.06	0.03	0.70	0.43	1.17	104.28
TPY	239.80	269.15	7.24	3.95	1.93	11.26	0.05	1.51	0.81	8.54	281.75
YRF	99.47	227.15	7.53	2.25	2.29	19.86	0.05	1.25	2.66	4.56	262.50
FHK	134.70	175.20	7.56	3.03	2.92	8.47	0.04	0.93	1.79	3.32	322.85
QDZ	119.15	250.15	7.53	2.29	2.11	7.34	0.03	0.76	2.66	4.02	311.80
YJQ	47.85	118.70	6.69	2.08	2.13	12.81	0.03	0.91	2.48	2.42	320.80
SLQ	20.38	70.78	7.14	1.85	2.26	15.50	0.03	0.99	2.00	1.71	283.50
Average	83.32	144.09	7.01	2.12	2.07	12.13	0.04	0.98	1.63	3.34	242.70
±SD	76.59	94.57	0.54	1.00	0.44	3.74	0.02	0.26	0.95	2.31	97.21
GB3838-2002 limit value(1)*	10	300	10	---	10	50	1	10	50	---	---
WHO(2004)**	300	1000	5	70	2000	5000	3	10	10	---	---
CMC, acute***	---	---	16	470	---	120	1.8	65	340	---	---
CMC, chronic****	---	1000	11	52	---	120	0.72	2.5	150	---	---

* GB3838-2002, Environmental Quality Standard for Surface Water (GB3838-2002) (2002) China.

**WHO (2004), Guidelines for Drinking Water Quality, third ed. World Health Organization, Geneva.

***CMC, acute (Criterion maximum concentration in freshwater for National Recommended Aquatic Life Criteria) https://www.epa.gov/(EPA 2009)

****CMC, chronic (Criterion continuous concentration in freshwater for National Recommended Aquatic Life Criteria) https://www.epa.gov/ (EPA 2009)

Table 4 Heavy metal concentration (mg/kg) in sediment sample of Fenghe river basin and the reference background value in water (mg/kg).

Sites	Mn	Cr	Ni	Cu	Zn	Cd	Pb	As	Sr
TPY	672.50	50.66	21.06	19.25	74.33	0.18	30.69	262.10	409.00
YRF	708.20	62.21	26.43	27.94	81.07	0.23	31.80	281.30	313.20
FHK	736.40	79.01	34.01	48.10	125.10	0.33	33.33	264.80	221.50
YJQ	652.00	67.00	30.03	30.14	96.56	0.23	28.63	261.20	243.70
SLQ	615.25	61.29	23.68	18.21	74.90	0.48	26.56	182.20	347.25
Average	676.87	64.03	27.04	28.73	90.39	0.29	30.20	250.32	306.93
±SD	42.33	9.20	4.58	10.76	19.12	0.11	2.38	34.83	68.38
Soil background value (Shannxi)	557	62.5	28.8	21.4	69.4	0.094	21.4	11.1	166
Wei River(Shannxi)	NA	91.3	25.6	21.2	66.1	NA	21.4	NA	NA
Yellow River(China)	NA	41-128	NA	NA	NA	NA	26-78	14-48	NA
ASV	NA	90	68	45	NA	0.3	20	13	NA

ASV, average shale value (Turekian and Wedepohl 1961);

Table 5 Pearson Correlation matrix between heavy metal concentrations in water and sediment

Water	Mn	Fe	Cr	Ni	Cu	Zn	Cd	Pb	As	Sr	Ti
Mn	1										
Fe	0.894**	1									
Cr	0.679	0.835**	1								
Ni	0.946**	0.850**	0.753*	1							
Cu	0.402	0.484	0.814*	0.601	1						
Zn	-0.177	-0.015	0.095	-0.079	0.051	1					
Cd	-0.168	-0.348	-0.355	-0.281	-0.302	-0.024	1				
Pb	0.748*	0.644	0.493	0.772*	0.255	0.450	-0.042	1			
As	0.161	0.526	0.703	0.317	0.661	0.292	-0.553	0.110	1		
Sr	0.574	0.712*	0.817*	0.758*	0.801*	0.034	-0.629	0.412	0.802*	1	
Ti	0.958**	0.873**	0.591	0.887**	0.230	0.019	-0.143	0.859**	0.131	0.489	1
Sediment											
Mn	1										
Cr	0.508	---	1								
Ni	0.572	---	0.966**	1							
Cu	0.783	---	0.913*	0.941*	1						
Zn	0.654	---	0.924*	0.946*	0.976**	1					
Cd	-0.414	---	0.300	0.063	-0.039	0.041	1				
Pb	0.988**	---	0.391	0.467	0.710	0.583	-0.495	1			
As	0.774	---	0.139	0.342	0.468	0.344	-0.873	0.800	1		
Sr	-0.432	---	-0.940*	-0.979**	-0.854	-0.869	-0.097	-0.313	-0.275	1	
Ti	-0.091	---	0.535	0.369	0.207	0.178	0.756	-0.230	-0.453	-0.443	1

* Significant to probability level 0.05.

** Significant to probability level 0.01.

Table 6 Total interpretation variance and rotation component matrix of the principal components/factors of the Fenghe river in water and sediment samples

Parameters	Water			Sediment	
	PC1	PC2	PC3	PC1	PC2
Mn	0.966	0.185	-0.170	0.616	0.691
Fe	0.819	0.467	-0.032	----	----
Cr	0.575	0.727	0.058	0.991	-0.129
Ni	0.899	0.378	-0.081	0.978	0.063
Cu	0.269	0.796	0.003	0.954	0.271
Zn	-0.027	0.077	0.994	0.944	0.169
Cd	-0.014	-0.698	0.064	0.189	-0.921
Pb	0.861	0.011	0.475	0.507	0.771
As	0.032	0.918	0.235	0.264	0.924
Sr	0.436	0.866	-0.011	-0.936	0.043
Ti	0.982	0.071	0.037	0.468	-0.719
Eigenvalue	4.713	3.648	1.315	5.576	3.414
% of total variance	42.848	33.165	11.953	55.760	34.144
Cumulative % total variance	42.848	76.013	87.966	55.760	89.904

Extration method: principal component analysis.

Factor loadings: Varimax normalized (value rendered in italics are loadings>0.700)

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Figure 6 The average factor contribution ration for heavy metals in (a) water and (b) sediment in the Fenghe River, Shannxi.

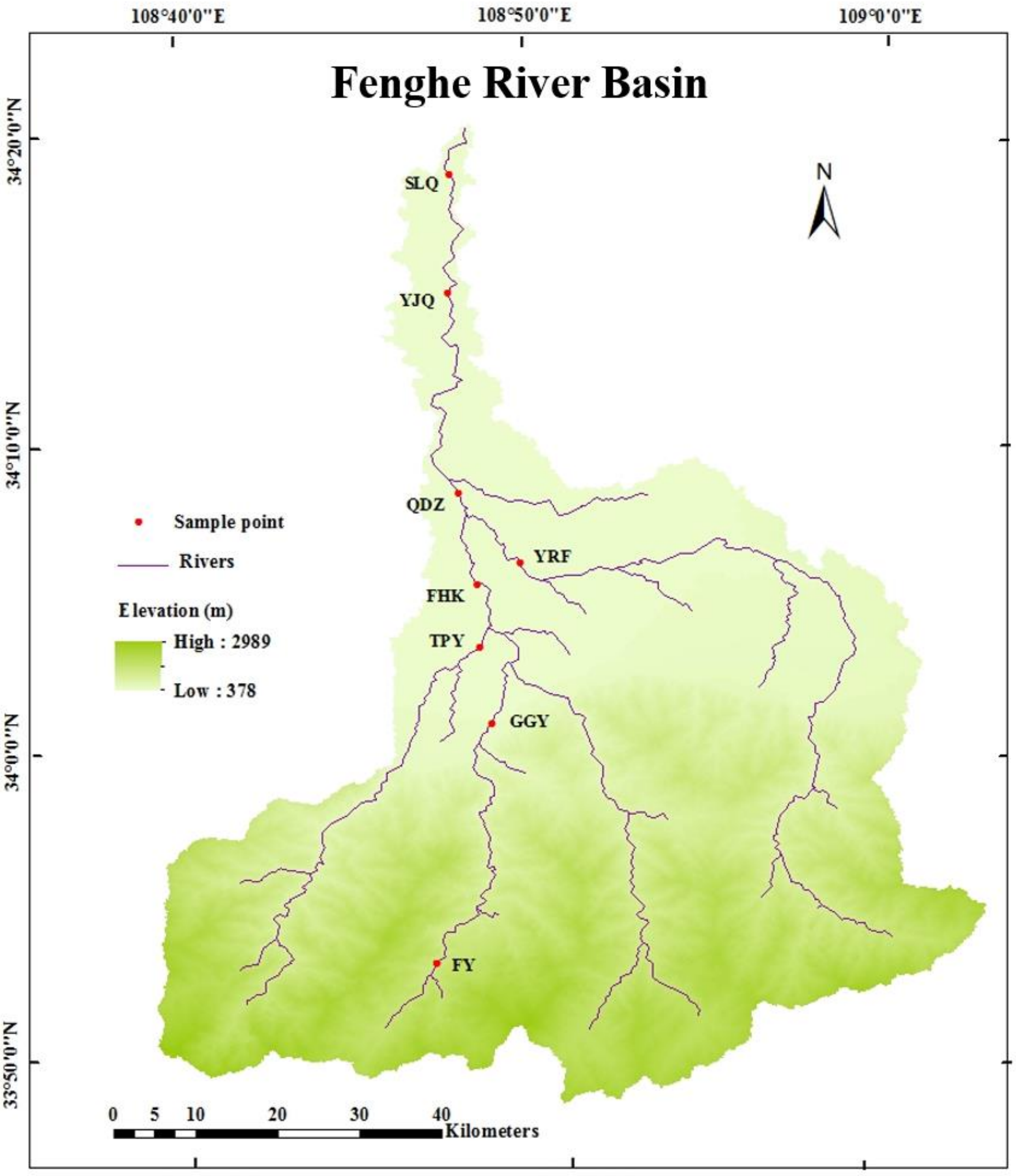


Figure1 The Map of the study area with sampling locations.

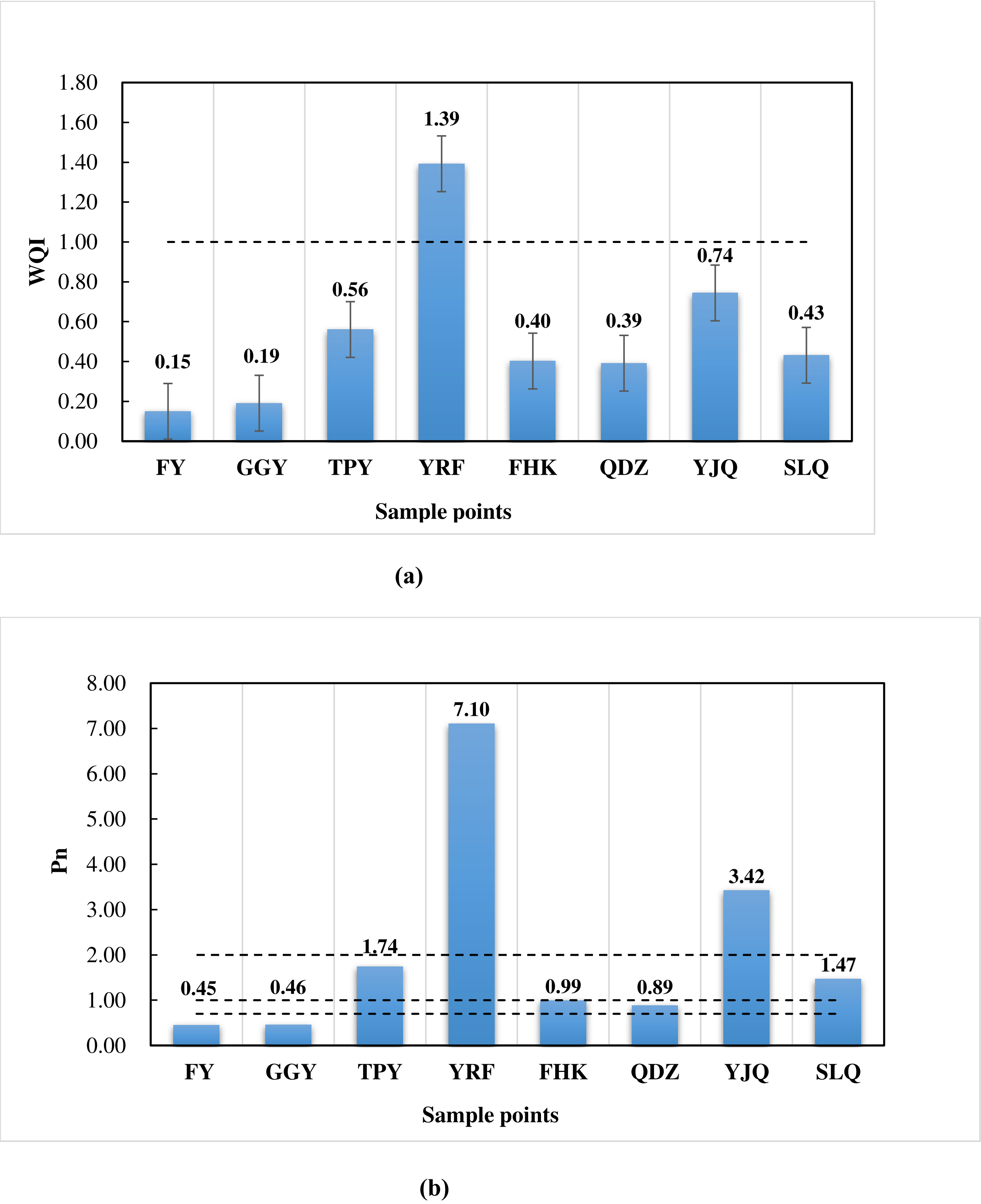
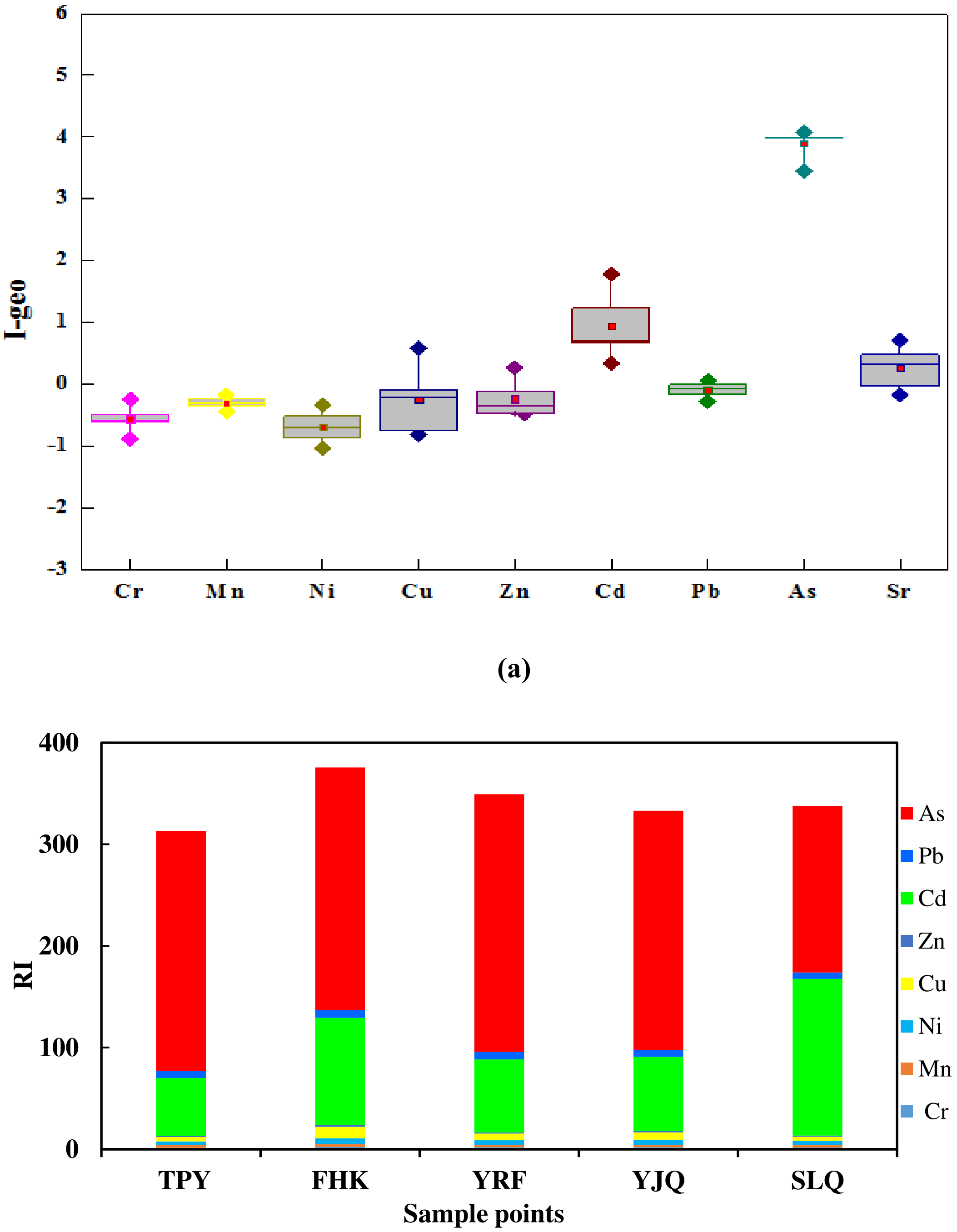


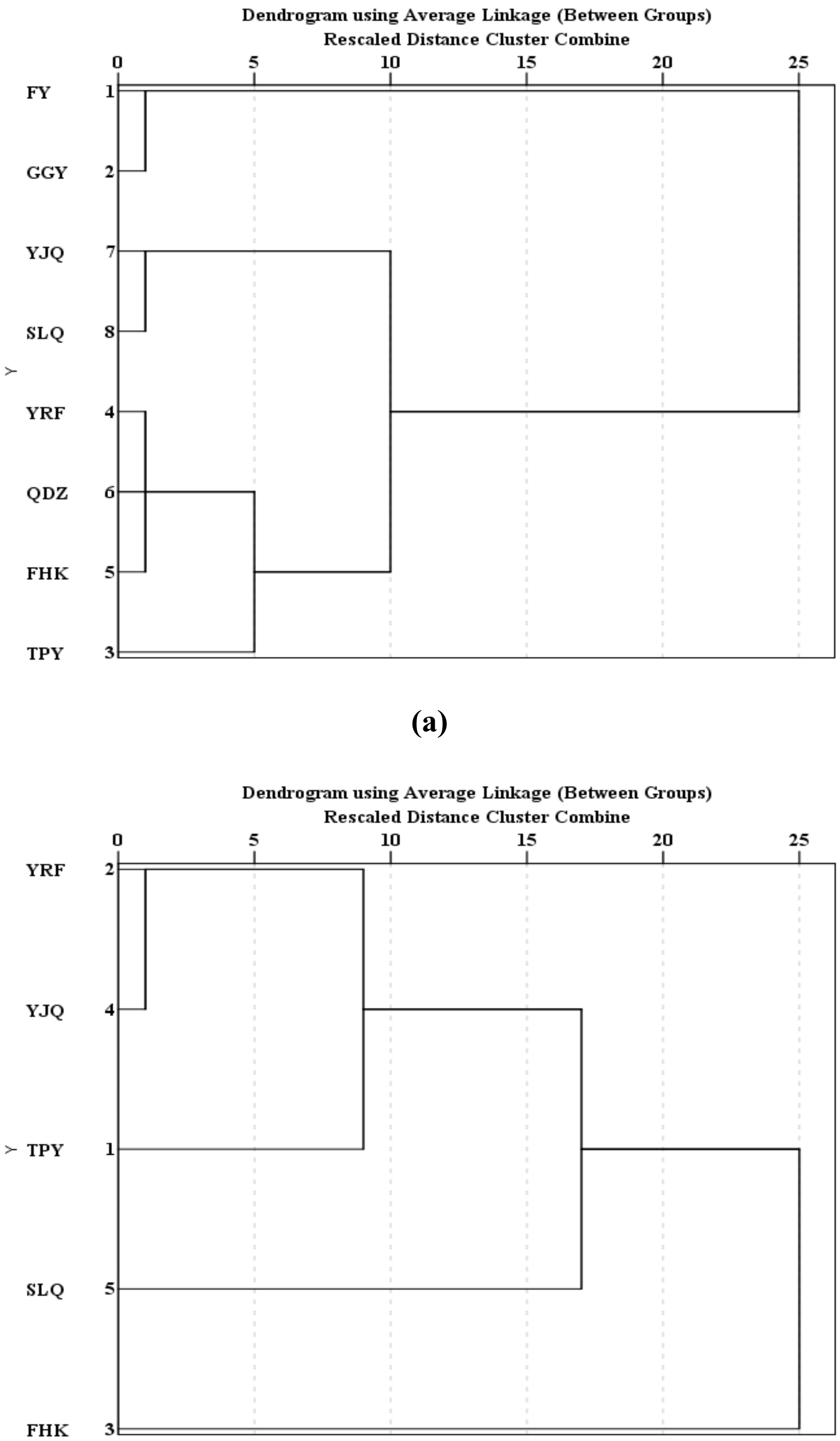
Figure 2 The comprehensive quality index (WQI) and Nemero index (Pn) of heavy metal in water in Fenghe river basin.



(a)

(b)

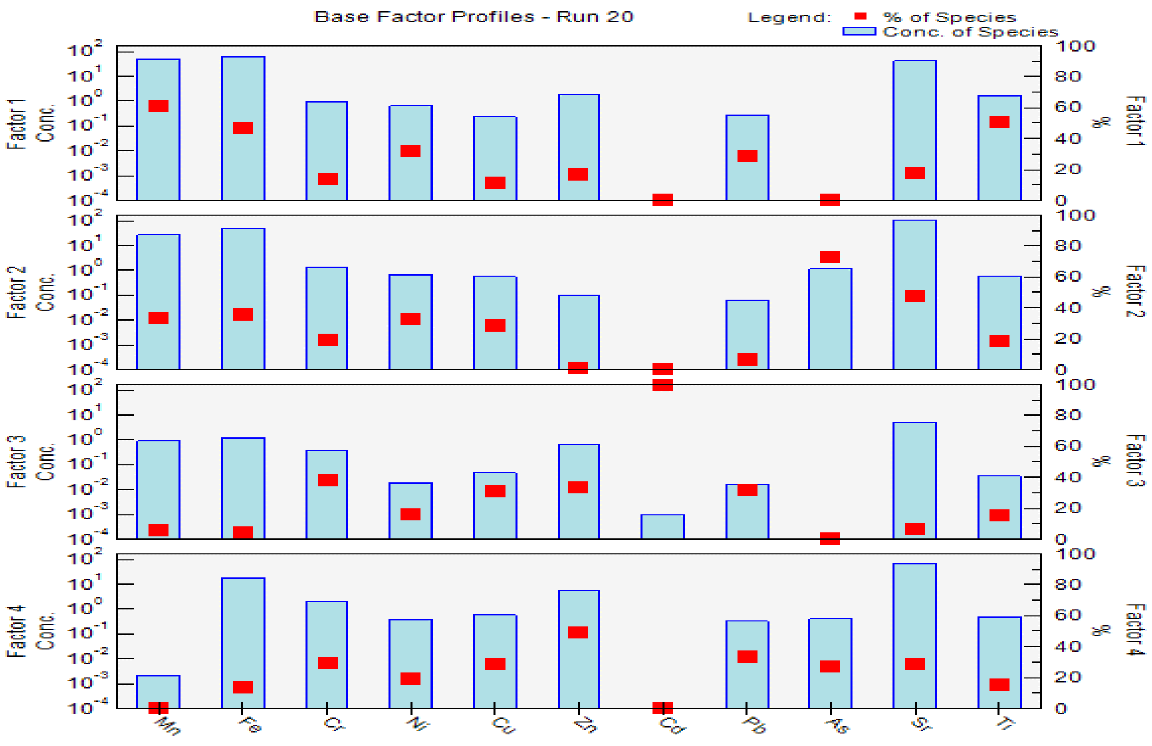
Figure 3 The geological accumulation index (I-geo) and potential ecological risk index (RI) of heavy metal in sediment in Fenghe River Basin.



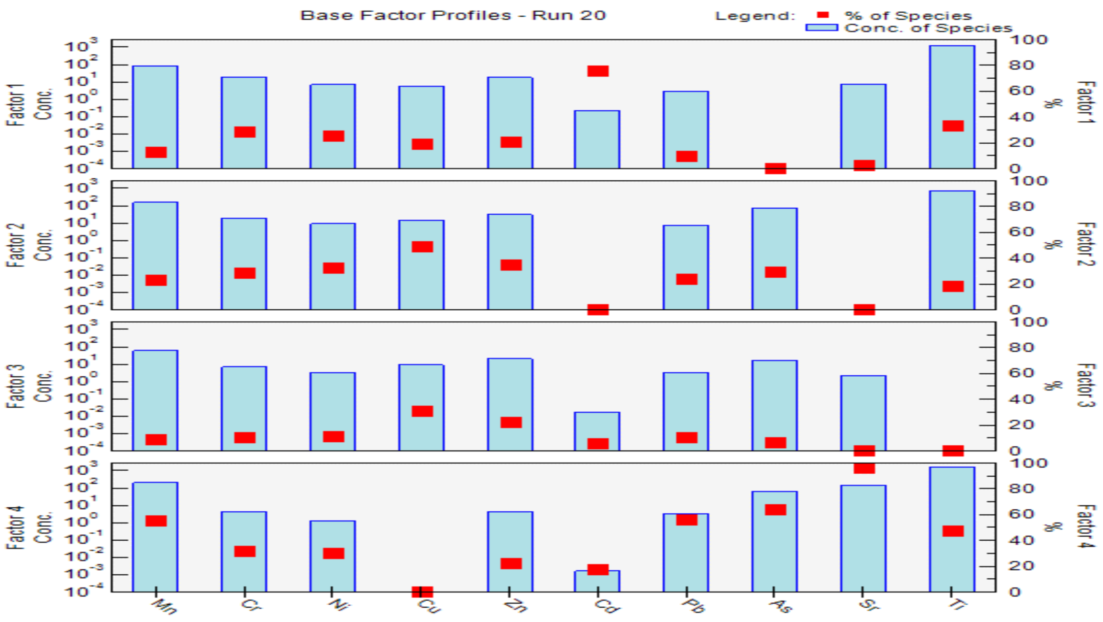
(a)

(b)

Figure 4 Dendrogram of cluster analysis amongst the parameters of Fenghe river in water(a) and in sediment(b) samples.

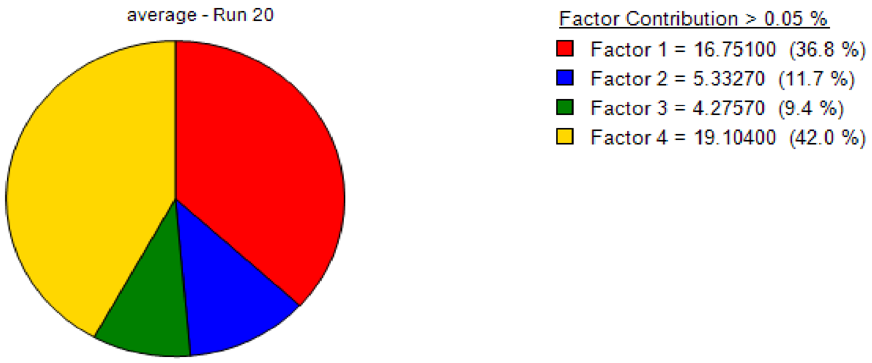


a) **Water**

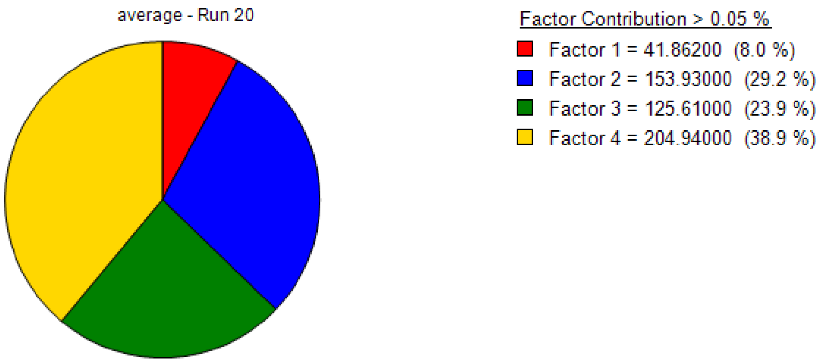


b) **Sediment**

Figure 5 Results of PMF source apportionment modeling for heavy metals in (a) water and (b) sediment in the Fenghe River, Shannxi.



a) Water



b) Sediment

Figure 6 The average factor contribution ration for heavy metals in (a) water and (b) sediment in the Fenghe River, Shannxi.

Figures

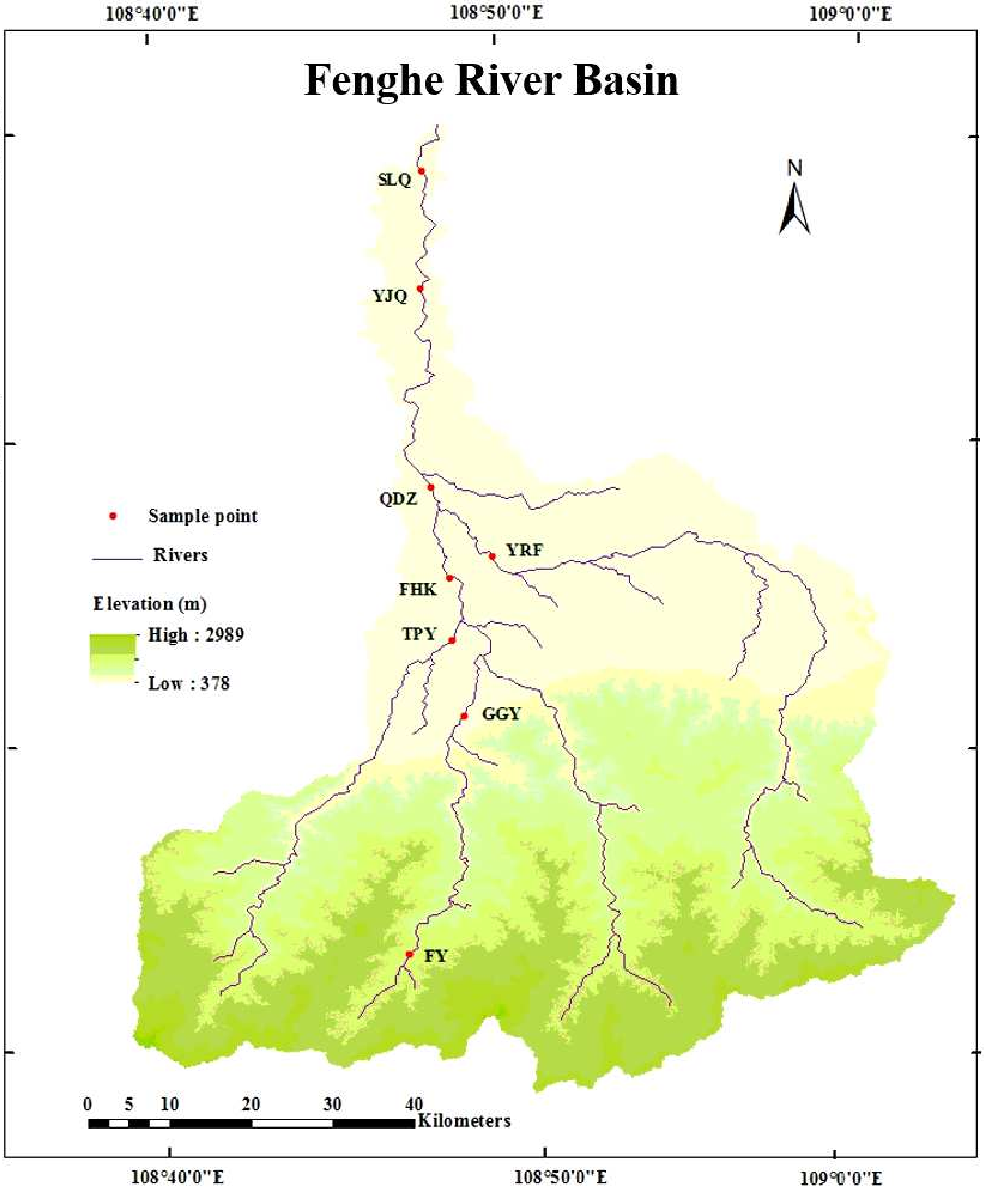
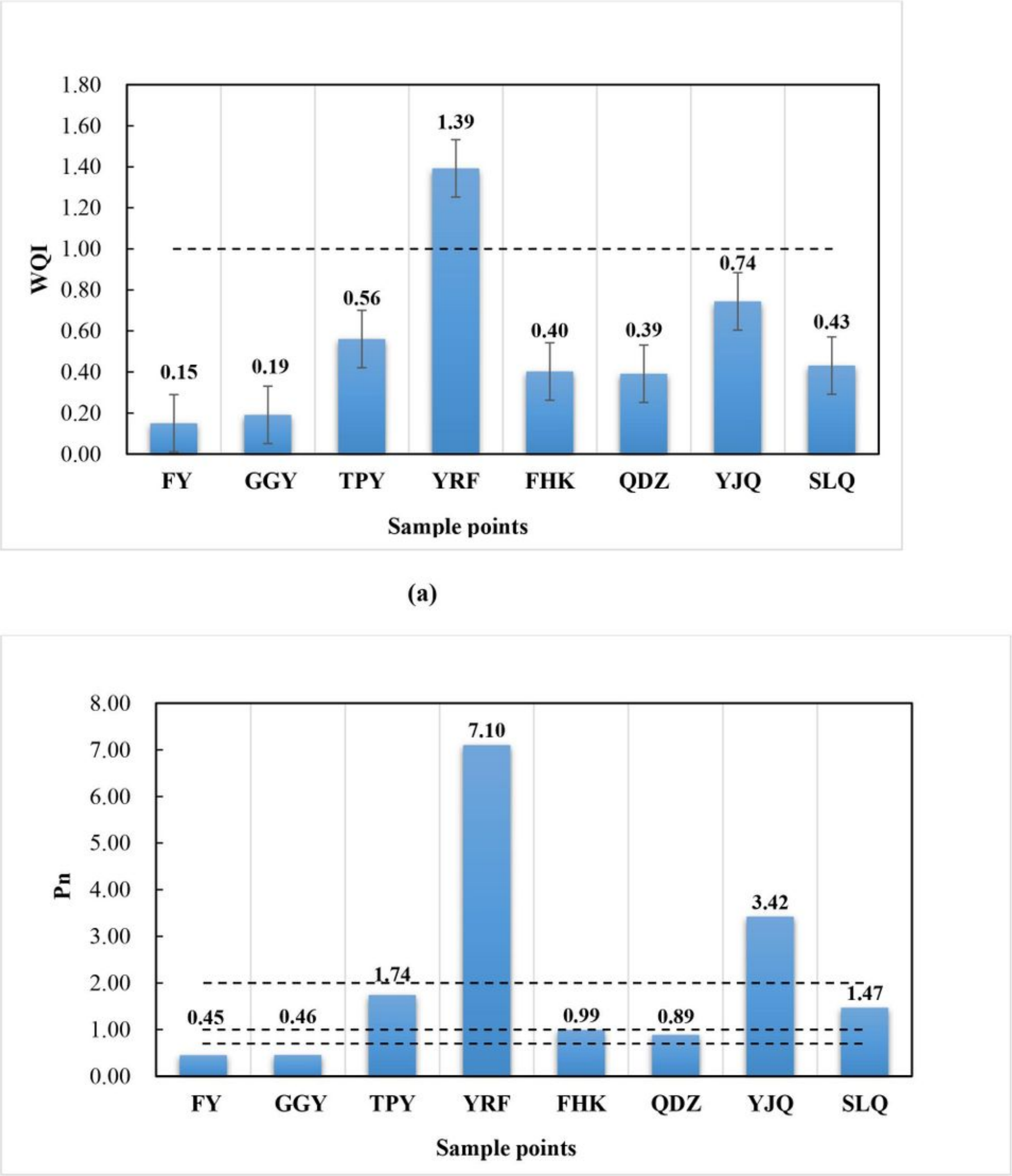


Figure 1

The Map of the study area with sampling locations. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

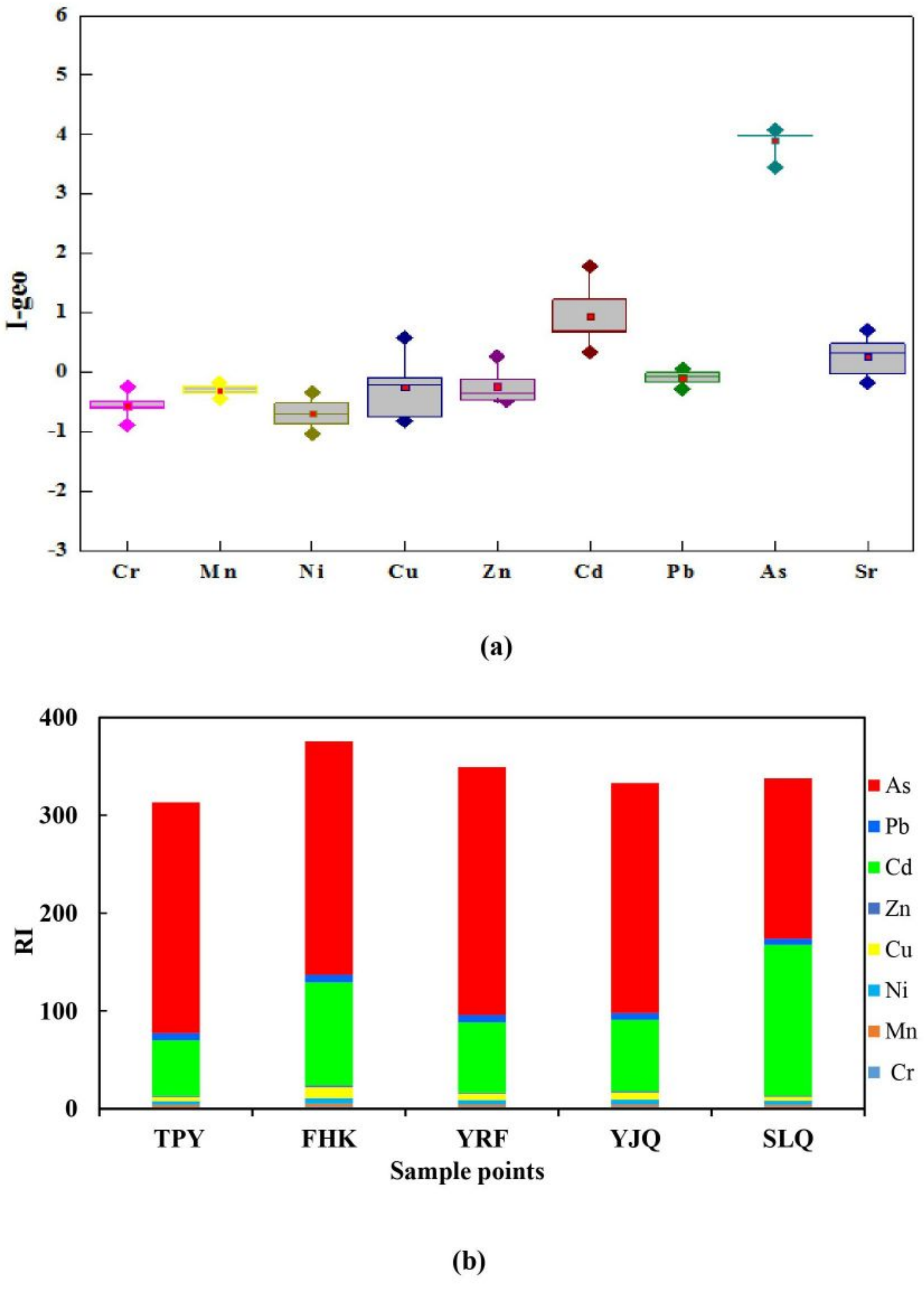


(a)

(b)

Figure 2

The comprehensive quality index (WQI) and Nemero index (Pn) of heavy metal in water in Fenghe river basin.



(a)

(b)

Figure 3

The geological accumulation index (I-geo) and potential ecological risk index (RI) of heavy metal in sediment in Fenghe River Basin.

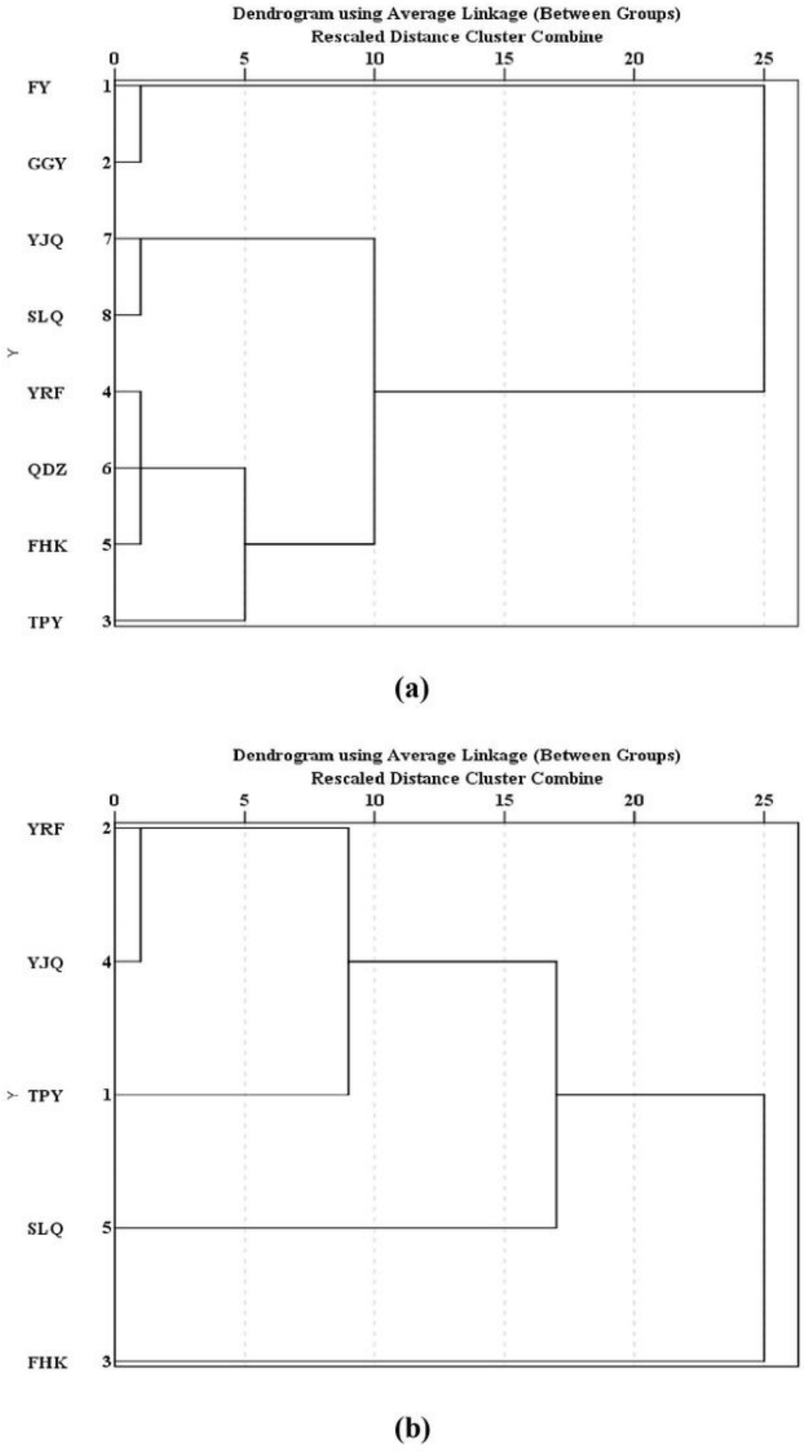
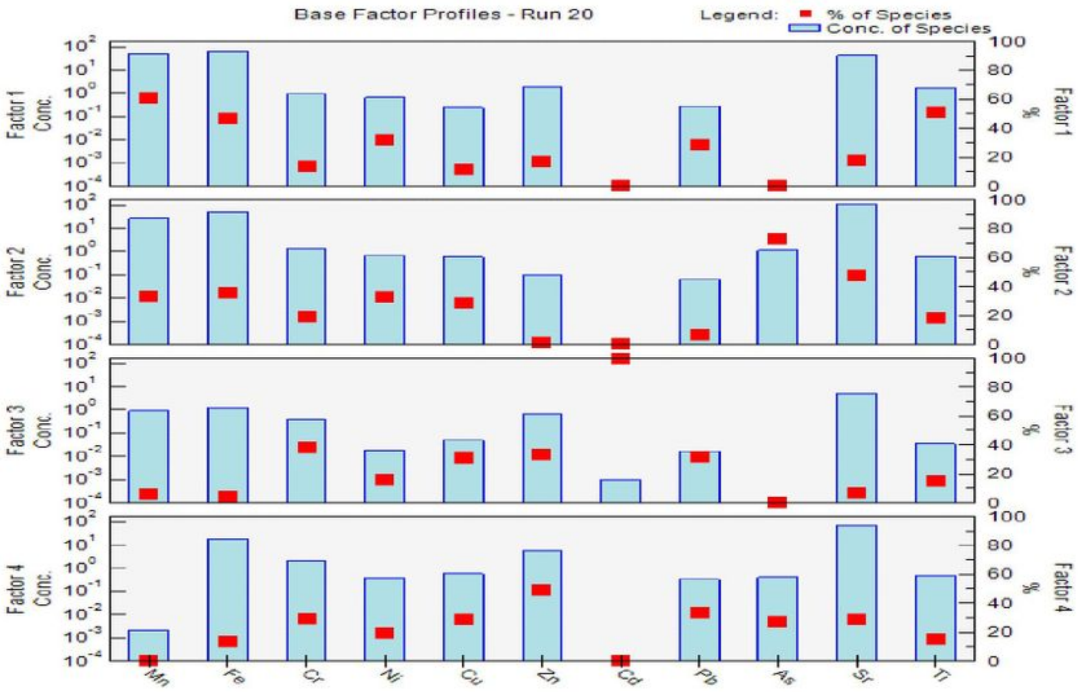


Figure 4

Dendrogram of cluster analysis amongst the parameters of Fenghe river in water(a) and in sediment(b) samples.

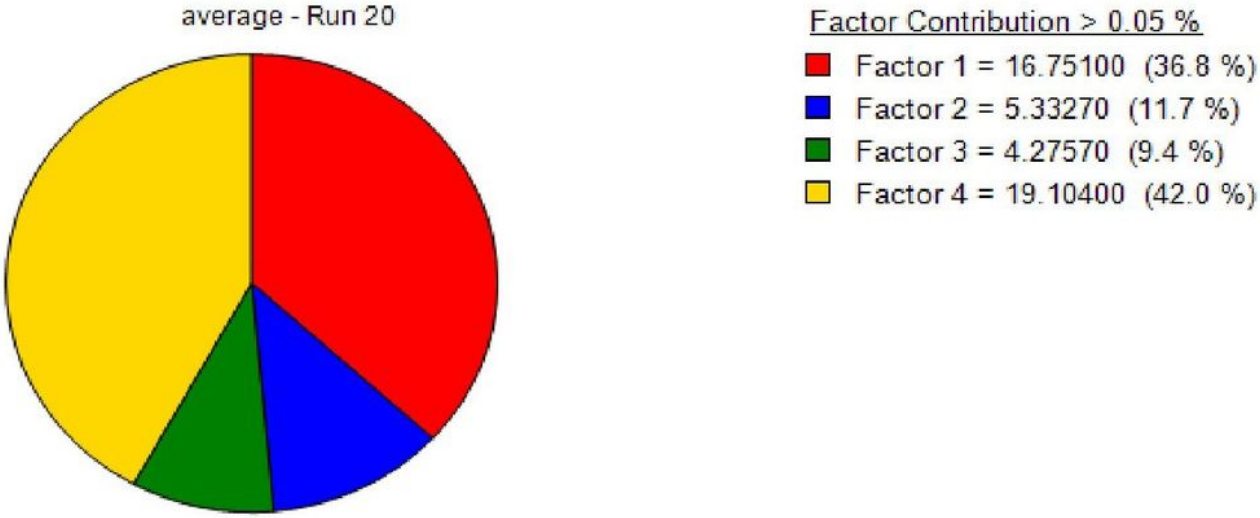


a) Water

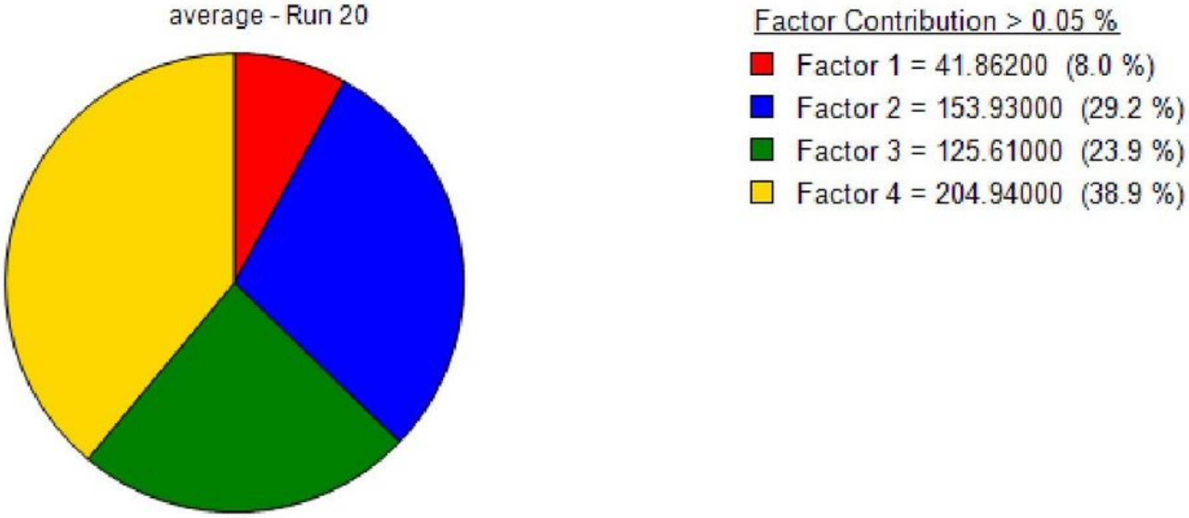
b) Sediment

Figure 5

Results of PMF source apportionment modeling for heavy metals in (a) water and (b) sediment in the Fenghe River, Shannxi.



a) Water



b) Sediment

Figure 6

The average factor contribution ration for heavy metals in (a) water and (b) sediment in the Fenghe River, Shannxi.