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RESEARCH ARTICLE

Accumulation and source of heavy metals in sediment of a reservoir near an industrial park of northwest China

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Abstract The accumulation and source of heavy metals As, Ba, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn in the surface sediment of a reservoir near an industrial park of northwest China were determined by enrichment factor and multivariate statistical analysis. Multivariate statistical analyses, i.e., factor analysis, cluster analysis, and correlation coefficient analysis, were used to identify the possible sources of the heavy metals. The results show that the mean concentrations of As, Ba, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn in the reservoir sediment are higher than their corresponding concentrations in the control sample, indicating all analyzed heavy metals accumulated in the surface sediments. The values of the mean concentrations of heavy metals in the surface sediment divided by their corresponding concentrations in the control sample increase in the order of Ba = Cr < Co = Pb < V < Ni < Cu = Zn < As < Mn. The enrichment factor values of Ba and Cr in the surface sediment samples are < 2, revealing minimal enrichment, while the enrichment factor values of As, Co, Cu, Mn, Ni, Pb, V, and Zn are in the range of 2–5, displaying moderate enrichment. Combining the results of correlation coefficient analysis, factor analysis, and cluster analysis, three main sources of these heavy metals were identified. As, Co, Cu, Mn, Ni, and V have mixed sources of natural and industrial sources and local consumption residues; Pb and Zn mainly originate from industrial activities, while Ba and Cr primarily originate from natural sources.

Keywords sediment, heavy metal, multivariate statistical analysis, source, reservoir

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1 Introduction

In recent decades, heavy metal accumulations in the environment have earned increased attention due to their toxicity and persistence in environment and subsequent accumulation in aquatic habitats (Facchinelli et al., 2001; Sin et al., 2001; Upadhyay et al., 2006; Varol, 2011). Sediments have traditionally been analyzed in sedimentological and geochemical exploration studies to assess anthropogenic impacts on the aquatic environment (Santos Bermejo et al., 2003; Farkas et al., 2007; Wang et al., 2014a). Sediments are the largest source of metals in the aquatic environment (Daskalakis and O'Connor, 1995; Wang et al., 2014a). They play an important role in contamination assessment because not only are they the final carrier of heavy metals (Sin et al., 2001; Varol, 2011), but also a potential secondary source of contaminants (Varol, 2011). Furthermore, sediments are represent a record of environmental impact over time, and they are often studied to determine the overall pollution in a specific region.

In terms of accumulation and source of pollutants, enrichment factors (*EF*s) have been widely applied to distinguish the origins of heavy metals in air, water, sediment, and soil (Zoller et al., 1974; Covelli and Fontolan, 1997; Reimann and de Caritat, 2000; Glasby et al., 2004; González-Macías et al., 2006). Three fundamental assumptions to the *EF* concept are 1) the low variability in concentration for the reference elements relative to the elements of interest, 2) the similarity in regional distribution patterns for various reference elements, and 3) the conservation of crustal element ratios through various compartments of the ecosystem (Reimann and de Caritat, 2005). However, many studies have ignored these intrinsic assumptions and have directly or indiscriminately normalized element concentrations to an average crustal value, despite the fact that Blaser et al. (2000) suggested that local background values may provide a more meaningful basis for calculating *EF*s than average crustal values, and Liu et al. (2003) demonstrated that multivariate analyses could be useful in determining the normalizer for anthropogenic heavy metals. Nevertheless, high *EF*s do not conclusively demonstrate human influence on heavy metals when the assumptions are not met (Reimann and de Caritat, 2005).

Multivariate statistical techniques, such as correlation coefficient analysis, factor analysis, and cluster analysis, are used frequently for the apportionment of contamination sources (Han et al., 2006; Ye et al., 2011) by grouping sampling sites and metals. Multivariable statistical analysis provides an alternative method to identify pollution sources, to apportion natural versus anthropogenic contributions, and to give indications about transport processes and environmental conditions. Factor analysis and derivative methods have been widely used in geochemical applications to reach the objective (Facchinelli et al., 2001; Manta et al., 2002; Filgueiras et al., 2004; Borůvka et al., 2005). Cluster analysis is often coupled with factor analysis to check results and provide grouping of individual parameters and variables (Facchinelli et al., 2001; Tariq et al., 2006; Upadhyay et al., 2006).

Nowadays, numerous studies on metal contamination in soil, plants, water, and sediment have been performed (Fang et al., 2003; Cicek and Koparal, 2004; Hsu et al., 2006; Mandal and Sengupta, 2006; Zhao et al., 2007; Pen-Mouratov et al., 2008; Rehman et al., 2008; Sharma and Tripathi, 2008; Vega et al., 2008) and are well documented in developed countries (for example U.S.A., Germany, Japan), while only limited information is available in developing countries, including China (Fang et al., 2003; Han et al., 2006; Duzgoren-Aydin, 2007; Zhao et al., 2007). China is one of the largest developing countries with the largest population in the world. The rapid urbanization and industrialization in China over the last few decades have been accompanied by unprecedented environmental changes (Lu et al., 2003; Yang et al., 2011; Chen et al., 2012), especially in the medium and small cities with poor environmental management and protection.

Baoji, the second largest industrial city of Shaanxi Province in northwestern China, has undergone rapid urbanization and industrialization, as well as resource exploitation in the recent decades, causing massive environmental issues (Lu et al., 2009, 2010). Changqing industrial park, located in northeast Baoji, is one of the city's most important industrial parks. In 2009, lead levels in the blood of children exceeded the standard limit of China in this industrial park. Our early work showed that the dust of this industrial park has elevated heavy metals (e.g., As, Co, Cr, Cu, Pb, and Zn, etc.) concentrations due to local industrial activities (Wang et al., 2014b). The surface dust in the industrial park and the atmospheric particles from industrial activities would enter the local aquatic environment by rain runoff and atmospheric deposition. Information about the effects of industrial activities on the local aquatic environment is lacking. The main objectives of this study were to investigate the contamination level of toxic heavy metals As, Ba, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn in the surface sediments of a reservoir near Changqing industrial park and to differentiate the sources of the studied heavy metals from the natural and other anthropogenic sources through enrichment factors and multivariate statistical analysis approaches.

2 Materials and methods

2.1 Study area

Baoji (33°34'–35°06' N, 106°18'–108°03' E) is located at the western edge of the Guanzhong plain about 180 km west of the provincial capital Xi'an. Wangjiaya reservoir (Fig. 1), an artificial lake, is located in about 20 km northeast of Baoji city. It was built in the middle-lower reach of the Qian River in 1970s. The western and eastern parts of the reservoir are surrounded by farmlands, uncultivated lands, and villages. A main road and railway run parallel to the reservoir in the east. In the northern part, the Qian River enters the reservoir, and nearby on the northeast side lies Changqing industrial park (Fig. 1).

Changqing industrial park lies in Changqing town, in the northeastern part of Baoji city. The main industrial activities in Changqing industrial park are lead-zinc smelting, coking, and coal-fired power generation (Wang et al., 2014b). The smelting plant with a lead-zinc smelting capacity of 300,000 tons per year and the coking plant with the coking capacity of 700,000 tons per year were founded in 2000 (Wang et al., 2015). The coal-fired power plant has been in operation since 2001. The power plant with 8.0×10^8 kWh annual production capacity consumes low-quality bituminous coal reserves from Huating of Gansu, and produces ~704,000 tons of fly and bottom ash per year from $>$ 3,600,000 tons of coal. A filter system (filtering bag) was installed in 2006 to reduce the particulate emission through the 160 m stack (Lu et al., 2012). Most industrial wastewater from the plants of Changqing industrial park discharged into the Qian River after treatment. There is no domestic sewage system in Changqing town. The town is surrounded by Loess Plateau on its northeast and southwest. Qian River traverses the town from northwest to southeast. Approximately 20,000 people live in the industrial park and 10,000 people live in the surrounding villages. Many households located directly along the reservoir releases waste waters into the reservoir. The climate of the study area is a typical temperate continental monsoon climate (hot rainy summers and cold dry winters) with the annual average temperature and the annual precipitation of 11.5°C and 610 mm, respectively (Wang et al., 2014b). The annual sunlight is about 2,057 h. The prevailing wind direction is from east to west.

2.2 Sampling and experimental analysis

Thirty-four sediment sampling sites were selected in Wangjiaya reservoir (Fig. 1). At every sampling site, surface sediment samples (0–20 cm) were collected manually using a grab sampler. A background sediment sample was collected from the upstream area of the Qian River before it enters the Wangjiaya reservoir. The sediment in this control point was not influenced by anthropogenic activities. The control sample is a composite sample of 5 sub-samples. The exact location (longitudes and latitudes) of each sampling site was recorded by a hand-held global positioning system (GPS) instrument.

All collected sediment samples were stored in double-sealed polyethylene bags, labeled, and then stored in the refrigerator at 4°C in the laboratory. Sediment samples were then dried for about 24 hours by a freeze-drying machine and then flipped, crushed, and sieved through a 1.0 mm nylon sieve to remove stones, dead organisms, and coarse debris before splitting the samples by halving and mixing. One half was stored prior to analysis of pH, organic matter content, magnetic properties, and particle composition, whereas the other was ground by a vibration mill and sieved through a 0.075 mm mesh nylon mesh. All handling was carried out without contacting with metals, to prevent potential cross-contamination (Lu et al., 2010).

X-ray fluorescence (XRF) samples were prepared by weighing out 4.0 g milled sediment samples that were then placed in the pressure-instrument (YYJ-260) mold, flattened, filled with boric acid, and crushed into a 32 mm diameter round pellet under 30 t pressure. The concentrations of As, Ba, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn in these sediment samples were determined by wavelength dispersive X-ray fluorescence spectrometer (XRF, PANalytical PW-2403 apparatus) (Lu et al., 2010; Zhang et al., 2015). For quality assurance and quality control (QA/QC), duplicate samples and standard refer-

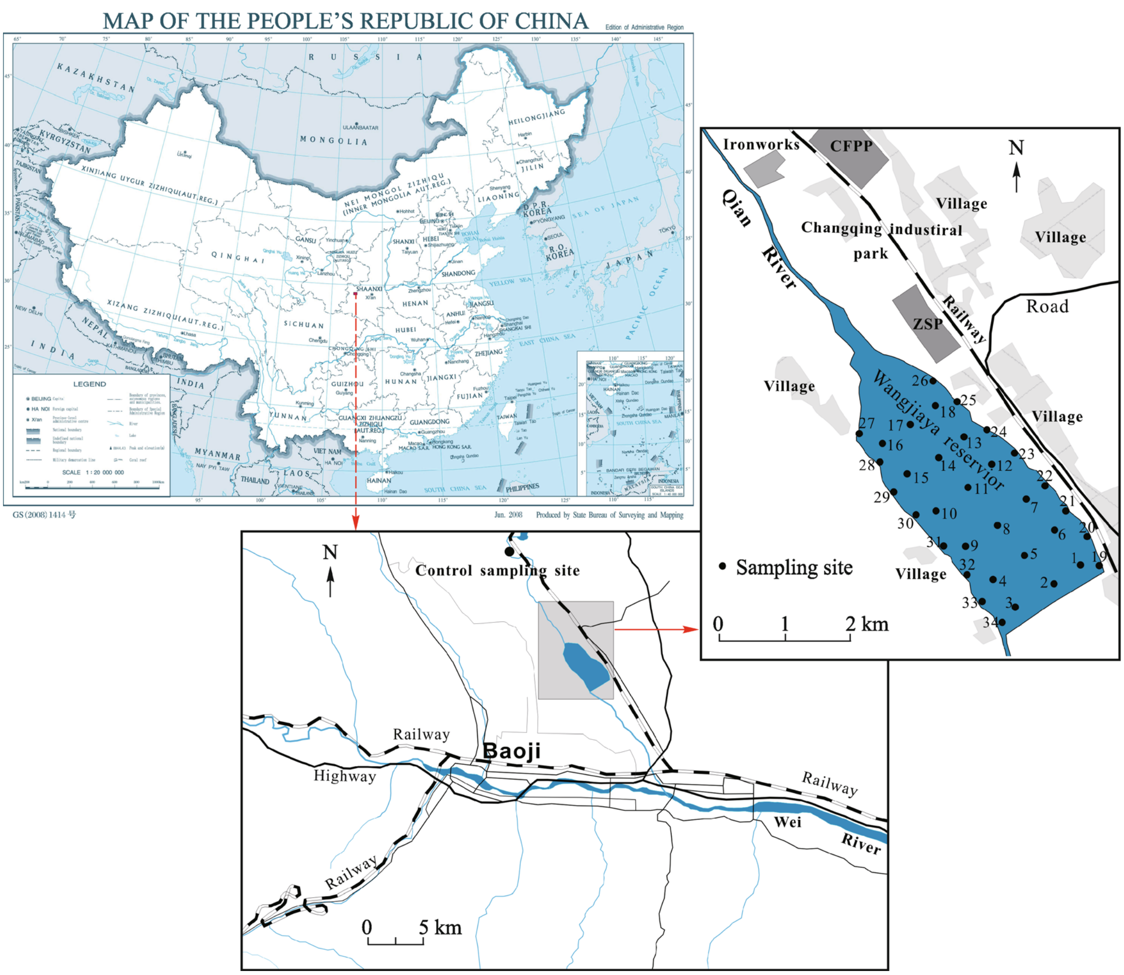

Fig. 1 Study area and sampling sites on Wangjiaya reservoir. CFPP: coal-fired power plant; ZSP: zinc smelting plant.

ence materials (GSS-1 and GSD-12) were analyzed using the same procedures, and the relative errors were less than 5%.

2.3 Enrichment factor analysis

Enrichment factor (*EF*), defined as the ratio of the concentration of the observed metal to the reference element in the sample of interest, is a useful indicator reflecting the status and the degree of environmental contamination (Feng et al., 2004; Mil-Homens et al., 2006), and a good tool to differentiate between metals originating from anthropogenic activities and those from natural sources (Meza-Figueroa et al., 2007; Chen et al., 2014). The *EF* has been mathematically calculated by the following equation:

$$EF = [C_x/C_{ref}]_{Sample}/[C_x/C_{ref}]_{Background},$$

where C_x is the concentration of the element of interest and C_{ref} is the concentration of the reference element for normalization. The element with low occurrence variability, e.g., Al, Fe, K, Mn, Sc, Ti, Zr, and Sr, etc., is often used in geochemical studies as reference element (Reimann and de Caritat, 2005; Han et al., 2006; Turner and Simmonds, 2006; Meza-Figueroa et al., 2007). In this work, the element Zr has been selected as the reference element because Zr is relatively hard to transport and transfer during the process of weathering (Mao et al., 2013) and is very stable in the investigated samples.

EF analysis can assist in determining the degree of metal contamination (Meza-Figueroa et al., 2007; Lu et al., 2009; Chen et al., 2014). $EF \leqslant 2$ means a deficiency of this metal or a minimal enrichment, $2 < EF \leqslant 5$ corresponds to moderate enrichment, $5 < EF \leqslant 20$ signifies significant enrichment, $20 < EF \leqslant 40$ indicates very high enrichment, and $40 > EF$ means extremely high enrichment (Lu et al., 2009; Chen et al., 2014). *EF* analysis can also assist in differentiating anthropogenic sources from natural ones. A value of *EF* close to 1 indicates a natural origin, whereas a value > 10 is considered to originate mainly from anthropogenic sources (Han et al., 2006; Chen et al., 2014).

2.4 Multivariate statistical analysis

To identify the relationship among heavy metals in the sediment samples and their possible sources, correlation coefficient analysis, factor analysis (FA), and Hierarchical agglomerative cluster analysis (CA) were performed using the statistics software package SPSS version 19.0 for Windows. In this study, Pearson's correlation matrix was used to measure the correlation relationship between different heavy metals (Tume et al., 2011).

FA and CA are the most common multivariate statistical methods used in environmental studies (Han et al., 2006; Tokalıoğlu and Kartal, 2006; Lu et al., 2010; Zhang et al., 2015). FA is used to reduce complex variables and extract latent factors (principal components, PCs) for analyzing relationships among the observed variables (Meza-Figueroa et al., 2007; Chen et al., 2012). FA relies upon an eigenvector decomposition of the covariance or correlation matrix (Han et al., 2006; Zhang et al., 2015). The original data matrix is first decomposed into a matrix of factor loadings and a matrix of factor scores plus a residual (Chen et al., 2008). The factor loading matrix is then rotated to obtain the rotated component matrix. Factor scores are obtained with the principal component analysis after varimax rotation and Kaiser normalization of variables. In this study, only principal factors that have eigenvalues > 1 were extracted from the variables after varimax rotation.

CA classifies a set of observations into two or more mutually exclusive unknown groups based on a combination of internal variables (Lu et al., 2010; Chen et al., 2012). To explore the interrelationship and correlation of analysis data, CA is usually coupled with FA to check the analysis results and to group individual parameters and variables (Facchinelli et al., 2001; Han et al., 2006; Lu et al., 2010). The purpose of CA is to discover a system of organizing observations where a number of groups/variables share observed properties. In the current study, CA was used to evaluate the sources similarities of heavy metals.

3 Results and discussion

3.1 Descriptive statistics of heavy metals in surface sediments

The descriptive statistical results of heavy metal concentrations in surface sediments of the Wangjiaya reservoir, as well as the corresponding concentration values of the control sample, are shown in Table 1. Table 1 shows that the arithmetic means of all measured heavy metals in the sediment samples except for Zn are close to their geometric means and medians, while the arithmetic mean of Zn is higher than its geometric mean and median, which indicates that the concentration variation of Zn in the sediment samples is larger than other heavy metals. The coefficients of variation (CVs) for all heavy metals also confirm this point. The CV of Zn is significantly higher than the CVs for other heavy metals.

The arithmetic mean concentrations, geometric mean concentrations, and medians of all analyzed heavy metals in the surface sediments are higher than their corresponding concentrations in the control sample, showing that the heavy metals accumulated in the sediment of the Wangjiaya reservoir. The sums of all analyzed heavy metals concentrations in the sediment of the Wangjiaya reservoir (1,583.9 to 2,054.8 $mg \cdot kg^{-1}$) are higher than in the control sample (1,163.8 $mg \cdot kg^{-1}$), which further confirms the effect of local human activities on the

Table 1 Heavy metal concentrations in surface sediments of Wangjiaya reservoir and control sample ($mg \cdot kg^{-1}$)

Elements	Max	Min	Mean	GM	Median	SD	CV/%	Kurtosis	Skewness	Control sample
As	19.4	6.5	14.7	14.5	15.1	2.4	16.3	3.7	−1.2	8
Ba	617.9	514.3	554	553.7	552.1	19.3	3.5	2.9	0.7	502.1
Co	20.6	12.9	18	17.9	18	1.4	7.9	3.9	−1.4	13.6
Cr	124.1	86.4	96.1	95.9	95.2	6.6	6.9	9.1	2.3	87.2
Cu	46.9	24.3	37.8	37.6	38.1	4.3	11.3	2.1	−0.5	22.9
Mn	1,121.6	685.8	950.5	944.2	974.8	107.4	11.3	0.2	−0.7	393.8
Ni	55.5	29.7	46.7	46.4	47.3	5	10.8	2.9	−1.0	29.4
Pb	42.3	28.6	35	34.9	35.2	3.2	9.1	−0.2	0.3	26.2
V	126.1	92.9	115.3	115	116.4	7.7	6.6	1.4	−1.1	80.6
Zn	334.6	65.4	101.9	97.7	93.5	42.8	42.2	28.4	5.1	61.4

GM: geometric mean; SD: standard deviation; CV: coefficient of variation (CV = SD/Mean*100).

Wangjiaya reservoir.

The 17th sampling site is located near the river entrance and the hydrodynamics here are stronger than at other sites. Particle size analysis indicates that the sediment particle size in 17th sampling site is coarser than at other sampling sites. The sediment from this site has the lowest heavy metal concentration (1,583.9 $mg \cdot kg^{-1}$). Concentrations of Cu, Mn, Ni, Pb, and Zn in all sediment samples and As in all sediment samples except sample 17 are obviously higher than the corresponding concentrations in the control sample. Their CVs are also relatively higher, which suggest As, Cu, Mn, Ni, Pb, and Zn, especially As and Zn, were significantly affected by the local anthropogenic activities (e.g., lead-zinc smelting and coal combustion for power generation). The values of the mean concentrations of heavy metals in sediment samples from the Wangjiaya reservoir divided by their corresponding concentrations in the control sample decrease in the order of Mn > As > Zn = Cu > Ni > V > Pb = Co > Ba = Cr.

In the study area, the maximum concentrations of As, Cu, Mn, Ni, and Zn in the sediments are 2.3, 2.0, 2.8, 1.9, and 5.4 times their corresponding concentrations in the control sample, respectively, and their mean values are 1.8, 1.7, 2.4, 1.6, and 1.7 times the corresponding concentrations in the control sample, respectively. Therefore, it is necessary to carry out essential measures to prevent further enrichment of these heavy metals in the sediment.

3.2 Enrichment factor analysis results

Enrichment factors (*EF*s) of all analyzed metals were calculated for each surface sediment sample relative to the corresponding concentration values of the control sample, with Zr chosen as the reference element. The calculated results of *EF* of heavy metals in the study are presented in Table 2. The *EF* values of As, Ba, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn are in the range of 1.26–4.09, 1.27–2.09, 1.27–2.73, 1.13–2.20, 1.53–3.66, 2.03–5.40, 1.47–3.38, 1.32–2.84, 1.36–2.93 and 1.38–8.86, with an average of 3.12, 1.85, 2.23, 1.85, 2.79, 4.09, 2.68, 2.25, 2.41, and 2.79, respectively. The mean *EF* value and 82.4% *EF* values for both elements Ba and Cr are < 2, revealing deficient to minimal enrichment of Ba and Cr in the surface sediments.

The mean *EF* value of As, Co, Cu, Ni, Pb, V, and As in

Table 2 The calculated results of EF and the samples percentage of different *EF* values

Element	*EF*				Samples/%				
	Max	Min	Mean	SD	$EF \leqslant 2$	$2 < EF \leqslant 5$	$5 < EF \leqslant 20$	$20 < EF \leqslant 40$	$40 < EF$
As	4.09	1.26	3.12	0.67	5.9	94.1	0	0	0
Ba	2.09	1.27	1.85	0.18	82.4	17.6	0	0	0
Co	2.73	1.27	2.23	0.34	20.6	79.4	0	0	0
Cr	2.2	1.13	1.85	0.23	82.4	17.6	0	0	0
Cu	3.66	1.53	2.79	0.49	5.9	94.1	0	0	0
Mn	5.4	2.03	4.09	0.77	0	94.1	5.9	0	0
Ni	3.38	1.47	2.68	0.46	5.9	94.1	0	0	0
Pb	2.84	1.32	2.25	0.32	14.7	85.3	0	0	0
V	2.93	1.36	2.41	0.36	11.8	88.2	0	0	0
Zn	8.86	1.38	2.79	1.16	8.8	88.3	2.9	0	0

SD: standard deviation.

94.1%, Co in 79.4%, Cu in 94.1%, Ni in 94.1%, Pb in 85.3%, and V in 88.2% of the surface sediment samples, are in the range of 2–5, indicating these heavy metals in the surface sediments are moderately enriched with respect to the control sample. For Mn, 94.1% of the *EF* values and 5.9% of the *EF* values are in the range of 2–5 and 5–20, respectively, with the mean *EF* value in the range of 2–5, indicating that Mn in the surface sediments is moderately to significantly enriched. The mean *EF* and 88.3% *EF* values for Zn are in the range of 2–5 showing moderate enrichment, while 8.8% of *EF* values are < 2 and 2.9% of *EF* values are > 5, indicating deficient to minimal enrichment and significant enrichment, respectively. The average *EF* values of As (3.12), Ba (1.85), Co (2.23), Cr (1.85), Cu (2.79), Mn (4.09), Ni (2.68), Pb (2.25), V (2.41), and Zn (2.79) are > 1, indicating that all analyzed heavy metals in the surface sediments were more or less affected by human activities. The assessment of *EF* based on the control sample as reference demonstrates that the accumulation of heavy metals in the reservoir sediments is mainly related to the human activities around the reservoir, e.g., the industrial discharge in the Changqing industrial park.

3.3 Correlation coefficient analysis results

The correlation among heavy metals can provide some information on the sources and pathways of heavy metals (Manta et al., 2002; Lu et al., 2010). Pearson's correlation coefficient of heavy metals in sediment samples from the Wangjiaya reservoir are presented in Table 3. A significantly positive correlation at the $P < 0.01$ significance level was found among As, Co, Cu, Mn, Ni, and V. The elemental pairs Pb-As (0.439) and Pb-Zn (0.494) had a significantly positive correlation at the $P < 0.01$ significance level, and the Pb-Cu pair (0.388) had a significantly positive correlation at $P < 0.05$ significance level. Based on the research of Lu et al. (2010), Saeedi et al. (2012), and Li et al. (2013), if the correlation coefficient between the heavy metal factors is positive, these factors may have a common source, mutual dependence, and identical behavior during transport.

3.4 Factor analysis results

Factor analysis (FA) was applied to assist in the source identification of heavy metals in the sediments by applying varimax rotation with Kaiser Normalization. By extracting the eigenvalues and eigenvectors from the correlation matrix, the number of significant factors and the percent of variance explained by each were calculated. The KMO (Kaiser–Meyer–Olkin) test value (0.665) and Bartlett's test value of sphericity (334.170) show that the concentration data of heavy metals in sediment from the Wangjiaya reservoir are suitable for factor analysis. FA results shown in Table 4 display factor loadings with a varimax rotation, as well as the eigenvalues and communalities calculated using the software package SPSS 19.0. The results show that there are three eigenvalues > 1 and that these three factors were extracted which explain 78.9% of the total variance. The first factor explains 49.1% of the total variance and loads heavily on As, Co, Cu, Mn, Ni, and V. Factor 2 is loaded by Pb and Zn, accounting for 15.7% of the total variance. Factor 3, dominated by Ba and Cr, explains 14.1% of the total variance. The relations among the heavy metals based on the three factors are illustrated in Fig. 2 in three-dimensional space.

3.5 Cluster analysis results

The results of hierarchical clustering for the studied heavy metals are presented in Fig. 3 as a dendrogram. Dendrograms can vividly reflect the proximity and the link among the heavy metals. The heavy metal concentrations data were standardized by means of *z*-scores and Euclidean distance for similarities in the variables were calculated. The hierarchical clustering was performed on the standardized data applying Ward's method. The distance cluster represents the degree of association

Table 3 Pearson's correlations matrix for the heavy metal concentrations in the Wangjiaya reservoir

	As	Ba	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
As		0.140	0.000	0.367	0.000	0.000	0.000	0.009	0.000	0.505
Ba	−0.258		0.275	0.070	0.729	0.528	0.993	0.370	0.945	0.106
Co	0.685^{**}	−0.193		0.124	0.000	0.000	0.000	0.307	0.000	0.577
Cr	−0.160	0.315	−0.269		0.107	0.538	0.062	0.320	0.417	0.229
Cu	0.806^{**}	0.062	0.774^{**}	−0.281		0.002	0.000	0.023	0.000	0.468
Mn	0.613^{**}	−0.112	0.714^{**}	−0.109	0.523^{**}		0.000	0.360	0.000	0.715
Ni	0.764^{**}	0.002	0.841^{**}	−0.324	0.974^{**}	0.599^{**}		0.052	0.000	0.368
Pb	0.439^{**}	−0.159	0.180	−0.176	0.388^{*}	0.162	0.336		0.071	0.003
V	0.743^{**}	−0.012	0.868^{**}	−0.144	0.799^{**}	0.870^{**}	0.845^{**}	0.314		0.601
Zn	0.118	−0.282	−0.099	−0.212	−0.129	−0.065	−0.159	0.494^{**}	−0.093	

The left lower part is correlation coefficient; the right upper part is significant level. * Correlation is significant at $P < 0.05$ (two-tailed). **Correlation is significant at $P < 0.01$ (two-tailed).

Table 4 Rotated component matrix for data of surface sediments from the Wangjiaya reservoir

Elements	Component			Communalities
	1	2	3	
As	**0.820**	0.302	−0.140	0.783
Ba	0.004	−0.141	**0.843**	0.731
Co	**0.895**	−0.081	−0.233	0.862
Cr	−0.195	−0.078	**0.726**	0.572
Cu	**0.922**	0.122	0.029	0.866
Mn	**0.786**	−0.058	−0.106	0.632
Ni	**0.947**	0.041	−0.052	0.901
Pb	0.302	**0.864**	−0.005	0.838
V	**0.954**	0.039	0.000	0.911
Zn	−0.185	**0.820**	−0.287	0.789
Eigenvalue	4.91	1.57	1.41	
% of total explained variance	49.1	15.7	14.1	
% of cumulative total explained variance	49.1	64.8	78.9	

Extraction method: Factor Analysis. Rotation method: Varimax with Kaiser normalization. Rotation converged in 5 iterations.

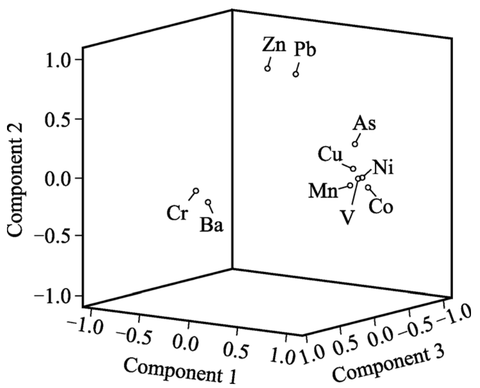

Fig. 2 Factor analysis results in the three-dimensional space: plot of loading of the three factors.

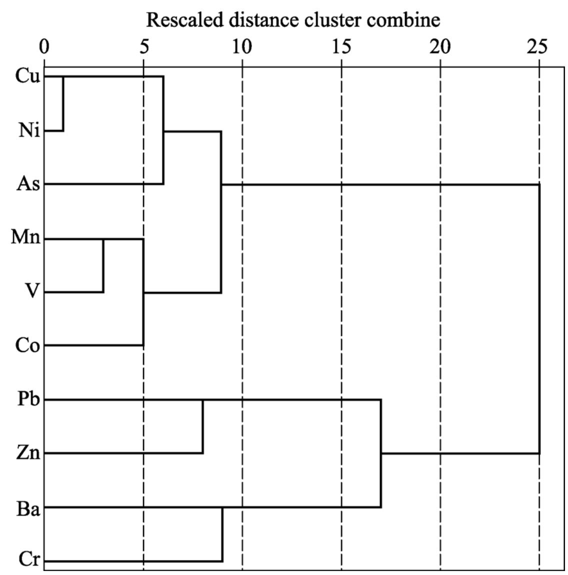

Fig. 3 Dendrogram results of cluster analysis based on Ward method hierarchical cluster analysis for 10 elements.

between elements. The lower the value on the distance cluster, the more significant was the association. A criterion for the distance cluster of between 10 and 15 was used in the analysis. Figure 3 shows three clusters: 1) As-Co-Cu-Mn-Ni-V; 2) Pb-Zn; 3) Ba-Cr, in total agreement with the FA results.

3.6 Heavy metals sources identification

Three main sources of the studied heavy metals in sediments from the Wangjiaya reservoir could be identified according to the concentrations, enrichment factor analysis, correlation coefficient analysis, factor analysis and cluster analysis:1) As, Co, Cu, Mn, Ni, and V have mixed sources of natural sources, industrial sources and local consumption residues; 2) Pb and Zn mainly originate from industrial activities; 3) Ba and Cr mainly originate from natural sources.

One group of elements consisting of As, Co, Cu, Mn, Ni, and V have a significantly positive correlation in the correlation coefficient analysis. They belong to Factor 1 and are classified together in CA (Cluster 1), implying a possible common source. The coefficient of variations (CVs) of As, Cu, Mn, and Ni and their concentrations in all the sediment samples except for As in the site #17 sample are clearly higher than their corresponding concentrations in the control sample, demonstrating they mainly originated from anthropogenic sources. However, the coefficients of variation (CVs) of Co and V in the sediments are relatively low, and their concentrations in most sediment samples from the Wangjiaya reservoir are slightly higher than or close to their corresponding concentrations in the control sample, indicating that Co and V largely originated from a natural source.

Wang et al. (2014b) shows that higher concentrations of As were found in the dust samples collected from the surrounding environment of the coal-fired power plant, while the higher concentrations of Cu were found in the dust samples from the surrounding environment of lead-zinc smelting plant. There are no other industries in the Changqing industrial park besides the lead-zinc smelting plant, the coking plant, and the coal-fired power plant. So, this finding shows that As in the dust from the study area was mainly contributed by the coal combustion, and Cu in the dust primarily contributed by the lead-zinc smelting plant. The dust with elevated heavy metals in the industrial park can directly discharge into the Wangjiaya reservoir with rainfall or snowmelt runoffs and thus influence the sediment heavy metal contents and aquatic ecosystem without treatment. Moreover, there is no domestic sewage system in the surrounding villages, and we have found some sewage outlets discharge directly into the river along the Wangjiaya reservoir. In addition, atmospheric deposition and industrial wastewater can also affect heavy metal concentrations in the aquatic environment and the sediment. Considering the concentrations, enrichment factor analysis, the coefficient of variation, and the multivariate statistical analysis results, one can conclude that As, Co, Cu, Mn, Ni, and V have mixed sources of natural and industrial sources and local consumption residues.

A second group of elements consisting of Pb and Zn is strongly positively correlated in the correlation coefficient analysis, FA (Factor 2) and classified together at a relatively higher level in CA (Cluster 2), indicating Pb and Zn in the sediments share similar impact factors. The concentrations of Pb and Zn in all the sediment samples are higher than the reference concentrations in the control sample, and the maximum concentration of Zn in the surface sediments samples is 5.4 times the reference values. The coefficient of variations (CVs) of Pb and Zn, especially Zn, in the sediments are significantly high. Furthermore, the average *EF* values of Pb and Zn are 2.25 and 2.79, respectively, corresponding to moderate enrichment. The lead-zinc smelting activities are the main source of Pb and Zn in the local surface environment (Wang et al., 2014b). Considering the concentration and the coefficient of variation, one can conclude Pb and Zn in the sediments mainly originate from local industrial sources, such as dust emissions and the effluent emissions with heavy metals from the Changqing industrial park.

A third group of elements consist of Ba and Cr. Ba and Cr share the same principal component (Factor 3) in FA, and they join together at a relatively higher level in CA (Cluster 3), implying a possible common source. Concentrations of Ba at all sites and Cr at all sites except site 15 from the Wangjiaya reservoir are approximately equal to, or slightly higher than, their corresponding values of the control sample, and their CVs are relatively low, which suggest they are mainly controlled by natural factors. Moreover, the enrichment factor results indicate that Ba and Cr are deficient to minimal enrichment in the sediment samples. Therefore, Ba and Cr mainly originate from natural sources.

4 Conclusions

The accumulation and source of As, Ba, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn in the surface sediments of the Wangjiaya reservoir, NW China have been studied in this work. All analyzed heavy metals were accumulated in the surface sediments and their mean concentrations were higher than their corresponding concentrations in the control sample, particularly As, Cu, Mn, and Zn. The mean concentrations of heavy metals in surface sediments of the Wangjiaya reservoir divided by the corresponding concentrations in the control sample decrease in the order of Mn > As > Zn = Cu > Ni > V > Pb = Co > Ba = Cr. Enrichment factor analysis indicates that Ba and Cr in sediment samples of the Wangjiaya reservoir came mainly from natural sources; while As, Co, Cu, Mn, Ni, Pb, V, and Zn in the surface sediments, especially Pb and Zn, were mostly influenced by human activities. Three main sources of different heavy metals in surface sediments of Wangjiaya reservoir were identified according to correlation coefficient analysis, factor analysis and cluster analysis, coupled with enrichment factors. As, Co, Cu, Mn, Ni, and V have mixed sources of nature, industrial sources and local consumption residues; Pb and Zn mainly originate from industrial activities.

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