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PAPER

Geochemistry and environmental assessment of major and trace elements in the surface sediments of the Wei River, China

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The development of western China in the past decade has led to increased discharges of wastewater and river pollution. The Wei River is the largest tributary of the Huang He River, but its geochemistry has not been thoroughly investigated. Sixty-three bed-surface sediment samples were collected from the Wei and analyzed for 24 elements by WDXRF; objectives for the study were to investigate the geochemical properties of the sediments; identify sources, and assess pollution levels and environmental risks. Major and trace element concentrations were comparable with those in other large rivers in China, but potentially hazardous trace elements (PHTEs) were lower than in the Yangzi or Pearl Rivers; most likely due to dilution of contaminants by the large sand inflows into the Wei and a lower level of industrialization. Nonetheless, pollution and risk analyses demonstrate slight contamination of Cr, Mn, Nb, Ni and Zn, moderate contamination of Cu and Pb, and strong contamination of As at some locations. Adverse biological effects from Ni and Cu are possible and are likely from As. Statistical and spatial analyses indicate that agriculture runoff and industrial wastewater discharge contribute to the contamination of this river. A comprehensive environmental management strategy, realistic national standards for wastewater discharge, and rigid enforcement are needed to address river pollution in China.

1. Introduction

Human activities, including metal mining, smelting and finishing, coal combustion, refuse incineration, fossil fuel burning, and agricultural practices, have released countless tons of trace elements into the environment.[1] Aquatic ecosystems continuously receive potentially hazardous trace elements (PHTEs) from natural and anthropogenic sources; these pose serious threats because of their toxicity, persistence, and tendency to bioaccumulate.[2] Many PHTEs concentrate in river-bed sediments but later are flushed to sensitive receiving basins, such as lakes, reservoirs and coastal areas.[3,4]

Elevated sediment and soil metal concentrations can have adverse impacts on food quality and safety, crop production, and public health, and these concerns have attracted widespread attention.[5,6] Sediments concentrate metals from aquatic systems, and they represent an appropriate and strategic medium for monitoring contamination.[7,8] Studies of major and trace elements in sediments and assessments of sediment quality are therefore critical steps in assessing environmental pollution.[8]

A western-region development strategy has been implemented in China, and numerous industrial plants have been built in western China during the past decade. As a result, large volumes of industrial wastes have been discharged into the Wei River, the largest tributary of the Huang He (Yellow) River, especially in

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Environmental impact

Information on the concentrations, distributions, and sources of trace elements in river surface sediments from China is still sparse. This paper presents a systematic study of major and trace elements in surface sediments from the Wei River in a rapidly developing area of western China. Multivariate statistical techniques, along with an analysis of pollutant distributions, showed that both industrial and agricultural activities contribute to the pollution of this river. Pollution and risk analyses demonstrate slight to strong levels of contamination at some locations and possible adverse biological effects from Ni, Cu, and As. Rigorous national standards for wastewater discharge and rigid enforcement are urgently needed to address river pollution in China.

Table 1 Chemical and physical properties of the Wei River summarized from previous studies[12,13]

Property	Value	Property	Value
pH of water[a]	7.3–8.5	Conductivity (μs cm^{-1})[a]	90–600
Dissolved oxygen (mg L^{-1})[a]	0.8–8.7	Biochemical oxygen demand (mg L^{-1})[a]	1.0–39.2
NH_3–N (mg L^{-1})[a]	0.2–10.5	NO_3–N (mg L^{-1})[b]	0.2–5.8
Petroleum (mg L^{-1})[a]	1.7–6.4	Total water amount (m^3 a^{-1})[a]	103.5 × 108
Redox (μs cm^{-1})[a]	70–225	Chemical oxygen demand (mg L^{-1})[a]	3.0–43.1
Volatile phenol (mg L^{-1})[a]	0.7–3.6		

[a] Work of Yang *et al.*[13] [b] Work of Wang and Wang.[12]

areas of the Guanzhong Plain in Shaanxi Province. This has led to serious environment pollution (Table 1) and health concerns.[9,10] In the summer of 2009, 615 children in Fengxiang County (~15 km east to Baoji city) were found to have blood lead levels significantly above the national standard,[11] and 163 children were poisoned with Pb. These adverse effects were traced to discharges of PHTEs from the chemical and metallurgical plants and paper mills surrounding the Wei River.[11]

Due to the seriousness of these events, a special project entitled "Major Projects on Control and Rectification of Water Body Pollution" has been developed to study and control the pollution around the Wei River. Plans have been made to invest ~5 billion US dollars to deal with the water pollution in China. Studies have been conducted to investigate the water quality such as dissolved oxygen, chemical oxygen demand, biological oxygen demand, NH_3–N, and organic matter, in the Wei River[10,12,13] (Table 1); however, to our knowledge, there have been no comprehensive investigations of trace element contaminants in surface sediments of the Wei. One prior study was conducted by Lei *et al.*,[14] but for that study only six samples were retrieved from a section of the river that runs through Xi'an (from east Xianyang to the Jinghe River mouth, see Fig. 1).

This paper presents the results of a study of major and trace elements in surface sediments from the Wei River. The three objectives for the study were (1) to investigate the geochemical properties of surface bed sediments; (2) to identify their natural and anthropogenic sources through the use of principal component and cluster analysis; and (3) to assess the pollution levels and the ecological/environmental risks posed by the PHTEs.

2. Study area

The Wei River has a length of 818 km and a drainage area of 134 300 km. The upper reaches of the river, and the tributaries to the north, such as the Jing and Luo Rivers, flow through the Loess Plateau and deliver large amounts of fine-grained calcareous silt to the Wei. These heavy loads of suspended sediments cause a yellowish color in the river. The northern branches are generally long while the southern branches are shorter but provide greater volumes of water.[10] The topography of the drainage area of the Wei River is complex, with a mountainous area in the west and an alluvial plateau and the Loess Plateau to the east. Most of the drainage areas are covered with thick loess.

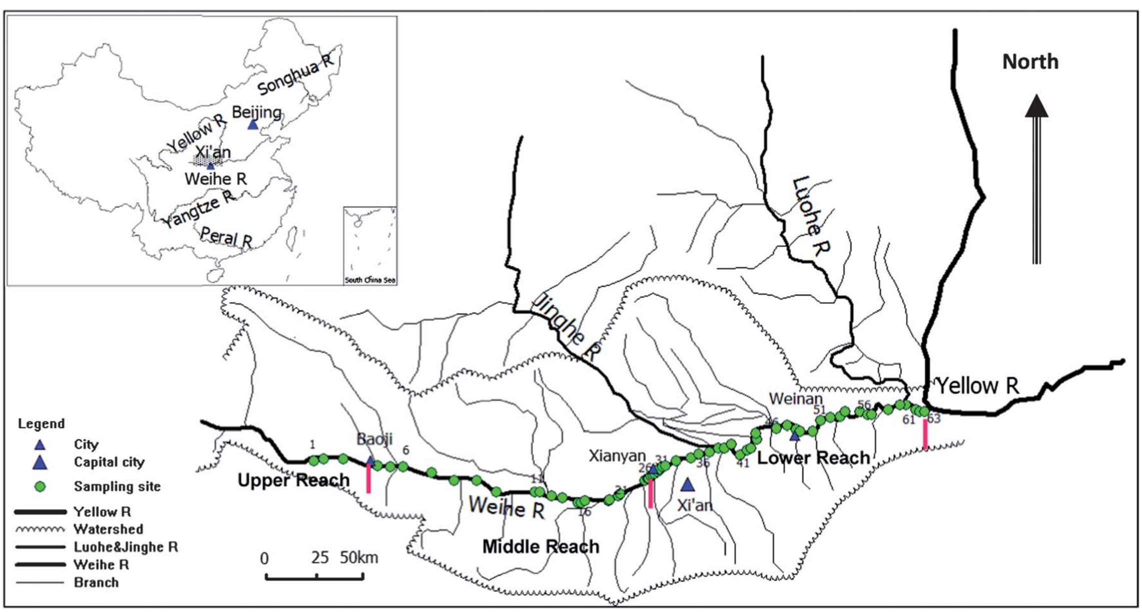

Fig. 1 Locations of surface sediment sample collections from the Wei River (the three red vertical lines mark the upper, middle and lower reaches of the river).

Annual river discharge at the Xianyang Station is about 5.4 billion m^3, and the annual sand transport is about 0.17 billion tons.[12]

The Wei River Valley is the earliest center of Chinese civilization and also the location of China's first major irrigation projects. Historically, the drainage area of the Wei River was famous as a food production region, and agriculture remains extremely important there. At present, the area accounts for about 64% of the population, 52% of the cultivated land, 72% of the irrigated areas, and 80% of the gross domestic product for Shaanxi province.[10] The wastewater discharges around the Wei River are mainly located in two parts (east of Baoji City and from Xianyang to the mouth of the Jinghe River, see Fig. 2).

The region has a continental climate with an annual averaged temperature of 6 to 13 °C, precipitation of 500 to 800 mm, and evapo-transpiration of 1000 to 2000 mm (mean values based on observations since the 1950s).[13] The river can be divided into three parts, with the upper reach from the Heyuan County in Gansu Province to Baoji City, the middle reach from Baoji to Xianyang, and the lower reach from Xianyang to the mouth of the Tongguan River (Fig. 1). This study focuses on the part of the river that flows through Shaanxi Province because of concerns over the large number of industries there.

3. Materials and methods

3.1. Sample collection

Sampling was conducted during April 2008, and a total of 63 surface bed sediment samples was collected (Fig. 1) using a plastic grab sampler. Each sample analyzed was composed of three sub-samples, which were taken from the top 5 cm of sediment of the riverbank within a ~30 m distance. These sub-samples were initially stored in clean, sealed, polythene bags and then returned to the laboratory in the Institute of Earth and Environment in Xi'an. All sub-samples were dried in an oven at 40 °C for 2 days. The dried sub-samples were passed though a 1 mm plastic sieve to remove large plant roots and gravel-sized materials. Each set of three sub-samples collected was then compiled into one sample with the same weight (100 g per sample) and homogenized.

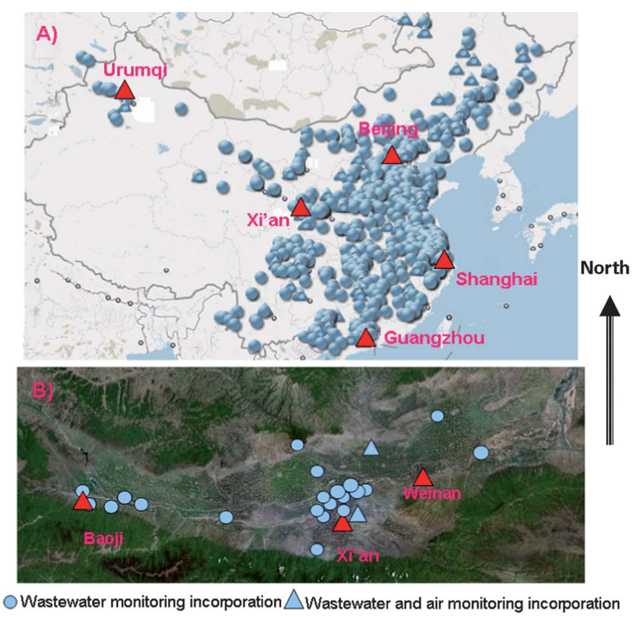

Fig. 2 (A) Locations of the main wastewater discharges in China, indicating the distribution of sources for water pollution; (B) locations of the main wastewater sources around the Wei River (from http://www.ipe.org.cn), which highlight the pollution sources to the east of Baoji and around Xi'an (from Xianyang to the Jinghe River mouth).

3.2. Experiments

Grain size analyses were carried out following pretreatment with H_2O_2 to disaggregate the particles and wet sifting. The sand (>63 μm), coarse silt (2–20 μm), fine silt (20–63 μm) and clay (<2 μm) volume fractions according to Folk classification[15] were analyzed with the use of a X-ray sedigraph.[8]

Organic carbon (OC) and total nitrogen (TN) contents were determined using a CHNOS elemental analyzer (Vario EL III, German) with acid pretreatment.[4] The overall analytical precision calculated from acetanilide standards and duplicates was estimated as ±3% for OC and ±4% for TN.

Each sample was ground and homogenized with a polypropylene mortar and sieved though a 200 mesh (diameter 63 μm) sieve in preparation for the elemental analyses. Major and trace elements were analyzed with the use of an Axios advanced wavelength dispersive X-ray fluorescence unit (WD-XRF; PANalytical, Ea Almelo, The Netherlands). Each 5 g composite sample was compacted into a disc of 32 cm diameter under 30 tf for the XRF analysis. Calibration was conducted with a set of up to 28 national certified reference materials (Soil GBW 07401-GBW07416 and Sediments GBW 07301-GBW07312). Analytical uncertainties were verified by parallel analysis of two national standards (GBW07408 and GBW07312). The certified values, arithmetic means obtained from ten replicate analyses, minimum detection limits, and relative standard deviations of 24 elements in national standard (GBW07408) are reported in Table 2.

3.3. Methods

Principal component analysis (PCA) is widely used to extract a small number of latent factors from complex datasets with the goal of making the results more readily interpretable.[16] In our study, PCA with the VARIMAX normalized rotation was used to identify presumptive sources for groups of trace elements. Principal factors extracted from the variables were retained if their eigenvalues were >1.0. Cluster analysis (CA), was employed to further group the elements based on similarities in the patterns in their concentrations. CA was carried out using Ward's method with squared Euclidian distances. SPSS for Windows, version 11.5 (SPSS Inc, USA) was utilized for the multivariate statistical analysis.

Enrichment factors (EFs) have been used to identify elements whose concentrations are higher than those expected from natural sources, and they have commonly been used to infer anthropogenic influences.[17–19] EFs are calculated from the equation

$$EF = (C_n/\mathrm{Th})_{[\mathrm{sample}]}/(B_n/\mathrm{Th})_{[\mathrm{background}]}$$

Table 2 Certified values, arithmetic means obtained from ten replicate analyses, minimum detection limits (MDL) and relative standard deviations (RSD) of 24 elements (the unit for the first 7 elements is % and unit of mg kg^{-1} for others) in national standard (GBW07408)

Elements	Certificate values	Obtained values	MLD	RSD
Na	1.27	1.24	0.07	2%
Mg	1.42	1.46	0.06	2%
Al	6.31	6.29	0.20	1%
Si	27.35	27.39	0.59	1%
K	2.00	2.04	0.07	1%
Ca	5.90	5.72	0.15	1%
Fe	3.13	3.16	0.31	1%
Ti	3800	3811.6	319.2	1%
Ba	480	481.5	47.8	3%
Rb	96	97.8	10	2%
Sr	236	235.0	18.5	1%
Y	26	25.64	2.6	2%
Zr	229	235.4	22.9	1%
Nd	32	29.3	10.6	11%
Th	11.8	13.2	4.2	9%
Nb	15	14.7	2.2	3%
Cr	68	66.7	8.0	2%
Mn	650	651.7	56.6	1%
Co	12.7	12.4	2.7	6%
Ni	31.5	30.9	2.9	3%
As	12.7	12.3	5.9	8%
Cu	24.3	22.7	4.1	6%
Pb	21	20.2	3.5	6%
Zn	68	65.9	6.8	2%

where $(C_n)_{[sample]}$ is the concentration of the element of interest in a sample and $(B_n)_{[background]}$ is the element's concentration in Shaanxi soils,[20] which are 6.87% for Al, 9.2 mg kg^{-1} for As, 2.23% for Ca, 10.1 mg kg^{-1} for Co, 53.9 mg kg^{-1} for Cr, 20.0 mg kg^{-1} for Cu, 2.73% for Fe, 0.63% for Mg, 482.0 mg kg^{-1} for Mn, 8.92 mg kg^{-1} for Nb, 23.4 mg kg^{-1} for Ni, 20.9 mg kg^{-1} for Pb, 66.1 mg kg^{-1} for Zn, and 12.8 mg kg^{-1} for Th. The rationale for choosing Th as a reference element is presented in Section 5.3. For sediments, EFs close to unity point to a crustal origin while those greater than two can be considered to have a non-crustal source.[16]

The Geoaccumulation Index (I_{geo}) introduced by Muller[21] was used to assess metal pollution in the sediments. I_{geo} is calculated using the equation

$$I_{geo} = \log_2(C_n/1.5B_n)$$

where C_n and B_n are the same as in the EF calculation. The I_{geo} values for sediments can generally be classified as uncontaminated ($I_{geo} < 0$), slightly contaminated ($1 < I_{geo} < 0$), moderately contaminated ($1 < I_{geo} < 2$), moderately to strongly contaminated ($2 < I_{geo} < 3$), strongly contaminated ($3 < I_{geo} < 4$), strongly to extremely contaminated ($4 < I_{geo} < 5$), and extremely contaminated ($I_{geo} > 5$).[21]

The sediment quality guide proposed by Long *et al.*[22] has been used to assess the toxicity of sediments and was used for that purpose in our study. This approach is based on the relationship between the measured concentrations of chemicals and observed biological effects (such as mortality or impairment of growth or reproduction in living organisms). In this study, the Effects Range-Low (ER-L) and Effects Range-Median (ER-M) concentrations were used to approximate these threshold values. ER-L is designed to represent concentrations below which biological effects are rarely observed while ER-M represents concentrations above which the incidence of adverse effects is increased by 60% to 90%.[22]

4. Results

4.1. Sediment features

Sediments of the Wei River can be characterized as sandy silts, with silt (including both coarse and fine silt) composing 70.4% and sand of 21.1% of the dry weight on average (Table 3). Correlation coefficient analysis (Table 4) suggests that elemental concentrations vary as a function of the sediments' grain size. As grain size decreases, the concentrations of Al, As, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Rb, Pb and Zn increase, but Si and Na decrease. All measured PHTEs concentrate in finer particles, and therefore these elements are more readily transported, potentially influencing the lower reaches of the Wei, and possibly even the Yellow River.

The OC contents range from 0.14 to 1.62%. The TOC concentrations, like those of the PHTEs, are highest in the finest particles (Table 4). Since organic matter can act as a metal carrier,[23] the strong correlations of OC with the PHTEs (Table 4)

Table 3 Descriptive statistics for major (the units for the first 7 elements are %) and trace element concentrations (unit of mg kg^{-1}) in surface sediment samples, and sediment characteristics: grain size (as % contents of clay, fine silt, coarse silt and sand) and organic matter (OC% concentrations and C/N ratio) for the Wei River

Elements	Average	Minimum	Maximum	SD[a]	CV[b]	Skewness
Na	1.52	1.13	1.89	0.17	0.11	−0.55
Mg	1.14	0.39	1.49	0.23	0.2	−0.97
Al	5.82	4.66	6.87	0.43	0.07	−0.1
Si	29.73	25.95	36.08	1.75	0.06	0.84
K	1.94	1.62	2.76	0.23	0.12	1.34
Ca	4.99	2.17	6.37	0.69	0.14	−1.43
Fe	2.65	1.13	3.49	0.44	0.17	−0.89
Ti	3689.3	1448.96	5693.56	602.01	0.16	−1.08
Ba	563.53	439.52	975.72	110.16	0.2	1.7
Rb	92.29	64.9	122.17	10.82	0.12	0.35
Sr	232.45	173.19	303.39	24.85	0.11	1
Y	25.34	11.3	42.84	4.7	0.19	−0.19
Zr	291.18	92.66	631.06	104.16	0.36	0.92
Nd	29.54	10.27	55.57	7.74	0.26	0.03
Th	11.75	6.58	18.03	1.83	0.16	0.67
Nb	14.12	10.97	17.48	1.59	0.11	−0.02
Cr	65.41	24.79	84.84	11.93	0.18	−1.33
Mn	557.67	254.28	751.07	91.82	0.16	−0.55
Co	9.53	4.65	13.86	1.92	0.2	−0.43
Ni	26.33	13.25	37.24	4.81	0.18	−0.33
As	17.17	6.05	111.62	19.3	1.12	3.81
Cu	25.75	9.33	65.65	12.19	0.47	1.4
Pb	25.74	10.65	64.11	9.82	0.38	2.32
Zn	78.86	29.98	157.74	33.78	0.43	0.81
% TOC	0.68	0.14	1.62	0.38	0.56	2.51
C/N	6.2	3.1	10.8	2.2	0.35	0.19
% Clay	8.5	2.5	22.4			
% Fine silt	36.5	8.5	79.2			
% Coarse Silt	33.9	6.2	63.1			
% Sand	21.1	0	81.8			

[a] SD = Standard deviation. [b] CV = Coefficient of variation, which is defined as average (arithmetic mean) divided by SD.

Table 4 Correlation coefficients between elements of surface sediments of the Wei River, grain-size distribution (in micrometers) and organic carbon (OC)[a]

Components	<2.0	2.0–20.0	20–63	>63	OC
Na	*−0.440*	*−0.374*	0.269	0.208	**−0.543**
Mg	**0.512**	**0.507**	0.055	**−0.579**	**0.498**
Al	**0.609**	**0.603**	−0.129	**−0.544**	**0.640**
Si	**−0.614**	**−0.579**	0.038	**0.591**	**−0.618**
K	0.135	0.200	**−0.739**	*0.354*	0.275
Ca	**0.509**	**0.470**	−0.039	*−0.476*	**0.512**
Ti	0.347	*0.367*	*0.407*	**−0.690**	0.230
Fe	**0.639**	**0.630**	−0.102	**−0.595**	**0.639**
Ba	−0.197	−0.136	**−0.486**	**0.519**	−0.089
Rb	**0.465**	**0.540**	**−0.743**	0.006	**0.608**
Sr	−0.074	0.062	**−0.468**	0.312	−0.040
Y	0.275	0.225	**0.548**	**−0.659**	0.117
Zr	−0.245	−0.344	**0.616**	−0.116	*−0.406*
Nd	0.298	0.125	**0.505**	*−0.462*	0.213
Th	0.234	0.134	*0.421*	−0.013	0.274
Nb	0.203	*0.393*	0.140	*−0.483*	0.042
Cr	**0.478**	*0.386*	0.290	**−0.644**	*0.421*
Mn	**0.625**	**0.623**	−0.202	**−0.509**	**0.634**
Co	**0.717**	**0.699**	−0.183	**−0.606**	**0.673**
Ni	**0.540**	**0.529**	−0.071	**−0.509**	**0.592**
As	**0.624**	**0.554**	−0.088	**−0.535**	**0.636**
Cu	**0.732**	**0.604**	−0.255	**−0.475**	**0.877**
Pb	**0.624**	**0.609**	**−0.496**	−0.276	**0.825**
Zn	**0.717**	**0.699**	−0.183	**−0.606**	**0.673**
OC	**0.688**	**0.503**	−0.383	−0.282	

[a] Bold denotes significance at the 0.01 level (2-tailed), and italics denotes significance at the 0.05 level (2-tailed).

Table 5 Rotated component matrix of principal component analysis (PCA) for elements in the surface sediments of the Wei River. (PCA loadings >0.5 are shown in bold.)

	Component			
Element	1	2	3	Extraction
Ti	0.286	**0.688**	**0.622**	0.942
Rb	0.243	**−0.937**	−0.032	0.937
Sr	−0.167	**−0.849**	−0.032	0.749
Y	0.179	**0.573**	**0.750**	0.923
Zr	−0.323	**0.569**	**0.584**	0.770
Nb	**0.743**	0.006	0.428	0.736
Ba	−0.151	**−0.920**	−0.280	0.948
Nd	0.036	0.394	**0.779**	0.764
Th	0.267	−0.016	**0.850**	0.794
Si	**−0.857**	−0.451	−0.055	0.941
Fe	**0.848**	0.336	0.356	0.958
Mg	**0.820**	0.510	0.155	0.957
Ca	**0.595**	**0.643**	0.136	0.786
Na	**−0.916**	−0.098	0.066	0.853
K	0.033	**−0.952**	−0.252	0.972
Cr	**0.551**	**0.667**	0.354	0.874
Mn	**0.852**	0.144	0.255	0.813
Co	**0.737**	0.193	0.249	0.643
Ni	**0.864**	0.294	0.272	0.907
Cu	**0.889**	−0.099	−0.002	0.800
Zn	**0.866**	−0.067	−0.013	0.754
As	**0.683**	−0.072	−0.381	0.617
Pb	**0.777**	−0.271	−0.198	0.717
Al	**0.851**	−0.032	0.237	0.781
Initial eigenvalues	9.928	6.317	3.691	
% variance	41.37	26.32	15.38	
Cumulative %	41.37	67.69	83.07	

suggest that organic matter may enhance the transport of these elements.

4.2. Element concentrations and distributions

The average (arithmetic mean) concentrations of major elements in Wei River sediments followed the order Si > Al > Ca > Fe > K > Na > Mg > Ti (Table 3). All of these elements had a coefficient of variation (CV, *i.e.*, the standard deviation divided by the mean) <0.2. Skewness for the distributions of these major elements varied between −1.4 and 1.3, suggesting relatively narrow spatial variations. The CVs for As, Cu, Pb and Zn were generally greater than or very close to 0.40, but all other trace elements showed lower variances, with CVs <0.40 (Table 3). Spatial distributions of selected elements, presented graphically in Fig. 2, show relatively homogeneous concentrations for most of the elements, but As, Cu, Pb and Zn showed comparatively larger variations.

4.3. Principal component analysis (PCA)

Three factors from the PCA were retained (Table 5) because their eigenvalues exceeded the commonly used threshold value of unity; these factors accounted for 83.1% of the total variance in the data. Factor 1 was loaded with almost half of the elements analyzed, namely Na, Si, Cu, Zn, Ni, Mn, Al, Fe, Mg, Pb, Co, As, Ca and Cr; this factor accounted for 41.4% of the total variance. Na and Si were negatively correlated with the other elements in this group. The loadings for As, Ca and Cr on Factor 1 were lower than 0.7, and this may imply quasi-independent behavior. Factor 2 had strong loadings of Rb, Sr, Ba, K, Ti, Cr, Ca, Y and Zr, and it accounted for 26.3% of the total variance, but Rb, Sr, Ba and K were negatively loaded. The third factor, which accounted for 15.4% of the total variance, was loaded with Th, Nd, Y, Ti and Zr.

The 3-D plot of the PCA loadings (Fig. 3) naturally shows results similar to those in Table 5, but it presents a more nuanced grouping of the elements. The plot separates Factor 1 into two

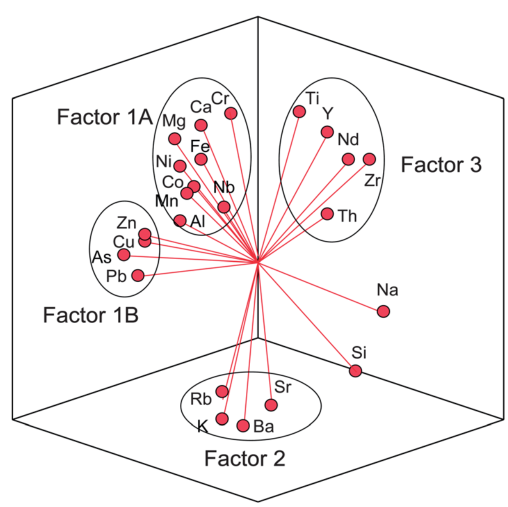

Fig. 3 Three dimensional PCA loading plot for 24 major and trace elements in the surface sediments of the Wei River.

parts (Factors 1A and 1B). With no discernible influence from the quasi-independent elements such as Ti, Cr, Ca, Y and Zr (Table 5), Factor 2 was dominated by Rb, Sr, Ba and K which were the negatively loaded elements. The elements in Factor 3 as revealed by the 3-D plot were very similar to those identified in the PCA (Table 5).

4.4. Cluster analysis (CA)

Five groups can be recognized from the cluster analysis: (1) Ba, K, Rb and Sr; (2) Si and Na; (3) Ti, Y, Nd, Zr and Th; (4) Cr, Ni, Co, Mn, Fe, Ca, Mg and Al; and (5) As, Pb, Cu, Zn and Nb (Fig. 4). The first three groups correspond to PCA Factors 2 and 3 in the PCA, and Si and Na which formed a separate group (Fig. 3) and were negatively correlated with the other elements in the Factor 1 (Table 5). Nb was moved from the Factor 1A to Factor 1B (Fig. 3) in the CA.

5. Discussion

5.1. Spatial patterns of the trace elements

Relatively small spatial variations were observed for almost all of the measured elements, and this is reflected in their low CV values (Fig. 2). The concentrations of As, Cu, Pb and Zn showed somewhat greater variability than the others (Fig. 2). The patterns of relatively high and low concentrations of these four elements in the Wei River sediments generally follow one another, and the Pearson's correlation coefficients between them varied between 0.56 and 0.86 ($p < 0.001$). Relatively high concentrations of the more variable elements occurred in two regions, the first to the east of Baoji City, which has numerous industrial waste discharges, and the second from Xianyang to the Jing River mouth, the most-densely populated part of the study

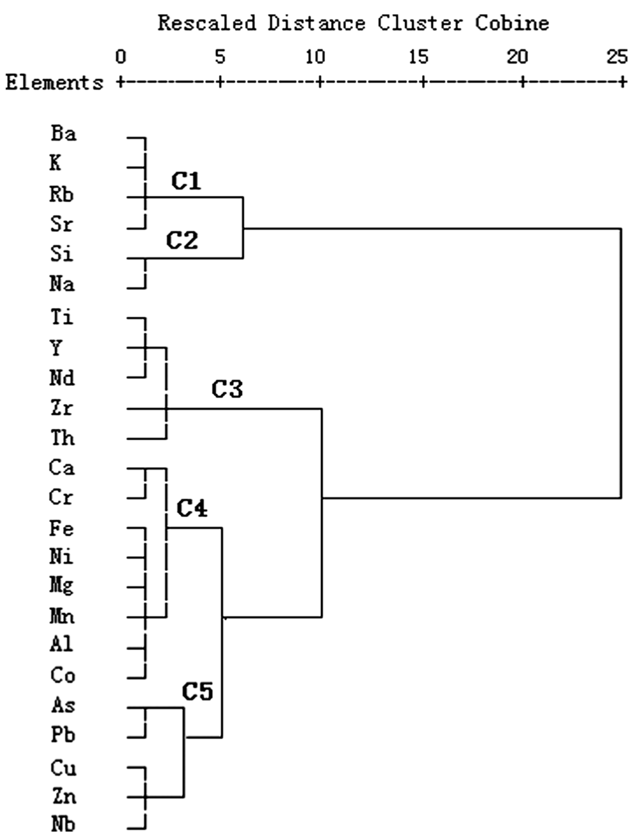

Fig. 4 Hierarchical dendogram for 24 elements obtained by Ward's hierarchical clustering method. The distances reflect the degree of correlation between different elements. Five clusters are identified and denoted as C1 to C5.

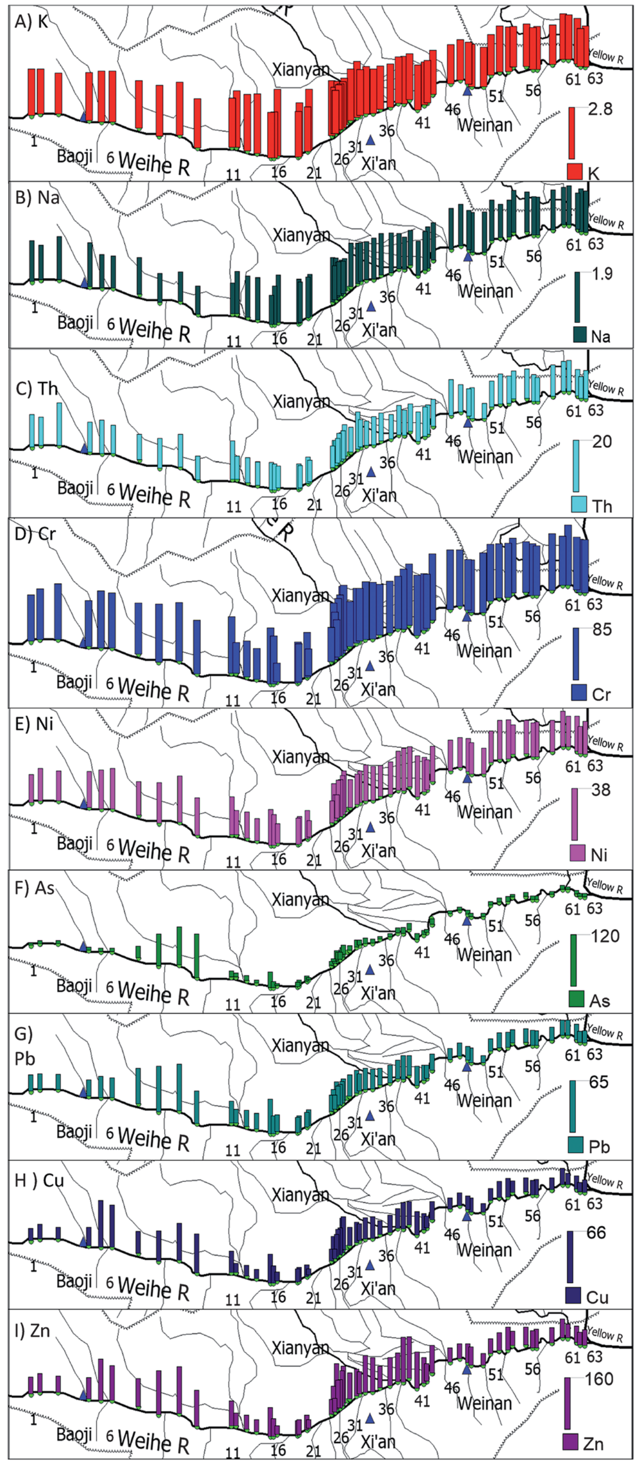

Fig. 5 Spatial distributions of selected elements assigned to different groups by cluster analysis (see Fig. 4).

area (Fig. 5). The highest concentrations of As, Cu, Zn and Pb (111.6, 65.6, 157.7 and 64.1 mg kg^{-1}, respectively) occurred to the east of Baoji City (Fig. 2), where blood lead levels were found to be high.[11] In this region, there are many small chemical and metallurgical plants and paper mills,[24] and their discharge of wastewater is not strongly regulated.

By comparing surface bed trace element contents in the Wei River with those from other large rivers in China[25–27] (Table 6), we find that their average concentrations are generally comparable. As the largest tributary of the Yellow River, it is not surprising that the Wei sediments have trace element contents very close to those reported for the Yellow River.[26] However, compared with the Yangzi and Pearl Rivers, which pass through the most heavily industrialized regions in south China, including the Changjiang and Pearl River Deltas, the concentrations of Cr, Mn, Co, Ni, Cu, Pb and Zn, are generally lower in the Wei. Although these elements are often impacted by pollution sources, the low apparent levels of contamination may be explained by the relatively large inflows of sand caused by the erosion of the Loess Plateau and the comparatively lower level of industrialization along the Wei (Fig. 5A). On the other hand, compared with Shonghua River (Table 6) the Wei River has similar Co concentrations, but relatively higher levels of Cr, Mn, Ni, Cu, As and Pb, and lower levels of Zn. Finally, the PHTE concentrations in the Wei River are comparable with those in other rivers around the world but generally fall into the lower range of those concentrations (Table 6).

Indeed, the overall pattern of relatively high levels of PHTEs in the rivers of south China and lower levels in north China is consistent with the industrial development in southern and eastern China over the past three decades. The large inputs of sand originating from the surrounding deserts and sand lands in north China, *e.g.* the Songhua and Nunjiang Sands contribute to the lower, weight-based, PHTE concentrations observed in the north.

5.2. Source identification

PCA and CA both produced similar results in terms of the elemental groupings (see Section 3.2. and 3.3). Five groups were identified: (1) Ba, K, Rb and Sr; (2) Na and Si; (3) Nd, Th, Ti, Y and Zr; (4) Al, Ca, Co, Cr, Fe, Mg, Mn, Nb and Ni; and (5) As, Cu, Pb and Zn, and the simplest interpretation of these results is that the groups are related to their sources and in some cases also influenced by chemical or physical processes. In fact, the first three groups are dominated by crustal elements, and these results can be interpreted to mean that many if not most of the elements are mainly associated with natural materials.

An additional point to consider is that elements delivered to river systems by erosive processes and subsequently transported in the river water under high pH conditions[28,29] may form groups as a result of similarities in their chemical properties and behavior. For instance, K, Ba, Rb and Sr in Group 1 of the CA are all large-ion lithophile elements. These elements are mainly concentrated in both acidic and alkaline rocks of the earth's upper crust, and they tend to be relatively mobile.[30,31] Rb generally coexists with K in K-rich minerals, such as K-feldspar and biotite, *etc.*[32] Si and Na in Group 2 of the CA are major elements, and they are mainly concentrated in quartz and feldspars, respectively. Furthermore, the concentrations of Si and Na vary with the size distributions of sediments on the Loess Plateau,[33,34] and the close relationship between them is most readily explained by the fact that they both are most abundant in intermediate and coarse-sized loess sediments.[33] The negative correlations of fine particles with Si and Na (Table 4) support this argument. Ti, Y, Nd, Zr and Th in CA Cluster 3 can be classified as immobile lithogenic elements, and they can be regarded as representing general variations in the abundance of mineral matter.[31,35]

Based on the analysis of the distributions of the various elements, the EF and I_{geo} analyses, and the relationships to grain size (Table 4), the remaining elements are presumed to have been influenced by anthropogenic activities, and for the purposes of discussion, they can be further classified based on the PCA (Fig. 3) and CA (Fig. 4) results. The first group is composed of Cr, Ni, Co, Nb, Mg, Mn, Ca, Fe and Al, and therefore it includes both major and trace elements, and this suggests a mixed source resulting from a combination of natural and agricultural activities.

In the last three decades, chemical fertilizers and agrochemicals have become widely used in China, and their application in the study area in particular has become commonplace. Indeed, the usage of fertilizers in Shaanxi province has greatly increased in the past several decades, from 1.2×10^5 thousand tons in 1977 to 11.8×10^5 thousand tons in 2004.[36] Lime and phosphate fertilizers are generally the major sources for trace elements

Table 6 Comparison of concentrations of As, Co, Cr, Cu, Mn, Ni, Pb and Zn (the potentially hazardous trace elements in this study) in sediments from the Wei River and other selected rivers

Locations	As	Co	Cr	Cu	Mn	Ni	Pb	Zn	References
Wei River, China	17.20	9.50	65.40	25.80	557.70	26.30	25.70	78.90	This study
Yellow River, China	na	10.98	64.77	17.80	433.6	26.71	29.49	60.3	Yang and Li[26]
Yangzi River, China	na	15.14	77.95	47.56	828.9	40.93	50.49	116.2	
Pearl River, China	na	16.2	71.4	54.5	908	37.7	97.1	202	Zhang and Wang[27]
Songhua River, China	5.56	9.55	46.3	20.7	529.0	17.4	22.7	83.1	Lin .*et al.*[25]
Brahmaputra River	na	14.5	100.8	na	na	80.4	9.6	78.1	Ramesh *et al.*[44]
Nile River, Egypt	na	15–40.4	37.1–233.0	124.9	125–1008.2	<0.0005	4.6–94.9	146.6–522.3	El Bouraie *et al.*[45]
Tigris River, Turkey	2.1–12.4	18.4–515.6	72.1–158.4	98.7–2860.3	786.2–1681.8	122.1–534.6	146.2–660.1	146.7–1061.5	Varol *et al.*[46]
Danube River, Europe	9.0–68.9	na	35.3–139.0	31.3–662.9	442–1379	24.6–142.8	14.7–107.6	83–622	Woitke *et al.*[47]
Rive Po, Italy	na	na	na	62.1	na	82.8	52.9	269.5	Farkas *et al.*[48]
Colorado River, USA	1–20	na	48–74	7–50	na	na	5–29	62–113	Daessle *et al.*[49]
South Platte River, USA	2.8–31		33–71	18–480	410–6700		19–270	82–3700	Heiny and Tate[50]

among the inorganic fertilizers,[37] and they contain high levels of PHTEs as well.[38] In addition, China also uses significant quantities of compound fertilizers; these amounted to $\sim 1.2 \times 10^7$ tons (in net nutrients) in 2005.[39] Ca and Mg were found to have relatively high EFs (both higher than 2) and I_{geo} values (0.56 and 0.24, respectively, Fig. 6), and this supports the notion that agricultural runoff is a source for this group.

The final group of elements, composed of As, Cu, Pb and Zn, is the most likely to have been strongly affected by industrial wastewater and sewage sludge. These four elements had the highest CVs of all measured elements. Their highest concentrations (Fig. 2), EFs (15.7 for As, 3.5 for Cu, 3.1 for Pb, and 2.9 for Zn) and I_{geo} values (3.6 for As, 1.1 for Cu, 1.0 for Pb, and 0.7 for Zn) were all observed to the east of Baoji where several large enterprises such as the Shaanxi non-ferrous metals smelting works, Baoji cement Ltd., Baoji textile process material Ltd., Baoji Bangfen paper mill Ltd. are located (Fig. 5). These factories commonly discharge industrial and hazardous wastes.[40] In 2008, over 700 paper mills were located around the Wei River.[41] About 4.7×10^8 tons of wastewater were discharged annually into the Wei River in the 1980s; the discharge increased to 9.6×10^8 tons in 2000,[42] and now the river receives about 78% of the industrial wastewater and 86% of the domestic wastewater from domestic and industrial discharges.

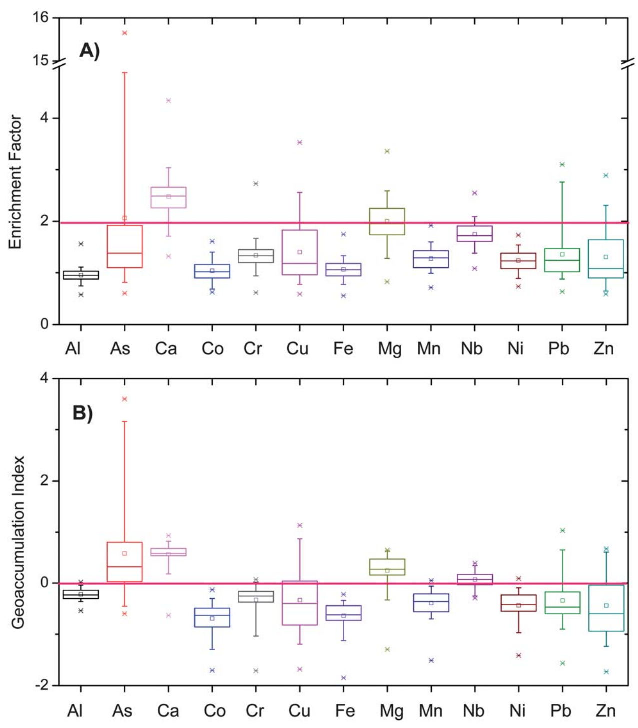

Fig. 6 Box–whisker plots of the enrichment factors (EFs) and geoaccumulation indices (I_{geo}) calculated for elements in Clusters 4 and 5 in Fig. 4, which were suggested to have anthropogenic origins (see text). The boxes enclose the 25^{th} to 75^{th} percentiles; whiskers represent the 5^{th} and 95^{th} percentiles; crosses mark outliers ($<5^{th}$ or $>95^{th}$ percentiles); lines inside the boxes are the medians; squares inside the box show the arithmetic means. The values of zero for I_{geos} and 2.0 for EFs are highlighted with red lines to indicate possible human contamination.

5.3. Pollution and risk assessment

An accurate assessment of pollution levels depends on the selection of appropriate reference elements and valid background values for the EF and I_{geo} calculations. Al, Fe and Ti are commonly used as references in EF analysis.[17–19,35] However, according to the source analysis presented above (see Section 5.2), Al and Fe apparently have been impacted by human activities. Of the lithogenic group of elements (see PCA analysis in Section 4.2), thorium had the lowest CVs and the highest loadings, suggesting that it is the least mobile lithogenic element, and for this reason Th was selected as the crustal reference element.

The EFs and I_{geo} index for Clusters 4 and 5 from the CA analysis, which were suggested to have anthropogenic origins (see Section 5.2), are presented in Fig. 6 in the form of Box–Whisker plots. Average EFs for all measured elements, except Ca and As, were generally lower than 2.0, which suggests that human activities generally have little apparent influence on surface sediments of the Wei River. The average EFs for Ca and As were higher than 2.0 (2.5 and 2.1, respectively), suggesting a modest human impact on the concentrations of these two elements overall. However, the EF for As in Wei sediments from the east of Baoji was 15.7, indicating strong contamination in that area.

I_{geo} values show patterns and results similar to those of the EFs (Fig. 6). Co and Fe had I_{geo} values less than zero, indicating a non-contamination status. Al, Cr, Cu, Mn, Ni, Pb and Zn also had average I_{geo} values that were negative, but their maximum I_{geo} values were positive (and for Cu and Pb even higher than unity), suggesting slight to moderate contamination from these elements in some locations. As noted above, the generally low apparent levels of pollution in the Wei River can be explained, at least in part, by the large silt and sand inputs into the Wei from the Loess Plateau in North Shaanxi; these inputs of natural materials dilute the polluted sediments and mask the influences from anthropogenic sources. The annual sediment discharge into the Wei River is 5.2×10^8 tons, and this amounts to 31.3% of the total discharge of sediments into the Yellow River.[43] As, Ca, Mg and Nb had mean I_{geo} values in the range of 0 to 1, implying overall slight contamination by these elements. Arsenic had its highest I_{geo} values of 3.6 at locations east of Baoji City, indicating strong contamination there, most likely due to industrial wastewater discharge (see Section 4.3).

Effects Range-Low and Effects Range-Median values (Fig. 7) have been proposed by Long *et al.*[22] as reference points for environmental assessments. Expressed as ER-M:ER-L (both in units of mg kg^{-1}), they are 8.2:70 for As, 81:370 for Cr, 34:270 for Cu, 20.9:51.6 for Ni, 46.7:218 for Pb and 150:410 for Zn. Examination of the observed concentrations for the Wei River sediments shows that Cr, Zn and Pb concentrations were generally lower than their ER-L values, but a few samples did exceed their ERL values. These results indicate that occurrences of adverse biological effects due to these elements will be low except for a few cases. In contrast, As, Ni and Cu had concentrations generally higher than their ER-Ls, indicating greater possibilities of adverse biological effects for these elements. Arsenic showed concentrations higher than its ERM value east of Baoji City, indicating that it is the element of greatest concern in terms of adverse biological effects.

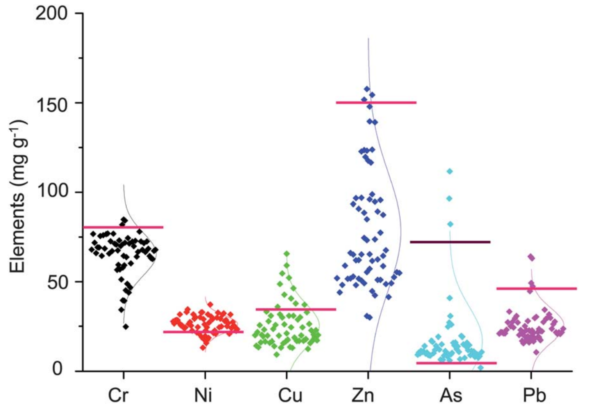

Fig. 7 Comparison of concentrations of Cr, Ni, Cu, Zn, As and Pb with their corresponding Effects Range-Low (ER-L, horizontal red line) and Effects Range-Median (ER-M, horizontal brown line) values. Only As had concentrations higher than its corresponding ER-M value.

6. Conclusions

This is the first systematic study of the concentrations, distributions, and probable sources of selected trace elements in the surface sediments of the Wei River. The geochemical processes influencing their distributions and potential environmental risks have been evaluated. The levels of both major and trace elements were comparable with those in other large rivers in China and around the world. PCA and CA identified five presumptive sources for the elements, and these were interpreted based on the elements' chemical properties and their occurrence in various natural and anthropogenic sources. The concentrations of Cu, Pb, Zn and As showed the greatest variability, and these elements were concluded to be the most strongly perturbed by human activities, especially the discharge of industrial wastewater and sewage sludge.

Relatively high concentrations of the four elements of concern occurred in two areas (1) east of Baoji City, which is where large quantities of the industrial wastewater are discharged, and (2) from Xianyang to the mouth of the Jinghe River, which is the most densely populated part of the study area. The Wei River is located in northwest China and river bed PHTEs in that part of the country are generally lower than in southeastern China. Although large volumes of wastes and wastewater are discharged into the Wei annually, that material is diluted by the large silt and sand inflows from the Loess Plateau; this dilution effect helps explain the relatively low apparent contamination of the PHTEs despite the industrial discharges and runoff. Future studies of water chemistry, biota, *etc.* are needed to more fully assess pollution in the Wei River system. Moreover, the possibility of adverse biological effects from As, Ni and Cu implied by the observed levels of contamination in parts of the Wei confirms the urgency for implementing effective environmental management practices. It is critical that rigorous national standards for wastewater discharge be enacted and rigidly enforced to control water pollution in China.

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