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# Influence of ore deposits on river sediment compositions in Dan River drainage, China

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## ABSTRACT

We mainly investigated trace element contamination of surface sediments in the Dan River drainage, the source of drinking water for the South to North Water Transfer Project, China, to determine trace element sources and associated levels of risk. Sediment samples were collected at 95 sites along the Dan River in connection with field surveys, and total element concentrations were determined using inductively coupled plasma-mass spectrometry (ICP-MS). Concentrations of most elements were lower than background levels; however, toxic heavy metals, such as As, Cd, Pb, and Sb, showed extremely high concentrations at sites associated with nearby metal ore deposits. Moreover, the spatial variations of contamination by some heavy metals were directly related to the distributions of metal ore deposits in the North and South Qinling terrains; sediment samples with especially high concentrations of Sb and As were from the North Qinling terrain, while sediments with especially high concentrations of Cd and Pb were from the South Qinling terrain, suggesting that metal ore distributions and associated mining activity strongly influence the distribution of heavy metals and heavy metal contamination in the Dan River drainage. Multivariate techniques, including Pearson correlation, hierarchical cluster, and factor analysis, were used to assess the sources of metal contamination. Results indicate that distributions of Al, Ba, Cu, Fe, Mg, Mn, Pb, Sn, Ti, V and Zn are controlled by natural sources; Co and Cr by a combination of geological and anthropogenic inputs; whereas As, Cd, Ni, Sb, and Pb appear to be primarily of anthropogenic origin. The ecological risk associated with heavy metal contamination of sediments was rated as moderate, based on an assessment using geo-accumulation index ($I_{geo}$), enrichment factor (EF), potential ecological risk index (RI) and mean probable effect concentration quotient ($m_{PECQ}$).

## 1. Introduction

Because trace metals in sediments are partitioned from the surrounding water, they represent a potential source reservoir of metals that can be released into the hydrological cycle, thereby affecting the quality of aquatic systems. The increasing worldwide contamination of aquatic systems with thousands of industrial and natural pollutants is a critical environmental problem (Schwarzenbach et al., 2006). Sediments are regarded as the ultimate sink for heavy metal cations (Gibbs, 1973), which have therefore been widely used as environmental indicators; thus, stream sediment monitoring can present important information about the extent of pollution in drainages (Acosta et al., 2014; Mirzaei et al., 2014; Singh et al., 2002; Wang et al., 2014; Yuan et al., 2014). River systems in many parts of the world have been contaminated by high concentrations of heavy metals; these include the Yangtze River (Wen et al., 2013; Yang et al., 2014; Zhang et al., 2009), Yellow River (Zhang and Liu, 2002; Zhang and Marie, 1988), Pearl River (Cheung et al., 2003), and Songhua River (Lin et al., 2008) in China, the Seine River in France (Meybeck et al., 2007), the Medway River in the UK (Cundy et al., 2005), the Odiel River in Spain (Borrego et al., 2002) and the Ganges River in India (Singh, 2001). The presence of heavy metals in sediments suggests the possibility of both geological and anthropogenic inputs to watershed (Acevedo-Figueroa et al., 2006; Adamo et al., 2006). Weathering and erosion of deposits enriched in heavy metals naturally generate a high proportion of heavy metal-bearing particles into river systems. Thus, natural surface processes determine background levels of trace metals in river sediments, while anthropogenic activities such as mining and urbanization can lead to abnormally high accumulations of metals.

Trace metals in sediments can be released into overlying water, thereby posing risks to benthic and pelagic biota (Hudson-Edwards, 2003), as well as contaminating drinking water source areas. Hence, data on trace metal concentrations in sediments play an important role in monitoring and evaluating environmental risks, and in mitigating the risks by various remedial measures (Chapman and Wang, 2001; Foster and Charlesworth, 1996; Sarkar et al., 2004).

The South to North Water Transfer Project in China is one of the largest water projects in the world. The project was designed to address

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the water shortage issues in North China, by diverting 45 billion $m^3$ of water per year from the lower (via the eastern route), middle (via the middle route), and upper (via the western route) reaches of the Yangtze River in South China (Jiang, 2009; Zhang, 2009). The middle route, which has been in the process of construction for many years, has an expected annual transfer capacity of 13 billion $m^3$. Via this route, water is collected from Danjiangkou Reservoir on the Han River, a tributary of the Yangtze River, and diverted to North China, including to the areas of Beijing, Tianjin and other main cities along the route, where it will be used for domestic, irrigation, and industrial purposes (Dong et al., 2011d). However, as noted in previous studies, the water quality in the source areas of the Danjiangkou Reservoir, as well as in the reservoir itself and along the middle route, has been severely degraded in recent years (Bu et al., 2010; Li and Zhang, 2010a, 2010b; Li et al., 2008, 2011).

Danjiangkou Reservoir, with a water surface area of 745 $km^2$, is located at the juncture of Hubei and Henan provinces (Fig. 1). Since construction of the reservoir in the 1970s, water quality has improved downstream of the reservoir, indicating that sources of contamination in the drainage are in upstream regions; levels of nitrogen and $COD_{Mn}$ in the reservoir are also relatively high (Li et al., 2009). The spatial distribution of trace elements in the upper Han River suggests that levels of contamination in Danjiangkou Reservoir are particularly high (Li and Zhang, 2010b). Li et al. (2008) found that concentrations of toxic heavy metals (e.g., As, Pb and Sb) in the water of Danjiangkou Reservoir exceeded World Health Organization (WHO) standards, and suggested that the contamination poses health risks in the region.

The water quality of Danjiangkou Reservoir is controlled mainly by inputs from the Dan River and Han River drainages, which are the primary source areas for reservoir waters. As compared with other rivers in the reservoir drainage, the Dan River is the dominant influence on water quality, as it flows directly into the reservoir; thus, heavy metal-bearing sediments are deposited directly into reservoir waters. In addition, sediments with high concentrations of heavy metals can contaminate flowing water after a period of sediment storage, resulting in later pollution of reservoir waters. While Danjiangkou Reservoir is an important source of water for both domestic consumption and agricultural irrigation, few studies have been conducted on heavy metal contamination of surface sediments in reservoir source areas.

The present study focuses on the Dan River drainage, which originates in the Shangzhou region, Shaanxi Province, and flows through the North Qinling and South Qinling geological terrains. Several metal ore deposits are located in the drainage, including for example Sb, Ni, and Pb ore bodies. This study characterized the concentration and spatial distribution of 17 trace elements and heavy metals, based on a study of total 95 sediment samples from the Dan River drainage; elements include those that are naturally occurring, as well as those with an anthropogenic origin. Sources of heavy metal pollution were identified based on an integrated geological and statistical analysis, and the sediment contamination and associated risk levels were evaluated by risk indices, including the geo-accumulation index ($I_{geo}$), enrichment factor (EF), potential ecological risk index (RI) and probable effect concentration quotient ($m_{PECQ}$), thus providing an accurate representation of sediment quality within the drainage. The research will promote and contribute to effective management and conservation strategies of drinking water sources, and also help to improve public health in populations served by the inter-basin South to North Water Transfer Project.

## 2. Site description and geology of the catchment area

The Dan River (formerly known as Dan Shui) drainage (109°30′–112°00′ E, 32°30′–34°10′ N), located in Shaanxi and Henan provinces, China, is the longest tributary of the Han River. The Dan River rises in Heilongkou County in the Qinling Mountains and then flows southeast through Shangluo City, Danfeng County, Shangnan County, Xixia County and Xichuan County, before flowing directly into Danjiangkou Reservoir located on the Han River. The Dan River drainage, with an area of 16,812 $km^2$, is ~2000 m wide and 443 km long, and spans an elevation of 200–2500 m (Fig. 1). Most of the Dan River drainage is mountainous, and well vegetated. The climate in the drainage basin can be considered as north sub-tropic monsoon, with an annual mean temperature of 11 °C–14 °C, and extreme maximum and minimum temperatures of 40.5 °C and −12 °C, respectively. The multiannual mean precipitation in the drainage is 743.5 mm, while the annual potential evaporation varies from 979.3 mm in upstream areas to 1557.5 mm in downstream areas. The temporal distribution of precipitation throughout the year is strongly heterogeneous. More than 80% of the total

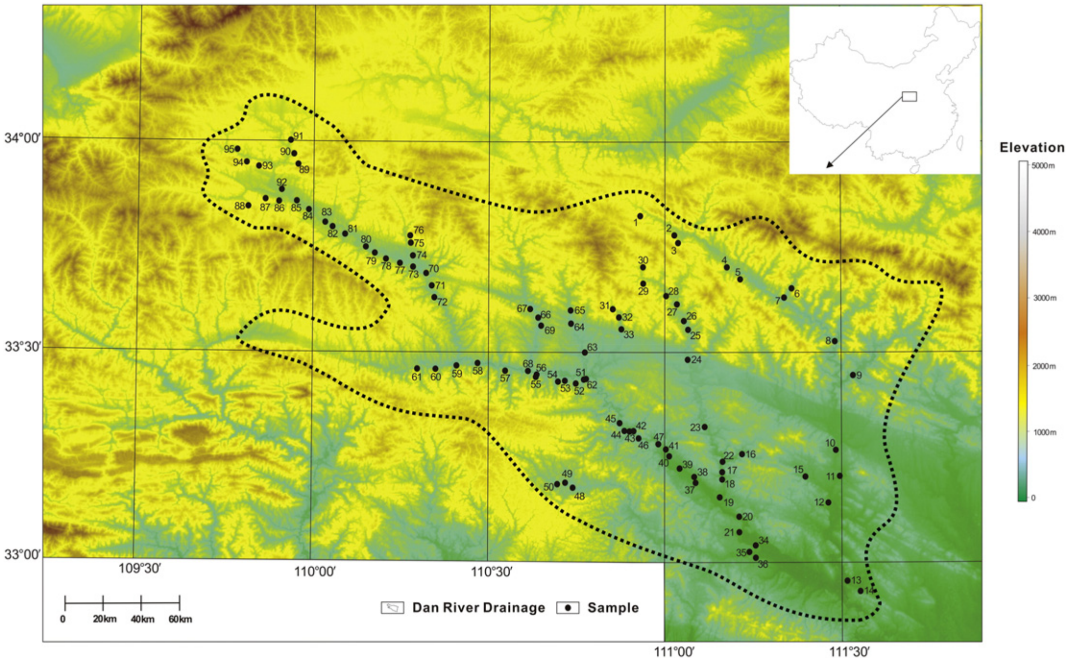

Fig. 1. Sampling sites and drainage systems of the Dan River drainage, China.

annual precipitation falls in the rainy season between May and October and less than 20% of the total falls from November to April (Li et al., 2008). In addition, floods and rainstorms occur frequently in the drainage during the rainy season, especially during July–September.

The Dan River drainage which flows across the Qinling orogen is comprised of the North Qinling belt and the South Qinling belt, which are separated by the Shangdan suture zone (Dong et al., 2011c; Shi et al., 2013). The North Qinling belt is comprised mainly of Precambrian basement units, Neoproterozoic and Lower Paleozoic ophiolites, and volcanic-sedimentary assemblages. From north to south, the Kuanping, Erlangping and Qinling groups and the Songshugou Proterozoic ophiolite are separated from one another by thrust faults or ductile shear zones (Dong et al., 2011a). The Shangdan suture zone is marked by a discontinuously exposed tectonic mélange, which consists mainly of ophiolitic assemblages and arc-related volcanic rocks, traditionally referred to as the Danfeng Group. The South Qinling belt is characterized by thin-skinned structures, including a south-vergent thrust–fold system comprising pre-Sinian basement and overlying Sinian and Phanerozoic sedimentary rocks (mainly Sinian to Carboniferous clastic, clay, and carbonate rocks) (Dong et al., 2011b). A few upper Paleozoic–Lower Triassic clastic sedimentary rocks are present in the northern part of the South Qinling belt (Xu et al., 2014). In addition, the Qinling orogenic belt, which is associated with multiple tectonic events, crust–mantle exchange, effects of geological fluids, and emplacement of minerals, has become one of the most important metal ore resources in the world (Mao et al., 2011). The Qinling orogen is rich in Mo, Au, Ag, Pb, and Zn deposits, which are dispersed throughout the orogen, siderophiles (Fe, Ni, and V) and Cu deposits located near the Shangdan suture zone, and large volumes of mafic rocks and Sb located mainly in the North Qinling region and north of Xunyang. In the catchment area of the Dan River drainage, Sb ores are distributed mainly in the North Qinling terrain area; some other metal ores (Ni, Fe, and Cu) are exposed in the South Qinling terrain area. The locations of the metal ores are shown in Fig. 2. According to Geological Report of Luanchuan Sheet (1964), Neixiang Sheet (1961), Shangnan Sheet (1961), Shangxian Sheet (1958), Yunxian Sheet (1959), Henan Bureau of Geology (1961), Henan Bureau of Geology (1964), Shaanxi Bureau of Geology (1958), Shaanxi Bureau of Geology (1959) and Shaanxi Bureau of Geology (1961), there are differences of mining and processing extent between the metal ore deposits in the study area. In the North Qinling terrain area, Sb and Pb ore deposits have been mined for several decades. Fe, Cu and V ore deposits in the South Qinling terrain area were being mined and processed during the last fifty years, whereas Ni and Pb ores were rarely mined due to their low exploiting values (low grade and distributed widely).

## 3. Materials and methods

### 3.1. Sample collection and analytical methods

Nighty-five river surface sediment samples were collected using a grab sampler in August, 2013 (Fig. 2). The lithology of sediments was classified as mud, silt and sand by the dominant size, which is similar to the categorization of sedimentary rocks (observed in the field) (Table S1). All of them were freeze-dried, homogenized, and crushed slightly for chemical analyses. The metal concentrations in sediments were determined by the following procedure: Aliquots (0.1 g) of sediment samples were decomposed in a digestion vessel with a mixture of 5 ml nitric acid ($HNO_3$) and 3 ml hydrofluoric acid (HCl). The mixture was heated in a MARS microwave digestion system (CEM Corporation, USA) for 20 min at 190 °C (Qin et al., 2014). After cooling, the digest was quantitatively transferred into a 50 ml PTFE crucible and evaporated to dryness at 320 °C in a fume hood until the acid solution was evaporated completely. After then, 2 ml nitric acid ($HNO_3$) was injected into the solution and then transferred into a 100 ml glass tube, filled up by super purified water, homogenized, and stored at 4 °C until measured by ICP-MS. The selected trace elements including Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sb, Sn, Ti, V and Zn were analyzed by inductively

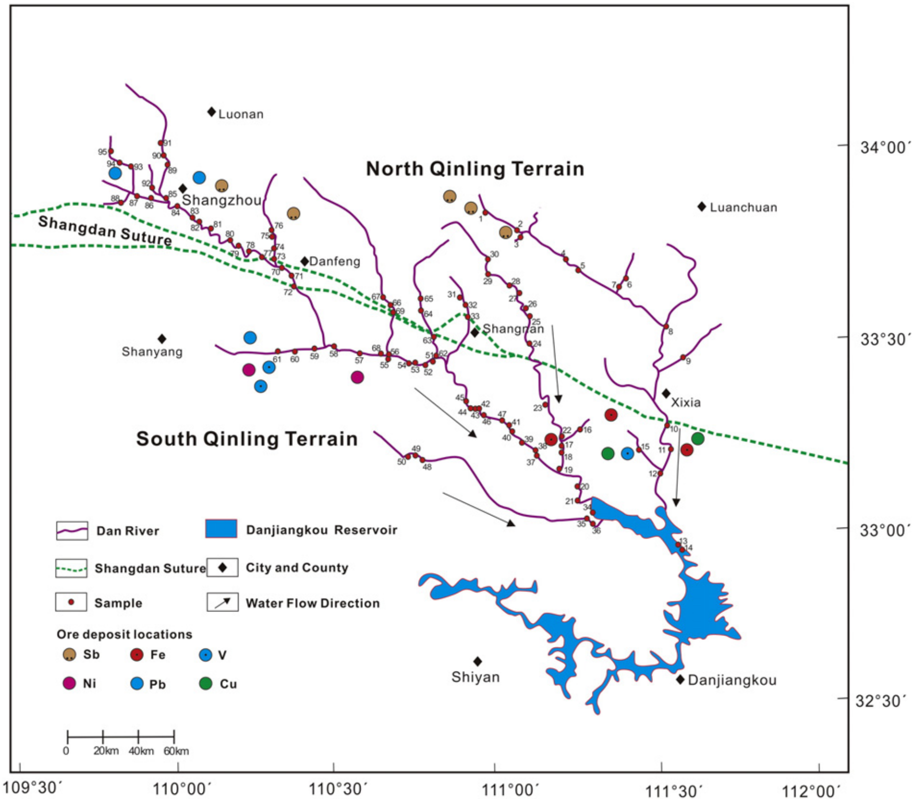

**Fig. 2.** The Dan River drainage showing tributary rivers and located metal ore deposits, after the 1/200,000 Geological Ore Map and report of Luanchuan Sheet (1964), Neixiang Sheet (1961), Shangnan Sheet (1961), Shangxian Sheet (1958) and Yunxian Sheet (1959).

**Table 1**
Recovery percentage (%) of the trace elements in the standard samples using ICP-MS.

| Al | As | Ba | Cd | Co | Cr | Cu | Fe | Mg | Mn | Ni | Pb | Sb | Sn | Ti | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 107.2 | 111.4 | 106.9 | 97.8 | 90.7 | 90.6 | 90.4 | 101.7 | 105.5 | 97.2 | 90.0 | 95.3 | 96.9 | 98.1 | 98.8 | 94.0 | 96.5 |

coupled plasma mass spectrometry (ICP-MS) at the Chinese Research Academy of Environmental Sciences. For accurate and credible results of Al, Fe, Mg and Mn, samples were diluted by 150 times when detecting these elements, due to their high concentrations than the others. Method validation and quality control samples were done by using a standard reference material. All specimens and standard samples were analyzed in batches, which included a procedural blank. A good agreement was found between the data generated and those certified by the standard samples, and the recovery percentages ranged from 90.0% (Ni) to 111.4% (As) (Table 1).

### 3.2. Data analysis

Data analysis was carried out using SPSS 19.0 and Surfer 10.0 for Windows. Relationships among the considered variables were tested using Pearson's coefficient as a non-parametric measure with statistical significance set priori at $p < 0.05$ (Han et al., 2006). Hierarchical cluster analysis (HCA) was applied to group objects (cases) into categories or clusters on the basis of similarities within a cluster and dissimilarities between different clusters with respect to distance between objects (Monjerezi et al., 2011). In the present study, R-model hierarchical agglomerative CA was performed on the normalized data set using squared Euclidean distances as a measure of similarity and Ward's method to obtain dendrograms. Q-model CA was also studied to get stations in the same category with the similar source of pollutants, indicating high concentration sites controlled by metal ores. Factor analysis (FA) was employed to find and interpret the structure of the underlying data set through a reduced new set of orthogonal (non-correlated) variables (total factors), arranged in decreasing order of importance (Gielar et al., 2012). FA was conducted to identify the main influencing factors of trace metal element distribution. Besides considerable data reduction, total factors can explain the entire multidimensional data set variability without losing much original information. The Kaiser–Meyer–Olkin (KMO) and Bartlett's test were introduced to evaluate the validity of FA, and a >0.5 of KMO and significant Bartlett's test were requisite before the FA (Mao et al., 2012; Zhou et al., 2007a, 2007b). FA with varimax rotation of standardized component loadings was conducted for extracting and deriving factors and those factors with eigenvalue > 1 were retained. Contour maps were obtained by kriging interpolation method and created with Surfer 10.0.

### 3.3. Risk assessment

The ecological risks of heavy metals in sediments were assessed using four different methods including geo-accumulation index ($I_{geo}$), enrichment factor (EF), potential ecological risk index (RI) and probable effect concentration quotient ($m_{PECQ}$). The geoaccumulation index ($I_{geo}$) was first proposed by Müller (1969) to assess the degree of metal contamination in aquatic sediments by comparing observed concentrations with background values (Eq. (1)):

$$I_{geo} = \log_2[(C_n/(1.5 \times B_n)] \tag{1}$$

where $C_n$ is the concentration measured in the sediments and $B_n$ is the geochemical background concentrations (Table 2). In this study, the background geochemical compositions of the river sediments in China were chosen as the background values for calculating the $I_{geo}$ values (Yan et al., 1995). The constant 1.5 allowed us to analyze natural fluctuations in the content of a given substance in the environment and to be a correction factor due to lithogenic effluents (Lin et al., 2008). The following classification was given for the $I_{geo}$ by $<0$ = practically unpolluted (level 0), 0–1 = unpolluted to moderately polluted (level 1), 1–2 = moderately polluted (level 2), 2–3 = moderately to strongly polluted (level 3), 3–4 = strongly polluted (level 4), 4–5 = strongly to very strongly polluted (level 5), and >5 = very strongly polluted (level 6).

Enrichment factor (EF) was performed to determine whether metals in sediments were of anthropogenic origin (Sinex and Helz, 1981).

**Table 2**
Concentrations of trace elements and heavy metals in the surface sediments of the Dan River drainage, China (unit in μg/g), and comparison with other rivers.

| | Min | Max | Mean | S.E. | Background values of sediments in China[a] | Several rivers in China and the world | | | | | | UC[d] | PECs[e] | PRV[f] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Amazon[b] | Ganges[b] | Congo[b] | Garonne[b] | Mississippi[b] | Yangtze[c] | | | |
| Al | 469.80 | 8301.00 | 3884.19 | 1668.08 | 68,824 | 115,000 | 77,000 | 117,000 | 118,000 | 88,000 | 65,375 | 77,440 | | |
| As | 1.88 | 13.71 | 7.97 | 2.85 | 9.1 | 5.3 | | 3.8 | | 14.6 | | 2 | 33 | 15 |
| Ba | 9.70 | 390.30 | 53.16 | 42.16 | 499 | 700 | 490 | 790 | 815 | | | 668 | | |
| Cd | 0.03 | 8.30 | 0.80 | 0.90 | 0.14 | | | | | 1.4 | 0.26 | 0.102 | 4.98 | 1 |
| Co | 0.32 | 2.04 | 0.81 | 0.33 | 12 | 41 | 14 | 25 | 39 | 21 | | 11.6 | | |
| Cr | 1.72 | 23.69 | 4.69 | 2.69 | 58 | 193 | 71 | 175 | 255 | 72 | 78.9 | 35 | 111 | 90 |
| Cu | 0.83 | 15.09 | 2.13 | 1.59 | 21 | 266 | 30 | | 51 | 42 | 30.7 | 14.3 | 149 | 50 |
| Fe | 439.50 | 3018.00 | 1688.65 | 487.14 | 30,800 | 55,000 | 37,000 | 71,000 | 58,000 | 47,400 | 33,394 | 30,890 | | |
| Mg | 80.70 | 4746.00 | 672.63 | 590.02 | 7800 | 11,200 | 12,400 | 5800 | 17,300 | | | 13,510 | | |
| Mn | 14.93 | 122.46 | 39.76 | 17.76 | 682 | 1030 | 1000 | 1400 | 1700 | 1300 | 766 | 527 | | |
| Ni | 0.18 | 12.64 | 1.91 | 1.60 | 24 | 105 | 80 | 74 | 33 | 55 | 31.8 | 18.6 | 48.6 | |
| Pb | 0.64 | 49.35 | 3.40 | 5.26 | 25 | 105 | | 455 | 381 | 45 | 27.3 | 17 | 128 | 70 |
| Sb | 0.03 | 13.47 | 0.68 | 1.88 | 0.73 | 1.9 | | 1.0 | | | | 0.31 | | |
| Sn | 0.09 | 0.47 | 0.25 | 0.08 | 3.3 | | | | | | | 2.5 | | |
| Ti | 94.65 | 641.10 | 281.01 | 89.54 | 4200 | 7000 | 5300 | 8400 | 5000 | | | 3117 | | |
| V | 2.36 | 28.63 | 6.59 | 3.64 | 80 | 232 | | 163 | 150 | | | 53 | | |
| Zn | 2.00 | 154.35 | 12.76 | 19.26 | 68 | 426 | 163 | 400 | 874 | 184 | 94.3 | 52 | 459 | 175 |

[a] Background values of sediments in China (Yan et al., 1995).

[b] Concentrations of trace elements in the surface sediments of Amazon River, Ganges River, Congo River, Garonne River, and Mississippi River (Martin and Meybeck, 1979, and references therein).

[c] Concentrations of trace elements in the surface sediments of Yangtze River (Zhang et al., 2009).

[d] Average contents in the upper continental crust (Wedepohl, 1995).

[e] Probable effect concentrations (Ingersoll et al., 2001).

[f] Preindustrial reference level (Hakanson, 1980).

Normalization of metal concentration was used to compensate for the natural variability of heavy metals in sediments (Loring, 1991). Here we selected Fe as the normalize reference element for calculation of the heavy metal enrichment factor (EF), and metal-to-Fe ration in upper continental crust (UC) as the background values. In this study, the EF was calculated for all toxic TM using the following equation (Eq. (2)):

$$\mathrm{EF} = ([\mathrm{TM}/\mathrm{Fe}])_{\mathrm{sample}}/([\mathrm{TM}/\mathrm{Fe}])_{\mathrm{UC}}. \tag{2}$$

In this equation, the concentrations of TM and Fe in the UC were taken from Wedepohl (1995) (Table 2). So far, five degrees of contamination defined by EFs have been commonly adopted: EF < 2, deficiency to low enrichment; EF = 2–5, moderate enrichment; EF = 5–20, significant enrichment; EF = 20–40, very high enrichment; and EF > 40, extremely high enrichment (Sutherland, 2000).

Hakanson (1980) suggested a potential ecological risk index to assess the degree of contamination for sediments in the aquatic system quantitatively. And this risk index has been proved as a highly effective tool to assess the overall contamination of aquatic sediments. According to Hakanson's methodology, the potential ecological risk (RI) of sediments was defined as (Eqs. (3) and (4)):

$$\mathrm{Er}^{\mathrm{i}} = \mathrm{Tr}^{\mathrm{i}} \times \left({\mathrm{C}_{\mathrm{s}}}^{\mathrm{i}}/{\mathrm{C}_{\mathrm{n}}}^{\mathrm{i}}\right) \tag{3}$$

$$\mathrm{RI} = \Sigma \mathrm{Er}^{\mathrm{i}}. \tag{4}$$

In these equations, i represents a given element, $\mathrm{Tr}^{\mathrm{i}}$ is the toxic response factor of element i (Cd 30, As 10, Pb 5, Cu 5, Cr 2, and Zn 1), $\mathrm{C}_{\mathrm{s}}^{\mathrm{i}}$ is content of element i in the samples, $\mathrm{C}_{\mathrm{n}}^{\mathrm{i}}$ is the preindustrial reference level (PRV) of element i (Table 2), and $\mathrm{Er}^{\mathrm{i}}$ is the potential ecological risk factor for element i. The RI values of <150, 150 to 300, 300 to 600, and >600 stand for low, moderate, considerable, and very high levels of ecological risk for the river.

The probable effect concentrations (PECs), developed by Ingersoll et al. (2001), were intended to identify the contaminant concentration thresholds. Harmful effects on sediment-dwelling organisms were expected to occur frequently, if levels in the samples above these concentrations. The PECs have been adopted as an informal tool to evaluate sediment chemical data in relation to possible adverse effects on aquatic system. A probable effect concentration quotient (PECQ) was calculated for each heavy metal in each sample by dividing the concentration of a kind of metal by the PECs for that metal.

$$\mathrm{PECQ}_{\mathrm{i}} = \mathrm{C}_{\mathrm{i}}/\mathrm{PECs}. \tag{5}$$

In this equation, i represents a given element, $\mathrm{PECQ}_{\mathrm{i}}$ is the probable effect concentration quotient of element i, $\mathrm{C}_{\mathrm{i}}$ is content of element i in the samples. The reliable normalized PECs included: arsenic (33.0 μg/g), cadmium (4.98 μg/g), chromium (111 μg/g), copper (149 μg/g), lead (128 μg/g), nickel (48.6 μg/g), zinc (459 μg/g) (Table 2). A mean PECQ ($\mathrm{m}_{\mathrm{PECQ}}$) was then calculated for each sample by adding the individual quotient for each chemical and dividing this sum by the number of reliable PECs evaluated. The $\mathrm{m}_{\mathrm{PECQ}}$ values of ≤0.1, >0.1–1.0, and >1.0 indicate relatively uncontaminated sediments, moderately contaminated sediments, and highly contaminated sediments, respectively.

## 4. Results and discussion

### 4.1. Heavy metals in surface sediments

The ranges and mean concentrations of elements in surface sediments are summarized in Table 2; data were collected for Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sb, Sn, Ti, V, and Zn. Based on mean values, the metal elements can be divided into three groups: (1) dominant metals with concentrations of >100 μg/g, including Al (3884.2 μg/g), Mg (672.6 μg/g), Fe (1688.6 μg/g) and Ti (281.0 μg/g); (2) metals with concentrations of 10–100 μg/g, including Ba (53.2 μg/g), Mn (39.8 μg/g) and Zn (12.8 μg/g); and (3) relatively low-concentration trace elements (concentrations < 10 μg/g), including As (8.0 μg/g), Cr (4.7 μg/g), Cd (0.8 μg/g), Co (0.8 μg/g), Cu (2.1 μg/g), Ni (1.9 μg/g), Pb (3.4 μg/g), Sb (0.7 μg/g), Sn (0.3 μg/g) and V (6.6 μg/g) (Fig. 2).

The mean concentrations of trace metals in the Dan River drainage were much lower than background values for river sediments in China, with the exception of concentrations of Cd, Sb, and As (Table 2). However, peak concentrations of As, Cd, Pb, Sb, and Zn were much higher than background values, and were much higher than mean concentrations observed in surface sediments in other rivers of the world (Table 2). The concentrations of most trace metals were, on the other hand, much lower than mean concentrations worldwide. Levels of several toxic heavy metals (e.g., Cd and As) in Dan River sediments were much higher than worldwide averages in other rivers, whereas levels of Sb were comparable to levels in other rivers.

The box plots in Fig. 3 show variations in trace metal concentrations in river sediments in the Dan River drainage. Extremely high concentrations of elements, including Ba, Cd, Cr, Cu, Mg, Mn, Ni, Pb, Sb, Ti, V, and Zn, were found in Dan River sediments; these unusually high concentrations generally occurred in sediments located downstream from metal ore deposits. Extremely high Sb concentrations in surface sediments were obtained from sites 1, 2, 3, 5, and 74, all of which are located near to Sb ore deposits, and, to a lesser degree, from sites 4, 10, 11, 73, and 75. The concentrations of Co, Cu, Mn, Pb, Ti, V and Zn were highest at site 15, which is very close to several ore deposits, including V, Fe, and Cu ore deposits. Sample site 61, which is in the vicinity of Ni, V, and Pb ore deposits showed relatively high concentrations of Cd, Ni and Zn. Sediments from sites 10 and 11, located near Cu and Fe ore deposits, showed relatively high concentrations of Cr, Cu and Pb, and Cu, respectively. Concentrations of Pb were relatively high at sites 1, 12, 54, 72, 74, 79, 83, and 94, all of which are located near metal ore deposits. In addition, concentrations of Cr and V were relatively high at sites 22 and 16, respectively, probably on account of Fe and V ore bodies located nearby. Generally, high concentrations of metals decreased dramatically away from metal ore deposits, which were the source of the contamination. The results therefore suggest that metal ore deposits are the dominant influence on heavy metal pollution in the Dan River drainage sediments.

The spatial distribution of trace metals in Dan River drainage surface sediments is presented in Fig. 4 and Table 3. Generally, Sb was the dominant heavy metal in the North Qinling terrain, whereas Cd, Cu, Mn, Ni, Pb, and V were the dominant metals in the South Qinling terrain. This pattern is probably the result of different types of metal ore deposits and lithologies in the North and South Qinling terrains. Sediments from the Shangdan suture zone exhibit relatively high concentrations of Cr, Fe, Sb, and Pb; the high Cr and Fe contents are associated with ophiolites in the suture zone, whereas concentrations of Sb and Pb may be the result of transport process of metal-bearing sediments in the vicinity of Sb. Overall, the distributions of heavy metals in surface sediments are controlled mainly by occurrence of metal ore deposits and metal-enriched rocks in the catchment area.

### 4.2. Contamination and risk assessment of trace elements in surface sediments

The $\mathrm{I}_{\mathrm{geo}}$, EF, RI, and PECQ values for each element were calculated to assess contamination and risk assessment of trace elements in the surface sediments (Table 4). According to the $\mathrm{I}_{\mathrm{geo}}$, most trace metals were classified as level 0 (unpolluted), except As, Cd, Sb, and Pb. For As, the highest level of pollution in the catchment was considered to be level 1 (unpolluted to moderately polluted). Our data show very strong (level 6) Cd pollution in the South Qinling terrain and strong pollution (level 4) in the North Qinling terrain and the Shangdan suture zone. The highest level of Sb pollution (level 5; strongly to very strongly polluted) occurred in sediments from the North Qinling terrain, and low levels of Sb pollution (level 1; unpolluted to moderately polluted)

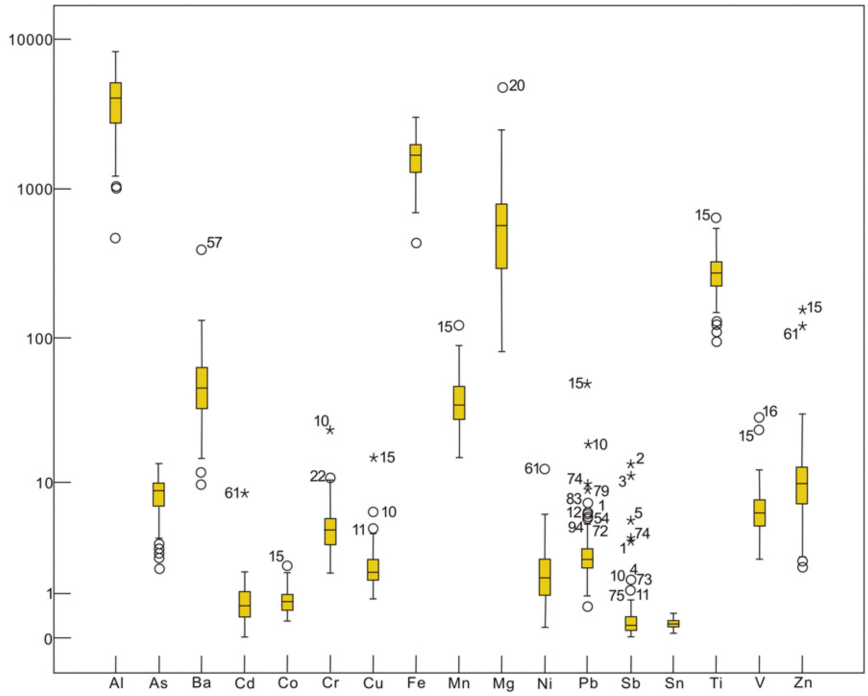

**Fig. 3.** Box and whisker plots showing the variation of trace elements and heavy metals in the surface sediments within the Dan River drainage (unit in μg/g).

occurred in the South Qinling terrain and the Shangdan suture zone. The extent of Pb pollution was low (level 0; unpolluted) in the North Qinling terrain and the Shangdan suture zone, but level 1 (unpolluted to moderately polluted) in the South Qinling terrain.

As shown in Table 4, the peak and mean EF values for most trace metals showed no significant differences between the three areas (North and South Qinling terrains and the Shangdan suture zone), and the EF level in most areas was less than 5. However, the average EFs of As and Cd were greater than 40 in all three areas, indicating extremely high enrichment in the entire Dan River drainage. The mean EFs of Sb in the North Qinling terrain were nearly twice and four times higher than in the Shangdan suture zone and the South Qinling terrain, respectively. The average EF values for Pb in the drainage were less than 5, but peak values were greater than 40 in the South Qinling terrain.

According to the potential ecological risk index (RI), sediments in the Shangdan suture zone and the North Qinling terrain showed low-moderate and considerable levels of ecological risk, respectively, while sediments in the South Qinling terrain showed low to extremely high risks. Individually, Cd in the sediments presented much more risk than other metals (As, Cr, Cu, Pb, and Zn). Overall, heavy metals in the Dan River drainage sediments showed low-considerable ecological risks. The results of risk assessments were in accordance with the metal distribution pattern recorded in the sediments. Higher risks were found in sediments of the South Qinling terrain than in the other two areas. For individual metals, Cd and As showed much higher risks than did the other metals, and should be listed as prior pollutants in the studied area.

The mean probable effect concentration quotient ($m_{PECQ}$) of the sediments was 0.04–0.12 for the North Qinling terrain, 0.07–0.16 for the Shangdan suture zone, and 0.07–0.42 for the South Qinling terrain, indicating that sediments in the Dan River drainage were uncontaminated to moderately contaminated by trace metal elements;, values for Cd, were relatively higher than values for other trace elements. The $m_{PECQ}$ values for trace elements were greater than 0.1 at some sites, such as at site 61, indicating that these trace elements would pose moderately adverse biological risks.

### 4.3. Source identification of heavy metals in sediments

Various multivariate techniques such as Pearson correlation analysis, hierarchical cluster analysis, and factor analysis, have been used to identify sources of heavy metals, to interpret spatial variations and complex environmental data matrices, and to assess the ecological status of natural and anthropogenic systems. A hierarchical cluster analysis showed the presence of homogenous groups of metal elements in sediments of the Dan River drainage (Fig. 5). The metals were clustered roughly into four primary groups. The first cluster consisted of most trace metals (As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sn, Ti, V and Zn), many of which were contaminants. The second cluster was Mg, which may be derived from both rock materials and anthropogenic sources on the account of its high mobility. The third and fourth cluster was Fe and Al, respectively, which are typically associated with parent rock materials. A factor analysis (FA) approach was applied to further identify sources of elemental components; a Kaiser–Meyer–Olkin (KMO) value of >0.7 (0.732) and a significant Bartlett's test (<0.001) demonstrated the validity of the FA. Table 5 shows the results of the factor loadings with a varimax rotation, as well as eigenvalues.

Five principal components (PCs) with eigenvalues greater than 1 explained 74.8% of the total variance. The first PC, which accounted for 39.2% of the total variance, was represented by high loadings of Cu, Pb, V, and Zn, and moderate loadings of Mn. Most PC1 elements are lithophile elements, occurring at low concentrations and low enrichment factors, and which are derived mainly from weathering and erosion of catchment rocks. Their concentrations showed significant positive correlations with one another ($p < 0.01$), suggesting that they were derived from similar sources. The elements Cu, Pb, and Zn tend to be geologically associated with one another, on account of their similar chemical properties (Hanesch and Scholger, 2002; Nriagu, 1996). The element V, which commonly exists as a negative ion (Breit et al., 1991), was first identified from vanadinite ($Pb_5(VO_4)_3Cl$). All forms of Cu, Pb, Zn, and Mn are highly soluble in aqueous brines in their divalent forms due to the formation of stable chloride complexes, whereas oxidation leads to rapid precipitation of oxide and oxyhydroxide minerals

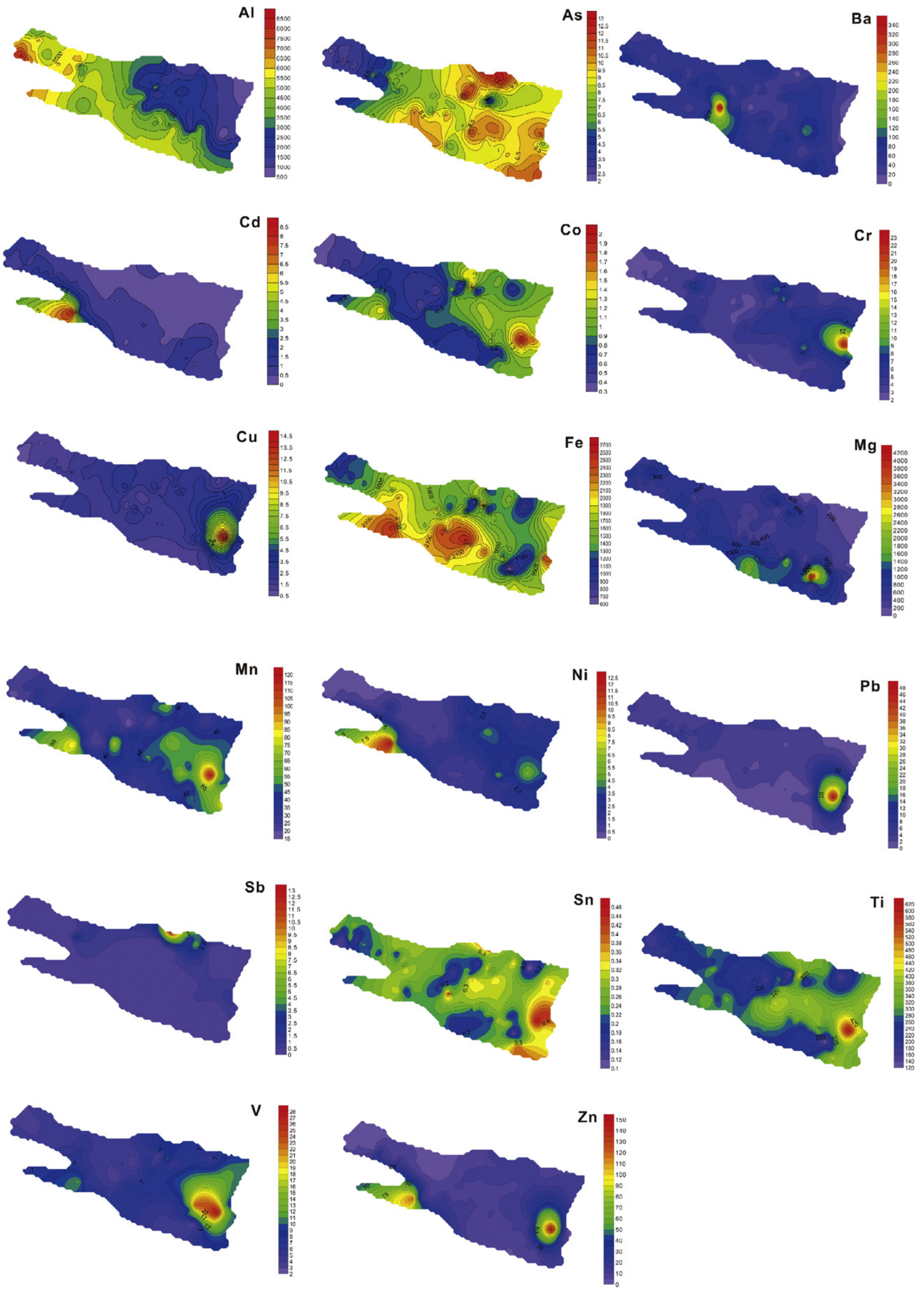

**Fig. 4.** Contour maps of trace elements and heavy metals' values of surface sediments in the Dan River drainage (unit in μg/g).

**Table 3**
Concentrations of trace elements in the surface sediments of the three terrains of the Dan River drainage, China (unit in μg/g).

| | North Qinling terrain | Shangdan suture | South Qinling terrain |
|---|---|---|---|
| Al | 3910.15 | 3833.82 | 3870.55 |
| As | 6.70 | 7.36 | 9.36 |
| Ba | 48.23 | 43.95 | 60.11 |
| Cd | 0.66 | 0.78 | 0.94 |
| Co | 0.71 | 0.77 | 0.91 |
| Cr | 4.13 | 6.34 | 4.85 |
| Cu | 1.88 | 2.19 | 2.36 |
| Fe | 1401.67 | 1913.28 | 1916.71 |
| Mg | 566.02 | 527.37 | 810.54 |
| Mn | 31.94 | 36.88 | 48.08 |
| Ni | 1.55 | 1.60 | 2.32 |
| Pb | 3.12 | 4.88 | 3.33 |
| Sb | 1.07 | 0.65 | 0.30 |
| Sn | 0.24 | 0.28 | 0.26 |
| Ti | 246.59 | 285.43 | 313.60 |
| V | 5.58 | 6.03 | 7.71 |
| Zn | 9.43 | 10.86 | 16.46 |

(Sager, 1992). The element V is commonly most stable in nature in its pentavalent form, and $VO_4^{3-}$ tends to be incorporated into the insoluble minerals with positive metal cations (Colina et al., 2005; Wehrli and Werner, 1989).

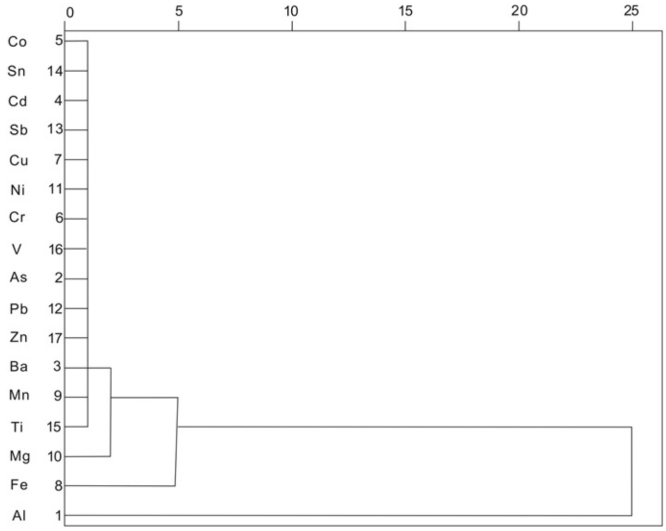

**Fig. 5.** Dendrogram showing clustering of trace elements according to Ward's method using squared Euclidean distance.

**Table 4**
The index of geoaccumulation ($I_{geo}$), enrichment factor (EF), potential ecological risk factor (Er), and probable effect concentration quotient (PECQ) of trace elements in the surface sediments of the Dan River drainage, China.

| | Al | As | Ba | Cd | Co | Cr | Cu | Fe | Mg | Mn | Ni | Pb | Sb | Sn | Ti | V | Zn | $m_{PECQ}$ | RI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *North Qinling terrain* | | | | | | | | | | | | | | | | | | | |
| $I_{geo}$ | | | | | | | | | | | | | | | | | | | |
| Min | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | | |
| Max | <0 | 1 | <0 | 4 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | 5 | <0 | <0 | <0 | <0 | | |
| EF | | | | | | | | | | | | | | | | | | | |
| Min | 0.22 | 17.89 | 0.31 | 11.37 | 0.65 | 1.37 | 1.35 | 1.00 | 0.19 | 0.79 | 0.22 | 1.45 | 1.85 | 1.05 | 1.13 | 1.43 | 0.95 | | |
| Max | 2.48 | 262.63 | 4.13 | 371.36 | 3.15 | 5.95 | 7.37 | 1.00 | 2.71 | 3.36 | 7.65 | 8.12 | 1043.12 | 3.46 | 3.25 | 4.60 | 13.89 | | |
| Mean | 1.18 | 80.10 | 1.72 | 148.91 | 1.35 | 2.57 | 2.93 | 1.00 | 0.96 | 1.35 | 1.86 | 4.14 | 73.26 | 2.11 | 1.75 | 2.33 | 4.18 | | |
| Er | | | | | | | | | | | | | | | | | | | |
| Min | | 2.06 | | 6.11 | | 0.06 | 0.20 | | | | | 0.31 | | | | | 0.03 | | 15.76 |
| Max | | 15.06 | | 378.32 | | 0.82 | 1.43 | | | | | 3.74 | | | | | 0.45 | | 385.59 |
| PECQ | | | | | | | | | | | | | | | | | | | |
| Min | | 0.06 | | 0.01 | | 0.02 | 0.01 | | | | 0.00 | 0.01 | | | | | 0.00 | 0.04 | |
| Max | | 0.42 | | 0.34 | | 0.09 | 0.03 | | | | 0.10 | 0.07 | | | | | 0.07 | 0.12 | |
| *Shangdan suture* | | | | | | | | | | | | | | | | | | | |
| $I_{geo}$ | | | | | | | | | | | | | | | | | | | |
| Min | <0 | <0 | <0 | 1 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | | |
| Max | <0 | 1 | <0 | 4 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | 1 | <0 | <0 | <0 | <0 | | |
| EF | | | | | | | | | | | | | | | | | | | |
| Min | 0.31 | 32.54 | 0.51 | 50.68 | 0.76 | 1.48 | 1.18 | 1.00 | 0.36 | 0.84 | 0.59 | 1.58 | 4.44 | 1.26 | 1.21 | 1.34 | 1.71 | | |
| Max | 1.22 | 116.63 | 2.03 | 195.94 | 2.19 | 13.82 | 8.57 | 1.00 | 1.05 | 1.89 | 4.08 | 22.44 | 96.50 | 3.52 | 2.18 | 3.40 | 11.77 | | |
| Mean | 0.78 | 61.92 | 1.07 | 120.90 | 1.10 | 3.18 | 2.64 | 1.00 | 0.62 | 1.14 | 1.48 | 5.06 | 35.13 | 1.83 | 1.50 | 1.89 | 3.66 | | |
| Er | | | | | | | | | | | | | | | | | | | |
| Min | | 5.62 | | 41.98 | | 0.10 | 0.33 | | | | | 0.42 | | | | | 0.08 | | 52.34 |
| Max | | 9.98 | | 282.41 | | 0.31 | 1.04 | | | | | 1.79 | | | | | 0.19 | | 290.92 |
| PECQ | | | | | | | | | | | | | | | | | | | |
| Min | | 0.12 | | 0.05 | | 0.02 | 0.01 | | | | 0.01 | 0.02 | | | | | 0.01 | 0.07 | |
| Max | | 0.35 | | 0.26 | | 0.21 | 0.04 | | | | 0.08 | 0.15 | | | | | 0.07 | 0.16 | |
| *South Qinling terrain* | | | | | | | | | | | | | | | | | | | |
| $I_{geo}$ | | | | | | | | | | | | | | | | | | | |
| Min | <0 | <0 | <0 | 1 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | | |
| Max | <0 | 1 | <0 | >5 | <0 | <0 | <0 | <0 | <0 | <0 | <0 | 1 | 1 | <0 | <0 | <0 | <0 | | |
| EF | | | | | | | | | | | | | | | | | | | |
| Min | 0.17 | 32.38 | 0.28 | 23.99 | 0.73 | 1.04 | 1.03 | 1.00 | 0.14 | 0.67 | 0.51 | 0.63 | 3.89 | 0.72 | 1.11 | 1.33 | 1.62 | | |
| Max | 3.32 | 344.43 | 11.01 | 970.43 | 5.02 | 7.40 | 30.13 | 1.00 | 24.69 | 6.62 | 8.27 | 82.87 | 59.65 | 5.31 | 5.87 | 15.42 | 84.73 | | |
| Mean | 0.87 | 84.80 | 1.57 | 165.13 | 1.39 | 2.45 | 3.14 | 1.00 | 1.42 | 1.62 | 2.22 | 4.08 | 17.07 | 1.82 | 1.71 | 2.61 | 6.06 | | |
| Er | | | | | | | | | | | | | | | | | | | |
| Min | | 6.95 | | 28.16 | | 0.08 | 0.29 | | | | | 0.13 | | | | | 0.08 | | 39.93 |
| Max | | 13.05 | | 1778.79 | | 0.37 | 3.59 | | | | | 9.87 | | | | | 2.27 | | 1791.07 |
| PECQ | | | | | | | | | | | | | | | | | | | |
| Min | | 0.19 | | 0.03 | | 0.02 | 0.01 | | | | 0.01 | 0.01 | | | | | 0.01 | 0.07 | |
| Max | | 0.36 | | 1.67 | | 0.10 | 0.10 | | | | 0.26 | 0.39 | | | | | 0.34 | 0.42 | |

**Table 5**
Results of principal component analysis (PCA) for trace elements and heavy metals in the Dan River drainage, China.

| PC | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| % of variance | 39.23 | 12.46 | 9.48 | 7.3 | 6.38 |
| Al | −0.273 | −0.785 | −0.002 | 0.053 | **0.39** |
| As | 0.022 | **0.857** | 0.128 | 0.045 | 0.133 |
| Ba | 0.113 | −0.139 | 0.028 | −0.141 | **0.774** |
| Cd | 0.011 | −0.326 | 0.06 | **0.905** | 0.025 |
| Co | 0.471 | **0.592** | 0.521 | 0.223 | −0.143 |
| Cr | 0.349 | **0.383** | **0.385** | 0.023 | −0.265 |
| Cu | **0.926** | 0.238 | 0.149 | 0.072 | −0.054 |
| Fe | −0.19 | −0.057 | **0.889** | 0.121 | 0.057 |
| Mn | **0.467** | 0.244 | **0.463** | 0.383 | −0.016 |
| Mg | −0.17 | −0.036 | −0.157 | 0.111 | **0.675** |
| Ni | 0.296 | 0.431 | 0.24 | **0.729** | −0.083 |
| Pb | **0.954** | −0.071 | 0.015 | 0.014 | −0.03 |
| Sb | 0.027 | **0.462** | 0.056 | −0.055 | −0.087 |
| Sn | 0.429 | 0.163 | **0.626** | 0.045 | −0.127 |
| Ti | 0.423 | 0.272 | **0.75** | 0.026 | −0.195 |
| V | **0.713** | 0.324 | 0.354 | 0.164 | −0.053 |
| Zn | **0.737** | 0.04 | 0.03 | 0.609 | −0.004 |

The second PC, which accounted for 12.5% of the total variance, showed positive loadings on As, Co, Cr and Sb, and negative loadings on Al. The elements As and Sb showed a significant correlation ($p < 0.05$), representing their origins mainly from weathering of enriched rock sources or industrial sources, such as mining districts and smelting plants (Welch and Lico, 1998); As and Sb show similar environmental characteristics, resulting in the association of the two elements in nature (Filella et al., 2002). The elements Cr and Co can replace one another through isomorphism in minerals (Spasovski, 2009). In compounds, Co occurs as a major metallic component in combination with S and As in sulfidic cobaltite (CoAsS), safflorite (CoAs$_2$), glaucodot ((Co,Fe)AsS), and skutterudite (CoAs$_3$) minerals (Ma and Bruckard, 2009; Sampson and Hriskevich, 1957). Aluminum may be derived primarily from the crust, as it is one of the most abundant mineral components in crustal rocks (Pekey et al., 2004). The inverse relationships between Al and As, Co, Cr, and Sb are indicative of external inputs of these elements. Hence, Al may be attributable to mixed geological and anthropogenic origins, especially as related to mining activities along the drainage.

The third PC, which accounted for 9.5% of the total variance, showed primarily contributions of Cr, Fe, Sn, and Ti, and partially of Mn, most of which are siderophile elements. Iron is relatively immobile in aquatic systems, with respect to natural geological processes such as weathering, erosion, and transportation (Gentner, 1977). The relatively low concentrations of PC3 elements indicate that they are from natural sources, which is also confirmed by their strong geochemical correlations (Table 6).

The fourth and fifth PCs, which accounted for 7.3% and 6.4% of the total variance, respectively (Table 6), were characterized by Cd and Ni, and Ba, Mg, and Al, respectively. The Dan River drainage shows heavy Cd contamination from north to south. The highest concentrations of Cd and Ni were found at site 61, which is in the vicinity of Ni, Pb, and V ores, indicating a source related to metal ore deposits. However, these ore deposits have not been mined based on the references until now, due to their low industry and economic values. The extremely high concentrations of Cd and Ni at site 61 could be caused by the weathering of the mineralized rocks. Moreover, concentrations of Cd and Ni may also be related to electroplating processes and battery fabrication; the Ni–Cd battery is one of the most common batteries in use, and the batteries are produced by many factories in Shaanxi and Henan provinces (Armand, 2001; Feng et al., 2010). In addition, fertilizers are an important source of Cd and Ni (Kashem and Singh, 2002). The elements Ba, Mg and Al are naturally abundant in earth materials (Krishna et al., 2009); PC4 was therefore attributed to natural and anthropogenic sources, whereas PC5 was attributed to natural sources.

**Table 6**
Pearson correlation matrix of trace elements and heavy metals in the Dan River drainage, China.

| | Al | As | Ba | Cd | Co | Cr | Cu | Fe | Mn | Mg | Ni | Pb | Sb | Sn | Ti | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 1 | | | | | | | | | | | | | | | | |
| As | **−0.595**$^{**}$ | 1 | | | | | | | | | | | | | | | |
| Ba | **0.320**$^{**}$ | −0.057 | 1 | | | | | | | | | | | | | | |
| Cd | **0.321**$^{**}$ | **−0.222**$^{*}$ | −0.006 | 1 | | | | | | | | | | | | | |
| Co | **−0.636**$^{**}$ | **0.492**$^{**}$ | −0.167 | 0.02 | 1 | | | | | | | | | | | | |
| Cr | **−0.446**$^{**}$ | **0.280**$^{**}$ | −0.161 | −0.06 | **0.647**$^{**}$ | 1 | | | | | | | | | | | |
| Cu | **−0.448**$^{**}$ | **0.265**$^{**}$ | −0.021 | −0.002 | **0.670**$^{**}$ | **0.483**$^{**}$ | 1 | | | | | | | | | | |
| Fe | 0.084 | 0.154 | −0.001 | 0.161 | **0.312**$^{**}$ | 0.196 | −0.01 | 1 | | | | | | | | | |
| Mn | **−0.289**$^{**}$ | **0.304**$^{**}$ | −0.09 | 0.236$^{*}$ | **0.674**$^{**}$ | **0.361**$^{**}$ | **0.569**$^{**}$ | **0.322**$^{**}$ | 1 | | | | | | | | |
| Mg | **0.352**$^{**}$ | −0.058 | 0.143 | 0.073 | **−0.196** | **−0.219**$^{*}$ | −0.189 | −0.073 | −0.134 | 1 | | | | | | | |
| Ni | **−0.418**$^{**}$ | **0.361**$^{**}$ | −0.079 | **0.511**$^{**}$ | **0.729**$^{**}$ | **0.484**$^{**}$ | **0.466**$^{**}$ | 0.178 | **0.563**$^{**}$ | −0.144 | 1 | | | | | | |
| Pb | −0.185 | 0.014 | 0.016 | 0.051 | **0.393**$^{**}$ | **0.341**$^{**}$ | **0.879**$^{**}$ | −0.114 | **0.439**$^{**}$ | −0.124 | **0.230**$^{*}$ | 1 | | | | | |
| Sb | **−0.251**$^{*}$ | **0.256**$^{*}$ | −0.076 | −0.078 | **0.290**$^{**}$ | 0.147 | 0.129 | −0.036 | 0.117 | −0.133 | 0.131 | 0.054 | 1 | | | | |
| Sn | **−0.258**$^{*}$ | 0.18 | −0.048 | 0.089 | **0.656**$^{**}$ | **0.493**$^{**}$ | **0.535**$^{**}$ | **0.335**$^{**}$ | **0.453**$^{**}$ | **−0.211**$^{*}$ | **0.435**$^{**}$ | **0.410**$^{**}$ | **0.279**$^{**}$ | 1 | | | |
| Ti | **−0.437**$^{**}$ | **0.315**$^{**}$ | −0.178 | −0.025 | **0.793**$^{**}$ | **0.470**$^{**}$ | **0.559**$^{**}$ | **0.554**$^{**}$ | **0.626**$^{**}$ | **−0.272**$^{**}$ | **0.409**$^{**}$ | **0.397**$^{**}$ | 0.182 | **0.646**$^{**}$ | 1 | | |
| V | **−0.468**$^{**}$ | **0.310**$^{**}$ | −0.028 | 0.065 | **0.781**$^{**}$ | **0.447**$^{**}$ | **0.786**$^{**}$ | 0.178 | **0.608**$^{**}$ | **−0.215**$^{*}$ | **0.552**$^{**}$ | **0.596**$^{**}$ | 0.132 | **0.495**$^{**}$ | **0.703**$^{**}$ | 1 | |
| Zn | **−0.235**$^{*}$ | 0.147 | −0.01 | **0.549**$^{**}$ | **0.487**$^{**}$ | **0.215**$^{*}$ | **0.743**$^{**}$ | 0.033 | **0.572**$^{**}$ | −0.111 | **0.644**$^{**}$ | **0.737**$^{**}$ | 0.014 | **0.318**$^{**}$ | **0.400**$^{**}$ | **0.625**$^{**}$ | 1 |

$^{**}$ Significance at the 0.01 probability level.
$^{*}$ Significance at the 0.05 probability level.

### 4.4. Metal ore effect

Previous studies have indicated that heavy metals and metalloids in the rivers could be derived from the weathering of the mineralized rocks (Förstner and Wittmann, 1981). More commonly, mining and ore processing contribute toxic heavy metals into the aquatic system, and also represent important potential hazards for water, biodiversity, and food chains (Macklin et al., 2006; Monterroso et al., 2014; Natarajan et al., 2006; Tapia and Audry, 2013). Both on-going and historic mining activities can release large quantities of heavy-metal-bearing mineral particles into fluvial environments (Hudson-Edwards, 2003). In recent years, several serious contamination incidents have occurred worldwide, including leakage of acidified copper water in Tingjiang, China (2010), failure of the main tailings dam at Aznalcollar, Spain (1998) (Grimalt et al., 1999), and contamination of the Danube River at Bahia Mare, Romania (Macklin et al., 2006). In addition to these highly publicized disasters, other less well known chemical hazards associated with ore development exist, Including metal release from mechanically unstable and non-remediated mine tailings and abandoned mine galleries, and biotic effects on organisms living near or downstream from ore bodies. These processes lead to slow steady contamination of the environment, and to a rise in background levels of contamination. In the river drainages worldwide, toxic metals (such as As, Cd, Pb and Sb) are highly concentrated in mining areas and their surroundings. Fluvial transport is one of the processes responsible for dispersion of elements and environmental contamination. Grosbois et al. (2001) found that in the Spokane River Basin, USA, surface sediments were enriched in Pb, Zn, As, Cd, Sb, and Hg relative to local background levels, on account of mining and related activities.

According to the spatial distribution and characterization of heavy metals reported in this study, the Dan River drainage is influenced by the locations of ore bodies within the drainage. The metallogenic belt located in the Qinling orogen is famous throughout the world, and hosts a variety of ore metals including Mo, Sb, Pb, Zn, V, and Ni (Mao et al., 2008; Zhai and Santosh, 2013). The ore deposits in the Dan River drainage in the North Qinling terrain are completely different from those of the South Qinling terrain. In the North Qinling terrain, Sb ores are the primary ore deposits and have been well mined, followed by secondary Pb ore deposits. However, in the South Qinling terrain, many types of ores are present, including unmined ores (Ni and Pb ores) and well mined ores (V, Cu and Fe). As a result, sediment contaminations in the North Qinling terrain is primarily by Sb and As, mainly caused by mining and smelting activities, while in the South Qinling terrain, contamination by Cd and Pb predominates, along with extremely high concentrations of Cr, Cu, Mn, Ni, Ti, V, and Zn at specific sites, resulting from both natural weathering and anthropogenic mining. A dendrogram representing Q-model CA shows three major clusters (Fig. S1): cluster 1 (sites 1, 13–14, 16, 18, 20, 25, 27, 30, 34–38, 44, 46–47, 51–53, 55–56, 60–61, 63–64, 66–69 and 73–74), cluster 2 (sites 2–12, 15, 22–24, 26, 28, 29, 31, 33, 62, 65 and 75), and cluster 3 (sites 17, 19, 21, 32, 39–43, 45, 48–50, 54, 57–59, 70–72 and 76–95); these clusters are based mainly on the distribution of sample sites with respect to metal ores, located mainly in the southwestern metal ore terrain (Ni, Pb and V), the eastern metal ore terrain (Sb, Fe, V, and Cu), and the northern–western–middle metal ore terrain (Pb and Sb), respectively (Fig. 1). Cluster 1 includes sites with extremely high concentrations of Cd, Ni, Pb, Sb, V, and Zn; cluster 2 includes sites with extremely high concentrations of Co, Cr, Cu, Mn, Pb, Sb, V, and Zn; and cluster 3 includes sites with extremely high concentrations of Pb. In particular, all sites with relatively high metal concentrations in surface sediments were in the vicinity of related metal ores, indicating a strong positive correlation between heavy metal contamination and ore-related activities. The distribution of metal elements in the ores and sediments is controlled primarily by their chemical and geological behaviors; hence, the accumulation of metals follows regular patterns.

The predominant ore mineral containing Sb is sulfide stibnite ($Sb_2S_3$) (McCallum, 2005). The element As appears frequently with Sb together by long term geological process, due to their similar chemical properties. Greenockite (CdS), the only cadmium mineral of importance, is nearly always associated with sphalerite (ZnS) and galena (PbS) (Deore and Navrotsky, 2006; Patterson, 1985), an association that is related to the geochemical similarities of Cd, Pb, and Zn, which makes geological separation difficult. Consequently, Cd is produced mainly as a byproduct of mining, smelting, and refining sulfidic Zn ores, and, to a lesser extent, Pb ores. Lead is usually found in ores in association with Zn, and Cu, and is extracted together with these metals. The main Pb mineral is galena (PbS); and other common Pb minerals are cerussite ($PbCO_3$) and anglesite ($PbSO_4$) (Ramdohr, 1969). Therefore, high concentrations of specific metals in surface sediments of the Dan River drainage are associated with specific ore deposits, resulting in the different metal contamination patterns observed in sediments of the catchment areas of the North and South Qinling terrains. The development of planning policies and regulations that is relevant to the prevention of heavy metal contamination from ore deposits and processing areas is of utmost importance.

## 5. Conclusions

The levels of most trace metals in surface sediments of the Dan River drainage were lower than levels reported from other rivers in China and worldwide. Nevertheless, peak values of several heavy metals, including As, Cd, Pb, and Sb, were much higher than background levels, indicating the potential for serious ecological impacts. While levels of heavy minerals tend to decrease dramatically with increasing distance from metal ore deposits, metal deposits and related activities have nevertheless led to high accumulations of potentially toxic heavy metals in surface sediments.

Multivariate statistical analyses demonstrate that in the Dan River drainage, concentrations of Al, Ba, Cu, Fe, Mg, Mn, Pb, Sn, Ti, V, and Zn are controlled mainly by natural processes and inputs, concentrations of Co and Cr are controlled by a combination of geological and anthropogenic inputs, whereas concentrations of As, Cd, Ni, Sb and Pb are controlled primarily mainly by anthropogenic inputs. The spatial distributions of heavy metals in surface sediments are controlled mainly by the regional distribution of metal-enriched rocks and metal ore deposits in catchment areas. In the North Qinling terrain, Sb and Pb are the dominant heavy metals accumulating in sediments, on account of widespread Sb ores, whereas in the South Qinling terrain, Cd, Mn, Ni, Pb, and V are the dominant heavy metals in sediments, on account of widespread Ni, V, Cu, Fe, and Pb ores. The relatively high concentrations of Cr and Fe in the Shangdan suture zone might be related to the presence of ophiolites in this region.

Contamination and risk assessment of As, Cd, Pb, and Sb in surface sediments of the Dan River drainage require attention to mitigate potential hazards. The element Sb is likely to pose greater risks than other metals in the North Qinling terrain; on the other hand, Cd is likely to pose greater risks in the South Qinling terrain. Individually, specific sites (such as site 61), pose hazards related to the presence of multiple different types of metal ore deposits located in the proximity, and which show a moderate potential for adverse biological effects. Overall, sediment contamination in the Dan River drainage poses relatively serious potential risks, and countermeasures to the impacts of ore-related activities such as mining, smelting and tailings storage should be strengthened to control heavy metal pollution.

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