

Distribution of potentially toxic elements in sediment of the Anning River near the REE and V-Ti magnetite mines in the Panxi Rift, SW China

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ABSTRACT

To clarify the impact of developing world-class REE and V-Ti magnetite mines on the distribution of potentially toxic elements (As, Cd, Co, Cu, Cr, Hg, Ni, Pb, Tl, U, and Zn) in adjacent aqueous sediments, thirty sediment samples from the Anning River and seventeen ore samples from the Panxi Rift of China were investigated. The results from this study suggest the following: (1) Mining activities have resulted in severe pollution of sediment by potentially toxic elements, especially Pb with an average concentration of 213.8 mg/kg, which is much higher than the probable effect concentration (PEC) and background values. (2) Different kinds of mines caused the enrichment of different elements in surface sediments. Heavy to extreme enrichment of Pb (EF = 45) and U (EF = 18) was observed in sediment near the Mianning REE mine, and severe enrichment of Pb (EF = 54), As (EF = 18), Cd (EF = 13) and U (EF = 8) was observed in sediment near the Lugu iron mine. (3) Concentrations of Pb and As in sediment that were extremely higher than the PEC indicate probable toxicity and support the need for further speciation analysis. (4) The joint application of distribution characteristics analysis (DCA) and robust regression (RR) was useful in identifying the source of potentially toxic elements in sediment near mining areas. Distribution characteristics analysis of risk elements can qualitatively suggest outliers, and robust regression can quantitatively identify whether a high concentration of a risk element can be classified as an outlier compared to a reference element.

1. Introduction

Contamination by inorganic trace metals and metalloids in aqueous environments has increasingly attracted attention from governments and residents due to their toxicity and threat to organisms. Most potentially toxic elements that are contained in water can be adsorbed by colloids and/or particles suspended in water, which are eventually deposited as sediment (Kimball et al., 1995; Atkinson et al., 2007). Therefore, concentrations of Cr, Cd, Hg, Cu, Fe, Zn, Pb and As in sediment are usually 100–10,000 times higher than those in ambient water (Yi et al., 2011).

Sediment plays an important role not only as a sink that accommodates potentially toxic elements but also as a source that releases them into the water (Chen et al., 2016; Shi et al., 2015). Physico-chemical conditions (e.g., pH and Eh) and the chemical composition of water can significantly affect the migration and transformation of risk elements (Eggleton and Thomas, 2004; Wang et al., 2014; Wang et al., 2016). Some risk elements that originate from bottom sediment can

gradually accumulate in plants, and then in animals, through the food chain (Peralta-Videa et al., 2009). The fraction of risk elements that is transferred into biomass heavily depends on the speciation and bioavailability of the different risk elements in sediment. The bioaccumulation effect of risk elements within the food chain has a descending order where bottom material > demersal fish and benthic fauna > middle-lower layer fish > upper-middle layer fish > water (Yi et al., 2011). Therefore, bottom sediment serves as a sensitive indicator of pollution by risk elements in an aquatic environment.

Source identification, risk evaluation, and pollution assessment of potentially toxic elements in river sediment contribute significantly to protecting river ecosystems and sources of drinking water (Grygar et al., 2013; Shi et al., 2016). Surface water in the southwest part of China is the major source of drinking water for local residents, but there is a large number of mineral resources distributed along the river system. The presence of these mineral resources raises a significant contradiction of ecologic and economic needs. The Anning River, located in the Panxi Rift, is a good example of this contradiction.

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Although the Anning River provides drinking water for millions of people and agricultural irrigation, the development of abundant world-class mines (the largest V-Ti magnetite mine and the third largest REE mine in the world) along the river considerably increases the risk of pollution in the river. Previous studies have indicated that the slopping and smelting of V-Ti magnetite is a primary source of pollution in soil and sediment (Teng et al., 2003, 2011). In addition, REE mines host low-radioactivity ores that are rich in U and Pb (Qin et al., 2008) and can cause severe environmental contamination (Xu et al., 2015). Nevertheless, the overall distribution and pollution status of potentially toxic elements in the Anning River remains unknown. Therefore, it is necessary to perform a systematic and comprehensive study of the distribution of and degree of pollution by potentially toxic elements in the sediment of the Anning River. The objectives of this study are (1) to investigate the impact of REE, iron ore and V-Ti magnetite mining in the Panxi Rift on the distribution of potentially toxic elements in surface sediment of the Anning River; and (2) to identify the natural and anthropogenic sources of the risk elements and evaluate the degree of pollution in aquatic sediment.

2. Materials and methods

2.1. Study area and geologic background

The Anning River is located in the southwest part of Sichuan Province, China. It originates at Jibeishan Mountain in Xide County, then flows through the Mianning, Xichang, Dechang, Miyi areas and ultimately integrates with the Yalongjiang River in Yanbian County of Panzhihua City (Fig. 1). The river flows from north to south along the Panxi Rift, with an overall decrease in elevation from 4750 m to 950 m. Its length, flow rate, and drainage area are 326 km², 231 m³/s, and

11,150 km, respectively. The catchment area is in a subtropical monsoon climate zone. There is abundant rainfall with an average annual rainfall > 1000 mm. The average annual temperature ranges from 17 to 19 °C. The highest temperatures can reach 21–24 °C, usually occurring in July, whereas the lowest temperatures can reach 8–11 °C, usually occurring in December.

The Anning River Basin is a subsiding area of the Panxi Rift and hosts a thick layer of Quaternary sandy gravel. The regional geology is characterized by abundant folds and faults. Magmatic rock is primarily distributed in the western part of the Anning River Basin, and sedimentary rock is distributed in the eastern part of the basin. Abundant mines are located along the east side of the rift, including the Maoniuping REE mine and the Panzhihua V-Ti magnetite mine (Fig. 1).

The Panxi region of the Anning River Basin (from Panzhihua to Xichang) is located in the transitional zone between the Qinghai-Tibet Plateau, the Yunnan-Kweichow Plateau and the Sichuan Basin (Shao et al., 2014). This basin is not only one of the most important grain-producing areas in southwest China but also a key ecological barrier for the upper reaches of the Yangtze River. In this basin, the Anning River is not only utilized as a water resource for agricultural activities but also a source of drinking water for millions of people. Despite the important ecological functions of the Anning River, many world-class ore mines are located along the river (Niu et al., 2003; Pang et al., 2010) including the Maoniuping REE mine (the third largest REE mine in world) (Xu et al., 2007; Chao et al., 2008) and the V-Ti magnetite mine (the largest V-Ti mine in world) (Pang et al., 2010; Hou et al., 2011).

2.2. Sampling and analysis

2.2.1. Sediment

To investigate the status of pollution in the river, thirty-two samples

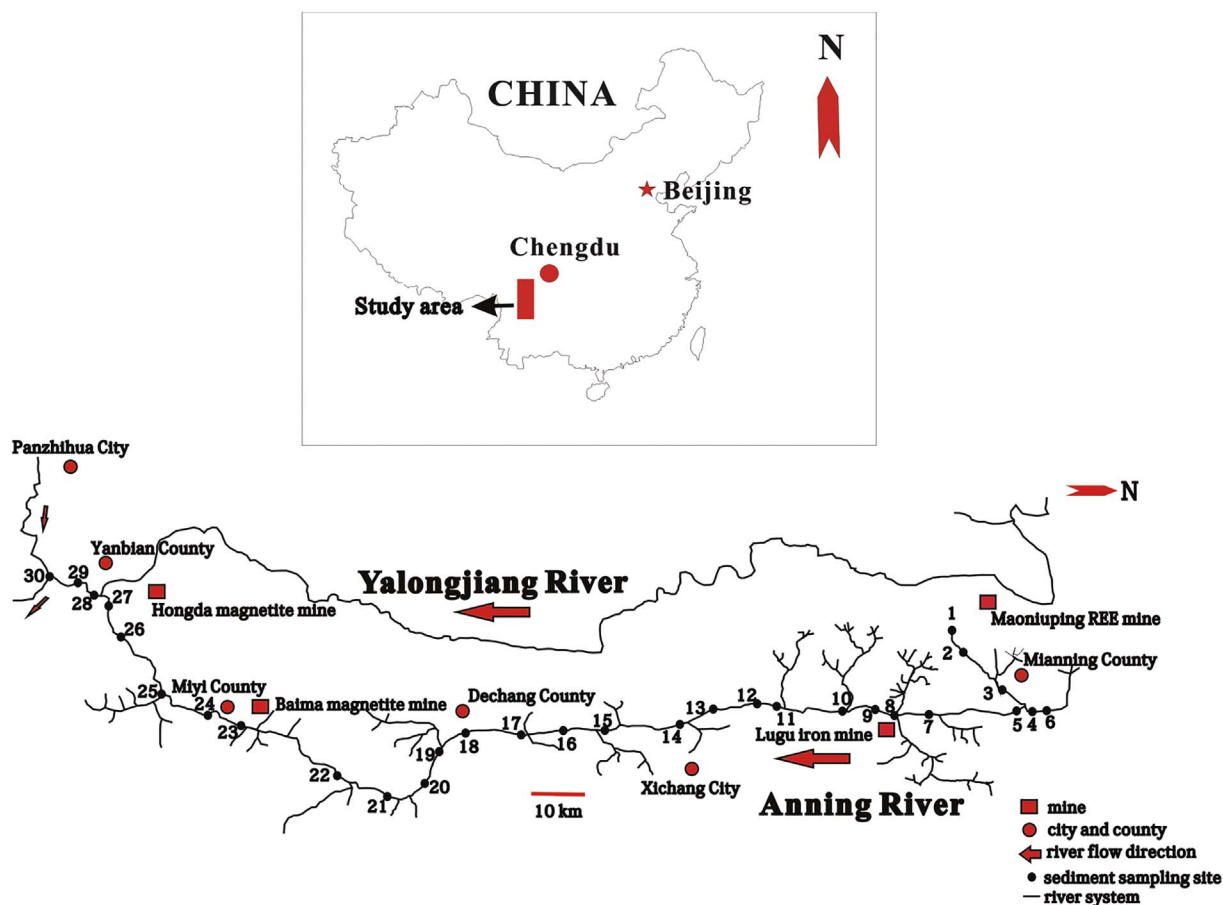


Fig. 1. Location of study area and sediment sampling sites along the Anning River.

of surface sediment were collected (0–10 cm below the water-sediment interface) using a flag-gravity corer (Serial No. XDB0205, China) in June 2012. After large particles and rotten plants were removed, sediment samples were stored in polypropylene plastic sample bags. Ten percent of each sediment sample was retained as a duplicate for the analyses. The sediment was primarily composed of fine silt and clay, with a small fraction of sand. When dried, aggregates in the sediment sample were disaggregated by hand with a wooden hammer. Most of the sand fraction was removed with a 100-mesh sieve (pore size < 150 µm). Most of the sediment had a small fraction of sand. Two samples (from sites located upstream) were omitted from further analyses because sand accounted for a significant proportion of the sample mass, such that a small volume of sediment was retained after sieving. Residual fine sediment particles (grain size < 150 µm) were digested with a mixture of HNO₃, HClO₄ and HF. National reference materials of stream sediment (No. GBW07310, No. GBW07312 and No. GBW07309) of China were used as a comparison. In addition, reference sediment samples No. GBW07310 and No. GBW07312 were jointly used to obtain standard curve line. Reference material No. GBW07309 (As: 0.089 ± 0.015, Cd: 0.26 ± 0.05, Co: 14.4 ± 1.8, Cr: 85 ± 10, Cu: 32 ± 3, Mn: 620 ± 30, Ni: 32 ± 4, Pb: 23 ± 4, Ti: 0.550 ± 0.025, U: 2.6 ± 0.6, Zn: 78 ± 5 mg/kg; Al₂O₃: 10.58 ± 0.15, Fe₂O₃: 4.86 ± 0.11%, TOC: 0.46 ± 0.05) was analysed in order to obtain a spiked recovery for all measured elements. Deionized water and analytical-grade chemicals were used for the analyses. As and Hg concentrations were measured using atomic fluorescence spectrometry (AFS) with recovery percentages ranging from 96% to 104%. For measuring As and Hg using AFS, the sample was first dissolved using heated 1 + 1 aqua regia in a boiling water bath. After the solution was cooled and made to be acidic (adjusted using 10% HCl), an ascorbic acid reducing agent (thiourea) was added to the solution. A high-intensity hollow cathode lamp was used as the excitation light source in testing the intensity of fluorescence of the As and Hg atoms. The concentrations of Cd, Co, Cr, Cu, Ni, Pb, Ti, Zn and U were measured using inductively coupled plasma mass spectrometry (ICP-MS, ELAN 6100DCRC-e of Perkin Elmer Co.) with the recovery percentages ranging from 94% to 102%. Total Al, Si and Fe were analysed using X-ray fluorescence (XRF). The concentration of total organic carbon (TOC) was determined by titration with K₂Cr₂O₇ (Cr exists as + VI). In the oxidation-reduction reaction, Cr(VI) was reduced to Cr(III) by organic carbon. According to the stoichiometric relationship, the concentration of TOC in sediment can be determined by Cr(III), which was measured using a spectrophotometer (Schumacher, 2002).

2.2.2. Ore samples

To investigate the relationship between mine development and sediment contamination, seven ore samples from the Maoniuping REE mine, four ore samples from the Lugu iron mine, and six ore samples from the Baima and Hongda V-Ti magnetite mines were collected. Crushed powder from the ore samples was analysed using X-ray fluorescence (XRF).

2.3. Chemometric multivariate analysis

To explore the sources of and correlations among risk elements contained in the sediment, cluster analysis (CA), discriminant analysis (DA), linear correlation analysis (LCA), and robust regression (RR) were performed on the data matrix using the software SPSS (Version 19.0) and Eview (Version 8.0). The details of each method are summarized below.

2.3.1. Cluster analysis (CA)

The goal of Q-cluster analysis is to identify groups of similar sites based on similarities within a group and differences among different groups. CA is useful for exploring potential groupings, especially when there is no clear classification pattern. The Anning River flows through

different functional regions, past different mines and across different strata, and therefore, a grouping classification for the thirty sediment samples was essential before the contaminant sources and correlations among risk elements could be identified. In this method, the most similar sediment sites are grouped together until all sites are assigned to a group. A Q-cluster analysis with the “Between Group” linkage method was used in this study. The results of CA for the sediment samples are presented in Fig. 3-a.

2.3.2. Discriminant analysis (DA)

Discriminant analysis is a supervised technique. It can construct a discriminant function that reflects the difference between different groups (Singh et al., 2004), as shown by Eq. (1):

$$F(G_i) = k_i + \sum_{j=1}^n w_{ij} p_{ij} \quad (1)$$

where i is the number of groups (G_i), k_i is a constant inherent to each group, n is the number of parameters that are used to classify a set of data matrices into a given group, and w_{ij} is the weight coefficient that is assigned by DA to a given selected parameter (p_{ij}). CA and DA can be jointly used to separate sediment samples and risk elements into different groups. In this study, CA and DA were jointly used for group classification of the sediment samples. The results of CA for sediment sites are presented in Fig. 3-b.

2.3.3. Robust regression

Pollution by potentially toxic elements in sediment due to human activity can be indicated as outliers for a group or dataset. Geochemical normalization of risk elements with a reference element (e.g., Fe or Ti) is an important way in which outlier risk elements are identified, compared to natural background values. Due to the existence of outliers, an abnormal distribution (non-Gaussian distribution) within the dataset can lead to the misuse of methods that assume a normal (Gaussian) distribution within the dataset (Grygar and Popelka, 2016). Therefore, it is necessary to use regression analysis based on reference elements to identify outlier risk elements. The results of ordinary least squares (OLS) and robust regression (RR) are presented as a comparison (Fig. 4). The results of the robust regression (M-estimate, huber) was plotted (Fig. 5) to identify the outliers (possible pollution) because it is insensitive to outliers, compared with ordinary least squares.

2.4. Enrichment factor

The enrichment factor (EF) is a geochemical index that reflects the degree of enrichment of risk elements. The EF is defined by Eq. (2) (Ergin et al., 1991) and was constructed based on the assumption that there should be a linear relationship between the reference element and other elements in sediment that is free of anthropogenic contributions.

$$EF = (Me/Fe)_{\text{sample}} / (Me/Fe)_{\text{background}} \quad (2)$$

The updated average concentrations of trace elements in sediment from the Yangtze paraplatform (Shi et al., 2016) were selected as background values in this study because the Anning River is located in the western part of the Yangtze paraplatform. Due to its stable chemical behaviour and abundance in the crust, Fe was used as a reference element for normalization, but Fe was first normalized based on Ti as a reference element. EF values were interpreted as follows: (1) no enrichment for $EF < 1$; (2) minor enrichment for $1 < EF < 3$; (3) moderate enrichment for $3 < EF < 5$; (4) moderately severe enrichment for $5 < EF < 10$; (5) severe enrichment for $10 < EF < 25$; (6) very severe enrichment for $25 < EF < 50$; and (7) extremely severe enrichment for $EF > 50$.

Table 1

Statistics of heavy metals in sediment of Anning River and data from other literatures.

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Tl	Zn	U	Fe	Mn	Ti	pH	Corg
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%	%	%		%
Min	1.08	0.183	3.2	24.6	9.9	0.006	5.2	15.3	0.159	65.1	1.46	0.93	0.06	0.34	7.82	0.1
Max	136	2.15	48.4	438	162	0.089	108.0	1166	1.07	313	35.2	15.08	2.18	5.96	9	1.21
Mean	17.88	0.70	17.4	103.9	49.9	0.024	36.0	213.8	0.605	125.2	6.90	4.48	0.25	0.93	8.47	0.41
Median	11.1	0.55	14.1	75.3	43.35	0.016	33.2	45.5	0.542	101	3.155	4.10	0.14	0.53	8.545	0.3
Elemental abundance in upper continental crust ^{a,b}	5.7 ^a	0.06 ^a	15 ^a	73 ^a	27 ^a	0.08 ^b	34 ^a	15 ^b	0.55 ^a	75 ^a	2.6 ^a	5.08 ^b	0.078 ^b	0.66 ^b	n. r.	n. r.
Background values in Yangtze paraplatform of China ^c	9	0.175	14	68	24	0.053	30	25	n. r.	77	2.8	3.43	0.075	0.45	n. r.	n. r.
TEC ^d	9.79	0.99	n. r.	43.4	31.6	0.18	22.7	35.8	n. r.	121	n. r.	n. r.	n. r.	n. r.	n. r.	n. r.
PEC ^d	33	4.98	n. r.	111	149	1.06	48.6	128	n. r.	459	n. r.	n. r.	n. r.	n. r.	n. r.	n. r.

n. r. means no data reported. Data of elemental abundance in upper continental crust is from (a) Hu and Gao (2008) and (b) Lee and Yao (1970); Data of background values in Yangtze paraplatform of China is from (c) Shi et al. (2016); Data of TEC (threshold effect concentration) and PEC (probable effect concentration) are from (d) MacDonald et al. (2000).

3. Results and discussion

3.1. Statistics of risk elements in sediment of the Anning River

The average, median, and range of concentrations of metals and metalloids in the sediment from the Anning River are presented in Table 1. The average concentrations of all measured risk elements (except Hg and Fe) were higher than concentrations in the upper continental crust (Hu and Gao, 2008) and background concentrations established for the Yangtze paraplatform of China (Shi et al., 2016). A comparison of the median and mean indicated that the distribution of Fe, Ni and Cu varies slightly at all sites. The average values of As, Cr, Pb, and U were much higher than their median values, suggesting that they had more extreme outliers that significantly increased the average concentration. This is especially apparent for Pb, which had an average concentration of 213.8 mg/kg, which was approximately four times larger than the median (45.5 mg/kg). Generally, the median values for risk elements in a dataset can represent the background level of the risk element only if the majority of samples in the dataset are unpolluted. Median values of Co, Ni, Tl, and Ti are close to corresponding to the elemental abundance reported for the upper continental crust (UCC) (Table 1), indicating that pollution of these elements in the Anning River is limited. However, median values of As, Cd, Pb, Zn, and U were significantly higher than UCC elemental abundances (Hu and Gao, 2008), suggesting that these elements were generally enriched in the sediment samples, which may be related to local geological background levels (Table 1).

3.2. Distribution of potentially toxic elements in river sediment

3.2.1. Cd, Pb, U and Tl in sediment near the Maoniuping REE mine

3.2.1.1. Content of risk elements in REE ore. Chemical analyses of ore samples (n = 7) from the Maoniuping REE mine showed that the average concentrations of Cd, Pb, U and Tl were 0.43, 1377, 31 and 1.0 mg/kg, respectively.

3.2.1.2. Distribution of risk elements near the REE mine. The concentrations of Cd, Pb, U and Tl in sediment showed similar trends along the river (Fig. 2-a, e, i, m). For comparison, the concentrations of Cd, Pb, U and Tl in the upstream and midstream samples were much higher than in downstream samples. They were enriched at AS1 (near the Maoniuping REE mining region) and gradually decreased in abundance from AS1 to AS8, but they increased at AS9 (near the Lugu mining region). Finally, the four elements gradually decreased from AS9 to AS30, except Cd, which displayed some localized peaks.

The sediment near mining regions (near AS1 and AS9) had significantly higher concentrations of Cd, Pb, U and Tl than other sites. Moreover, the concentrations of Cd, Pb, U and Tl in sediment decreased

with increasing distance from the REE mine. Another study that was focused on the depth-distribution of Cd in sediment cores suggested that the corresponding timing of the Cd peak in the sediment core correlated to the temporal initiation of mining activity (Xu et al., 2015). All of these data suggest that the significant enrichment of Cd, Pb, U and Tl in upstream sediment is likely related to the development of the Maoniuping REE mine.

3.2.2. As, Cd, Pb, U, Tl, Mn, Cu and Zn in sediment near the Lugu iron mine

3.2.2.1. Content of risk elements in Lugu iron mine ore. Ore samples from the Lugu iron mine (n = 4) had average concentrations of As, Cd, Pb, U, Tl, Mn, Cu and Zn of 20, 0.27, 87, 1.49, 0.55, 1259, 24 and 164 mg/kg, respectively. Enrichment of As, Pb, U, Cu, and Zn in ores increases the pollution risk of these elements for the local ecosystem.

3.2.2.2. Distribution of risk elements near the iron mine. As, Cd, Pb, U, Tl, Mn, Cu and Zn showed similar trends in the midstream sediment below site AS9, especially for As and Mn, which reached peak values at site AS9. The concentrations of these elements all sharply increased at site AS9 near the Lugu iron mine (Figs. 1 and 2-a, e, i, m) and gradually decreased with the increasing distance downstream of the Lugu iron mine. These trends suggest that the Lugu iron mine is an important source of these risk elements in the midstream parts of the Anning River. These results are similar to conclusions from a previous report (Wang et al., 2016) that investigated the concentrations of risk elements for seven sediment samples in the Anning River collected in 2014. However, most sampling sites in their study were different from the sites presented here. Site S4 (in their study) at the Lugu iron mine is close to site AS9 from this study. A comparison of the two sample sites revealed that the concentrations of As, Cd, Cr, Cu, and Pb (not Zn and Hg) that were measured in 2014 (Wang et al., 2016) were lower than the concentrations measured for this study in 2012. This temporal variation in concentration may be related to seasonal changes in the river or other factors. The trends in pollution of river sediment need continuous investigation in the future.

3.2.3. Co, Ni and Cr in sediment near the V-Ti magnetite mines at Hongda and Baima

3.2.3.1. Content of risk elements in V-Ti magnetite ore. Analyses of V-Ti magnetite ores from the V-Ti magnetite mines at Hongda and Baima (n = 6) showed that the average concentrations of Co, Ni, Cr, Fe and Ti were 100, 121, 37.8, 35,980 and 5928 mg/kg, respectively. Compared to the UCC value, the EF of Co, Ni, Cr, Fe, and Ti from the V-Ti magnetite mines were 6.67, 3.56, 0.52, 0.71 and 0.90, respectively. The enrichment of trace elements such as Co and Ni was significant, but the concentrations of Fe and Ti in the ore were close to UCC values, showing nonsignificant enrichment. This is contradictory to previously reported data for Fe (approximately 30%) and Ti (approximately

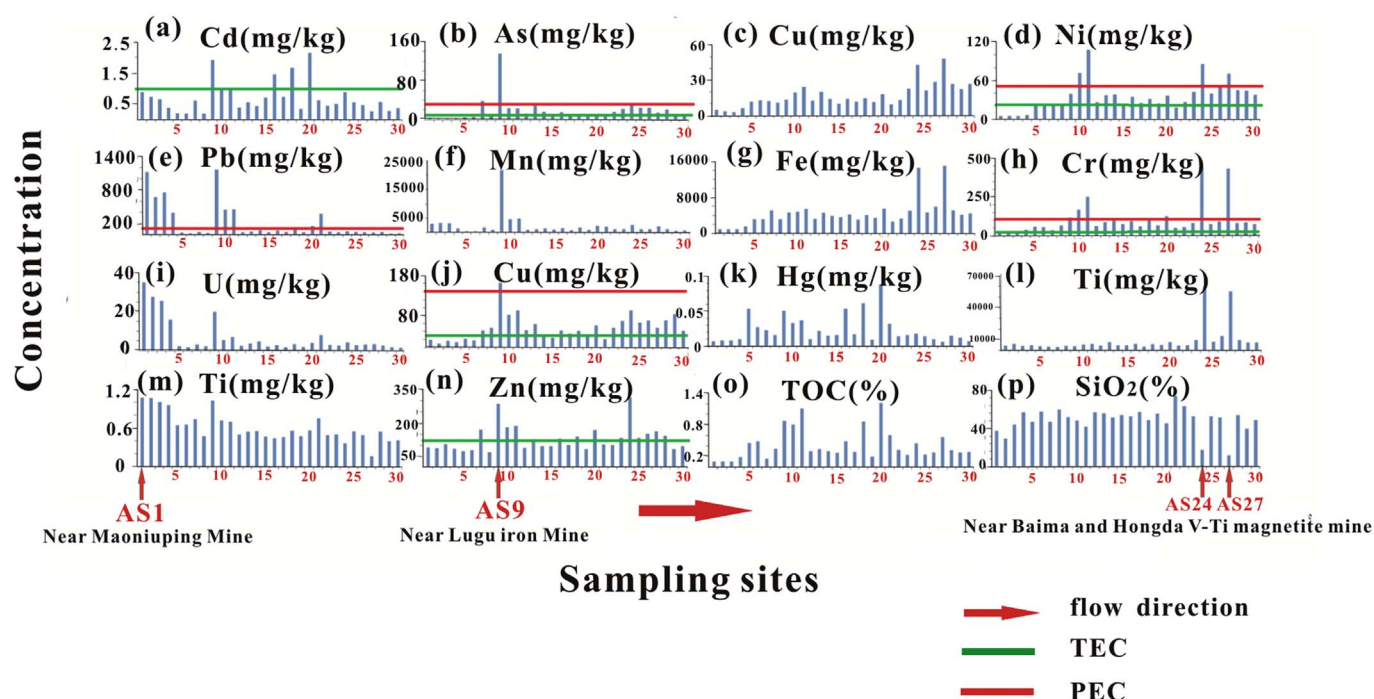


Fig. 2. Spatial distribution of major/trace elements and other parameters in the bottom sediment of the Anning River and its comparison to TEC (threshold effect concentration) and PEC (probable effect concentration).

8.42%). This indicates that the ore samples collected from the V-Ti magnetite mine were probably not the actual V-Ti magnetite ore, but rather, were the surrounding rock.

3.2.3.2. Distribution of risk elements in sediment near the V-Ti magnetite mine. Co, Ni, and Cr showed similar trends to Fe and Ti in the downstream sediment. The concentrations of these elements all sharply increased at AS24 and AS27, near the V-Ti magnetite mines at Baima and Hongda, respectively (Figs. 1 and 2-c, d, g, h, k, l). Moreover, the major constituent (SiO_2) in sediment also significantly decreased at AS24 and AS27. As a major component of rock-forming minerals (e.g., silicates), the SiO_2 concentration in sediment is related to the concentration of the parent rock. The rock classification of the V-Ti magnetite at Baima and Hongda is ultra-basic to basic, which is characteristically low in SiO_2 (usually < 45%) (Zhou et al., 2005). Compared to the concentration of SiO_2 in UCC (57.9%) (Lee and Yao, 1970), the concentrations of SiO_2 in sediment at AS24 (40.95%) and AS27 (37.19%) were much lower. These data suggest that the enrichment of Co, Ni, and Cr in downstream sediment was related to the development of the V-Ti magnetite mines at Baima and Hongda (Fig. 1). In addition, the high values suggest the importance of further investigating the speciation and bioavailability of Co, Ni and Cr in sediment at AS24 and AS27.

3.3. Risk of potentially toxic elements in sediment

3.3.1. General evaluation

A comparison of the average concentrations of risk elements in sediment from the Anning River with sediment quality guidelines (SQGs) (MacDonald et al., 2000) indicates that the concentrations of As, Cr, Cu, Ni, Pb and Zn in the Anning River sediment exceeded the TEC (threshold effect concentration) value (Table 1). This indicates that toxic effects of As, Cr, Cu, Ni, Pb and Zn are possible. This is especially true for Pb, which had an average concentration of 213.8 mg/kg, which is much higher than the PEC value of 128 mg/kg (MacDonald et al., 2000). These results suggest that Pb contamination in sediment of the Anning River was very severe, probably resulting in toxic effects for

local organisms.

The average concentration of Hg in the Anning River sediment was low, approximately 0.024 mg/kg (Table 1), and even the maximum value of Hg was only 0.089 mg/kg (Fig. 2- k). The highest value is still less than the TEC of 1.06 mg/kg (MacDonald et al., 2000). However, the distribution characteristics of Hg and TOC in sediment showed that the distribution of mercury in the Anning River sediment was related to organic materials (Fig. 2- k, o). Additionally, a linear correlation analysis of all thirty sites indicated that there was a significant positive linear correlation between Hg and organic materials (R^2 Hg-TOC: 0.64). This correlation is probably related to the particle size or other factors. Considering that the toxicity of Hg in sediment depends on its speciation (Clarkson, 1997; Kannan et al., 1998), a speciation analysis of Hg in the sediment is necessary before Hg toxicity can be assessed.

3.3.2. Specific evaluation at site

In general, concentrations of Cd and Zn at most sites were lower than their corresponding TEC values, except at sites near the Lugu iron mine (AS9) and near small towns (Fig. 2, AS16, AS18, and AS20 for Cd; AS24 for Zn). There were no sites where Cd and Zn exceeded the PEC value.

Concentrations of Cu, Pb and As at sites near the Lugu iron mine exceeded their corresponding PEC values (Fig. 2-b, j), especially As (136 mg/kg, approximately four times higher than the PEC value of 33 mg/kg) and Pb at AS9 (1166 mg/kg, approximately nine times higher than the PEC value of 128 mg/kg), suggesting that arsenic and lead contamination near the Lugu iron mine probably had a toxic effect on the local ecosystem. Similarly, the concentration of Pb in sediment near the Maoniuping REE mine ranged from 396 to 1124 mg/kg (from AS1 to AS4), all of which exceeded the PEC value. The concentration of Cr and Zn in sediment near the Baima and Hongda V-Ti magnetite mines also exceeded their respective PEC values. Cr contamination was especially severe (Fig. 2-d, h).

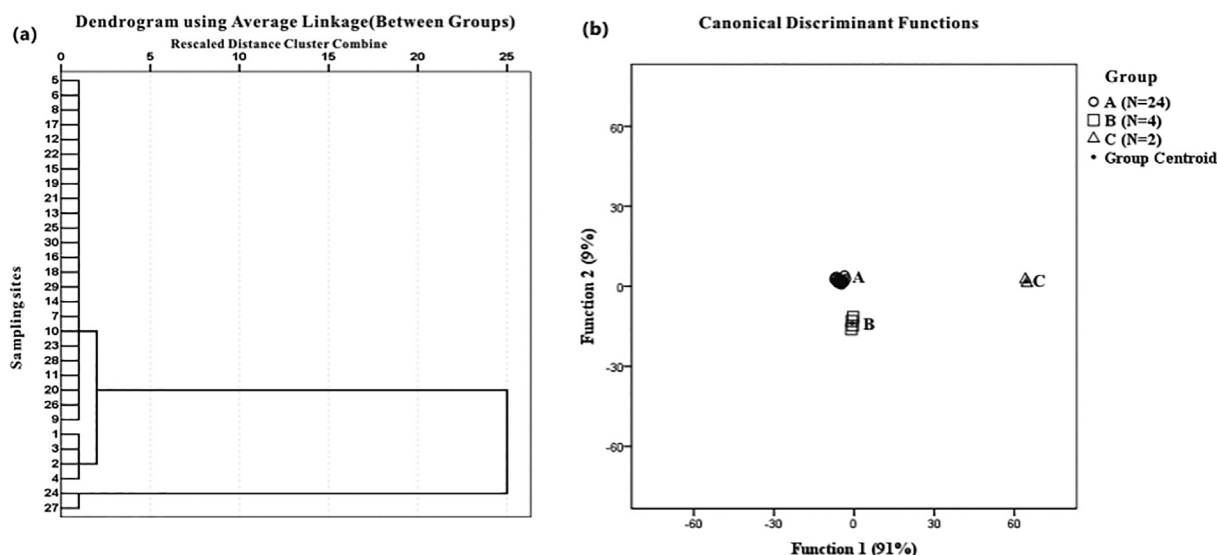


Fig. 3. Classification of sediment sites using the CA and DA.

3.4. General source identification of risk elements in sediment

3.4.1. Group classification of sediment sites using HCA and DA

Risk elements in river sediment are usually distributed unevenly in space because of the random distribution of pollution sources along the riverbank. To evaluate the general source of potentially toxic elements in the river sediment, a reasonable classification of different sites into different groups was important for further analysis. Grouping was based on the similarity of enrichment characteristics of risk elements among the sites. Therefore, cluster analysis (CA) and discriminant analysis (DA) were performed to classify thirty sites along the Anning River into different groups (Fig. 3). All of the sites were divided into three groups based on the distributions of all measured metals (Fig. 3-a): (1) Group A includes the twenty-four sites from AS5 to AS31, excluding sites AS24 and AS27; (2) Group B includes the four sites from AS1 to AS4; and (3) Group C includes two sites, AS24 and AS27. Group A primarily includes the sites along the midstream and downstream reaches of the river, Group B includes the four sites near the Maoniuping REE mine and Group C includes the two sites near the V-Ti magnetite mine.

Moreover, DA was used to test the suitability of group classification based on CA. The loadings and scores of two discriminant functions were presented (Fig. 3-b). The results of the DA indicated significant differences among the three groups, suggesting that the classification of the thirty sampling sites into three groups was suitable. The first (F1) and second (F2) functions explained 91% and 9% of the variance in the data, respectively. Therefore, general identification of sources of risk elements in sediment is discussed in three groups.

3.4.2. Source classification of risk elements of different groups using LCA and DCA

Linear correlation analysis among different trace elements was an important proxy that indicated whether the risk elements possibly have the same pollution source. However, recent research concerning the effect of sediment grain size on trace element enrichment indicates that smaller sized particles are inclined to be enriched in trace elements, which can result in the covariance of elements due to the grain size effect (Grygar and Popelka, 2016). The ratio of Al to Si in sediment can be regarded as an indicator of grain size. Therefore, linear correlation analyses among trace elements and Al/Si were also performed (Table 2).

3.4.2.1. Group A. Significant, positive linear correlations among As-Cu-Pb-Zn-U-Tl, Co-Cr-Ni, and Cd-Hg indicated common sources (Table 2).

Poor linear correlations between these trace elements with the index of sediment size (Al/Si) supported a nonsignificant effect of particle size on the linear correlations (Table 2). Moreover, a pollution assessment of sites from Group A indicated no significant pollution by As, Cu, Pb, Zn, U, and Tl, suggesting that the Group A elements were geologically sourced. Although there was no significant pollution by Co, Cr, and Ni for sites of Group A when compared to background values (Fig. 6), their spatial distribution indicated an obvious enrichment of Co, Cr, and Ni around AS9, near the Lugu iron mine (Fig. 2-c, d, h). Therefore, Co, Cr, and Ni possibly had a mixed geological and anthropogenic source. Enrichment of Cd and Hg in the sediment of Group A was obvious, especially at site AS9 near the Lugu iron mine and at three sites near local towns (sites AS16, AS18 and AS20) (Fig. 1), suggesting that Cd and Hg for Group A likely had anthropogenic sources.

3.4.2.2. Group B. Due to fewer sediment samples in this group, most linear correlations among trace elements were not statistically significant (Table 2). DCA revealed significant enrichments in Cd, Pb, U, and Tl in sediment near the REE mine (Fig. 2-a, e, i, m), suggesting that Cd, Pb, U, and Tl for Group B originated from the Maoniuping REE mine. No outliers of As, Co, Cr, or Ni at sites between AS1 and AS4 were observed (Fig. 2-b, c, d, h). Similarly, there was no enrichment in or pollution by As, Co, Cr, and Ni between sites AS1 and AS4 compared to the background values (Fig. 6). These results suggested that As, Co, Cr, and Ni had a geological or natural source.

3.4.2.3. Group C. Data from Group C were too few to make chemometric multivariate analyses, but spatial distribution characteristics (Fig. 2) clearly defined a contribution of Ni, Co and Cr from the V-Ti magnetite mines. However, the low concentrations of As, Cd, Pb, U, Tl, and Cu at sites AS24 and AS27 indicated a natural source.

3.5. Pollution identification based on robust regression

Risk elements As, Co, Cu, Cr, and Zn were positively correlated with Fe in sediment (Fig. 4-a, c, d, e, i) using OLS or RR. Regression lines by OLS and RR for elements As, Co, and Cr were very close to one another (Fig. 4-a, c, e), suggesting that the number of outliers for As, Co, and Cr were fewer than for other trace elements. Significant differences between OLS and RR lines for Cd, Cu, Hg, Ni, Pb, Zn and U indicated that more severe pollution by these elements was possible (Fig. 4-b, d, f, g, h, i, j), which can result in more outliers. However, outliers for U were mainly distributed at sites with a comparatively low Fe content, such as

Table 2
Linear correlations among risk elements and with the ratio Al/Si.

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Tl	Zn	U	Al/Si
Group A (N = 24)												
As	1											
Cd	0.461*	1										
Co	0.015	−0.036	1									
Cr	0.197	0.466*	0.411*	1								
Cu	0.818**	0.447*	0.404	0.533**	1							
Hg	0.181	0.811**	−0.183	0.359	0.147	1						
Ni	0.142	0.191	0.634**	0.922**	0.544**	0.077	1					
Pb	0.841**	0.565**	−0.068	0.480*	0.762**	0.368	0.343	1				
Tl	0.735**	0.396	−0.209	0.276	0.499*	0.402	0.181	0.836**	1			
Zn	0.827**	0.714**	0.261	0.550**	0.815**	0.426*	0.480*	0.801**	0.712**	1		
U	0.890**	0.543**	−0.099	0.362	0.739**	0.344	0.226	0.971**	0.837**	0.786**	1	
Al/Si	−0.444	−0.356	0.151	−0.364	−0.54*	−0.032	−0.266	−0.500	−0.225	−0.425*	−0.454	1
Group B (N = 4)												
As	1											
Cd	−0.302	1										
Co	0.898	−0.528	1									
Cr	0.803	−0.737	0.963*	1								
Cu	0.424	0.431	−0.017	−0.167	1							
Hg	0.341	−0.988*	0.607	0.799	−0.501	1						
Ni	0.541	−0.941	0.777	0.918	−0.391	0.972*	1					
Pb	−0.023	0.936	−0.361	−0.591	0.717	−0.945	−0.853	1				
Tl	−0.334	0.945	−0.426	−0.633	0.156	−0.889	−0.837	0.798	1			
Zn	−0.508	0.267	−0.785	−0.72	0.443	−0.408	−0.547	0.32	0	1		
U	−0.32.211	0.995**	−0.461	−0.684	0.5	−0.983*	−0.916	0.962*	0.929	0.243	1	
Al/Si	−0.632	0.829	−0.776	−0.909	0.186	−0.835	−0.974	0.769	0.698	0.413	0.891	1

* Correlation is significant at the 0.05 level (2-tailed).

** Correlation is significant at the 0.01 level (2-tailed).

sites AS1 to AS4 (Fig. 2-i and g), suggesting that the enrichment of U at those sites might be correlated with grain size because uranium typically occurs in large grains and/or heavy minerals that have a low concentration of Fe.

Outliers of As and Cu mainly appeared at site AS9 (Fig. 5-a), indicating the influence of the Lugu iron mine. Moreover, outliers of Pb and U were both located in the upstream region that is affected by the Maoniuping REE mine and the Lugu iron mine, which is in agreement with results of the distribution characteristics analysis. Outliers of Cr at sites AS24 and AS27 near the V-Ti magnetite mine were observed (Fig. 5-e) when Fe was used as a reference element. However, the high concentrations of Co and Ni at sites AS24 and AS27 (Fig. 2-c, d) were considered to be normal (Fig. 5-c, g). This strongly indicates pollution by Cr at sites AS24 and AS27. Outliers of Hg were mainly distributed in sites near towns, which is in agreement with the spatial distribution characteristics (Fig. 2-k). In summary, distribution characteristics analysis (DCA) of risk elements can qualitatively indicate possible outliers. However, robust regression (RR) can be used to quantitatively identify whether a high concentration of a risk element should be classified as an outlier or not because RR considers the natural background concentrations of the element. RR is more accurate than DCA in identifying

an outlier or pollution.

3.6. Enrichment factor (EF)

To evaluate the degree of pollution by risk elements in the sediment samples, an enrichment factor (EF) of all metals was calculated for the thirty sample sites, and the results are plotted in Fig. 6. Generally, the mean EF values of these metals followed the descending sequence: Pb (8.58) > Cd (3.73) > U (2.35) > As (1.76) > Cu (1.66) > Tl (1.34) > Zn (1.30) > Cr (0.96) > Ni (0.87) > Co (0.86) > Fe (0.84) > Hg (0.40). The EF of Pb showed severe enrichment at sites AS2 and AS4 (near the Maoniuping REE mine), sites AS10 and AS11 (near the Lugu iron mine) and site AS21; very severe enrichment at sites AS1 and AS3 (near the Maoniuping REE mine); and extremely severe enrichment at site AS9 (near the Lugu iron mine) (Fig. 6). The EF of U showed moderately severe enrichment at sites AS2, AS3, and AS4 (near the Maoniuping REE mine) and AS9 (near the Lugu iron mine); and severe enrichment at site AS1 (near the Maoniuping REE mine). The EF of As showed severe enrichment at site AS9 (near the Lugu iron mine) and minor enrichment at other sites (Fig. 6). The EF of Cd showed moderate enrichment at sites AS1, AS2, AS3, AS7, AS10, AS11, and

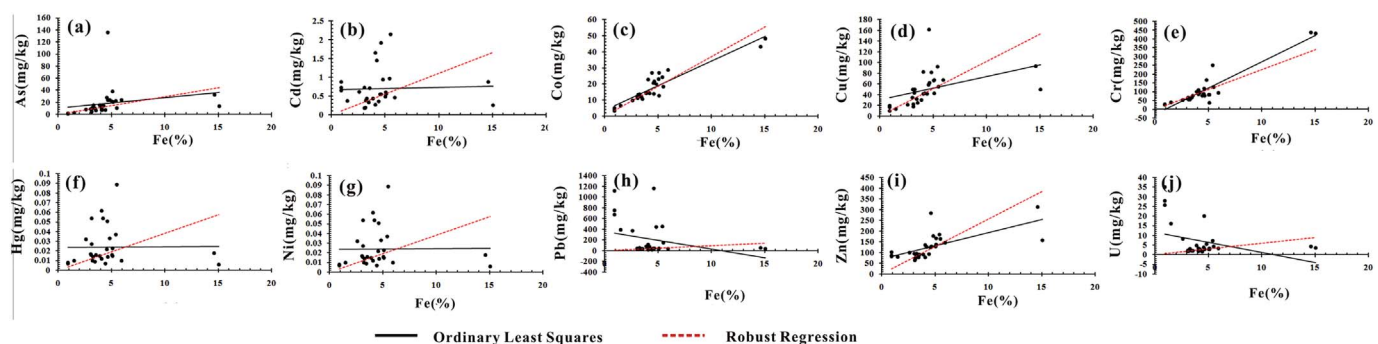


Fig. 4. Result of regression analysis between risk elements and Fe in sediment using ordinary least squares and robust regression.

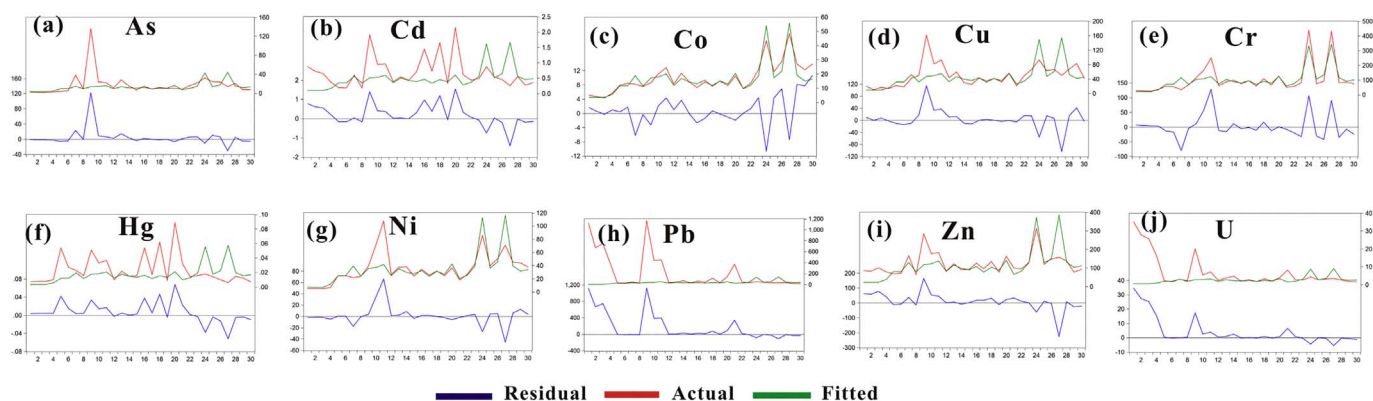


Fig. 5. Result of the risk elements (actual, fitted and residual) following the robust regression analysis (M-estimate).

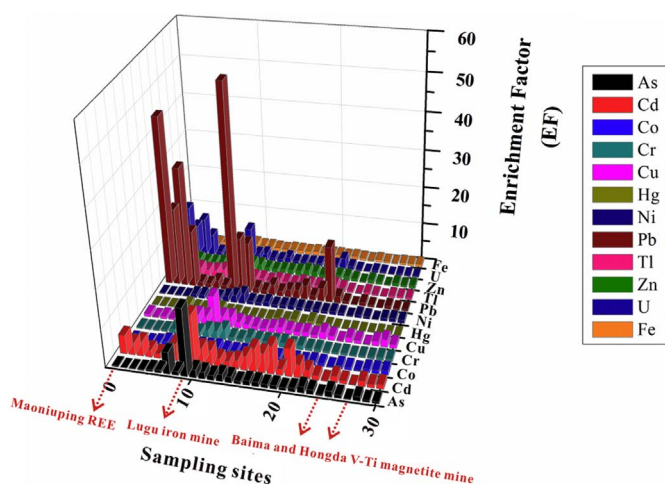


Fig. 6. Enrichment factor of risk elements and metalloids at all the sites.

AS15; significant enrichment at sites AS16, AS17, AS18 and AS20; and severe enrichment at site AS9 (Fig. 6). No significant enrichment of Fe in sediment was observed when Ti was used as a reference element. Enrichment in Cu, Tl, Zn, Cr, and Ni was minor. The order of sites in terms of descending metal enrichment is as follows: AS9 > AS1 > AS2 > AS3 > AS10 > AS11 > AS21 > other sites. These results suggest that the development of the Maoniuping REE mine and the Lugu iron mine probably led to the severe enrichment of Pb, Cd, As and U in upstream and midstream sediment samples.

4. Conclusions

Mining activities along the Panxi Rift have caused severe pollution of the sediment in the Anning River by risk elements, especially Pb pollution. Different mine categories have led to the enrichment of different risk elements. The Maoning REE mine caused significant enrichment of Pb, U, Cd, and Tl, and the Lugu iron mine caused the severe pollution by As, Cu, Ni and Cr.

In sediment samples taken from areas near the mines, there were much higher concentrations of Pb, As, Cr, and Ni than the PEC, suggesting a probable toxic effect of these metals, which needs further regulation and monitoring. The effective reduction of these mining pollution sources is important to protect the safety of the Anning River, which is the source of drinking and irrigation water for local inhabitants.

A joint application of distribution characteristics analysis (DCA) and robust regression (RR) was useful in identifying the sources of these potentially toxic elements. Distribution characteristics analysis (DCA) of risk elements qualitatively indicated the outliers, but robust

regression (RR) quantitatively identified whether a high concentration of a risk element could be classified as an outlier (compared to a reference element).

Enrichment factors of risk elements showed (1) severe to very severe contamination by Pb, moderate to severe contamination by U, and moderate contamination by Cd in sediment near the Maoniuping REE mine; (2) severe to extreme contamination by Pb, and moderate to heavy contamination by Cd, Cu, Zn and As in sediment near the Lugu iron mine; (3) moderate to heavy contamination by Cr and Co in sediment near the V-Ti magnetite mine; and (4) Tl was practically uncontaminated for all the sites except near the Maoniuping REE mining region.

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