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Occurrence and mobility of toxic elements in coals from endemic fluorosis areas in the Three Gorges Region, SW China

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ABSTRACT

Fluorine (F) is a topic of great interest in coal-combustion related endemic fluorosis areas. However, little extent research exists regarding the environmental geochemistry of toxic elements that are enriched in coals and coal wastes in traditional endemic fluorosis areas, particularly focusing on their occurrences and mobilities during the weathering-leaching processes of coals and coal wastes in the surface environment. This paper addressed the issue of toxic elements in coals and coal wastes in the Three Gorges Region, Southwest (SW) China, where endemic fluorosis has historically prevailed, and investigated the distribution, occurrence, mobility features, and associated potential health risks. For this purpose, a modified experiment combined with long-term humidity cell test and column leaching trial was applied to elucidate the mobility of toxic elements in coals and coal wastes. In addition, sequential chemical extraction (SCE) was used to ascertain the modes of occurrence of toxic elements. The results demonstrated that the contents of toxic elements in the study area followed the order: stone coals > gangues > coal balls > coals. Furthermore, modes of occurrence of toxic elements were obviously different in coals and coal wastes. For example, cadmium (Cd) was mainly associated with monosulfide fraction in coals, molybdenum (Mo) and arsenic (As) were mainly associated with carbonate and silicate in coal gangues and stone coals, chromium (Cr) mainly existed in silicate and insoluble matter in coal gangues and coal balls, thallium (Tl) mainly occurred in organic matter in stone coals and sulfide in coals, and the occurrence of antimony (Sb) varied with different kinds of samples. Moreover, a large amount of toxic elements released to the leachates during the weathering and leaching process, which might pollute the environment and threaten human health. Based on the geo-accumulation index (I_{geo}), single factor index (P_i) and Nemerow index (P_N), soils in the study area were mainly polluted by Cd, which constituted a potential risk to locally planted crops.

1. Introduction

Long-term environmental exposure to toxic elements can negatively impact human health, such as endemic diseases of chronic thallotoxicosis (Xiao et al., 2007), arsenosis (Li et al., 2013; Steinmaus et al., 2016), selenosis (Zhu et al., 2008; Long and Luo, 2017) and fluorosis (Dai et al., 2004; Ding et al., 2011), which have attracted intensive research attentions globally. There are two major kinds of endemic fluorosis reported in China, the water-drinking type and the coal combustion type. Previous research has believed that water-drinking endemic fluorosis results from excessive fluoride ingestion in groundwater (Chen et al., 2012), while coal combustion endemic fluorosis is caused by the intake of high levels of fluoride emitted from indoor combustion of F-rich coal balls or stone coals, using conventional stoves without chimneys venting the emissions outdoors (Dai et al., 2004; Luo, 2011; Chen et al., 2014).

Toxic elements tend to be released into the environment through the coal combustion process from fire power plant in urban areas and domestic coal combustion in rural areas (Zheng et al., 2007; Saikia et al., 2016). Particularly, the local environment in rural areas, where toxic element-rich coals occur and are widely used, may suffer from toxic element exposure, through indoor coal combustion and the natural weathering of coal wastes. The released amounts of toxic elements from indoor coal combustion are significantly dependent on their concentrations in local coals. Even though Chinese coals have normal contents for most trace elements compared to world coals (Dai et al.,

2012), certain areas possess coals with elevated concentrations of toxic elements. For instance, the brown coals in Shanxi Province are enriched in As and Cd (Zhang et al., 2004), the bituminous coals in SW Chongqing are characterized by high selenium (Se) and F contents (Chen et al., 2015), and coals in Guizhou Province are enriched in As and F (Dai et al., 2004).

The historic prevalence of coal-combustion related endemic fluorosis in Wushan and Fengjie Counties in the Three Gorges Region, SW China, has engendered great concern (Li et al., 2005). Particularly, a rural area of Jianping in Wushan County, has experienced severe fluorosis (Chen et al., 2007). Some researchers have considered that coal-combustion fluorosis is caused by using high-F coal balls or stone coal (Dai et al., 2004; Zheng et al., 2007). However, recent researches have indicated that local coal, stone coal and coal ball (home making by 75% local coal and 25% clay) in the Jianping area are rich in both high geogenic F and Cd, and thus local residents might suffer from a high health risk of chronic F-Cd poisoning (Tang et al., 2009; Liu et al., 2015). In this area, high F-Cd coals are used to burn for cooking, heating and drying harvested crops. As a result, F and Cd, emitted from local coal combustion, are easily absorbed by the drying crops, which might lead to excessive intake of F and Cd, giving rise to tooth and bone damage for local residents. Such fluorosis can be prevented by using either low F-Cd coal or chimneys that vent the emitted F and Cd outside of the home (Li and Zhang, 2005). Nevertheless, chronic fluoride poisoning in this area has occurred periodically. Another potential source of F and Cd for local residents in the Three Gorges Region may exist, in which a black shale zone with a high background of F and Cd is outcropped (Tang et al., 2009; Liu et al., 2015). In addition, long-term coal mining activities in this area have produced a large number of gangues, releasing F and Cd during the weathering process, which might pollute the local soil and constitute a potentially serious threat to the local public. However, little is currently known about the occurrence, mobility, and associated potential health risks of toxic elements in local coals and coal wastes. Consequently, this paper aimed to: (i) determine the distribution, occurrence, and mobility of toxic elements during the weathering process, using an integrated approach (combined with a humidity cell test and a column leaching test) and sequential chemical extraction (SCE); and (ii) assess the potential health risks of toxic elements in soils and clays in the Three Gorges Region, using a synthetic assessment (combined with geo-accumulation index, single factor index and Nemerow index).

2. Materials and methods

2.1. Study area

The study area is located in Wushan and Fengjie Counties (110°6′38″–109°17′2″ E, 30°37′57″–31°19′26″ N) of the Three Gorges Region, Chongqing, SW China (Fig. 1). The subtropical continental monsoon climate in this region is warm and humid, with an annual average precipitation of 1041 mm, elevation of 229–1095 m above sea level and a mean temperature of 18 ˚C.

The study area is geologically located in the Yangtze platform, at the cross-section of three structural units: the Daba mountain fault fold belt, the eastern Sichuan fold belt and the fold belt of Sichuan, Hubei, Hunan, and Guizhou Province in China. The study area presents a karstic topography, with mountains and hills constituting the main geomorphologic units. Local rock outcroppings include lithologies from the Silurian to the Jurassic periods, mainly composed of limestone, dolomite, siltstone, claystone and coal seam. Purple soil, yellow soil, paddy soil and limestone soil are the main local soil types.

Wushan County and Fengjie County, located in the Three Gorges Region, are traditional coal combustion related fluorosis areas, with a high geochemical background for F and Cd (Tang et al., 2009; Liu et al., 2013). Jianping, the most serious fluorosis area, historically featured long-term coal mining, but has now ceased mining and begun using low-F coals imported from coal mines outside of Wushan and Fengjie since 1983 (Li and Zhang, 2005). The past local coal mining activities and current coal domestic combustion practices might lead to negative impacts on the environment and human health.

2.2. Sample collection and preparation

A total of 124 samples, composed of 39 coals, 17 gangues, 13 coal balls, 10 clays, and 45 soils from 43 sampling sites of Wushan and Fengjie were collected (Fig. 1). Each sample was kept in polyethylene bags and air-dried in the laboratory. The soil and clay samples were crushed and ground to pass 200 mesh (75 μm) for major and trace element analysis. The coal and coal waste samples were crushed and divided into three aliquots. One was ground to pass 200 mesh for a trace metal analysis, the second was ground to pass 100 mesh (150 μm) for a sequential chemical extraction experiment, and the third was ground to 20–100 mesh powder for a leaching test. For trace mental determination, 50 mg sample powder (200 mesh) was oxidized with 3 ml conc. HNO_3 and 1 ml conc. HF in a Teflon steel pressure bomb for 24 h at 170 ˚C. After cooling, the bomb was heated on a hotplate to remove F, and the final solution was made up to 100 ml by the addition of 5% HNO_3 (Sager, 1993).

2.3. Sequential chemical extraction

Nine coal and coal waste samples were selected for a modified SCE (Tessier et al., 1979; Huggins et al., 2000; Norris et al., 2010). The detailed procedure was listed in Table 1. A 2.5g sample was placed into a 100 ml polyethylene centrifuge tube, 50 ml extraction solution was added, and then shook for 18 h. After centrifugation to separate supernatant and solid, the next extraction solution was added to the solid. Procedures in Table 1 were followed to obtain water-extractable, exchangeable, carbonate or monosulfide (sphalerite, galena, and chalcopyrite), silicate, disulfide (pyrite and marcasite), organic matter and insoluble fractions (zircon and titanium dioxide polymorph) (Huggins et al., 2000). The remaining insoluble residues were digested with HNO_3 and HF as described above. The extraction solution was heated on a hotplate to reduce the volume to 1 drop, 5 ml 50% HNO_3 was added and the final solution was made up to 50 ml by the addition of Milli-Q water. The recovery for elements was calculated as the sum of all fractions divided by the contents of elements from HNO_3 and HF digestion of the original sample. All of the samples routinely displayed a fine recovery from 86% to 106%.

2.4. Long-term leaching test

In order to determine the retention and transport characteristics of toxic elements in coals and coal wastes, a modification experiment combined with a long-term humidity cell test and a column leaching test was applied (Yu et al., 2014; Orndorff et al., 2015). Five samples of coals and coal wastes (200 g, 20–100 mesh) were placed in an enclosed column (diameter = 5 cm, height = 50 cm) with ports for input and output of air, respectively. During a 15 d cycle, dry air was passed through the columns in the first 7 d and then humidified air for the next 7 d. On the 15th day, 200 ml of simulated local acid rain (SO_4^{2-}: NO_3^- = 6.4: 1, pH = 5) (He et al., 2008) was used to flush each column, allowing contraction of each sample for approximately 2 h prior to draining into a collection flask. The filtered leachates were measured for trace metals, major elements, anions, and water chemical parameters shortly. The follow-ups were performed to begin an extended cycle, as mentioned above, for a total of 10 cycles.

All of the experiment and analysis in this study were conducted at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Science. Trace metals were determined using inductively coupled plasma mass spectrometry (ICP-MS, Agilent, 7700x U.S.A.), major elements were measured by inductively
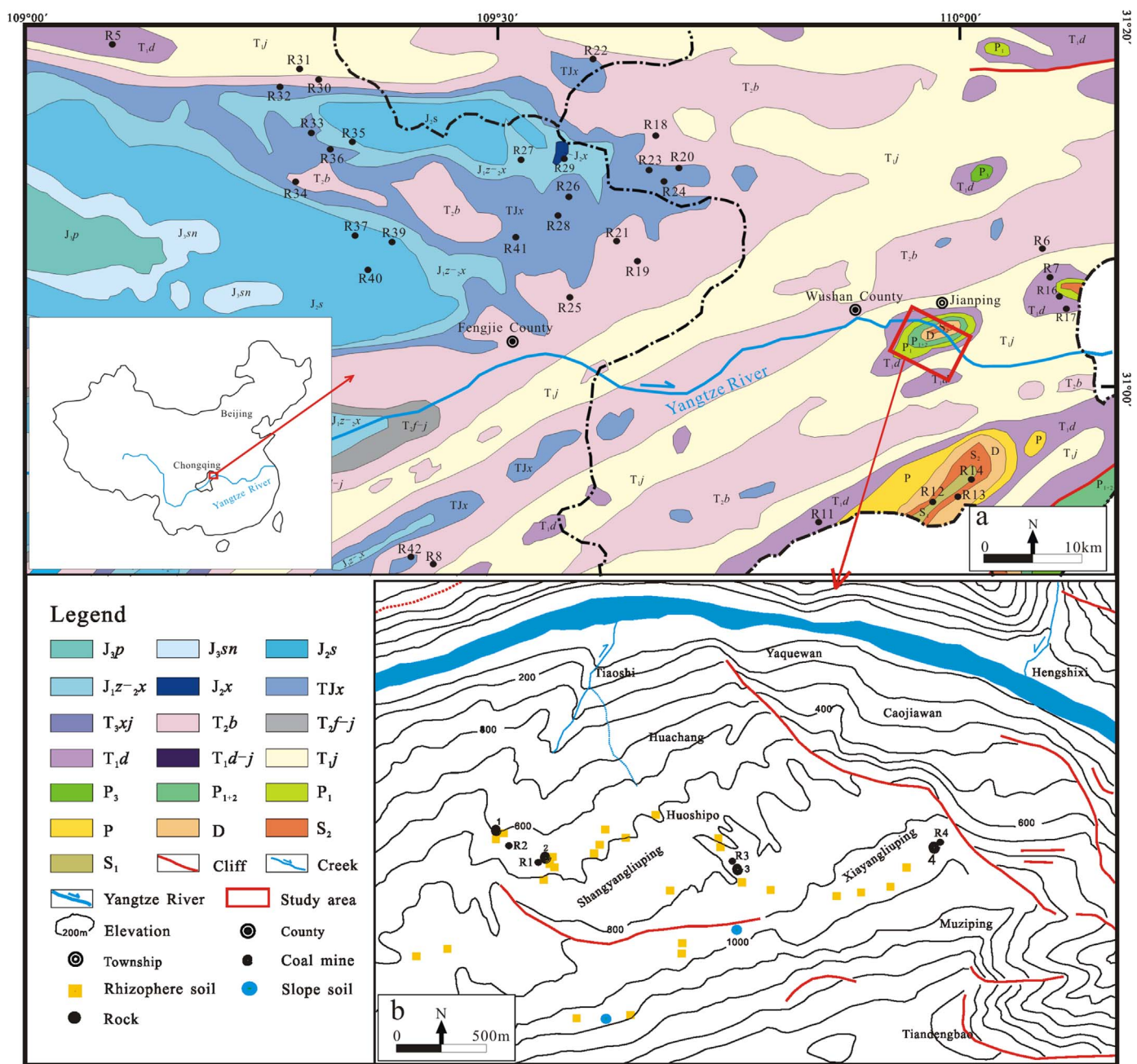
Fig. 1. Map of the sampling sites in the study area. a is the sampling sites for coals and coal wastes in Wushan and Fengjie Counties. b is the sampling sites for soils, stone coals, gangues and coal balls in the Jianping area, Wushan County.

Table 1
The sequential chemical extraction procedure.

Fractions	Reagents
Water-extractable	50 ml Milli-Q water, shaking for 18 h, centrifuged
Exchangeable	50 ml 1 M NH$_4$AC,shaking for 18 h, centrifuged
Carbonate	50 ml 3 M HCl, shaking for 18 h, centrifuged
Silicate	50 ml 50% HF, shaking for 18 h, centrifuged
Disulfide	50 ml 2 M HNO$_3$, shaking for 18 h, centrifuged
Organic matter	3 ml 0.02 M HNO$_3$ and 20 ml 30% H$_2$O$_2$ (pH = 2), shaking at 85 °C for 5 h, cooling, 12.5 ml 3.2 M NH$_4$Ac and 10 ml Milli-Q water, shaking for 30 min, centrifuged
Insoluble	Residuals were digested by HNO$_3$ + HF

coupled plasma-optical emission spectroscopy (ICP-OES, Wasst-mpx, U.S.A.), anions were analyzed by ion chromatography (Dionex, ICS-90, Sunnyvale, U.S.A.), and water chemical parameters were measured by a calibrated YSI Professional plus pH meter (YSI, Yellow Springs, OH, U.S.A.). X-ray powder diffraction (XRD) study was performed on powder samples using the PANalytical EMPYREAN X-ray diffractometer with CuKα radiation, running from 4° to 70° 2θ, with a step increment of 0.02° and a counting time of 25 s per step. The minerals in each case were identified by referencing the ICDD powder diffraction file.

Standard quality control procedures were applied in this study to control analytical precision and accuracy. An internationally certified reference materials (SLRS-5) and internal standards (Rh at 500 mg/L) were utilized during the test. International coal certified reference material (BCR 180), Chinese soil and rock geochemical certified reference materials (GBW07405 and GBW07108), and duplicates and regent blanks were digested and analyzed under the same conditions as

Table 2
Average concentration (mg/kg) of selected elements in coals and coal wastes in the study area.

	Cr	As	Se	Mo	Cd	Sb	Tl
Wushan County							
Coals	38.9 ± 20.60	6.29 ± 7.15	2.36 ± 2.37	6.66 ± 4.57	1.18 ± 0.84	1.28 ± 1.77	0.21 ± 0.06
Stone coals	504.8 ± 543.13	9.06 ± 7.46	28.50 ± 50.23	80.06 ± 146.01	39.95 ± 60.37	3.58 ± 2.80	1.08 ± 1.39
Gangues	179.1 ± 214.05	9.53 ± 7.58	19.43 ± 36.59	36.58 ± 61.86	13.32 ± 31.81	3.51 ± 4.89	0.96 ± 1.19
Coal balls	50.8 ± 31.87	11.23 ± 8.16	1.50 ± 0.71	8.35 ± 7.11	1.83 ± 2.80	2.17 ± 1.63	0.43 ± 0.16
Fengjie County							
Coals	28.1 ± 10.51	7.46 ± 11.08	1.15 ± 0.34	2.86 ± 3.05	0.18 ± 0.12	1.51 ± 1.42	0.33 ± 0.28
Gangues	126.1 ± 140.99	4.89 ± 5.10	1.29 ± 0.49	8.05 ± 17.62	2.29 ± 5.66	1.73 ± 1.17	0.80 ± 0.36
Coal balls	46.9 ± 4.14	9.24 ± 3.56	1.12 ± 0.11	2.14 ± 0.57	0.25 ± 0.15	1.90 ± 0.70	0.46 ± 0.08
Chinese coals[a]	15.4	3.79	2.47	3.08	0.25	0.84	0.47
World coals[b]	16	8.3	1.3	2.2	0.22	0.92	0.63

The uncertainties are the standard deviation of the mean value of samples.
[a] From Dai et al. (2012).
[b] From Ketris and Yudovich (2009).

the sampled particles for toxic elements. Recoveries of certified referenced materials were between 95 and 105%. Relative standard deviation (RSD) of duplicates were less than 10%. Concentration of toxic elements in blanks always gave values less than 2% of the measured contents in samples.

3. Results and discussion

3.1. Contents and affinities of toxic elements

Toxic element concentrations in local coals and coal wastes were listed in Table 2. Compared to the Chinese and world coals (Ketris and Yudovich, 2009; Dai et al., 2012), coals from Wushan and Fengjie were characterized by higher levels of Cd, Mo, Cr and Sb. Particularly, coals and coal wastes in Wushan were enriched for Cd and Mo. The concentration distribution of toxic elements exhibited the pattern of stone coals > gangues > coal balls > coals. In addition, Cd in coals, stone coals and gangues in Wushan were 1.2, 40.0 and 13.3 mg/kg, respectively, which is much higher than those in Fengjie County. Other toxic elements, such as Mo and Cr, exhibited distributions that were similar to Cd in the study area. Fengjie coals mainly occurred in the Late Triassic (T_3) or Early and Middle Jurassic (J_{1-2}) coal-forming period, whereas the coals from Wushan were formed in Late Permian (P_2). Previous research indicated that the arithmetic mean contents of trace elements in coals from the P_2 coal-forming period are higher than coals from the J_{1-2} period (Bai, 2003).

Affinities of elements in coals were analyzed by Pearson's correlation coefficients (R). As the host element for kaolinite, Al is usually utilized as an indicator for aluminosilicate minerals. Sulfide minerals in coal are presented as pyrite and marcasite, with S as the indicator for sulfide (Sia and Abdullah, 2011). The Pearson's correlation coefficients of element contents with respect to S and Al contents were plotted in Fig. 2. Li, Ti, Hf, Sc, Ga and Sn in coals exhibited obvious positive correlations with Al (r = 0.51–0.73, $p < 0.01$), indicating that they mainly possessed aluminosilicate affinity and might exist in clay partings in coals, such as kaolinite, montmorillonite, and other detrital minerals (Finkelman, 1994). Toxic elements (Tl, Cd, Mo, Se, Zn, and Cr) showed positive correlations with S (r = 0.52–0.81, $p < 0.01$) and Fe (r = 0.45–0.86), with a certain degree of sulfide affinity. They might occur in pyrite and other sulfides in coals, which was similar to coals from Inner Mongolia (Wang et al., 2011). Tl positively correlated with Cd (r = 0.97, $p < 0.01$) and Se (r = 0.97, $p < 0.01$) in stone coals in the Jianping area, implying an association with sulfides in stone coals.

The trace metal concentrations from nine selected samples, comprising four stone coals and one coal ball from the Jianping area, and two groups of coal and gangue from Wushan and Fengjie, were applied to elucidate the characteristics of the distribution, occurrence, and mobility of toxic elements. Fig. 3 showed that a number of metals in the

selected samples were much richer than Chinese coals.

Notably, the average concentration coefficient (CC = ratio of element concentration in selected samples vs. Chinese coals) for Cd in stone coals was up to 199, and the CCs were 40.3, 33.9, 31.8 and 16.9 for Cr, V, Mo and Se, respectively. Cu and U had CC values of 5–10, and 2–5 for As, Sb, Zn, Tl, P, Sc, Ga, Rb, Zr, Nb, Cs and Ta in coals and coal wastes. The other metals exhibited similar CCs (0.5–2) to Chinese coals (Fig. 3). Among them, the metals of Cd, As, Cr, Mo, Sb and Tl were enriched in local coals and coal wastes in the study area. Long-term exposure to these elements may result in environmental pollution and health risks.

3.2. Occurrence of toxic elements

The mode of occurrence of trace metals reveals chemically bound and physically distributed of elements, and insight into the occurrence of toxic elements in coals is meaningful for reducing their mobility in burning and weathering processes (Finkelman, 1994).

The changes for toxic elements upon SCE experiment varied greatly with element and sample type, as demonstrated in Fig. 4. It is notable that Cd in water-extraction of gangues presented high values, accounting for 22.0–29.7% (with an average of 25.8%). Water-extractable Cd in coals and stone coals ranged from 0.1% to 0.4% (mean at 0.2%), which displayed much lower values than 8.7% of coal ball. Moreover, a considerable number of Mo existed in water-extractable matter in the selected samples, which varied from 0.1% to 15.5% according the data. The dominated occurrence of Mo in selected samples were carbonate and silicate (with the average percentage of 24.1% and 25.5%, respectively). Since gangue samples were slightly weathered, a large number of Cd and Mo occurred in leaching solutions after simulation of weathering, Cd and Mo in gangues in the study area were easily released to the environment. In addition, water-extractable Cd and Mo were the most potentially bioavailable to plants and the food chain. Therefore, Cd and Mo in gangues posed a potentially great hazard to local public health.

The exchangeable fractions of elements were associated with clay minerals, humic acids, and hydrated oxides of iron and manganese (Tessier et al., 1979). Coal ball (R9) was made of 75% coal (R2) and 25% local clay in the Jianping area. The exchangeable fraction Cd in R9 was 22.7%, which is much higher than R2 (3.6%) and other samples (1.9–15.2%). Exchangeable Cd constituted one of the dominating fractions in soil samples in Jianping, with an average value of 21% (Liu et al., 2013). Hence, high exchangeable Cd in coal balls might be influenced by the fractions of local clay.

Cations associated with carbonates and monosulfides could be removed by HCl (Huggins et al., 2000). In this study, carbonates and monosulfides were the dominant fractions of Cd in samples, ranging from 19.9% to 73.9% (mean at 42.6%). This result was similar to
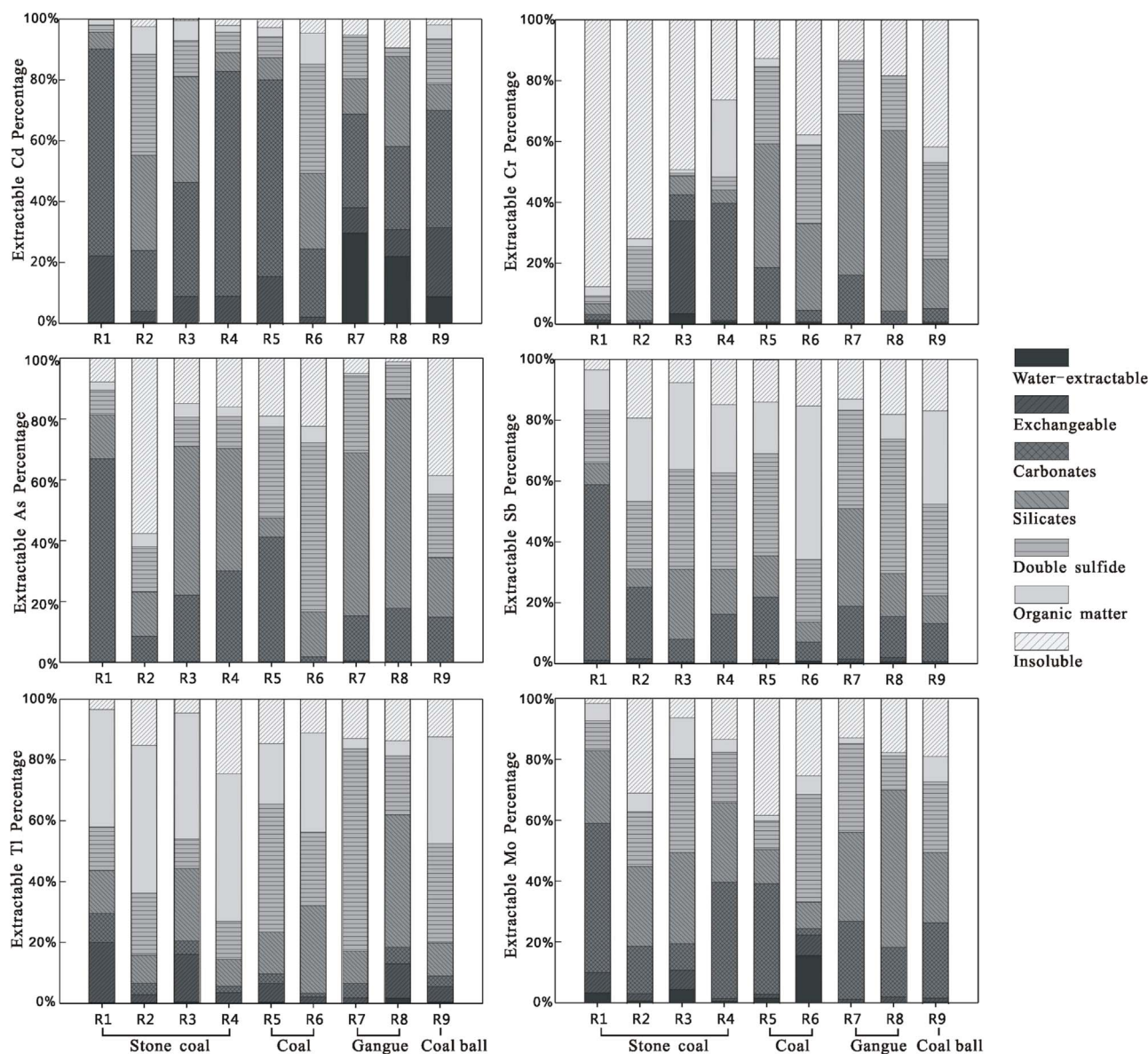
Fig. 2. Pearson's correlation coefficients of element contents with respected to Al and S in coals in the Three Gorges Region (n = 39).

previous studies which generally accepted that Cd in coal mainly occurs in solid phase in sphalerite (Finkelman, 1994; Huggins et al., 2000). Furthermore, Cd exists in silicate and sulfate fraction in coal and coal waste, with average percentages of 17.7% and 14.3%, respectively. On the contrary, a small amount of Cd associated with organic matter and insoluble matter in selected samples, with values ranging from 0.3% to 10.2% and 0.1% to 9.4%, respectively.

Cr associated with an insoluble fraction of stone coals (from 26.3% to 87.6%, with an average of 58.7%) was higher than that in other associations. This result suggested that most Cr in stone coals might occur in insoluble phases such as zircon or one of the titanium dioxide polymorphs (Huggins et al., 2000), which were not expected to be released in solutions under the conditions of SCE. Silicate-associated Cr was the dominant phase in gangues (with an average of 56.2%). Cr in coals and coal balls was nearly evenly distributed in silicates, double sulfides and insoluble fractions. A few Cr occurred in water-extractable, exchangeable, carbonate and organic matter in the samples. This phenomenon suggested that Cr was not readily leached by reagents, but rather occurred in stable phases and was difficult to release into the environment for most samples in the study area. This result was different from U.S. bituminous coal (Huggins et al., 2000) and Australian

coals (Riley et al., 2012).

Tl is a lithophile element in the environment with high temperature and low sulfur geological background. The ionic radius and chemical properties of Tl are similar to Rb and K during geochemical processes, such as metasomatism and bioaccumulation (McGoldrick et al., 1979). Tl is easily concentrated in K-rich silicate minerals such as micas and organic matter in coals (Antonia López Antón et al., 2013). However, Tl is also a chalcophile element, concentrated in sulfide minerals at low temperature combined with high sulfur geological environment (Kiseeva and Wood, 2015). Although the occurrence mode of Tl of coal in the study area has not been studied in great detail, it is generally accepted that Tl mainly occurs in sulfides and organic matter in coal (Riley et al., 2012; Antonia López Antón et al., 2013).

Organic matter association and sulfide association Tl were the dominant occurrence observed in this study. The mean percentage of organic bounded Tl was 44.3% in stone coals, 35.1% in coal ball and 26.3% in coals. Sulfide associated Tl occurred in gangues (mean at 42.9%), coals (mean at 33.2%), and coal ball (mean at 32.7%). However, a smaller portion of Tl was bounded to water-extractable matter (mean at 0.4%), exchangeable matter (mean at 7.5%), carbonates matter (mean at 4.2%) and insoluble matter (mean at 12.5%). Pearson's correlation

Fig. 3. Average concentration coefficients (CC, the concentration ratio of samples investigated vs. Chinese coals) of elements in coals (n = 2), gangues (n = 2), coal ball (n = 1) and stone coals (n = 4) in the Three Gorges Region. The concentration coefficients were normalized by averages of Chinese coal (Dai et al., 2012).

Fig. 4. Percentage of Cd, Cr, As, Sb, Tl and Mo in various fractions inferred from sequential chemical extraction.

Table 3
Concentration of elements in selected samples and average concentrations for their corresponding leachates taken after 10 leaching cycles.

Sample[a]		Before leaching				Leachate												
ID	Type	S %	Cd mg/kg	Cr mg/kg	Tl mg/kg	pH	Eh mV	Ec ms/cm	SO_4^{2-} mg/l	F⁻ mg/l	Fe mg/l	Ca mg/l	Cd ug/l	Cr ug/l	Tl ug/l	As ug/l	Sb ug/l	Mo ug/l
R1	SC	1.0	146.5	1050	3.4	6.94	197.4	2.0	1620	3.9	0.2	611	72.1	4.9	0.37	1.1	4.5	7326
R3	SC	1.3	23.6	1135	1.2	6.88	189.9	1.7	1352	2.3	6.7	555	146.3	64.9	0.35	1.9	1.9	13
R5	C	0.9	3.1	473	1.5	2.80	498.6	1.2	926	11.4	60.3	139	763.3	941.1	1.12	10.0	2.1	8
R7	G	1.5	2.7	183	0.8	7.05	178.5	2.1	1753	1.1	0.1	456	3.5	1.3	0.10	1.6	1.3	88
R8	G	0.5	16.3	102	0.7	6.40	211.6	0.3	129	1.7	0.2	47	20.8	5.3	0.25	8.1	2.6	171

[a] SC – stone coal, C – coal, G – gangue.

analysis showed that Tl was positively correlated with element S (r = 0.78, p < 0.01) in selected samples in the study area.

There was a small portion of water-extractable and exchangeable As in coal and coal waste in the study area. As principally occurred in silicate association in gangues (R7 and R8, mean at 61.2%) and stone coals (R3 and R4, with an average date of 44.6%). Double sulfide associated As was the dominant fraction for coal R6 (mean at 55.6%),

while As in coal R5 was mainly distributed in carbonated and double sulfide fraction (with the percentage of 41.0% and 29.9%, respectively). A large number of insoluble fraction As occurred in stone coal (R2, 57.6%) and coal ball (R9, 38.6%).

Sb was nearly uniformly distributed in carbonate, silicate, double sulfide and organic matter fraction, with the mean percentage of 19.4%, 14.0%, 29.4% and 22.4%, respectively. There was little water-
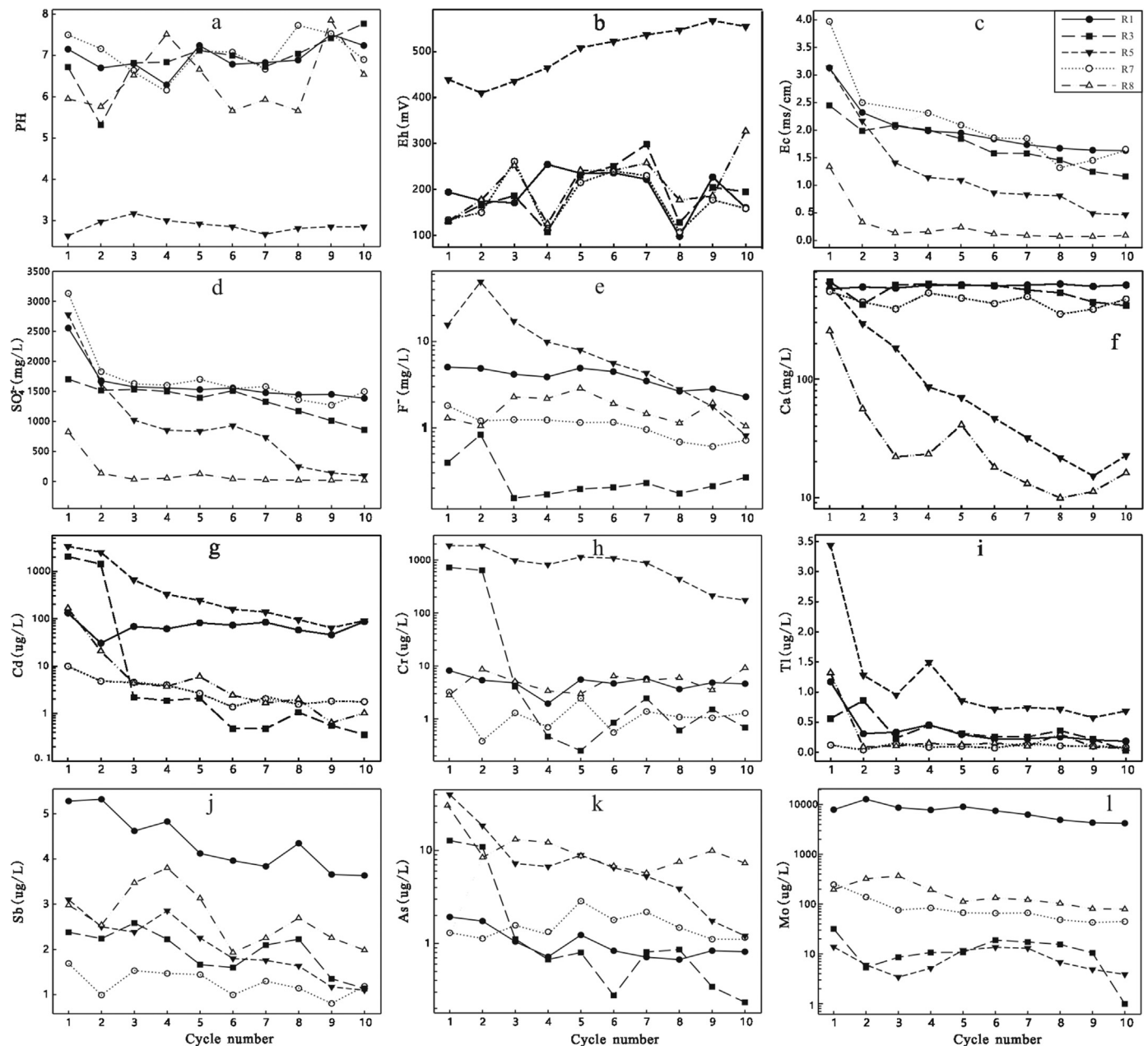
Fig. 5. Scatter diagrams of selected water chemical parameters, anions, major and trace elements leached from five selected samples. The 10 cycles of weathering and leaching test occurred over 20 weeks. Each cycle consisted of a 14 d weathered process (7 d dry air + 7 d humidified air) and leached on the 15th day.

extractable (mean at 0.3%) and exchangeable (mean at 0.8%) Sb existing in the selected samples. However, carbonate associated Sb was the dominant fraction in stone coal (R1, mean at 57.7%) and organic matter fraction was the main occurrence of Sb in coal (R6, mean at 50.5%).

3.3. Mobility of toxic elements

Stone coals (R1, R3), gangues (R7, R8) and coal (R5) were selected for a long-term weathering and leaching test. Sample information and scatter diagrams of element concentrations for leachates were presented in Table 3 and Fig. 5, respectively.

The pH values for stone coals (R1, R3) and gangues (R7, R8) were 6.94 ± 0.35, 6.88 ± 0.64, 7.05 ± 0.48 and 6.40 ± 0.77, respectively, remaining close to neutral and higher than simulated rainfall (pH = 5) throughout the whole experiment (Fig. 5a). A large number of Ca^{2+} released from those samples during the experiment (Fig. 5f), which

indicated the hydrolysis reactions of broken primary minerals and carbonate dissolution in the moderately weathered stone coals and gangues. This process might effectively buffer the pH near-neutral values, thereby reducing the rate of releasing and mobility of toxic elements.

Unlike stone coals and gangues, the pH for coal (R5) leachate was 2.80 ± 0.26, which is much lower than simulated rainfall and other leachates. The average concentration of Fe, SO_4^{2-} and F^- in this leachate were up to 66.34, 926 and 11.43 mg/l, respectively, but Ca^{2+} (139 mg/l) was lower than other leachates. Two reasons might explain the acidic pH in leachate of R5. First, the oxidation of pyrite and other sulfates in R5 released high levels of SO_4^{2-} and F^-, which resulted in high acidity of leachate. Second, low Ca^{2+} concentration in leachate indicated that a small quantity of carbonate dissolved during the leaching process, accounting for the low pH value in leachate. Furthermore, chalcophile elements were easily emitted from the weak acid extracting solution, and toxic elements (Cd, Cr, Tl and As) were in high concentrations in
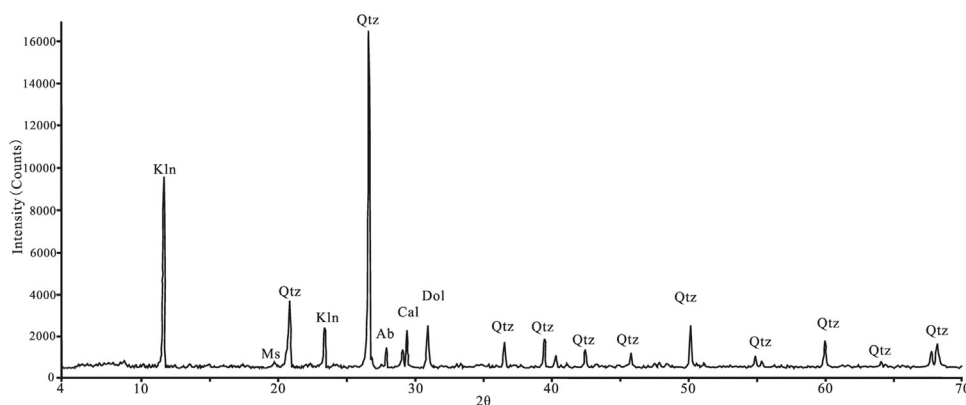
Fig. 6. Powder X-ray diffraction pattern of typical stone coal sample (R1) in the study area. Qtz, quartz; Kln, kaolinite; Dol, dolomite; Cal, calcite; Ms, muscovite; Ab, albite.

coal (R5) leachate. The weathering and leaching processes of the coals in the study area might produce acid mine drainage.

Fluorine in leachates of stone coals and gangues changed slightly throughout this experiment, but increased at first and then declined in coal leachates (Fig. 5e). Previous researches have shown that F mainly occurs in silicate minerals and clays, and that kaolinite is the prime carrier of F (Wang et al., 2011; Dehbandi et al., 2017). The X-ray diffraction result indicated that the typical stone coal sample (R1) was dominated by quartz, followed by kaolinite, and a minor amount of calcite, dolomite, muscovite and albite (Fig. 6). However, compared with gangue and stone coal, coal lacked silicate minerals, and thus F in coal leachate declined throughout the entire experiment.

Conductivity (EC) concentration in leachates decayed as the leaching progressed. Moreover, EC declined rapidly over the first four cycles and then decreased at a lower rate, this trend was similar to the patterns of Cd, Cr, As and Tl in leachates. The concentration of SO_4^{2-} in leachates decreased quickly in the first two cycles, and then flattened-out as the process reached a steady state. However, for R3 and R5, SO_4^{2-} in leachates still maintained a declining trend after the 6th cycle (Fig. 5d). The EC values in leachate represented readily extractable salts in parent rocks (Visconti and de Paza, 2012). In addition, the selected samples were slightly weathered in nature prior to the experiment, the initial responses of EC, SO_4^{2-}, Cd, Cr, As and Tl reflected a flush of readily soluble extractions from sample surfaces under the leaching condition of simulated acid rain. High EC (1.24–2.05 mS/cm) always coupled with high SO_4^{2-} (925–1753 mg/l) and Ca^{2+} (139–611 mg/l) in leachates (Table 3). According to the Pearson's correlation coefficient, EC values of leachates were positively correlated with SO_4^{2-} (r = 0.95, p < 0.01) and Ca^{2+} (r = 0.79, p < 0.01). This relation implied that SO_4^{2-} and Ca^{2+} were being generated as a result of kinetic weathering and leaching. A similar correlation was observed in acid-mine drainage from sulfides (Gray, 1996) and Illinois coal rejects (Huggins et al., 2012).

A large number of toxic elements, especially Cd, Cr, Mo and As, were observed to release into the leachates throughout the simulated leaching process (Table 3, Fig. 5). Toxic elements were easily released when flushed by simulated acid rain after long-term exposure in dry and humidified air. Pearson's correlation analysis indicated that Cd, Cr, As and Tl in leachates were positively correlated with Fe (r = 0.713, p < 0.01) and negatively correlated with pH (r = − 0.576, p < 0.01). Low pH value, indicating a high acidity environment, accelerated the dissolution of elements in coal during the leaching process (Komonweeraket et al., 2015). In this study, toxic elements might be segregated from pyrite in coals and coal wastes, and resulted in higher concentrations of toxic elements in leachates. Mo, having a positive correlation with Sb (r = 0.813, p < 0.01), was observed to heavily release from the selected samples and to change slightly during all of the leaching cycles, implying that Sb and Mo might have the same genesis and source in the study area. In general, weathering and leaching processes of these coals and coal wastes may help to increase

the concentrations of toxic elements in the aquatic system.

3.4. Potential health risks of toxic elements in the study area

The study area features a high geological Cd background, and Cd was enriched in local black shales (4.5–187 mg/kg), coals (11.5–53.4 mg/kg), arable soils (1.01–59.7 mg/kg), and other environmental samples (Tang et al., 2009; Liu et al., 2013, 2015). Toxic elements, especially volatile trace elements, can easily escape into the atmosphere during coal combustion. Coal mining activities in the study area produced a large amount of waste and gangues, from which the leaching processes could release Cd and other toxic elements into the environment. Consequently, they would pollute the air, deteriorate water quality, damage soil properties and contaminate agriculture products (Chen et al., 2014; Saikia et al., 2016). Finally, toxic elements might accumulate in the human body through the food chain and other pathways, which might lead to major health problems for the local public.

Concentrations of Cd and F in the urine of local residents in the Three Gorges Region revealed a reduced impact of F, but an increasing health threat of Cd (Tang et al., 2009). Daily Cd intake for populations in the study area was much higher than other places in the world, with local vegetables constituting the main source of Cd intake for residents (Liu et al., 2015). Obviously, the concentration of toxic elements in soils impacts on plants. In addition, coal balls in the study area are made by local clays, toxic elements in clay might be emitted through coal ball combustion. For these reasons, it is meaningful to evaluate the contamination of soils and clays in the study area.

To better determine the pollution degree of toxic elements in soils and clays in the Three Gorges Region, descriptive data analysis (range, average and pollution degree) of three kinds of indexes is performed in Table 4. The geo-accumulation index (I_{geo}) was normalized by the background values of Chinese loess (Yan et al., 1997). The contamination assessment of selected toxic elements in soils and clays were calculated using a single factor index (P_i) with the limiting values of environmental quality standards for soils in China. The integrative pollution degree of toxic elements in Wushan and Fengjie were evaluated by the method of the Nemerow index (P_N).

The Nemerow index indicated that soils in Wushan County were heavily polluted (the average value of P_N was 21.0), while Wushan clays were slightly polluted (the average value of P_N was 1.1). I_{geo} and P_i values revealed that Cd in Wushan soils were heavily contaminated, Cr, Tl, Sb and As in soils were slightly polluted. Cd and other toxic elements in soils might transfer through roots and stems to vegetables, resulting in the accumulation of toxic elements in edible portions of plants, such as grains or fruits. Soil and clays in Fengjie County were slightly polluted (the average values of P_N were 1.1 and 0.8, respectively). Cd constituted the main pollution element in Fengjie soils, with I_{geo} values varying from 0.2 to 2.5, indicating an unpolluted-to-moderate degree of pollution. Tl was the major polluted element in Fengjie

Table 4
Pollution indexes of toxic elements in soils and clays in the study area.

Samples		Geo-accumulation index					Single factor index				Nemerow index
		Cd	Cr	As	Tl	Sb	Cd	Cr	As	Sb	
Soils in Wushan	Range	0.8–7.1	−0.9 to 2.0	−1.2 to 0.4	−0.3 to 1.6	−1.0 to 1.3	1.6–72.7	0.5–8.0	0.3–0.9	0.2–0.6	1.8–73.4
	Average	3.4	0.3	−0.2	0.4	0.1	20.7	1.5	0.6	0.3	21.0
	Pollution	Strong	No- Moderate	No	No- Moderate	No- Moderate	Yes	Yes	No	No	Strong
Clays in Wushan	Range	−0.4 to 0.4	−0.1 to 0.2	0.3 to 0.8	0.1–0.4	−0.3 to 0.4	0.4–0.6	0.6–0.7	0.7–1.0	0.1–0.2	1.0–1.2
	Average	0.0	0.0	0.5	0.2	0.0	0.5	0.6	0.8	0.2	1.1
	Pollution	No	No	No- Moderate	No- Moderate	No	No	No	No	No	Slight
Soils in Fengjie	Range	0.2–2.5	−1.1 to 0.0	−1.2 to (−0.74)	−0.8 to (−0.2)	−1.0 to (−0.3)	0.5–2.8	0.3–0.6	0.2–0.7	0.1–0.2	0.6–2.9
	Average	0.8	−0.6	−1.0	−0.5	−0.6	1.0	0.4	0.4	0.1	1.1
	Pollution	No- Moderate	No	No	No	No	No	No	No	No	Slight
Clays in Fengjie	Range	−0.2 to 0.3	−0.5 to (−0.1)	−0.40 to 0	−0.4 to 0.3	−0.7 to (−0.4)	0.2–0.6	0.4–0.6	0.4–1.0	0.1–0.2	0.7–0.8
	Average	−0.2	−0.3	−0.2	0.0	−0.5	0.4	0.5	0.6	0.1	0.8
	Pollution	No	No	No	No- Moderate	No	No	No	No	No	Slight

clays (Table 4).

4. Conclusions

This study elucidated the distribution, occurrence, mobility, and potential health risks of toxic elements in coals and coal wastes in the fluorosis area of the Three Gorges Region in SW China. Compared with Chinese coals, Cd and Mo were enriched in local coals in the study area. Particularly, coal samples from Wushan County were characterized by higher toxic element concentration. The dominant occurrence of toxic elements in coals and coal waste were: carbonate and monosulfide fraction for Cd, carbonate and silicate fraction for Mo and As, silicate and insoluble fraction for Cr, and organic matter and sulfide fraction for Tl.

A large number of toxic elements, such as Cd, Mo and Cr, were easily released to the leachates during weathering and leaching process. The contamination assessment of toxic elements indicated that soils and clays in Wushan County were polluted by Cd, while soils and clays in Fengjie County were slightly polluted. In conclusion, toxic elements in the study area could be easily released from coal and coal waste weathering, and further polluted the soil and crops, posing a potentially dire risk to public health.

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