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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 $_i$n 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.,

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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