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Geochemical valuation and intake of F, As, and Se in coal wastes contaminated areas and their potential impacts on local inhabitants, Shaanxi China

Rahib Hussain · Kunli Luo

Abstract This study probe the human health risk of fluoride (F), arsenic (As), and selenium (Se) and their daily intake available quantity to human through different sources in different regions of Shaanxi, China. For this purpose, a number of samples, including coal and coal wastes, rocks, soil, and vegetables were collected from south Qinling Mountain stone-like coal (Geo type-I), Binxian-Jurassic (Geo type-II), Hancheng Permo-Carboniferous (Geo type-III), and countryside (Huanglong County) of Shaanxi province. All these samples were analyzed through atomic fluorescence spectroscopy and combustion hydrolysis methods. Results showed that Geo type-I was enriched with As, Se, and F, Geo type-II, III, and the countryside were slightly enriched with As and F and deficient in Se. The average daily intake (ADI) of Se in Geo type-I was 0.005–0.0045, Geo type-II 0.0005–0.0004, Geo type-III 0.0006–0.0005, and countryside 0.0002–0.001 in mg kg^{-1} day^{-1} adult–children, respectively, which was lower than the optimum level (0.06–0.075 mg kg^{-1}day^{-1}). ADI of As at Geo type-I was 0.0085–0.0075, Geo type-II 0.004–0.0037, Geo type-III 0.0008, and countryside 0.00022–0.00019 in mg kg^{-1} day^{-1} adult–children, respectively, which was above the acceptable range (10^{-6}–10^{-4}). ADI of F at Geo type-I was 0.0047–0.0041, Geo type-II 0.0098–0.0087, Geo type-III 0.002–0.0017 and countryside 0.0015–0.0013 in mg kg^{-1} day^{-1} adult–children, respectively. The toxicity level of Se and F at all the regions was lower than the NOAEL and LOAEL, while As was higher at Geo type-II and I. The extreme deficient of Se than the optimum range along with high F could deregulate the normal body growth especially causes bones and joint problems. However, the study found a rare patient with bone and joint disease (maybe Kashin–Beck disease) in the countryside. To find the exact cause of Kashin–Beck disease, the study needs further medical investigation in Se-deficient regions and their association with selenium deficiency and enriched fluoride.

R. Hussain · K. Luo (✉)
Institute of Geographic Sciences and Natural Resource Research, Beijing 100101, China
e-mail: luokl@igsnrr.ac.cn

R. Hussain
University of Chinese Academy of Sciences, Beijing 10080, China

Introduction

Coal is the major source of energy in China counted about 75% of total energy production and consumption (WEC 2013). However, the overuse of coal and dumping their wastes in surrounding environment may cause serious environmental and health problems. Among them, the major causes of environmental and health problems are toxic elements and gases production, coal dust generation, deteriorating water and air quality, affecting crops growths, land degradation, etc (Zhang and Da 2015). However, most of the elements are attributed to performing dual function both harmful and beneficial to humans (in optimum range) (Tang et al. 2009; Wu et al. 2008; You and Xu 2010).

Globally, the key source of exposure to F, As, Cd and Se is contaminated drinking water, food crops, pesticides as well as mining wastes. The largest contributor of F in the USA and China is drinking water, coal and food crops. In 1992, 1.4 million peoples of the USA were exposed to F contaminated water with a concentration of 2.0–3.9 mg L^{-1}, more than 2 million exposed to $\sim$ 4.0 mg L^{-1}, while in 2000, 162 million peoples were exposed to F contaminated water with a concentration of 0.7–1.2 mg L^{-1} (National Research Council 2006). Fluoride causes physiologic and pathologic disorders which led to endemic fluorosis, which had been considered a serious health problem in China, Japan, India, Africa and Mexico (Yang et al. 2003; Lu et al. 2000; Xiang et al. 2003). More than 73% coal burning fluorosis was observed in western Guizhou, eastern Yunnan, and southern part of Chongqing, Sichuan, and Shaanxi provinces (Daba region of Ziyang, Langao and Ankang counties) (Luo et al. 2011; Sun 2004).

Arsenic is a noxious and carcinogenic element mostly associated with coals and mineralized rocks, which is perilous to a living organism. The extremely high level of As was mostly observed in coal and water in different regions of China (Luo et al. 2004b). However, As in Yunnan lignite coal was 8.0–33.5 mg kg^{-1} (Han et al. 1996) and in anthracite coal of Laochang, China, was 6.2 mg kg^{-1} (Zhao et al. 1998). Luo (2005) reported that As content was found less than 10 mg kg^{-1} in Permo-Carboniferous strata of north China coal, which was similar to the previous average of As contents in the coal of China (3.8 mg kg^{-1}) (Ren et al. 2006) as well as global coal (7.9 mg kg^{-1}) (Palmer and Lyons 1996). Exposure to

As will surely cause skin lesion, peripheral vascular disease, polyneuropathy, hypertension and black foot disease of mental health, and DNA mutation (Zhang et al. 2000; Li et al. 2012b). Among the endemic arsenism, black skin lesion problems, therapeutic effects, malignant lymphoma, gallbladder carcinoma, ovarian carcinoma, and cervical cancer were mostly observed in the Inner Mongolia and some other parts of China (Yu et al. 2007; Ai et al. 2007).

Selenium performed a dual function because of the prescribed border between enriched and deficient is an optimum range. The optimum range is rather narrow but mostly observed sustainable in non-affected areas (Tan et al. 2002). Diet is the key source of Se for humans and other animals in the optimum range. However, both lowest and highest concentration caused Keshan and Kashin–Beck disease, bones, and joint problems as well as selenosis, etc (Wang and Gao 2001). Keshan and Kashin–Beck disease is an endemic cardiomyopathy disease that mainly affects younger children of age 2–12 years. However, it will also affect woman's of childbearing age (Hartikainen 2005). Keshan disease was mostly observed in the areas where the Se concentration was below 0.04 mg kg^{-1} in food crops (Li et al. 2012b), 3.08 mg kg^{-1} in soil with the high marginal level of 0.123–0.175 mg kg^{-1} (Tan et al. 2002). The excessive intake of Se caused selenosis, brittle hair and nails, red skin, paresthesia, and hemiplegia, which is mostly observed in many parts of south China (Cai et al. 2016a). However, in south Shaanxi and Hubei province, the endemic selenosis was reported at a rate of 50% morbidity in human, while it was also reported in chickens and Pigs (Dai et al. 2012; Baoshan et al. 2010).

Luo et al. (2002) reported that in north and south China the coal excavation and processing were 84 and 7%, respectively. Therefore, it is hypothesized that their environmental and health impacts will be higher in northern China as compared to the south, but also depends on the magnitude of toxic elements. Literature reviews revealed that there is a lack of comprehensive research to probe the magnitude of contamination, especially F, As, and Se and its associated health risk. The study aimed to probe the concentration of F, As, and Se in the soil, rock, coal and coal wastes, and daily intake foods. Therefore, the present study discusses the geographic distribution and correlation of the selected elements in coal and

coal wastes, soil, food, and plants and their available intake quantity and potential risk to the inhabitants of Shaanxi, China. It would be of great importance to assess the association between these selected elements, based coal, environment, and human health problems.

Methodology

Regional geology

The study was conducted in four different regions of Shaanxi province, according to different geological setup, enrichment, and abundance of elements in coal, rocks, and food crops. The area was divided into geological area 1 (Geo type-I), geological area II (Geo type-II), geological area III (Geo type-III), and countryside according to their geological features. The geological setup of the above-mentioned areas was explained here comprehensively.

Geo type-I

Geo type-I (south Qinling Mountain stone-like coal areas) is situated in between the latitude of 32°26′12.9″–32°28′7″N, and longitude of 108°56′25.5″–108°58′49″E extends 44 km from the Langao County, Ankang, south Shaanxi. Langao County of the south Qinling Mountains is important to study the Wenlock serious of Cambrian age (Rong et al. 2005; Fu et al. 2004). The study areas are near to Pinlgli County, where tectonics mostly belongs to Silurian, Proterozoic, while some of the areas belong to Permian and Triassic (Wang et al. 2017). According to Zhang et al. (1987), the geological characteristics of black shale rocks and coal are the Early Paleozoic, which is distantly spread in south China. The coal seams and black shale of the areas are widespread in Donghe Formation of the Lower Cambrian age (which are enriched with trace elements) (Zhang et al. 1987). However, the trace elements enriched coal seams and carbonaceous rocks could be caused by sulfide ores (Pyrite, Chalcopyrite, and Molybdenite) that absorbed the organic matters (Hanjie and Yuzhuo 1999; Zhenmin et al. 1997) as well as Se minerals (Selenium, Chalcomenite, Berzelianite, and Drysdallite (Zhu et al. 2000). In Daba areas of the south Qinling Mountain, coal and

contact rocks are also enriched with As (Luo 2005; Tang et al. 2002).

Geo type-II

Binxian (Huanglong coalfield) tectonics is located in the north of Ordos basin of northern Shaanxi Weibei uplift. The centralized tectonics from top to bottom are Quaternary, Neogene, Cretaceous, Central Chihuahua Formation, Luohe Formation, Yijun Formation, Jurassic Zhiluo Formation, Yan'an Formation, and Fuping Formation (Li et al. 2014; Ren et al. 2014). The upper segment mainly comprised of reddish-brown mauve mudstone, and sandy mudstone with partial sandstones. The entire basin has entered into tectonic evolution stage of sedimentary basin inland depression since the Late Paleozoic. However, at end of Triassic, the Indosinian movement uplift the whole basin. The top of Yanchang Formation in the Upper Triassic subjected to intensive weathering and river erosion. Gullies of the Yanchang Formation both vertical and horizontal undulating to paleo-geomorphology, where the ancient landscape is characterized by vast water system and gullies. Some studies reported that the Early Jurassic sedimentary system was mainly affected by ancient topography before the sedimentary movement (Wang et al. 2015; Zhao et al. 2001; Guo et al. 2001; Feng et al. 2017).

Geo type-III

Hancheng (Weibei coalfield) is located at the east edge of the Ordos basin in the eastern Shaanxi, which comprise a number of coalmines. In the northwest, it is connected to Weihe graben system. In NNE (Northnortheast), it is connected to Lyliang fold belt and Fenhe river graben system, while in the west it is connected to thrust-fold belt located at the west edge of Ordos basin (Xue et al. 2012). The study areas are located between the longitude 110°26′29″–110°31′29″E and latitude 35°35′–35°38′30″N, with an altitude of 650 m from the sea level (Fig. 1). The important topographies of the areas are; middle and high-grade coals belongs to Late Carboniferous and Early Permian. Tectonically, Weibei coalfield is located on Tongchuan belt at the southeast corner of the Ordos basin, which leaning toward northeast and southwest with an angle of 5°–15° (Wang 2010; Yao et al. 2009). The tectonic setting of the local areas
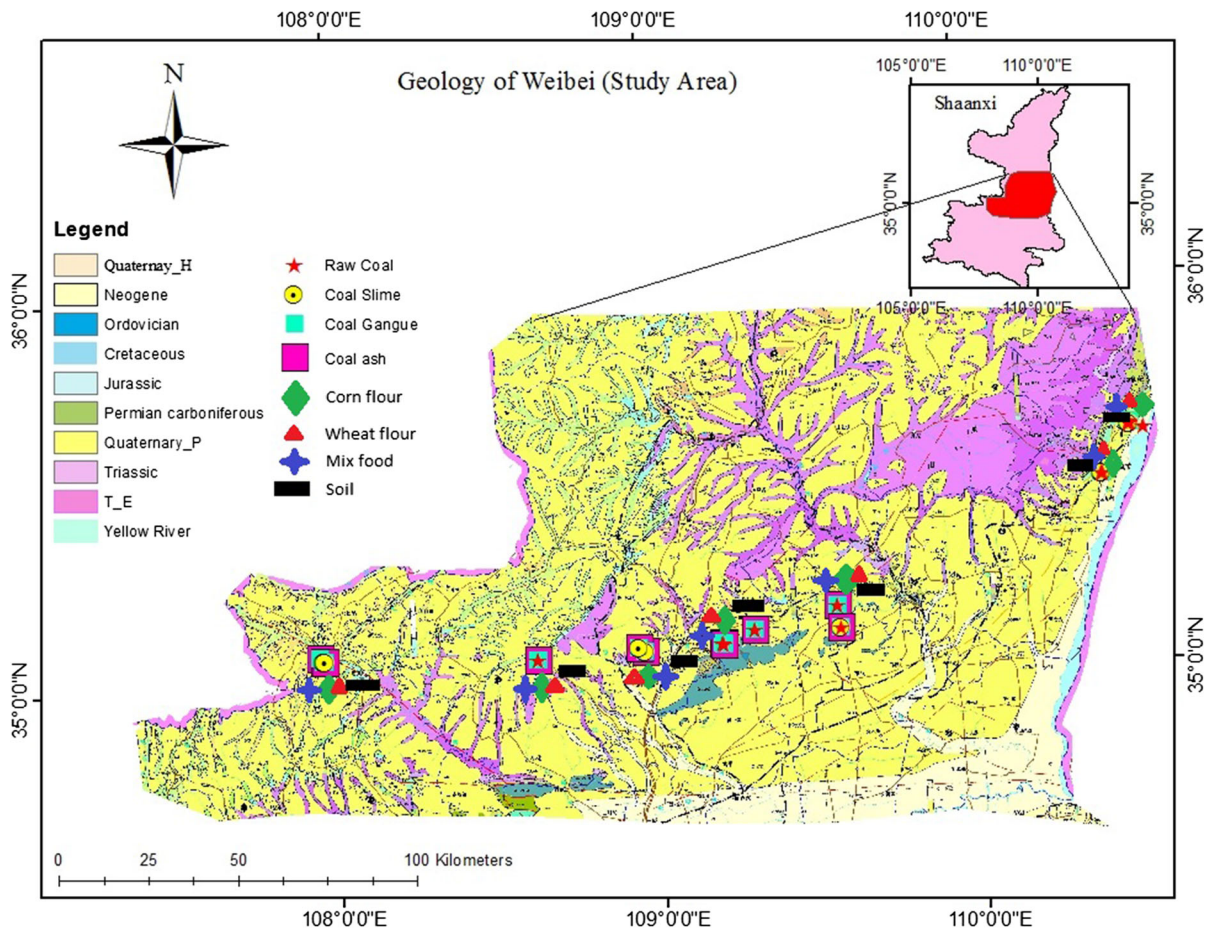
Fig. 1 Geological setting and samples sites location map of the study areas

divided into west and east zones. The West zone mostly extended to Pubai, Tongchuan, and some parts of the Chenghe district, while the east zone is expanded to Hancheng and some part of Chenghe district. The east zone has mostly normal thrust and fault with fewer folds. Relative to east zone, the west zone has numerous anticlines, synclines, and thrust faults (Wang 1996; Yao et al. 2009).

Countryside

Countryside area (Huanglong County) was selected because this is an endemic Kashin–Beck disease area, where the selenium concentration is very low in food, soil and rocks. The prevalence of Kashin–Beck disease is very high in the surrounding region. The study area was also selected to compare with other areas toxic element (As, F, and Se) existence. The study area is located between the longitude

$110°11'25''$–$110°40'56''$E and latitude $35°26'57$–$35°49'51''$N (Fig. 1). The study areas are located in the southern Ordos basin, whereas the surrounding rock and contacted areas of the Huanglong belong to middle Jurassic of Yan'an Formation (Wang et al. 2016).

Field visit and sampling

A field survey was carried out at coalfield-explored areas, i.e., Weibei coalfield (Hancheng coalmines), Huanglong coalfield (Binxian Jurassic coalmine), Langao Cambrian coalfield (Zhihe coalmines), and other connected areas, where there is a pretty coal uses. During field survey, a representative coal and coal wastes, affected and unaffected soil and foods crops samples were collected under the qualified geoscientists. A random sampling technique was applied according to the distribution of raw coal, coal gangue,

coal slime, and coal ash. It was also applied to collect affected and unaffected (uncontaminated areas) soils and food crops samples. Almost, 289 representative samples were collected from Hancheng County (coal and coal waste 36 samples, soil 19, plants and food 25) (Hussain et al. 2018), Binxian County (coal and coal waste 37, coal ash 39, soil 31, plants and food 118), Langao County (coal 09, rocks 06, coal ash 10, soil 20, plants and food 22), and countryside (foods 17 samples) using standard geological methods and materials (Table S1, S2, and S3).

Experimental procedures

All the air-dried samples were ground and passed through a sieve of 200-mesh size, while the plant samples were dried at 60 °C in the oven and mashed through a grinder of 80-mesh size. For Se and As determination, 0.05 g soil, coal and coal wastes samples (coal slime, coal ash, and coal gangue) were treated with 5:1 solution of HNO_3 and $HClO_4$, while for the plant digestion, 0.5 g samples were treated with 9:1 HNO_3 and $HClO_4$ (Ni and Luo 2015; Ni et al. 2016). After completing initial digestion, the solution was further processed through 3 mL (milliliter) of HCl (1:1 diluted), and then 1 mL of pure HCl in a sequence. This final solution is ready for Se and run through Hydride Generation Atomic Fluorescence Spectrometry (HG-AFS 9780 BJHG). For As determination, the above solutions were passed through thiourea-ascorbic acid reagent (2.5:2.5 g per 100 mL Water) and 1 mL HCl, and the final solutions were run through HG-AFS. The compatible detection limit (DL) of AFS is 0.01 μg L^{-1} (Luo et al. 2004a).

For the quality control and assurance, duplicate samples, blank reagents, and geological grade reference standard of GBW-07401, 07403, 07406 (followed by National Research Centre for Standard in China) were used in each samples batch to verify the accuracy and precision of the digestion methods and subsequent analysis (Wang et al. 2016), while the precision and accuracy of the instrument were found within confidence limit of > 98%.

Risk-based models

The aims of the risk-based models were to prediction chronic and acute toxicity as well as to predict no-effect and low-effect of various elements. It will rapidly evaluate the possible sources of elements in a specific human setting, where there is a concern for potential or actual human exposure to contamination. The models will also explore the cumulative or aggregate elemental exposures to population and dietary routes of environmental chemicals (Sørensen et al. 2012).

Geo-accumulation index (GAI) is a geo-statistical technique used to quantify the degree of contamination and their associated risk, which is determined by Eq. 1

$$GAI = \log_2\left(\frac{cn}{Bn \times 1.5}\right) \tag{1}$$

where Cn and Bn are the elemental concentration (mg kg^{-1}) of the current study and reference value (using Chinese standard values), respectively (Table S4), while 1.5 is the possible anthropogenic contamination existence in the reference areas. By comparing the results with risk grading, GAI are categorized into six grades; G-0 ($0 < GAI \leq 1$) reveals unpolluted, G-1 ($1 < GAI \leq 2$) slightly polluted, G-2 ($2 < GAI \leq 3$) moderate polluted, G-3 ($3 < GAI \leq 4$) moderate sever polluted, G-4 ($4 < GAI \leq 5$) sever polluted, G-5 ($GAI > 5$) revealed extreme high polluted (Hussain et al. 2015, 2018).

The health risk-based model along with NOAEL (No Observed Adverse Effect Level) and LOAEL (Lowest Observed Adverse Effect Level) was raised by US-EPA (IRIS 1991, 1987, 1995), which is the fundamental units for health risk assessment. Among these models, three major models were applied in the study as suggested by Liu et al. (2013a) and USEPA (2011) (Table S4). The average daily intake of food, coal dust, and soil is determined through Eqs. 2–4, respectively, while total health quotient (THQ) and total hazard index (HI) are determined through Eqs. 5, 6, respectively.

$$ADI = \frac{C \times IRf \times Ef \times ED}{BW \times At} \tag{2}$$

$$ADI = \frac{C \times InR \times Ef \times ED}{PEF \times At} \tag{3}$$

$$ADI = \frac{C \times IRs \times Ef \times ED}{BW \times At} \times 10^{-6} \tag{4}$$

$$THQ = \frac{ADI}{Rfd} \qquad (5)$$

$$HI = \sum_{i=1}^{n} ADI_i \qquad (6)$$

where ADI is average daily intakes (mg kg^{-1} day^{-1}), C is a concentration of elements in food, soil, and coal (mg kg^{-1}), EF—exposure frequency: 350 days years^{-1}; ED—exposure duration: 26 and 6 years (adult and children, respectively) (USEPA 2011). BW—body weight: 57.7 and 15 kg adult and children, respectively (Walpole et al. 2012); AT—average time for non-carcinogens (26 × 365 days) and carcinogen(365 × 70 days) (USEPA 2011). IRf—ingestion rate of food; IRs—ingestion rate of soil: 100 and 200 mg day^{-1} adult and children, respectively; InR—inhalation of coal dust 20 m^3 day^{-1}, CF—units conversion factor: 10^{-6}, Rfd—reference dose of specific elements in mg kg^{-1} day^{-1} (Table S4) (USEPA 2011; Liu et al. 2013a).

Results and discussions

Geo type-I

In south Shaanxi, the elemental contents of Se, As, and F (range) in different specific categories are presented in Table 1, while their respective results for each sample were given in supplementary file (Table S1). The corresponding concentration range of Se in stone-like coal (SLC) were 1.48–24.2 with an average of 12.0 mg kg^{-1}, which was considerably higher than all specific categories (i.e., vegetable both control and affected, coal ash, affected, and unaffected soil) except the black shale rock (surround the SLC's). In the current study, the Se concentration was higher than igneous hosted SLC (9.9-mg kg^{-1}), while lower than the carbonated hosted SLC (29.2-mg kg^{-1}) (Luo 2011). However, the Geo type-I Se was also much higher than the other studies (He et al. 2002; Ren et al. 2006; Finkelman 1993; Tang and Huang 2004; Dai et al. 2008). The range of Se in the surround black shale rocks was 1.3–42.5 (average 14.24) mg kg^{-1} (Table 1), which was higher than earth crust abundance (ECA) (0.05-mg kg^{-1}), US coal (2.8-mg kg^{-1}), Chinese coal 2.8 mg kg^{-1} as well as World coal (8.7-mg kg^{-1}) (Ketris and Yudovich 2009) (Table 2). The

concentration of Se in SLC ash was 0.85, 13.5, and 5.3 mg kg^{-1}, minimum, maximum, and average, respectively, which was comparably higher than Zhou et al. (2014) (4.3-mg kg^{-1}). The high amount of coal uses in China has focused attention on the released of toxic trace elements (TTE) especially Se, As, and F from coal extraction, and combustion. Selenium in the Geo type-I affected soil was 0.8–7.7 with an average of 2.8 mg kg^{-1}, while their range in control soil was 1.4–3.1 with an average of 2.46 mg kg^{-1} (Table 1), which was higher than the Zhou et al. (2014) (0.31-mg kg^{-1}) and lower than the Luo et al. (2004a) (26-mg kg^{-1}) and Du et al. (2018) (4.7-mg kg^{-1}). The observed range and average in both control and affected soil proved that the Se contamination in surround regions of Geo type-I is the geogenic origin, where the surrounding rocks and coal both have a major role in the distribution of contamination. Similarly, the Se range in the affected area's vegetable was 0.5–5.6 with an average of 2.6 mg kg^{-1}, while the Se range in control areas vegetable was 0.2–9.1 with an average of 3.5 mg kg^{-1}, (Table 1), which was extremely higher than Chinese food permissible level of < 0.3 mg kg^{-1} (GB 2011) and Zhou study 0.24 mg kg^{-1} (Zhou et al. 2014). The concentration of Se in surrounding region (Geo type-I) was high not only because of coal but the contact rocks have a similar role as a coal. The study proved that the higher concentration of trace elements in surrounding areas is due to the entire formation of both rock and coal as also reported by Dai et al. (2012).

The concentration of As in SLC was 3.3–124.9 mg kg^{-1} (average 42.6-mg kg^{-1}), which was higher than Luo (2005) (32-mg kg^{-1}). The As in rocks was 5.3–193.9 (average 53.3) in mg kg^{-1}, which was 10-fold lower than Ziyang County (SLC contact rocks) black shale rocks (534-mg kg^{-1}) (Luo 2005). Arsenic in coal ash was 4.7–107.9 (average 32.4) in mg kg^{-1} (Table 1), which was exactly equivalent to Zhou et al. (2014) study (32.4-mg kg^{-1}). The overall average (mg kg^{-1}) of As in SLC, contact rocks, and coal ash was higher than the Chinese coal (3.8), US coal (24) and ECA (1.8) (Table 2). Luo (2005) reported that in south Shaanxi igneous hosted SLC has > 32 mg kg^{-1} arsenic, which has a major role in the health problems. The concentration of As in affected soil was 7.7–68.0 mg kg^{-1} (average 35.3-mg kg^{-1}), while the concentration in control soils was 17.4–67.3 with an average of 41.5 mg kg^{-1}. The As in

Table 1 Basic statistical concentration (mg kg^{-1}) of the selected elements in a specific geological areas and samples

Areas	Specific	Se			As			F		
		Min	Max	Average	Min	Max	Average	Min	Max	Average
Geo type-I	Vegetables (affected areas)	0.5	5.686	2.66	0.622	3.608	1.388	0.01	8.111	3.092
	Vegetables (control areas)	0.256	9.191	3.498	0.254	44.456	8.741	0.332	6.437	2.638
	Stone-like coal (SLC)	1.481	24.203	12.041	3.309	124.91	42.66	321.5	885.4	680.48
	Rocks (SLC contact rocks)	1.269	42.455	14.24	5.358	193.91	53.35	283.05	931.9	618.3
	Coal ash	0.851	13.49	5.318	4.721	107.98	32.43			
	Affected soil	0.805	7.724	2.818	7.667	68.032	35.35			
	Control soil	1.415	3.111	2.467	17.48	67.369	41.52			
Geo type-II	Wheat	0.057	0.160	0.114	0.247	1.630	0.895	0.337	4.155	2.524
	Corn	0.027	0.041	0.035	0.242	0.385	0.308	0.496	1.003	0.714
	Mix food	0.057	0.167	0.105	0.467	1.124	0.779	0.456	2.123	1.302
	Local plants	0.091	0.126	0.106	0.489	1.360	0.874	2.816	3.906	3.257
	Raw coal	0.375	8.087	2.416	2.828	87.69	21.25	33.49	385.94	156.35
	Coal gangue	0.000	17.071	2.108	0.001	60.64	19.35	147.2	784.8	412.2
	Coal slime	0.450	3.521	1.351	10.940	19.62	15.29	312.6	457.7	385.8
	Coal ash	0.141	10.613	1.193	4.923	69.51	23.81			
	Soil	0.000	1.809	0.494	0.002	41.46	16.12			
Geo type-III	Wheat	0.032	0.158	0.101	0.041	0.148	0.085	0.075	0.447	0.267
	Corn	0.036	0.192	0.091	0.044	0.063	0.051	0.201	0.442	0.294
	Mix food	0.030	0.170	0.087	0.140	0.589	0.301	0.171	0.716	0.379
	Local plants	0.189	5.617	1.418	0.375	2.179	1.099	0.052	5.095	2.649
	Raw coal	4.781	26.400	10.927	0.284	21.33	10.10	102.8	485.2	273.5
	Coal gangue	0.574	10.656	3.539	3.403	27.47	10.31	237.6	595.7	363.9
	Coal slime	3.159	8.710	5.803	6.112	19.73	12.90	253.7	536.8	377.7
	Coal ash	0.753	15.943	9.558	3.244	26.26	14.60	88.8	453.2	228.6
	Soil	0.000	4.454	0.805	2.051	16.86	10.65			
Country side	Corn flour	0.013	0.031	0.022	0.055	0.086	0.064	0.022	0.625	0.312
	Wheat flour	0.027	0.059	0.041	0.091	0.328	0.184	0.048	0.763	0.293
	Mix food	0.018	0.582	0.237	0.065	0.143	0.106	0.051	0.358	0.227

Min minimum, *Max* maximum, *STDV* standard deviation

both the areas was higher than the Chinese soil permissible level of 11.2 mg kg^{-1} (SEPAC 1995), Japan soil standard (15-mg kg^{-1}) (EQSS 1991) and also higher than the Canadian soil standard (11-mg kg^{-1}) (Ministry of Environment 2011). The control soil has high concentration as compared to affected soil, which showed that elemental contents were not only released by coal, but it is a hidden treasure of Cambrian and other Paleozoic black shales in the Daba Mountains. Similarly, in both the areas (affected and unaffected), the As was higher than the

standard permissible level of China (0.5-mg kg^{-1}) (GB 2012) (Table 2).

Fluoride concentration in SLC was 321.5–885.5 with an average of 680.4 mg kg^{-1}, which was 8.7-fold higher than western China coal (Luo et al. 2011, 2004b). It was also higher than Zhaotong coal (40–124.5 mg kg^{-1}) (Liu et al. 2013b), and Bai study (157-mg kg^{-1}) (Bai et al. 2007), while lower than Daba mountain SLC (1689-mg kg^{-1}) (Luo 2011) (Table 2). However, the F content in SLC contacted rocks was 283–931.5 with an average of 618.3 mg kg^{-1}, which was lower than the Daba

Table 2 Provided internationally published selected elements concentration (mg kg^{-1}) for comparison and correlation

Standards and Ex-studies	Specific	Se	As	F
Finkelman (1993)	USA coal	2.8	24	98
Ren et al. (2006)	Chinese coal	2.78	3.8	131.3
SEPAC (1995)	China soil standard	0.29	11.2	478
JeffersonLab (2007)	Earth crust abundance	0.05	1.8	
Ministry of Environment (2011)	Canadian soil standard	1.2	11	0.05
EQSS (1991)	Japan soil standard	0.01	15	
GB (2012)	GB2762-2012 (veg.)		0.5	
Luo (2011)	South Shaanxi SLC (igneous hosted)	9.9	77.9	1689.8
Luo (2011)	SLC contact rocks	5.9	34.89	1089.1
Luo (2011)	SLC (Cambrian and Ordovician)	29.9	112.9	550.8
Bai et al. (2007)	Coal	2.28	4.09	157
Tang and Huang (2004)	Chinese coal	5	5	168
Dai et al. (2008)	China coal (Inner Mongolia)	2.47	3.79	130
Ketris and Yudovich (2009)	Coal	1.3	8.3	88
Ketris and Yudovich (2009)	Contact rocks	8.7	30	660
Zhou et al. (2014)	Coal gangue	3.42	27.3	
Zhou et al. (2014)	Coal ash	4.3	32.4	
Zhou et al. (2014)	Soil	0.31	20.9	
Zhou et al. (2014)	vegetable	0.24	0.5	
GB-2005	food		0.5	1.5

Mountain SLC (1089-mg kg^{-1}) (Luo 2011). Evidently, the F concentration was higher in surround rocks as compared to SLC. The results showed that the concentration of F in the surrounding region is not due to coal, but it is due to the entire formation of Cambrian shale. Similarly, the F contents in affected vegetable (locally grown in affected areas) were 0.01–8.1 with an average of 3.1 mg kg^{-1}, while the respective range in the control vegetables (control areas) was 0.3–6.4 with an average of 2.6 mg kg^{-1} (Table 1), which was higher than the southwestern China vegetables (coal affected vegetables) of 2.73 mg kg^{-1} and Chinese's standard for food (1.5-mg kg^{-1}) (GB/T2762-2005) (GB 2005).

Geo type-II

Selenium level in the Binxian Jurassic raw coal was 0.37–8.1 mg kg^{-1} (average 2.4-mg kg^{-1}). Selenium in the coal gangue was 0.0–17.1 mg kg^{-1} (average 2.1-mg kg^{-1}), which was higher than higher than the ECA (1.8-mg kg^{-1}) (JeffersonLab 2007), while desperately lower than the Zhou et al. (2014) (3.4-mg kg^{-1}) and World coal (8.3-mg kg^{-1}) (Ketris and Yudovich 2009) (Table 2). The average Se contents in

coal slime was 1.35 mg kg^{-1}, and in coal ash was 1.2 mg kg^{-1} (Table 1). The Se concentration (mg kg^{-1}) in Geo type-II raw coal and coal gangue was equivalent to the US coal (2.8-mg kg^{-1}) (Finkelman 1993), higher than the ECA (1.8-mg kg^{-1}) (JeffersonLab 2007), while lower than the World coal (8.3-mg kg^{-1}) (Ketris and Yudovich 2009). However, Se of the coal slime and coal ash was equivalent to ECA (1.8-mg kg^{-1}). In Binxian Jurassic, selenium in agriculture soil (0.5-mg kg^{-1}) was 1.7-fold higher than the Chinese soil reference standard (0.29-mg kg^{-1}) (SEPAC 1995). Most of the plants have potential to accumulate the elements up to maximum level. The average Se level in wheat flour was 0.11 mg kg^{-1} and corn grains was 0.035 mg kg^{-1}. Selenium in the mixed foods (Brassica *campestris*, Chinese's red pepper, rice, cabbage radish, garlic) was 0.057–0.17 with an average of 0.10 mg kg^{-1}, which was a bit lower than the Chinese food permissible level of < 0.3 mg kg^{-1} and Zhou study of 0.24 mg kg^{-1} (Zhou et al. 2014).

Arsenic concentration in Binxian Jurassic raw coal was 2.8–87.7 mg kg^{-1} (average 21.2-mg kg^{-1}), coal gangue 0.01–60.6 mg kg^{-1} (average 19.3-mg kg^{-1}). Arsenic of the Binxian Jurassic raw coal and coal

gangue was at least equivalent to the US coal (24-mg kg^{-1}) (Finkelman 1993) and extremely higher than the Chinese coal (3.8-mg kg^{-1}) (Ren et al. 2006), and Weibei coal (1.2-mg kg^{-1}) (Luo 2005) (Table 2). Arsenic concentration in Binxian Jurassic coal slime was 10.9–19.6 mg kg^{-1} (average 15.29-mg kg^{-1}), coal ash 4.9–69.5 (average 23.8-mg kg^{-1}) that was approximately equivalent to the Poland Fly ash (10.2–50.5 mg kg^{-1}) (Franus et al. 2015) and the US coal (24-mg kg^{-1}), while higher than the Ren et al. (2006) (3.8-mg kg^{-1}) and to the coal ash of Zhou et al. (2014) (4.3-mg kg^{-1}) (Table 2). Arsenic in Binxian Jurassic soil was 0.002–41.5 with an average of 16.1 mg kg^{-1}, which was slightly higher than the Chinese soil standard of 11.2 mg kg^{-1} (SEPAC 1995) and Huaibei coal mining contaminated soil (13.0-mg kg^{-1}) (Shi et al. 2013). Arsenic concentration in wheat flour was 0.25–1.6 mg kg^{-1} (average 0.89-mg kg^{-1}), while in corn grains was 0.24–0.38 mg kg^{-1} (average 0.31-mg kg^{-1}), which was higher than the maximum limit of Chinese standard for cereal products (0.5-mg kg^{-1}) (GB 2012), (Table 1). Arsenic in the mixed food (vegetables) was 0.47–1.1 mg kg^{-1} (average 0.78-mg kg^{-1}), locally grown plants 0.5–1.4 mg kg^{-1} (average 0.9-mg kg^{-1}) (Table 1), which was higher than Huaibei grains food (growing in mining contaminated soil) 0.034 mg kg^{-1} (Shi et al. 2013) and Zhaotong raw corn 0.007 mg kg^{-1} (Li et al. 2012a). The overall concentrations of As in food crops were higher than the Chinese maximum permissible level for foods (0.5-mg kg^{-1}) (grain and cereal crops) except corn grain, which was a bit lower than the Chinese standard (GB 2012).

Fluoride concentration in Binxian Jurassic raw coal was 33.5–385.9 mg kg^{-1} (average 156.4-mg kg^{-1}), coal gangue 147–784.8 (average 412-mg kg^{-1}), and coal slime 312.6–457.7 mg kg^{-1} (average 385.8-mg kg^{-1}) (Table 1). The observed concentration (mg kg^{-1}) was at least equivalent to ex-study of Weibei coalfield (150–500 mg kg^{-1}) (Luo et al. 2004b), while higher than the US coal (98-mg kg^{-1}) (Finkelman 1993), Chinese coal (131.3-mg kg^{-1}) (Ren et al. 2006), World coal (88-mg kg^{-1}) (Ketris and Yudovich 2009), and Inner Mongolia coal (130-mg kg^{-1}) (Dai et al. 2008). Similarly, the F concentration in Binxian County wheat flour was 0.3–4.1 mg kg^{-1} (average 2.5-mg kg^{-1}), corn grains 0.4–1.0 mg kg^{-1} (average 0.7-mg kg^{-1}), mixed food

0.46–2.1 mg kg^{-1} (average 1.3-mg kg^{-1}) and in locally grown plants was 2.8–3.9 mg kg^{-1} (average 3.3-mg kg^{-1}) (Table 1). Fluoride in wheat flour, corn flour, and mixed food was higher than the Chinese food standard of 1.5 mg kg^{-1} (GB 2005) and Zhaotong raw corn (1.50-mg kg^{-1}) (Li et al. 2012a).

Geo type-III

Selenium concentration in the Hancheng Permo-Carboniferous raw coal was 4.7–26.4 with an average of 10.9 mg kg^{-1}. Selenium in the coal gangue was 0.6–10.7 with an average of 3.5 mg kg^{-1}, which was equivalent to Zhou et al. (2014) (3.4-mg kg^{-1}), higher than the ECA (1.8-mg kg^{-1}) (JeffersonLab 2007), while lower than the World coal (8.3-mg kg^{-1}) (Ketris and Yudovich 2009) (Table 2). The Se contents in coal slime were 3.2–8.7 with an average of 5.8 mg kg^{-1}, while Se in the coal ash was 0.8–15.9 with an average of 9.5 mg kg^{-1} (Table 1). The overall Se concentration (mg kg^{-1}) in Geo type-III coal, coal gangue, coal ash, and coal slime was higher than the ECA (1.8-mg kg^{-1}) (JeffersonLab 2007), US coal (2.8 mg kg^{-1}) (Finkelman 1993), while equivalent to the World coal (8.3-mg kg^{-1}) (Ketris and Yudovich 2009). The Se concentration in nearby soil (0.8-mg kg^{-1}) associated with Permo-Carboniferous coal was 2.7-fold higher than Chinese soil standard (0.29-mg kg^{-1}) (SEPAC 1995). Similarly, the Se magnitude in wheat flour was 0.032–0.16 with an average of 0.10 mg kg^{-1}. The Se magnitude in corn grains of Geo type-III was 0.036–0.19 with an average of 0.091 mg kg^{-1}. Selenium in the mixed garden vegetables (Brassica campestris, Chinese red pepper, rice, cabbage radish, garlic) was 0.03–0.17 with an average of 0.087 mg kg^{-1}, which was extremely lower than the Chinese food permissible level of < 0.3 mg kg^{-1} (GB 2011) and Zhou study 0.24 mg kg^{-1} (Zhou et al. 2014). However, Se in local plants (especially ornamental plants and grasses) was 0.19–5.6 with an average of 1.4 mg kg^{-1}, which was higher than the Chinese food permissible level (< 0.3-mg kg^{-1}) (Table 1).

Arsenic in the Hancheng Permo-carboniferous raw coal was 0.28–21.3 mg kg^{-1} (average 10.10-mg kg^{-1}), and coal gangue 3.4–27.5 mg kg^{-1} (average 10.3-mg kg^{-1}) (Table 1). The As in Geo type-III coal and coal gangue was lower than the US coal (24-mg kg^{-1}) (Finkelman 1993) and extremely higher

than the Chinese coal (3.8-mg kg^{-1}) (Ren et al. 2006) and Weibei coal (1.2-mg kg^{-1}) (Luo 2005) (Table 2). Arsenic concentration in coal slime was 6.1–19.7 with an average of 12.9 mg kg^{-1}, while the As in coal ash was 3.2–26.3 with an average of 14.6 mg kg^{-1} lower than the Poland Fly ash (10.2–50.5 mg kg^{-1}) (Franus et al. 2015) and the US coal (24-mg kg^{-1}), while higher than the Ren et al. (2006) (3.8-mg kg^{-1}) (Table 1). Arsenic in the soil nearby the coal mining of Geo type-III was 10.6 mg kg^{-1}, which was almost similar to Chinese soil reference standard of 11.2 mg kg^{-1} (SEPAC 1995) and Huaibei coal mining contaminated soil (13.0 mg kg^{-1}) (Shi et al. 2013). The As concentration in wheat flour was 0.04–1.5 with an average of 0.085 mg kg^{-1}, which was lower than the maximum limit of Chinese standard for cereal products (0.5-mg kg^{-1}) (GB 2012), (Table 1). The As contents in corn grains were 0.05 mg kg^{-1}, which was lower than the Chinese permissible limit for cereal product (0.5-mg kg^{-1}) (Table 1). The As concentration in locally grown plants was 0.37–2.17 with an average of 1.1 mg kg^{-1} (Table 1), which was higher than Huaibei grains food (growing in mining contaminated soil) of 0.034 mg kg^{-1} (Shi et al. 2013) and Zhaotong raw corn of 0.007 mg kg^{-1} (Li et al. 2012a).

Fluoride concentration (mg kg^{-1}) in the Hancheng Permo-Carboniferous raw coal was 102.8–485.1 (average 273.5), coal gangue was 237.6–595 (average 363.9), coal slime was 253–536 (average 377.7), and coal ash was 88.8–453 (average 385) (Table 1). The above-observed concentrations were at least equivalent to ex-study of Weibei coalfield (150–500 mg kg^{-1}) (Luo et al. 2004b), while higher than the US coal (98-mg kg^{-1}) (Finkelman 1993), Chinese coal (131.3-mg kg^{-1}) (Ren et al. 2006), World coal (88-mg kg^{-1}) (Ketris and Yudovich 2009), and Inner Mongolia coal (13-mg kg^{-1}) (Dai et al. 2008). Similarly, the F concentration in wheat flour was 0.075–0.45 (average 0.27-mg kg^{-1}), corn grains was 0.2–0.4 with an average of 0.29 mg kg^{-1}. The F contents in mixed food were 0.17–0.7 with an average of 0.38 mg kg^{-1}, while the F content in locally grown plants (in coal wastes areas) was 0.05–5.1 with an average of 2.7 mg kg^{-1} (Table 1). Fluoride in wheat flour, corn flour, and mixed food was lower than the Chinese food reference level of 1.5 mg kg^{-1} and Zhaotong raw corn of 1.50 mg kg^{-1}. However, F in local plant growing in coal

contaminated areas was higher than the Chinese standard of 1.5 mg kg^{-1} (GB/T2762-2005) (Luo et al. 2011) and Zhaotong raw corn of 1.50 mg kg^{-1} (Li et al. 2012a).

Countryside

In the countryside, the selenium concentration in corn flour was 0.013–0.03 mg kg^{-1} (average 0.02-mg kg^{-1}), while Se concentration in wheat flour was 0.027–0.059 mg kg^{-1} (average 0.04-mg kg^{-1}). The Se concentration in mixed food crops was 0.018–0.58 mg kg^{-1} (average 0.24-mg kg^{-1}), which was equivalent to Chinese food permissible level (< 0.3-mg kg^{-1}) (GB 2011), while higher than the Zhou study (0.24-mg kg^{-1}) (Zhou et al. 2014). Among all the geological areas (i.e., Geo type-I, Geo type-II, and Geo type-III), the lowest possible concentration of Se was observed in Kashin–Beck disease areas (countryside, Huanglong County).

Arsenic concentration in the countryside corn grain was 0.05–0.086 mg kg^{-1} (average 0.064-mg kg^{-1}), which was lower than Geo type-III corn grains (Table 1). Arsenic concentration in wheat flour was 0.09–0.3 mg kg^{-1} (average 0.18-mg kg^{-1}), while the concentration in mixed food crops of the countryside was 0.06–0.14 with an average of 0.11 mg kg^{-1} (Table 1). The overall As concentration in the countryside was lower than the Chinese food permissible level of 0.5 mg kg^{-1} (GB 2012) and Huaibei grains food (growing in mining contaminated soil) of 0.034 mg kg^{-1} (Shi et al. 2013), while higher than the Zhaotong raw corn of 0.007 mg kg^{-1} (Li et al. 2012a).

Fluoride concentration in corn flour of countryside was 0.022–63 mg kg^{-1} (average 0.3-mg kg^{-1}), wheat flour was 0.048–0.76 mg kg^{-1} (average 0.29-mg kg^{-1}), while in mixed food crops 0.051–0.36 mg kg^{-1} (average 0.23-mg kg^{-1}). The F contents in wheat and corn flour of countryside were lower than Chinese standard (for grain and cereal product) of 1.5 mg kg^{-1} (Luo et al. 2011; GB 2005) and Zhaotong raw corn of 1.50 mg kg^{-1} (Li et al. 2012a) (Table 1).

The health implications pertaining to As in Geo type-I areas were higher than the Geo type-II, Geo type-III, and the countryside. The average daily intake of As in Geo type-I region was 0.0085 and 0.0075 mg kg^{-1} day^{-1} adult and Children, respectively. The

ADI of As in Geo type-II areas was 0.0042 and 0.0037, in Geo type-III was 0.0008 and 0.0008, while in countryside 0.0002 and 0.0001 in mg kg^{-1} day^{-1} adult and Children, respectively (Table 3). Similarly, the carcinogenic risk (total hazard quotient (THQ) and integrated hazard index (HI) of As in Geo type-I, Geo type-II, Geo type-III as well as the countryside were higher than the standard limit of 01 (Potential health risk level) set by the US-EPA (USEPA 2011) (Table 3). The potential risk of As in Geo type-I was included from moderate to extreme risk (Fig. 2b), Geo type-II was included from slight to extreme risk except for wheat flour (which caused no risk). Geo type-III caused slight to moderate sever risk except for food crops (which caused no risk), while the countryside was included in unpolluted and caused no risk (Fig. 2b). The toxicity level of As in Geo type-I was higher than both NOAEL and LOAEL, Geo Type-II was higher than NOAEL but equivalent to LOAEL, while Geo type-III and countryside were lower than both NOAEL (0.0008-mg kg^{-1} day^{-1}) and LOAEL (0.014-mg kg^{-1} day^{-1}) (IRIS 1995) (Fig. 3). The toxicity level of As at Geo type-I beyond the limit, which may cause a potential risk of skin cancer, lung cancer, black foot disease, liver and bladder cancer, lymphoma and leukemia (Tseng et al. 2002). The hyper-consumption of As contaminated food may cause mutagenic problems including disturbed chromatid chain, chromosomal aberration and inhibit DNA repair while teratogenic problems including placental barriers, skeletal anomalies, inhibiting skull development, and fetal problems are in great concern (Jack et al. 2003).

The average daily intake of Se by inhabitants in Geo type-I was 1.009 and 0.89, Geo type-II 0.0005 and 0.0004, Geo type-III 0.0006 and 0.0005, while in countryside 0.00007 and 0.00006 in mg kg^{-1} day^{-1} adult and Children, respectively (Table 3). However, the higher non-carcinogenic risk of Se was only observed in the adults of Geo type-I, while the HI trend of both adults and children was Geo type-I > Geo type-II > Geo type-III > countryside. The food crops at Geo type-I cause extremely severe risk, while at Geo type-II, Geo type-III, and countryside cause slight risk (while some food sample batch cause no risk). However, in this region, the low Se effects (Bones and joints problems) were observed (Fig. 2c). The toxicity level of Se at countryside zones and Geo type-III were extremely lower than the standard level (NOAEL 0.015 mg kg^{-1} day^{-1}, LOAEL 0.023 mg kg^{-1} day^{-1}), while Se in Geo type-I was a bit lower than the NOAEL and LOAEL. The deficient level of Se intake and their risk was Countryside < Geo type-III < Geo type-II < Geo type-I (Fig. 3). Selenium is essential to the human body at an optimum level (60–70 µg day^{-1}) (Hurst et al. 2010). The extreme

Table 3 Intake of selected toxic elements and their risk implication pertaining to human health

Areas	Specific	Adult			Children		
		Se	As	F	Se	As	F
Geo type-I (Cambrian)	ADI	0.005	0.00853	0.0047	0.0045	0.0075	0.0041
	THQ	1.009	28.4216	0.1167	0.8961	25.277	0.1035
	HI	29.547			26.277		
Geo type-II (Binxian Jurassic)	ADI	0.0005	0.0042	0.0098	0.0004	0.0037	0.0087
	THQ	0.1055	13.886	0.2465	0.0937	12.3556	0.2187
	HI	14.238			12.667		
Geo type-III (Permo-Carboniferous)	ADI	0.0006	0.0008	0.0020	0.0005	0.0008	0.0017
	THQ	0.1216	2.8372	0.0499	0.108	2.5375	0.0442
	HI	3.0087			2.6897		
Countryside	ADI	0.000216	0.000605	0.001507	0.000192	0.00054	0.00133
	THQ	0.04320	2.01628	0.03768	0.03834	1.78983	0.03345
	HI	2.09716			1.86163		

Unites; ADI = mg kg^{-1} day^{-1}, THQ = unitless, HI = unitless
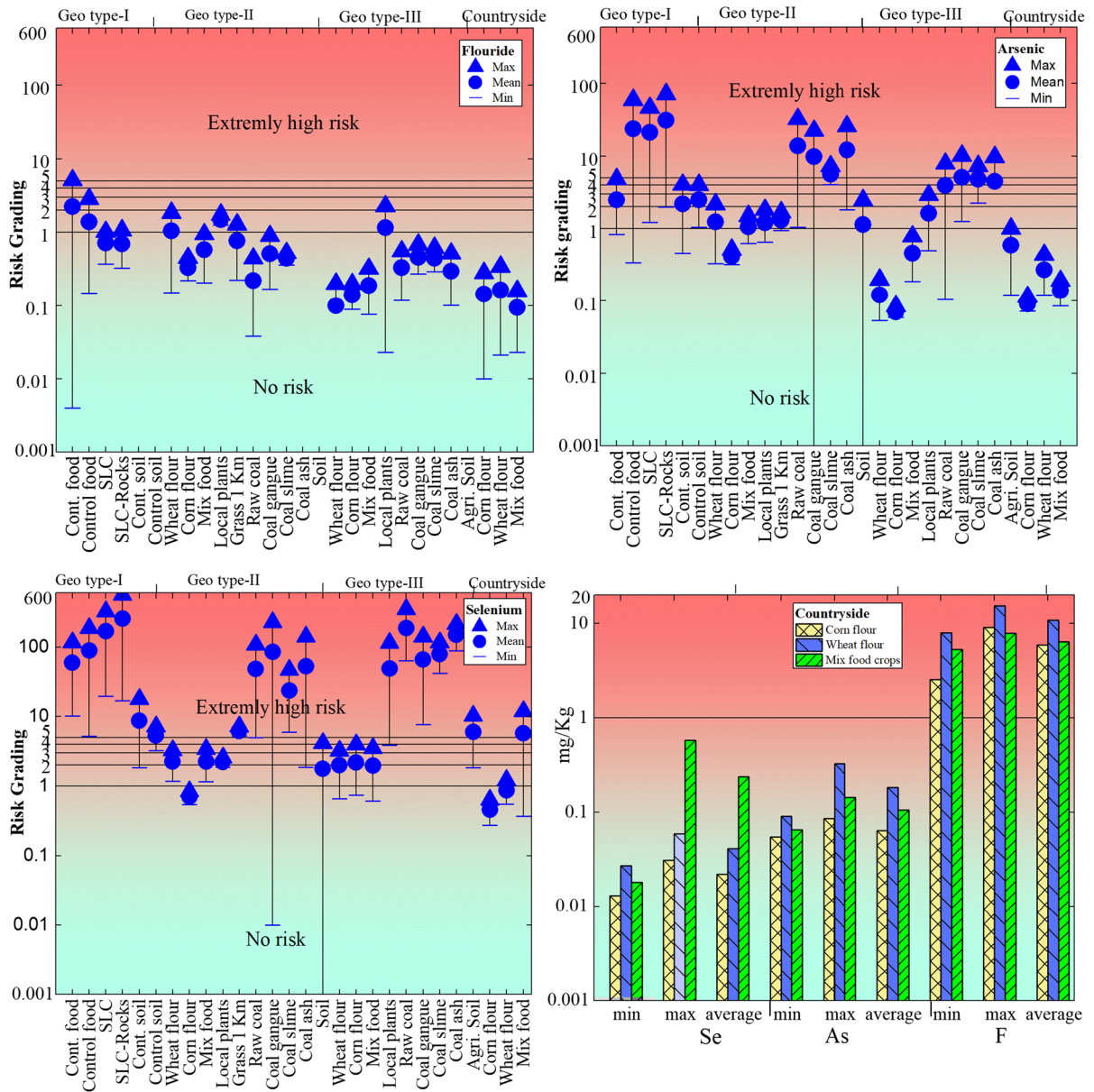
Fig. 2 Exposure pathway of toxic elements (As, F, Se) pertaining to different typical coal

deficient of Se at the countryside (Kashin–Beck disease areas), Geo type-III as well as in Geo type-II may cause a high risk of asthma, increasing the chance of Keshan disease (cardiomyopathy) and Kashin–Beck disease (Chen 2012; Cai et al. 2016b). The study observed extreme low availability of Se in food at Kashin–Beck disease areas, but a few minor patients were observed in the countryside of Shaanxi province. Many scientists reported that Keshan and Kashin–

Beck disease are caused due to Se-deficient food intake (Baoshan et al. 2010; Li et al. 2012b; Xiong et al. 2010; Tan et al. 2002; Hartikainen 2005; Wang and Gao 2001).

The F contamination was higher in the food crops of Geo type-I and in wheat and local plants of Geo type-II and III. The ADI of F in the Geo type-I was 0.0047 and 0.0041, in Geo type-II 0.0098 and 0.0087, in Geo type-III 0.002 and 0.0017, while in countryside 0.0015 and
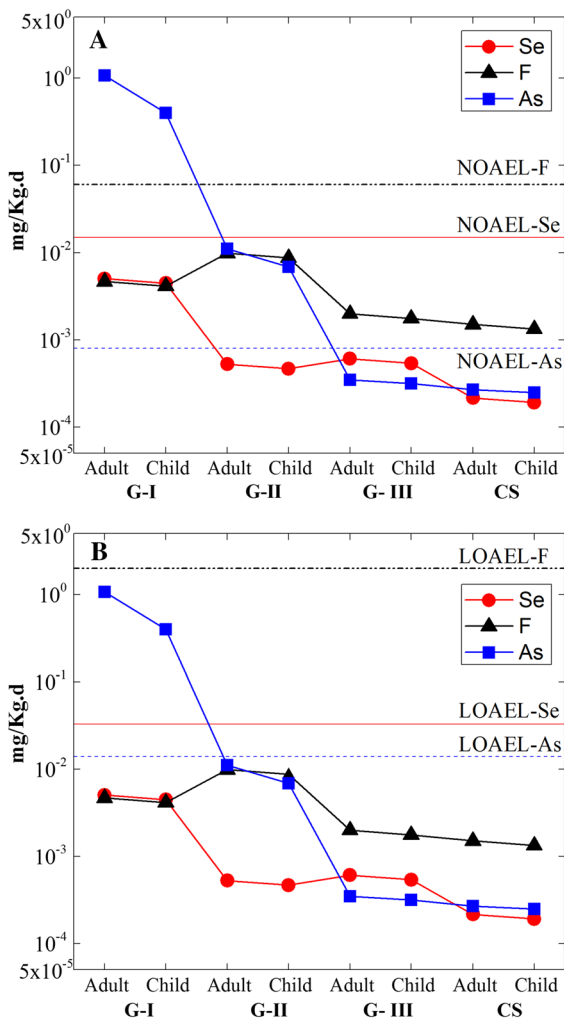
Fig. 3 The relationship between selected toxic elements intake and adverse health responses

0.0013 in mg kg^{-1} day^{-1} adult and children, respectively (Table 3). The non-carcinogenic risk of F in all the regions was lower than the standard risk level of 01 (USEPA 2011) (Table 3). However, the toxicity level of F was lower than the specific limits of NOAEL (0.06 mg kg^{-1} day^{-1}) and LOAEL (2.0 mg kg^{-1} - day^{-1}) (Fig. 3). The estimated toxicity trend of fluoride was Geo type-II > Geo type-I > Geo type-III > countryside. This seems that SLC and contact rocks caused moderate risk of fluoride-associated problems. Many scientists reported the observed F risks and problems in Geo type-I regions (Daba Qinling Mountain) (Luo 2011; Luo et al. 2011; Liu et al. 2013b; Dai et al. 2012). The current study has pointed out that there has been higher F concentration

in Geo type-I vegetable, coal, and contact rocks, which strongly correlated with Donghe/Liujiaping formation of the Lower Cambrian or other Paleozoic black shale of Daba Mountain geological sequences of south Shaanxi.

Conclusion

Geogenic toxic elements (As, Se, and F) in the environment are crucial source of health risk to human. The historic SLC and accompanying rocks are the major sources of F, As, and Se in south Shaanxi, while Permo-Carboniferous coal has a lower concentration of As, Se, and F followed by Binxian Jurassic and countryside. Arsenic in the Geo type-I i.e. SLC 5.2-fold, SLC-ash 2.2-fold, soil 3.3-fold, and vegetable 29-fold higher than the Hancheng Permo-Carboniferous regions (Geo type-III). Similarly, in Geo type-I, the Se in SLC 1.1-fold, SLC-ash 0.5-fold, soil 3.5-fold, and vegetable 40.1-fold higher than the Geo type-II, while much higher than the countryside. In Geo type-I, fluoride in SLC 2.5-fold and in vegetable 8.1-folds higher than the Permo-Carboniferous contacted regions. However, the fluoride in Cambrian SLC 2.0-fold, SLC-ash 1.4-fold, pertaining soil 2.6-fold, and vegetable 11.2-folds higher than the Binxian-Jurassic. The potential risk of As in Geo type-I and II associated with the coal, coal gangue, and coal ash is extremely severe, in Geo type-III moderate sever, while the countryside has no arsenic risk. The toxicity in Geo type-II and I is considerably higher than the standard limit of NOAEL, while the toxicity level of As is only higher in Geo type-I, which could cause a high chances of health problems.

Fluoride implication and intake situation were not exotic in the study areas, but the geo-accumulation was higher in vegetable of Geo type-I, while also observed in the local plants of Geo type-II. The toxicity trend of fluoride was Geo type-II > Geo type-I > Geo type-III > countryside. This seems the Cambrian SLC and Binxian Jurassic coal cause moderate risk of F associated problems, while lower (F implication) in Hancheng Permo-Carboniferous and countryside.

The high and low intake of Se than the optimum level will surely cause health problems. The toxicity level of Se is extremely lower than the optimum

range, and their trend was countryside < Geo type-III < Geo type-II < Geo type-I. The extreme deficient of Se in the countryside and Geo type-III counties could deregulate the normal body function. Selenium deficient also has a role in bone disease (especially Keshan and Kashin–Beck disease). However, the study found a rare patient in the countryside (Kashin–Beck disease areas) with bones diseases (expected Kashin–Beck disease). The study suggests crucial medical investigation of bones diseases and their association with selenium deficiency and high fluoride in the selenium-deficient regions of north Shaanxi.

Compliance with ethical standards

Conflict of interest The authors declare no conflicts of interest in this work.

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