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Abstract

Geochemical research of the impact of Se–Cu–Mo–V-bearing coal layers on the environment in Pingli County, Shaanxi Province, China

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Abstract

This paper presents a geochemical study on the impact of Se–Cu–Mo–V-bearing coal layers on the environment in Pingli County, Shaanxi Province, China. Analysed samples for environmental geochemical study (rock, soil and edible plant) were collected from the abandoned Dragon Village coal mine on the northern bank of the Pingli River, and the Shanliya coal mine area still in exploitation. Experiments on coal combustion were made in order to determine the amount of Se released from coal burned by local inhabitants. There are three main ways by which coal beds enhance Se, Cu, Mo, and V in the environment in the study area. First of all, supergene geological processes involving soils derived from the Se-bearing rocks and the weathering of coal are the main control on the redistribution of Se, Mo, and other trace elements in Pingli County. Coal seams in the Shanliya contain as much as 48 $\mu g\ g^{-1}$ Se, 452 $\mu g\ g^{-1}$ Mo, and 335 $\mu g\ g^{-1}$ Cu, whereas the soil has 0.85–7.10 $\mu g\ g^{-1}$ Se, 46–227 $\mu g\ g^{-1}$ Cu, and 8–29 $\mu g\ g^{-1}$ Mo. Selenium is enriched in the weathering crust of coal beds with values of 88.4 $\mu g\ g^{-1}$ Se in a calcareous sinter from the top of the weathering zone. Therefore, edible plants possible may accumulate Se, Zn, Cu, and Mo, for instance, with value above 20 $\mu g\ g^{-1}$ Cu from sesame and peanut growing in the area. Second, coal beds in the Dragon Village coal mine contain 96 $\mu g\ g^{-1}$ Se while the Se concentration of soils is high, ranging from 27 to 29.5 $\mu g\ g^{-1}$ Se. As a result, some plants have high Se contents (0.08–28 $\mu g\ g^{-1}$ Se). Variations in Se and Mo contents of the same plant species are due to large-scale geographical variations in environmental Se and Mo of soils and rocks. Finally, it is proposed that most of Se in the coal is released into atmosphere after combustion. The percentage of Se released from coal combustion containing 52.8–53 $\mu g\ g^{-1}$ Se from the Shanliya mine is 78% on average, whereas that from the coal containing 73–85 $\mu g\ g^{-1}$ Se from Dragon Village is 98%. Whenever it rains, the Se released in the atmosphere could recycle back to soils and plants on the ground.

Keywords: Coal mine; Combustion; Edible plant; Selenium; Chinese tea

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1. Introduction

Metals are of natural occurrence and are the essential components of global ecosystems (Allan, 1997). Biogeochemical studies of metal-tolerant plants, geobotanical indicators, and human activities in mining environments that cause metals to redistribute within the ecosystems have been reported by some geoscientists (Dunn et al., 1996; Paton and Brooks, 1996; Robinson et al., 1997; Äyräs et al., 1997; Benvenuti et al., 1997; Langedal, 1997; Sharmasarkar et al., 1998; Wright et al., 1998; Klukanová and Rapant, 1999; Yan et al., 1999; Zhang et al., 1999; Xiao et al., 1999; Qi et al., 1999; Liu, 2000; Zheng and Wang, 2000; Karen et al., 2001; Woo et al., 2002). The documented papers pertaining to trace element-rich black shales reported that the black shales have impacts on the eco-environmental system including soils, plants, animals, and human beings (Vine and Tourtelot, 1970; Lee et al., 1998; Loukola-Ruskeeniemi et al., 1998; Karen et al., 2001). The environmental importance of Se is attributed to its potential to cause either toxicity or deficiency in human beings, animals, and some plants within a very narrow concentration range (Lakin, 1972). Selenium is widely distributed in the Earth's crust with an abundance that has been estimated to be approximately 0.07 μg g^{-1} in China (Li and Ni, 1990). However, concentration of Se in different rocks and soils is variable. It is frequently found in great abundance in black shales, particularly in coal layers and carbonaceous cherts from the Ankang area of Shaanxi Province and the Enshi area of Hubei Province in China, where Se may be in excess of 100 μg g^{-1} Se, with 206.8 μg g^{-1} Se in carbonaceous shales and 280.6 μg g^{-1} Se in carbonaceous cherty shales. So, selenosis occurred in those areas (Zheng et al., 1992; Fang et al., 1995, 1996, 2002a,b; Li, 1997; Zhu and Zheng, 1999; Wen and Qiu, 1999; Fordyce et al., 2000). Selenium deficiency is linked to an endemic degenerative heart disease known as the Keshan Disease and degeneration of the articular cartilage between joints known as Keshan-Beck Disease (Yang et al., 1983; Tan et al., 1989; Lin, 1991), while selenium toxicity (selenosis) would have caused loss of hair and nail and disorder of nervous system in the human population in the Enshi area of Hubei Province and Ziyang County of Shaanxi Province in China (Yang et al., 1983; Zheng et al., 1992; Zhao et al., 1993). Although Se impacts on the environment have been extensively studied, Cu–Mo–V impacts on the environment in black shale and coal layer area are poorly understood. Human activities such as waste dumps of coal mine and coal combustion may cause a number of metals to redistribute though supergene geological processes including the soils derived from the rocks, and their weathering is the main factor controlling the distribution of trace element. As a result, some edible plants are of trace element enrichment. This paper presents the results of environmental geochemistry research on the impacts of coal mining on the environment in Pingli County, Shaanxi Province, PR China, indicating three ways by which coal beds enhance the concentration of Se, Cu, Mo, and V in the study area.

2. Geology and location

According to Zhang et al. (1987), coal in the Early Paleozoic black shales is a black caustobiolith with calorific capacity amounting up to more than 3347 J/g. The coal comprises poor coal with calorific capacities ranging from 3347 to 5020 J/g, good coal with calorific capacities ranging from 5020 to 12552 J/g, and best coal with calorific capacities of more than 12552 J/g. Coal from the Qinling coal zone (zone I in Fig. 1) is classified as the best coal with the calorific capacity ranging from 20920 to 29288 J/g. Therefore, this coal is mined and burned as daily fuel by local inhabitants.

A general description of the geological characteristics of black shales and coals in the Early Paleozoic black shales, which are widespread in Southern China, is given by Zhang et al. (1987). Their investigations suggested that palaeo-bacteria such as blue algae were the primary producer of organic matter in the Paleozoic sea, and organic matter in the Early Paleozoic black shales was deformed by late tectonic movements. The palaeo-biocoenosis of bacteria blue algae and tunicate not only supplied sufficient organic matter for forming the combustible deposits but also laid a foundation for the enrichment of accessory elements. Therefore, some coal layers were formed in the Early Paleozoic black shales. Pingli County is located at the Qinling coal zone (zone I in Fig. 1). Throughout the area coal seams and black shales are

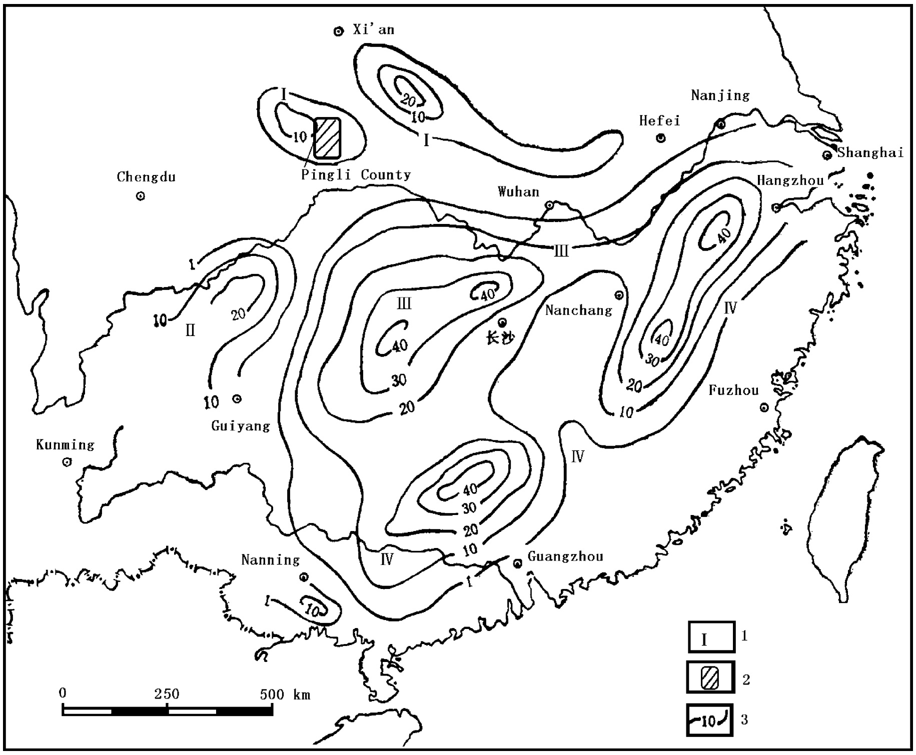

Fig. 1. Location of the area studied and the Lower Cambrian coal seams in China (modified after Zhang et al., 1987). 1—Coal zones and their numbers; I: Qinling zone; II: Yangtze zone; III: Southern China zone; 2—Location of the area studied; 3—Thickness of coal (in meter).

widespread in the Donghe Formation of the Lower Cambrian age enriched in trace elements. The Donghe Formation of the Lower Cambrian age comprises black carbonaceous shale, carbonaceous carbonate rock, coal seam-bearing rock, chert, and carbonaceous argillite in the area. Trace elements enriched in chert are supposed to be associated with sedimentation of volcanic exhalation or hydrothermal deposition at sea floor (Zhang et al., 1987; Li, 1997; Chen et al., 1998; Fang et al., 2002b). However, trace elements enriched in coal seams and carbonaceous rocks could be caused by sulfides, such as pyrite, chalcopyrite, and molybdenite in them, and absorption by organic matter (Zhang et al., 1987; Fan et al., 1991; Gao et al., 1997; Wen and Qiu, 1999) as well as Se minerals such as native selenium, chalcomenite, berzelianite, and drysdallite (Zhu et al., 2000).

Dragon Village coal mine was used for daily fuel by local inhabitants in the past. Outcrops of the Donghe Formation of the Lower Cambrian age comprise coal seams, carbonaceous chert, carbonaceous argillite, and carbonaceous carbonate rock. In general, strata-bound coal seams are measured up to 0.5–4 m in thickness and 100–200 m in length. The coal seams at the surface contain much pyrite and no copper mineralisation. The mine comprises more than 5 abandoned adits and 10 abandoned open-pits on a slope. Coal dumps and waste rock dumps, which mainly comprise black shales and black carbonaceous cherts, were left around these adits and open-pits and are weathering and fragmenting due to recent supergene process. Therefore, soils are derived from these dumps. Percolating water freely transports large amounts of Fe-bearing sulfosalts from the dumps and contaminates broader surrounding soils.

The Shanliya coal layers mined via underground mining adits are characterized by the buried occurrence of black shales and coal seams with copper mineralisation. In general, strata-bound coal seams are measured up to 0.5–3.6 m in thickness and 100–400 m in length. Copper-mineralised layers that occurred among the coal seams are 0.1–1.5 m thick and 10–60 m long. Pyrite, chalcopyrite, malachite, and covellite are found in copper-mineralised layers among coal seams. Sandy stone, muddy shale, limestone, calcareous shale, and soils cover most of coal beds. There are small outcrops of (generally less than 2.5 m^2) coal beds in low parts of the valley, which are coated by calcareous sinter and native sulfur. Percolating water and drain from adits in the mine carry fine coal-dust and Fe-bearing sulfosalts and contaminate the soils.

3. Material and methods

Environmentally geochemical samples (rock, soil, edible plant, and animal) were collected from the abandoned Dragon Village coal mine on the northern bank of the Pinglin River, and the Shanliya coal mine still under mining. Edible plants were sampled at each of these locations. Composite samples (300 g), comprising edible plants or grain crops including sesame, peanut, corn, wheat, potato, and sweet potato, were collected. Edible plants or animals include *Amorphophallus konjac K.·Kock*, *Gynostemma pentaphyllum*, mustard leaf, mulberry leaf, as well as Chinese blue tea and silkworm in the study areas. Different parts of Chinese tea trees, called the Shanliya Tea and the Baxian Tea, were sampled as here are special local teas enriched in Se. Samples of fresh plant were washed with river water in the field site so as to remove muddy dusts adhered to plants.

Rock samples were crushed as fine as 0.25 mm in a jaw crusher, and then, quartered, pulverised in a high-Al-ceramic crusher to 0.095 mm in size. Surface soil samples were collected from depths of 10 to 30 cm. Soil samples were kept in cotton bags and allowed to air-dry, then crushed in cotton bags with a stick to less than 0.275 mm in size, quartered and pulverised in a high-Al-ceramic crusher to less than 0.095 mm in size. Samples of edible plants were left in cotton bags and allowed them to be partially air-dried prior to removal of all moisture in an oven at a temperature of 40 °C to avoid loss of volatile compounds. The dried plant samples were crushed to 0.20 mm in size by means of a GWF-1 multiple crusher.

Water-soluble trace elements in samples of tea plant were processed by way of Chinese drinking tea. Steps involved in process are as follows: firstly, in order to remove dusts from tea samples, they should be washed two times with purified water at about 20 °C; secondly, the samples were put into an evaporative prior to removal of all moisture in an oven at a temperature of less than 60 °C; thirdly, 40 g of each sample and 600 ml of the deionised water were put in a container; fourthly, the samples were heated in the boiling water (at no more than 100 °C) to extract the water-soluble elements in the tea for 30 min by using an electric hot plate. Finally, the extractable solutions were condensed to 500 ml in a container for instrumental analysis.

Plant samples were digested and analysed according to Chinese National GB12393-90. Firstly, in order to remove dusts from the dried plant samples, they should be washed with water and then washed three times with deionised water. Secondly, the samples were put into an evaporative prior to removal of all moisture in an oven at a temperature of less than 60 °C. Thirdly, 5 g of dried plant samples were taken and put into a 50-ml-sized ceramic crucible for digestion. The plant samples were digested by total digestion, i.e., first digested by HNO_3 (1:1) and then by $HClO_4$. Finally, the solution dissolved by 4% HCl in a container was taken for instrumental analysis. Se in the samples was analysed by two-banded atomic fluorescence spectroscopy (AFS-220 type) with a detection limit of 0.01 ppm for Se. Mo, Cu, Zn, B, and V in the samples were analysed by the oscillography–polarography (JP-II) with a detection limit of 0.01 ppm for Mo and 0.10 ppm for Cu, Zn, B and V. Fluorine in the samples was analysed on a 752-mode spectrophotometer.

Rock and soil samples were processed by aqua regia. Se in the samples was analysed by two-banded atomic fluorescence spectroscopy (AFS-220 type). Cu, Zn, Mo, V, and B in the rock and soil samples were analysed by ICP.

Reagent blanks, duplicate samples, and Chinese National Standard Samples were put into each batch for data quality control. Chinese National Standard Samples comprise wheat GBW-08503, poplar leaf GBW-07604, and tea GBW-08506 (RSD$\leqslant$5% for all analysed elements in this study). The samples were analysed at the Northwest Analytic Centre of Trace Elements (Chinese National A-order Analytic Centre), attaching to Mineral and Geological Exploration Centre of Nonferrous metals of China.

Experiments on coal combustion were made in order to investigate the effects of the Se released from coal burned by local inhabitants on the atmosphere in the study area. Coal samples were collected, respectively, from the Shanliya and Dragon Village mines. Crushed, these samples were 0.105 mm in size using a jaw crusher, and then, 0.5 g of each sample was taken and put into a SRJX-8-18-type electric furnace at controlled and constant temperature to be burned for 2 h at 650 °C. The residues of samples were taken out and weighed on a photoelectric balance. Finally, the Se contents of coal samples before and after combustion were measured on an XDX-2A-type atomic fluorescence spectroscope. The following equations are employed to deal with the data:

(i) Percentage of loss=(loss – gross/sample – gross);
(ii) Gross of released Se=(sample – gross × Se content before burning)(residue – gross × Se content after burning);
(iii) Percentage of released Se = gross of released Se/(sample – gross × Se content before burning);
(iv) Percentage of residue = residue – gross/(sample – gross × Se content before burning).

4. Results and discussion

4.1. Case study 1: the Shanliya coal mine still under mining

Table 1 shows concentration of trace element in rocks, soils, and edible plants in the vicinity of the Shanliya coal mine, Pingli County, which is still under mining at present time. A sample of coal layers from the Shanliya mine contains 48 μg g^{-1} Se. Nevertheless, the coal layers are mostly overlain by carbonate rock, siltstone, and muddy sandstone. Selenium concentrations in soils from the Shanliya area range from 0.80 to 7.1 μg g^{-1} and Cu from 46 to 227 μg g^{-1}. Soils in the Shanliya area contain Zn contents ranging from 95 to 557 μg g^{-1} and Mo contents ranging from 3.8 to 29 μg g^{-1}, and V contents ranging from 196 to 1330 μg g^{-1}. Selenium is enriched in the weathering topsoil over the surface of coal seams, with values of 88.4 μg g^{-1} Se in a calcareous sinter from the top of the weathering zone. Selenium contents of the calcareous sinter are much higher than those of coals and Se-bearing black shales in the Shanliya area, indicating that Se could be enriched during weathering of these rocks under supergene geological processes. Sharmasarkar et al. (1998) have reported that Ca addition would enhance Se sorption, and that the distributions of SeO_3^{2-}–SeO_4^{2-}–SO_4^{2-} as the solution species, the sorbed fraction and the sorbed complexes are commonly observed in the presence of inorganic oxide of CaO. They considered that SeO_4^{2-} would be the predominant Se species in the solution (typical for mine soils) and could be bioavailable for plant uptake or aquifer contamination. The calcareous sinter derived from these Se-bearing rocks because of their weathering under supergene condition is readily soluble by water.

Table 1
Trace element contents of rocks, soils, and plants from the Se-enriched Shanliya area (μg/g)

Sample type	Se	Cu	Zn	Mo	V
Coal	48	335	950	452	2560
Carbonaceous limestone	1.7	75	330	–	648
Carbonaceous limestone	0.40	36	207	–	150
Soil 5 m away from the mine	7.1	227	557	–	1330
Soil 20 m away from the mine	2.8	85	130	29	420
Soil derived from limestone	0.80	46	340	–	166
Soil in a Chinese tea farm	1.1	105	130	8.0	304
Soil derived from limestone	0.85	55	95	9.0	248
Soil derived from carbonaceous limestone	1.6	90	160	3.8	196
Calcareous sinter	88	–	–	–	–
Mulberry leaf	0.17	8.8	29	2.0	1.9
Silkworm	0.84	–	–	–	–
Potato	3.0	11	29	7.6	0.45
Mustard leaf	2.5	15	107	14	9.0
Wheat	0.24	6.3	32	0.71	0.71
Sweet potato	4.5	4.5	8.8	0.75	0.58
Corn	0.02	1.7	14	1.1	0.36
Sesame	0.27	22	66	1.3	0.16
Peanut	0.09	21	37	3.1	0.13
Gynostemma pentaphyllum	0.84	14	2.5	3.7	3.0

There is one sample for each sample type as shown above. (–) Represents no analysed data.

Therefore, Se from it can easily migrate into mine soils.

Selenium concentrations in edible plants from the Se-rich Shanliya area are lower than those detected in an abandoned coal mine at Dragon Village, Pingli County (case study 2). But Se contents are still high (4.46 μg g^{-1} Se in sweet potato, 3 μg g^{-1} Se in potato, 2.47 μg g^{-1} Se in mustard leaf). And, Se is enriched in mulberry leaf, wheat, sesame, and *G. pentaphyllum* whereas Se concentrations of corn and peanut are within the normal range (Fang et al., 1995, 1996). Silkworms contain 0.84 μg g^{-1} Se, four times higher than that of mulberry leaf containing 0.17 μg g^{-1} Se. Silkworms live on mulberry leaves in the area, and the influence Se bioaccumulation in the food chain is demonstrated in the area. However, Cu contents in edible plants in the Shanliya area are within normal range (1.67–22 μg g^{-1} Cu). The soluble species of Se including SeO_3^{2-} and SeO_4^{2-} are predominant when in the presence of inorganic oxide of CuO (Sharmasarkar et al., 1998). So Se may share much in common with Cu with the respect to their migration in the presence of predominant Cu mineralisations. Zinc, Mo, and V concentrations in mustard leaf are higher than any other edible plants in the Shanliya area.

In summary, the supergene geological processes involving soils derived from and the weathering of the black carbonaceous rocks are the main factor controlling the distribution of Se, Mo, and other trace elements.

Table 2
Trace element contents of the same species of edible plant, soil, and rock from different areas (μg/g)

Area	Sample type	Se	Cu	Zn	B	Mo	V
Se-poisoned area	coal	95	50	227	20	55	1500
	coal	62	74	260	135	–	1470
	soil 2 m away from the mine	29.5	80	234	55	40	450
	soil 5 m away from the mine	27	75	145	135	70	125
	soil derived from coal seams	20	37	178	63	–	1320
	Gynostemma pentaphyllum						
	2 m away from the mine						
	stem	1.36	7.0	44	31	5.2	0.44
	leaf	1.59	7.0	44	11.1	7.4	1.9
	Gynostemma pentaphyllum						
	soil 5 m away from the mine						
	stem	0.29	8.5	18.5	16.1	0.82	0.95
	leaf	0.36	13.5	30	14.3	3.9	9.5
	Amorphophallus konjac K. Kock						
	in soil derived from coal	4.92	5.0	38.7	11.4	1.3	0.80
Se-rich area	carbonaceous shale	0.23	20	85	125	1.0	100
	carbonaceous shale	0.67	5	25	5	2.5	40
	siliceous rock	0.12	15	50	28	1.7	61
	soil	0.17	25	80	43	1.5	108
	soil	0.17	40	80	33	1.5	97
	soil	0.52	40	100	35	5.0	125
	soil	0.81	45	100	33	3.8	196
	stem of *Gynostemma pentaphyllum*	0.80	15	42.5	11	6.5	1.1
	stem of *Gynostemma pentaphyllum*	0.84	13.8	2.5	3.0	3.7	2.5
	Amorphophallus konjac K. Kock	0.79	5.8	26.5	11	4.0	0.98
	Amorphophallus konjac K. Kock	0.57	6.2	57.6	–	3.2	1.3
Se-normal area	soil	0.18	40	80	30	2.1	136
	Amorphophallus konjac K. Kock	0.13	3.8	42.5	3.0	0.82	0.38
Se-deficient area	*Amorphophallus konjac K. Kock*	0.04	18	45	–	0.80	2.8

There is one sample for each sample type as shown above. Se-deficient area is Shangluo area of Shaanxi Province. (–) Represents no analysed data.

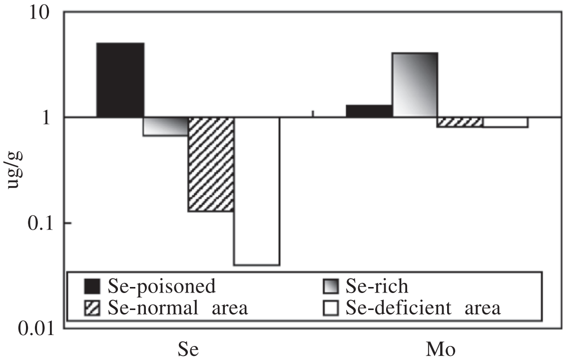

Fig. 2. Contents of Se and Mo in an edible plant, *A. konjac K. Kock*, from different parts of the Ankang area (one sample for each area).

4.2. Case study 2: an abandoned coal mine at Dragon Village, Pingli County

Selenium-poisoned (>21 μg g^{-1} Se), Se-rich (19–4.8 μg g^{-1} Se), Se-normal (0.46–0.26 μg g^{-1} Se), and Se-deficient (< 0.18 μg g^{-1} Se) areas in Shaanxi Province of China can be classified in relation to Se in the soils (Fang et al., 2002a). The coal beds and mine waste dumps on the environment are exemplified by case study 2 at Dragon Village mine. Localised geochemical differences are readily seen in comparisons of the Se contents of soils and *G. pentaphyllum* plant from four different areas: a Se-poisoned area in the vicinity of the Dragon Village mine, a Se-rich area, a Se-normal area, and a Se-deficient area (as listed in Table 2).

Selenium-rich coal from the Dragon Village mine contains 96.0 μg g^{-1} Se, consequently, Se contents in soils derived from the waste dumps of the coal mine also range from 27.0 to 29.5 μg g^{-1} Se. Furthermore, Zn, Mo, V, Cu, and B contents in soils from the Dragon Village coal mine are higher than those from the other recorded areas.

Due to the environmentally geochemical effects on the soils, Se, and Mo contents of *G. pentaphyllum*, Chinese healthy tea or herb growing in the vicinity of the Dragon Village coal mine are higher than those from the Se-enriched area and Se-normalized area (Table 2) away from the abandoned coal mine. It is also evident in the contents of trace elements in the plant *A. konjac K.·Kock* from the four different areas with different Se and Mo levels (Table 2 and Fig. 2). *A. konjac K.·Kock* in the soil derived from coals contains 4.92 μg g^{-1} Se, which is 123 times the value recorded in the Se-deficient area (containing 0.04 μg g^{-1} Se); 36 times that of the Se-normal area, and 6–9 times that of the Se-rich area. To sum up, the variations in Se contents of the plant species are due to large-scale geographical variations in environmental Se of the soils and rocks, implying that the weathering of the coal and waste dumps is mainly responsible for enhanced trace element contents to soils in the vicinity of the abandoned coal mine.

However, in Se-rich environment such as the Dragon Village, different plant species can accumulate Se from the soil in varying amounts. Previous studies (Fang et al., 1995, 1996, 2002a) indicate that high concentrations of Se were found in a variety of plant species (8.50 μg g^{-1} Se in potato, 6.35 μg g^{-1} Se in garlic, 15.3 μg g^{-1} Se in chilli, 16.0 μg g^{-1} Se in mung bean, 7.30 μg g^{-1} Se in radish, 28.0 μg g^{-1} Se and 50 μg g^{-1} Mo in radish leaf, and 43.9 μg g^{-1} Mo in soybean). The highest concentrations of Se and Mo were found in radish leaf, and the extremely high Se concentrations in edible plants from this area would normally be toxic to local residents and animals.

4.3. Trace element contents in the different parts of Chinese blue tea plant

Plants take up Se from the soil according to the amount and availability of the Se present in soils. The Se-rich Ziyang tea is a special local tea in China, which is grown in Ziyang County near Pingli County. Selenium in soils ranges from 0.094 to 23.53 μg g^{-1} Se while water-soluble Se in the soils ranges from 2.21 to 56.38 μg kg^{-1} Se in this tea planting area

Table 3
Contents of trace elements in different parts of Chinese blue tea plant from the area studied (μg/g)

Parts	*N*	Se	Mo	Cu	Zn	B	F	V	Cr
Sprout in spring	4	0.38	–	13	50	2.9	–	–	2
Leaf in autumn	4	0.05	1.3	10	22	3.8	2	2.3	0.28
Flower (autumn)	2	0.04	0.16	10	16.9	3	2.5	1.5	0.23
Sprout in autumn (Autumn Tea)	1	0.04	4.2	11	24	9	3.1	0.87	0.23
Sprout in spring (Maojian Tea)	2	0.48	0.14	13	35	3.4	2.9	0.04	0.88

N = total samples. (–) Represents no analysed data.

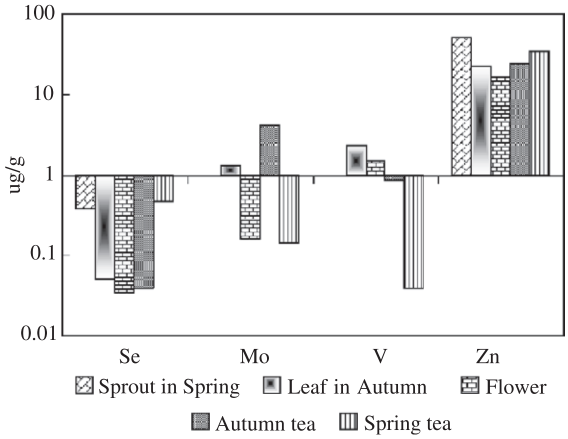

Fig. 3. Contents of Se, Mo, V, and Zn in different parts of tea tree in the Ankang area.

(Zhao et al., 1993). Selenium contents of Ziyang Tea range from 0.103 to 3.85 μg g^{-1} Se (Cheng et al., 1991). Table 3 and Fig. 3 show that Se, Mo, V, and Zn contents in the different parts of Chinese blue tea plant in Pingli County vary in numerous amounts. The highest concentrations of Se (0.48 μg g^{-1} Se) and of Zn (50 μg g^{-1} Zn) are found in the sprout of tea in spring season whereas Se contents in flower and leaf or sprout in autumn are lower ranging from 0.04 to 0.05 μg g^{-1} Se. The sprout of tea in autumn season has the highest Mo content (4.2 μg g^{-1} Mo). This is suggested that different elements are accumulated in different parts of Chinese tea trees with seasonal change. Sprouts of tea trees in spring (Maojian Tea) may be Se and Zn accumulators, while sprouts of tea trees in autumn (Autumn Tea) could be Mo and B accumulators. Autumn season (on same season) is the time that tea plant is in the period of pregnancy. The sprout of tea tree has to support that the tea tree bears its flowers and fruitages. It is supposed that photosynthesis of tea tree at this time could uptake more Mo and B from the soils, and store them in the sprout of tea tree due to both Mo and B is beneficial to become pregnant in relation to physiological action of tea plant.

The contents of F in the tea are less than 4 μg g^{-1} F, so it is not thought to be a major component of endemic fluorosis in Pingli County. The main cause of endemic fluorosis in Ziyang County is that the soil–corn–air system has been polluted by fluorine released from daily coal-burning by inhabitants themselves (Zheng, 1996). Owing to the close similarities in geological condition and ecosystem between Ziyang and Pingli counties in the Ankang area, endemic fluorosis may be caused by similar factors.

4.4. Experiments on the Se released from combustion of coal

Changes in Se contents of coals after and before burning are described in Table 4. On one hand, coals (BR-1, BR-2, and BR-3) from the Shanliya coal mine before the experiments of combustion contain 53–52.8 μg g^{-1} Se, and the residues after the combustion contain 19–17 μg g^{-1} Se. Loss gross of the samples (BR-1, BR-2, and BR-3) after the combustion ranges from 40.7% to 40.5%. On the other hand, coals (BR-4, BR-5, and BR-6) from the Dragon Village coal mine before the combustion experiments contain 85–

Table 4
Comparisons of Se contents in coal before combustion and residues after combustion

Location		Shanliya coal mine			Dragon Village coal mine		
Sample no.		BR-1	BR-2	BR-3	BR-4	BR-5	BR-6
Before burning	sample gross (g)	0.5	0.5	0.5	0.5	0.5	0.5
	Se (μg/g)	53	53	52.8	85	73	84
After burning	loss gross (g)	0.2036	0.2032	0.2027	0.1586	0.1575	0.1581
	residue gross (g)	0.2964	0.2968	0.2973	0.3414	0.3425	0.3419
	Se contents from residues (μg/g)	19	18.4	17	2.9	2.1	2
Percentage	loss gross (%)	40.72	40.64	40.54	31.72	31.5	31.62
Gross	released Se (μg)	20.81	21.04	21.35	41.51	35.78	41.35
Percentage	released Se (%)	73.7	79.39	80.87	97.67	98.03	98.37
Percentage	residues (%)	21.3	20.61	19.14	2.33	1.97	1.63

73 μg g^{-1} Se while the residues after the combustion experiments contain only 2.9–2 μg g^{-1} Se. Loss gross of the samples (BR-4, BR-5, and BR-6) ranges from 31.7% to 31.5%. The combustion experiments showed that Se contents decreased significantly in the residues after burning. The percentage of Se released from the coal of the Shanliya mine ranges from 73.7% to 80.87% with a mean value of almost 78%, whereas that from the coal of the Dragon Village mine range from 97.67% to 98.37% with a mean value of almost 98%, indicating that most of Se in the coal is released after combustion. As coals are one of the most important fuels for inhabitants, their daily burning could provide significant Se to the local atmosphere. Whenever it rains, the Se in atmosphere could be deposited back to the soils and plants on the ground.

5. Conclusions

Despite the biological difference between plants, results of environmental geochemistry research on black shales, coal seams, soils, and edible plants indicate that the coal seams and black shales do have a major influence on trace status of local ecosystems. The three main ways by which coal seams and black shales enhance Se, Cu, Mo, and V in the environment are demonstrated in the study area. Firstly, supergene geological processes including soils derived from these rocks and the weathering of these rocks are the main control on the distributions of Se, Mo, and other trace elements in Pingli County. Secondly, the variations in Se and Mo contents of the plant species are due to large-scale geographical variations in environmental Se and Mo of the soils and rocks. The Se, Mo, and Cu contents of soil near the coal mine are high, with Se ranging from 27.0 to 29.5 μg g^{-1} Se in soils derived from coal and waste dumps of the abandoned coal mine. All this indicates that the coal layers and waste dumps of the coal mine essentially related to human activities are predominantly responsible for the enhanced dispersion of trace elements to soils in the vicinity.

Thirdly, much Se from the coal will escape to the atmosphere during combustion as it is used as daily fuel by the local inhabitants. In the study area, it is suggested that the Se released from the combustion of coals by local inhabitants into atmosphere could recycle back to the ground when it rains.

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