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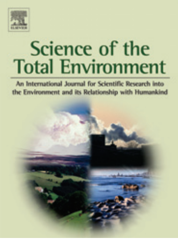

Distribution and transport of selenium in Yutangba, China: Impact of human activities

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ABSTRACT

Yutangba, one of the typical high-Se areas where a sudden incidence of Se poisoning occurred in 1963, is located in the northern part of Shuanghe town about 81 km SE of Enshi, Hubei Province, China. In this area, a comprehensive investigation was conducted on the distribution of Se in soils, plant species, stream water and sediment. The mean concentrations of Se were: total soil, 4.75±7.43 mg/kg ($n=150$); Corn seeds, 1.48±1.41 mg/kg ($n=20$); Agry wormwood, 1.68±1.27 mg/kg ($n=30$); Bracken fern, 0.63±1.61 mg/kg ($n=57$), and Central China dryoathyrium, 0.48±0.72 mg/kg ($n=39$); Stream water, 58.4±16.8 μg/L ($n=12$); stream sediment, 26.6±26.8 mg/kg ($n=11$). The spatial distribution of Se in soils and plants is significantly uneven and higher Se samples mainly distributed in the croplands and northwest Yutangba, while almost all the lower Se samples are located in undisturbed areas. 11 samples contained extremely high concentrations of Se, ranging from 346 to 2018 mg/kg with an average of 899±548 mg/kg, were found at croplands and discarded coal spoils in Yutangba.

The distribution of Se in Yutangba is related to the pathways of Se transport, which was caused by human activities such as stone coal conveyance by local villagers, mining of stone coal for use as a fuel or fertilizer, and discharging lime into cropland to improve soil. These activities caused variable addition of Se to the soil and further accumulation of Se in food chain. Therefore, human activities have played an important role in the distribution, transport, and bioavailability of Se. Yutangba is still a high risk area where Se poisoning may occur again, and so are almost all high-Se areas in Enshi Prefecture.

1. Introduction

Selenium is an essential trace element for human beings and animals. The range of healthy Se intake between levels that are toxic and those leading to Se-deficiency in humans is rather narrow (50–200 μg/day for adults, WHO, 1987; Navarro-Alarcón and López-Martínez, 2000). The distribution of Se on the earth's surface varies widely, forming Se-deficient and Se-excessive ecosystems which affect human and animal health (Tan and Huang, 1991; Presser, 1994; Wang and Gao, 2001; Tan et al., 2002). In China, selenium deficiency occurs in a geographic low-Se belt stretching from Heilonjiang Province in the northeast to Yunnan Province in the southwest. This Se-deficiency was linked to two endemic diseases: a degenerative heart disease known as Keshan Disease and osteoarthropathy (Kaschin–Beck Disease) which causes deformity of the affected joints (Tan and Huang, 1991; Tan et al., 2002). Selenium toxicity, which results in hair and nail loss and nervous system disorders in humans, has also

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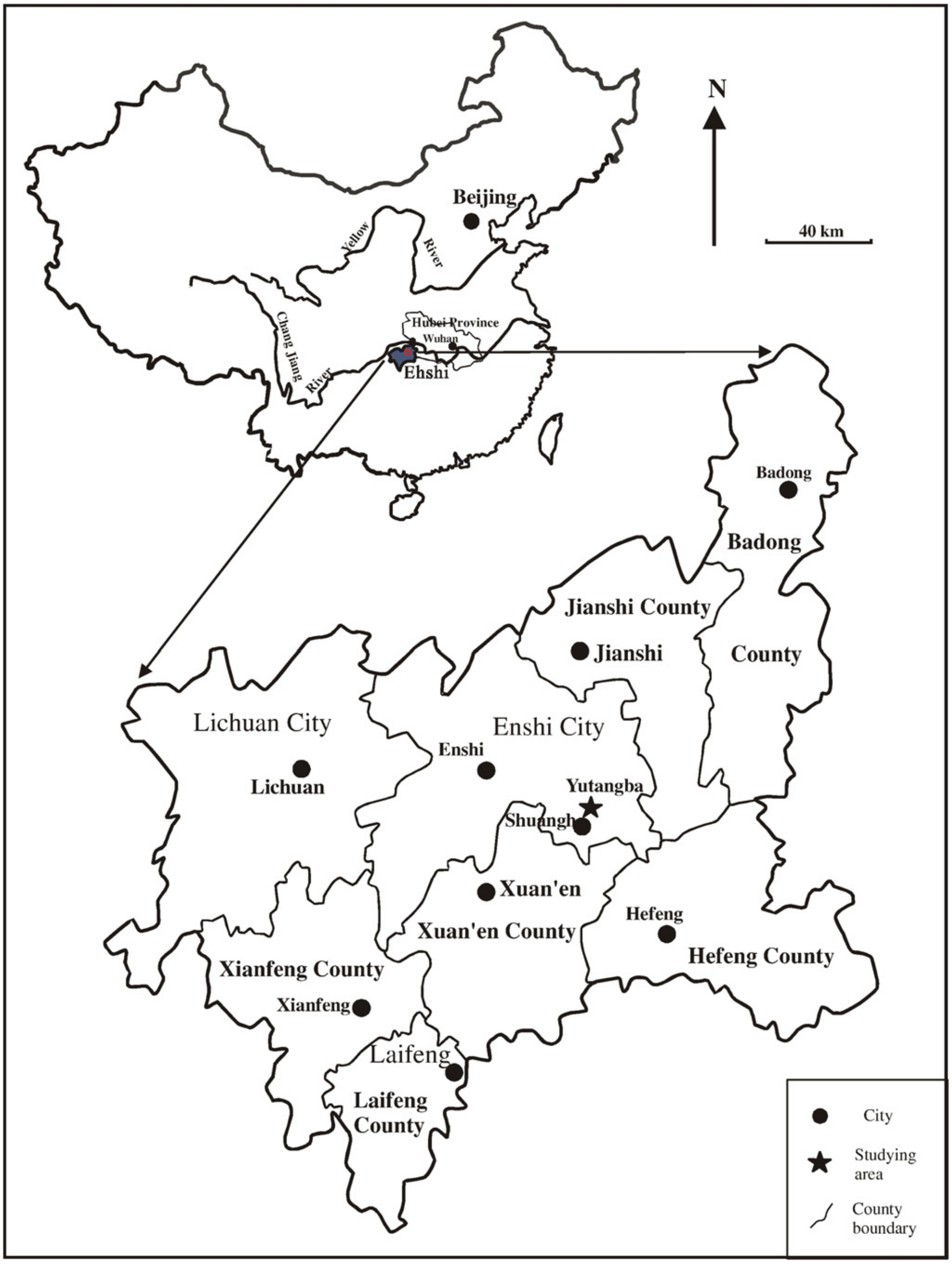

Fig. 1 – Sketch map showing the location of Yutangba, Shuanghe town of Enshi city, China.

been reported in two notable seleniferous regions: the Ziyang region in Shanxi Province and Enshi Prefecture in southwest Hubei Province (Yang et al., 1981, 1983; Mei, 1985).

In Enshi Prefecture, 477 cases of human Se poisoning and more than 10,000 cases of swine Se poisoning have been reported over the past 4 decades. Currently, cases of Se poisoning among swine and goats are still being reported in some high-Se villages (Mao et al., 1990, 1997; Mao and Su, 1993), and several human cases of Se poisoning, while sporadic, were reported again in recent years (Su, Hongcan pers. commun.). Yutangba is a small settlement located in the northern part of Shuanghe Town, approximately 81 km SE of Enshi City (Fig. 1), which is one of the typical high-Se areas in China (Zheng et al., 1992, 1993; Mao et al., 1997) where a sudden incidence of Se poisoning took place (Yang et al., 1981, 1983; Mao et al., 1990). A few people living in Yutangba experienced loss of hair and nails from early 1930s to 1961. However, in 1963, 19 of 23 local inhabitants manifested symptoms of Se poisoning, and all livestock died (Mao et al., 1990, 1997). Subsequently, villagers were forced to evacuate their homes.

In the Yutangba study area, from the northwest to the southeast, the sedimentary rocks are exposed in the following order: P_1m^2, P_1m^3, P_2w^{1+2}, P_2d^1, P_2d^2, T_1d^1 and T_1d^2 (Fig. 2 and see Table 1 for full description). Selenium is mainly present in the carbonaceous chert and carbonaceous shale (locally known as "stone coal") of the Lower Permian Maokou (P_1m^2, P_1m^3) and Wujiaping Formation (P_2w^{1+2}). These strata are located in an

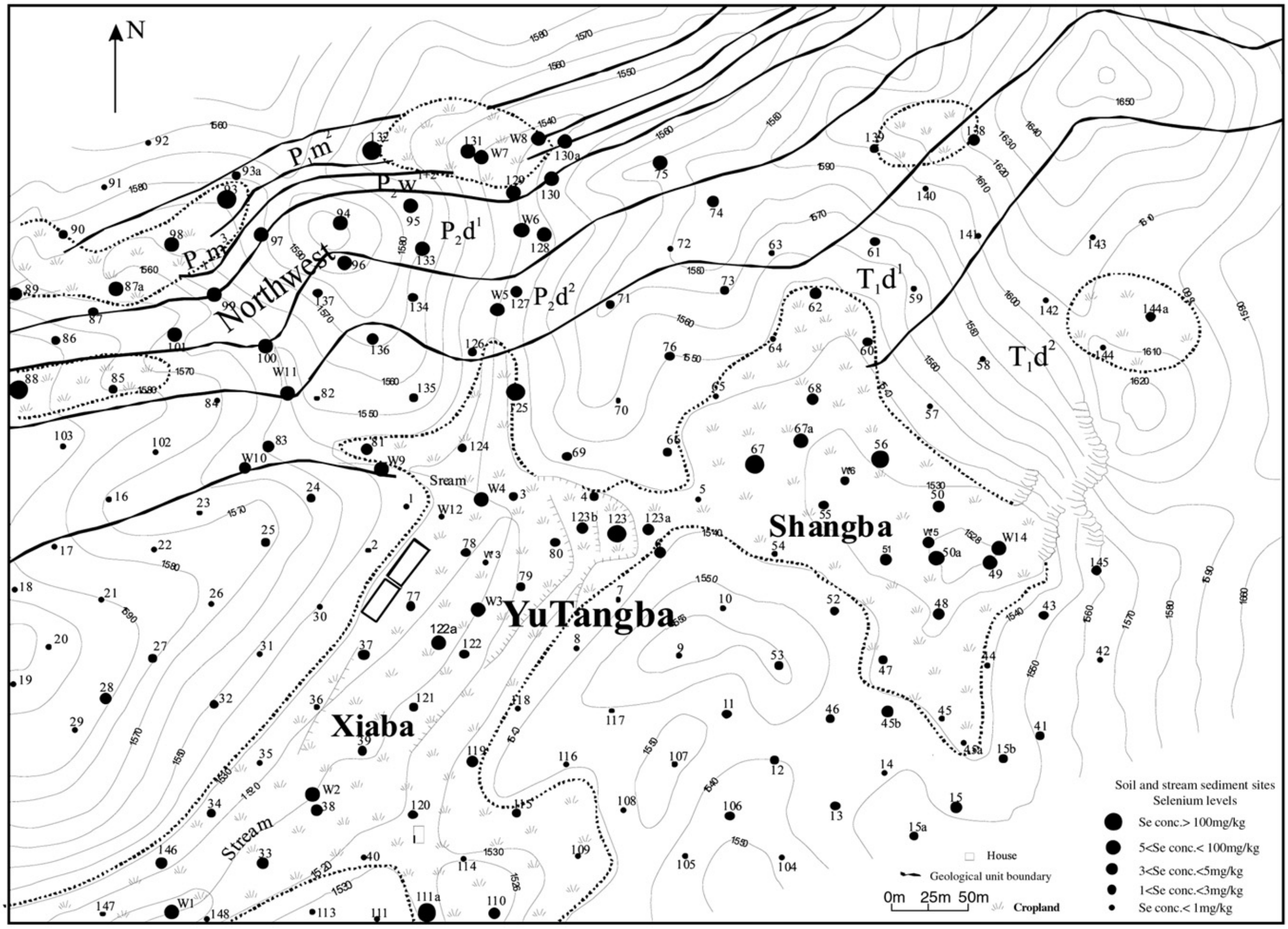

Fig. 2 – Sketch geological and topographic map of Yutangba showing locations of soil and stream sedimentary samples with selenium concentrations marked by classes.

upland ridge 210 m north of the farm building and main crop-growing area at Yutangba. The Se concentrations in the Se-rich carbonaceous rocks samples collected by Yang et al. (1981, 1983), Zheng et al. (1992) and Song (1989)were estimated to be 83,124 mg/kg, 6471 mg/kg and 8390 mg/kg, respectively. Furthermore, the different mechanism formations of native Se present in Yutangba were investigated and Se concentrations greater than 3% were found in some samples from carbonaceous mudstone (Zhu et al., 2004). These studies suggested a probable relationship between Se-rich carbonaceous rocks and Se poisoning in the local population. However, the bedrock that immediately underlies the main farm and crop-growing area at Yutangba principally comprises muddy shale (Dalong Formation P_2D^2) and a Triassic limestone (Daye Formation $T_1D^1$and T_1D^2) in which Se concentration is generally less than 0.5 mg/kg (Zheng et al., 1992, 1993; Mao et al., 1997). If the soil Se in cropland of Yutangba is derived directly from the immediate underlying bedrock, low concentrations should be expected. However, the Se content in some cropland soils in Xiaba and Shangba of Yutangba (Fig. 2) was in fact much greater than that expected according to the Se concentrations of the underlying bedrock. It was also greater than both the upper limit of 1.4 mg/kg baseline range for soil of western USA and is within the range of seleniferous areas in the world (Zheng et al., 1992). Therefore, it is necessary to understand the process of Se to be transported and the origin of high-Se in soils in Yutangba.

Fordyce et al. (2000) and Zhang et al. (1998) suggested that the localized lithological variations in high-Se villages can result in the considerable ranges of Se in various samples, and Se

Table 1 – Geological strata outcropped Yutangba area (from northwest to southeast)

Geological units	Era	Rock type
T_1d^2(Daye formation)	Triassic	Crystalline limestone and algal limestone
T_1d^1(Daye formation)	Triassic	Muddy shale and argillaceous limestone
P_2d^2(Dalong formation)	Permian	Dolostone, carbonaceous and muddy shale
P_2d^1(Dalong formation)	Permian	Calcareous siltstone, carbonaceous shale and siliceous rock
P_2w^{1+2}(Wujiaping formation)	Permian	Muddy siltstone, carbonaceous shale and siliceous rock
P_1m^3(Maokao formation)	Permian	Carbonaceous siliceous rock, carbonaceous shale and mudstone
P_1m^2(Maokao formation)	Permian	Algal limestone with flint nodule, siliceous rocks

availability to plants in the high-Se toxicity villages is controlled by the total soil Se concentration, pH, Fe oxyhydroxide and other factors such as organic matter (Fordyce et al., 1998). Furthermore, because the Se content in the villages is so variable, they proposed more detailed studies that would be required to understand more fully the relationships between the environmental (natural and man-made) controls and Se distribution (Fordyce et al., 1998). The study by Zhu and Zheng (2001) showed that micro-topographical features and leaching conditions were the primary factors affecting the Se content and distribution in soils and corn, but their work was just limited to the Shangba area of Yutangba, a small basin with 0.01 km^2, rather than the entire Yutangba area. In order to better understand the reason why Se is so variable in Yutangba, the pathways of Se transportation there, its uptake by plants and the presence of possible Se indicator plants, we conducted a comprehensive, more detailed field-screening study. Numerous samples, including soils, plants, water and stream sediments, were collected on an approximate grid-interval of 40 m that would allow the preparation of a Se concentration map identifying sites of low and high concentrations of Se in soils and plants. Furthermore, we sought to determine why Se is so variable and to evaluate the impact of the local inhabitant activities such as agricultural practices on the transport and bioavailability of Se.

2. Methodology

2.1. Sampling design

Unlike previous studies that were limited to the upper part of Yutangba (Zhu and Zheng, 2001), this study focuses on the entire Yutangba area (Fig. 2). The main crop is corn. The soils on the uncultivated hill slopes surrounding Yutangba are thin with poorly developed horizons. Thicker accumulation of soil occurs in the main cultivated basin at Yutangba but these soils also have poorly developed soil horizons as they comprise material transported from the surrounding hillsides or carbonaceous rock debris and lime introduced by farmers. The A, B, and C soil horizons can not be distinguished. Near-surface (0–30 cm) soil samples were collected on a larger area, smaller spacing. The sampling sites have a grid-like distribution with ~40 m intervals (Fig. 2). The means of collecting soil samples were similar to that described by Fordyce et al. (2000) but the distance between sub-samples was no more than 2 m apart and attention was paid to the different lithological strata units. Plant samples were also collected from the sampling sites but this depends on the grown plant species, which varied with location in Yutangba. It is difficult to collect the same plant species across the whole study area although we know that Se concentration varies from species to species and also varies in different parts of plants (Lakin, 1972; Maryland et al., 1991; Zhu et al., 2001). So, the main 4 plant species were selected. Corns (20 samples) were taken from the farms in basin, agry wormwood (*Artemisia argyi Leval. Et Vant*) leaves (29 samples) were mainly collected from Shangba (Fig. 2) and abandoned cropland, younger bracken fern (*Pteridium aguilium(L.) kuhn*; 58 samples) and central china dryoathyrium (*Dryoathyrium okaboanum(Makino) Ching*) leaves and stems (40 samples) were collected from hill slopes surrounding cropland. Several samples of other species were also collected from the hillsides, including several hupeh beautyberry (*Callicarpa gracilipes Rehd.*; 5 samples), japanese flowering fern (*Osmunda japonica thunb*; 1 sample), henry chestnut (*Castanea henryi(Skan)Rehd.et Wils*; 1 sample) leaves, and *taperleaf Camellia* (*Camellia caudata Wall*; 2 sample). Additionally, stream sediment and water samples were collected from the ephemeral stream in the center of Yutangba. Water pH was determined in-situ by pH-meter using 50 mL unfiltered water sample. Another 50 mL 0.45 μm filtered water was stored in 50 mL polypropylene corning tube after acidification on-site to pH<1 (0.01% HNO_3) by addition of 30% HNO_3. Water samples were later acidified further using concentrated HCl before Se analysis. Total samples collected were as follows: 161 soil samples, 150 plant samples, 16 stream sediment samples and 12 stream water samples.

2.2. Sample preparation

Soil and stream sediment samples, free of plant roots or detritus, were air dried in the field at ambient temperature, and then were ground in the laboratory in an agate-mortar to pass through a 120 mesh sieve (0.12 mm) and stored in air-tight plastic containers at room temperature(25 °C) for chemical analysis. Plant samples were successively washed with distilled water and deionized water, dried in an oven at approximately 40 °C and then ground into a powder (about 0.2 mm in size) in a plant sample grinder and stored at room temperature for Se analysis.

2.3. Sample analysis

All the samples were analyzed for Se by a DAN (2,3-diaminonaphthalene)-fluorescence spectrophotometry (Watkinson, 1966; Hall and Gupta, 1969; Hou et al., 1981). The detection limit was 0.002 μg/mL, the precision of the method was 3.6 CV% (n=6). The recovery of Se in international soil standards (GSS4, GSS5 and GSS6, China) ranged from 90.8% to 100.6%. Care must be taken during sample digestion with the mixture of HNO_3 and $HClO_4$, and the ratio was adjusted based on organic contents in different samples, especially for plant samples. In order to control the data quality, total Se in all soil samples and stream water were determined again by hydride generation-Atomic Fluorescence Spectrometry (HG-AFS. He et al., 2002). Briefly, soil sample was digested in concentrated HF(0.4 ml) and HNO_3(2.6 ml) in 30 ml (Teflon liner) Parr bomb (He et al., 2002; Rouxel et al., 2002). Before sealing, samples containing carbonate or organic-rich materials were left at room temperature for 2 h to degas. Sealed Parr bombs were placed in an oven heated at 150 °C for 16 h. After cooling, solution was transferred to 15 ml PFA beaker and taken to incipient dryness at 75 °C on a hot plate. The Se was transform to Se(IV) by adding 3 ml of 6 mol/L HCl and kept at 95–100 °C for 45 min. The solution was diluted to 25 ml with 0.72 mol/L HCl for final analysis. 1–3 ml filtered water sample was added 1 ml HNO_3 and then taken to incipient dryness, the other procedures were the same as above. Acceptable precision was 10% variability between duplicates when above two different methods was used.

3. Results

3.1. Distribution of selenium in soils

The concentrations of Se in most of the soil samples ranged from 0.41 to 42.3 mg/kg with an average of 4.75±7.43 mg/kg. 150 of the

161 soil samples fell within this range. The remaining 11 samples contained extremely high concentrations of Se, which were located at cropland and discarded coal spoils, ranging from 346 to 2018 mg/kg with a average of 899 ± 548 mg/kg ($n = 11$). This second group is considered separately because they stand out as outliers from the distribution of Se in the remaining soils. This suggests a different process that might lead to the extreme Se enrichment in the 11 highest samples and further study should be required. Accordingly, we suggest that the mean of the 150 lower results represents a normal range for soils in most of the field area. The geometric mean of Se concentration in these soils is 2.41 mg/kg, higher than the upper limit (1.4 mg/kg) of the expected 95% baseline range for Se in soil of the western U.S.A. (Presser et al., 1994), and is approximately 20 times greater than the average Se content (0.125 mg/kg) in Se-deficient areas (Keshan Disease and Kaschin–Beck Disease) and approximately 6 times greater than that (0.40 mg/kg) in Se-rich areas in China, respectively (Tan and Huang, 1991; Tan et al., 2002). The arithmetic mean of 4.75 ± 7.43 mg/kg of Se in soil is greater than that (3 mg/kg) in Se-excessive areas in China (Tan and Huang, 1991). However, the high coefficient of variation (156%) for Se in soil indicates that distribution of Se in soil is significantly uneven, as we observed in our previous study (Zhu and Zheng, 2001).

As shown in Fig. 2, soil samples can be further divided into three groups based on sampling sites, which were classified by cropland soil, undisturbed soil and those Se-rich soil samples mainly distributed in the higher elevation area in the northwest corner of Yutangba, where Se-rich rocks exposed. Se concentrations in soil are 3.37 ± 1.74 mg/kg (geometric mean of 2.89 mg/kg, $n = 60$), 1.14 ± 0.65 mg/kg (geometric mean of 0.98 mg/kg, $n = 60$) and 15.0 ± 11.7 mg/kg (geometric mean of 10.6 mg/kg, $n = 30$), respectively. In comparison with soil Se content reported by Fordyce et al. (2000) and Zhu et al. (2001), soil Se(15.0 ± 11.7 mg/kg) in northwest Yutangba is higher than that (9.46 mg/kg) in high-Se-toxicity (HT) villages. Se concentrations in cropland and undisturbed soils are less than those in high-Se-No-toxicity (HN) villages (7.06 mg/kg) and HT villages. The results we report here for cropland soil (3.37 ± 1.74 mg/kg) are slightly less than that of the less comprehensive previous study (4.06 ± 1.24 mg/kg; Zhu et al., 2001).

3.2. *Distribution of selenium in plants*

In the whole study area, the arithmetic mean of Se concentrations in 5 main species were (Table 2): *Corn seeds*, 1.48 ± 1.41 mg/kg (0.31 ~ 4.82 mg/kg; $n = 20$); *Agry wormwood*, 1.68 ± 1.27 mg/kg

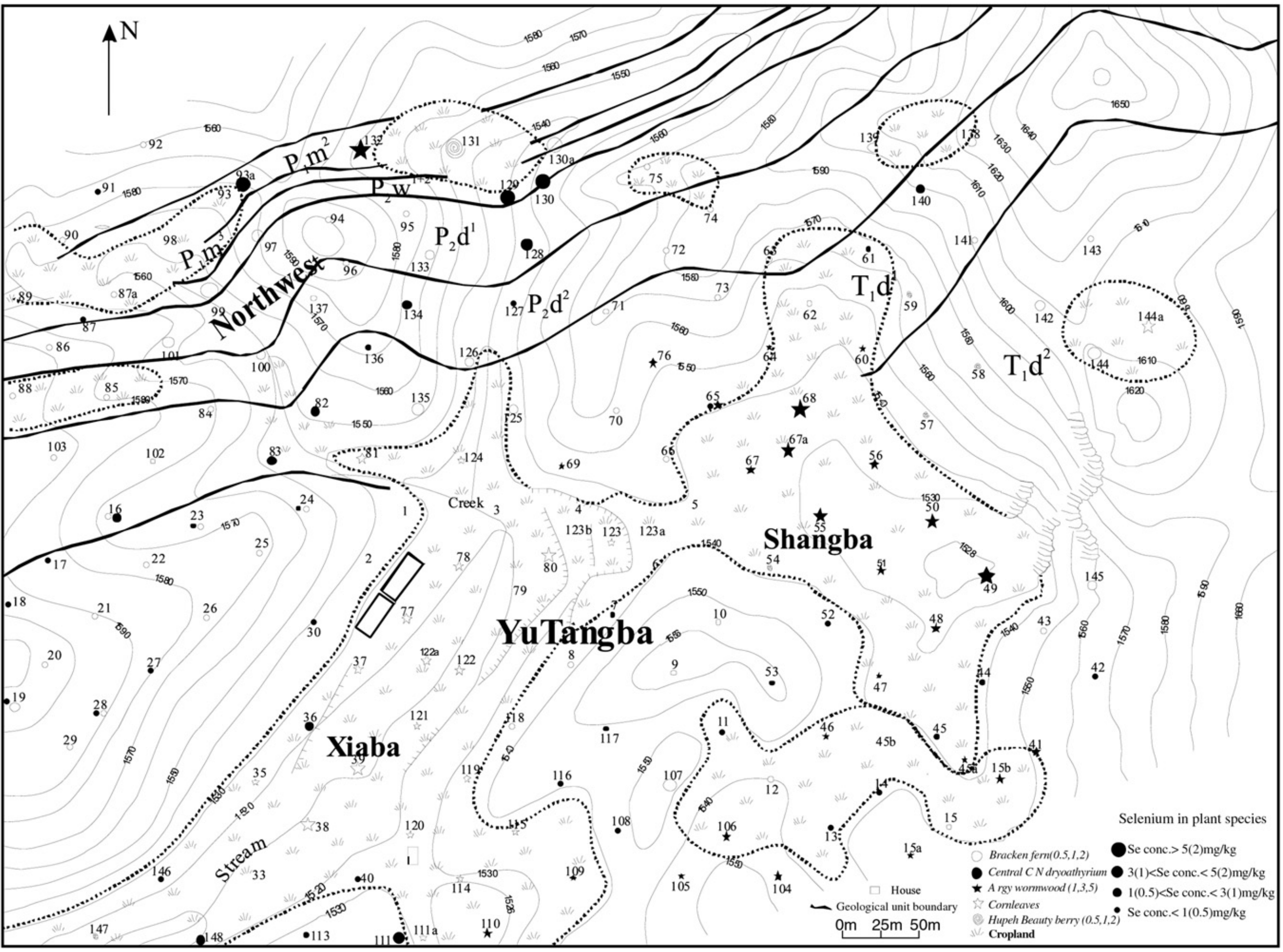

Fig. 3 – Sketch geological and topographic map of Yutangba showing locations of plant species with selenium concentrations marked by classes.

Table 2 – Summary of Se concentrations in the dominate plant species growing in Yutangba

Plant species	Min (Se mg/kg)	Max (Se mg/kg)	A (Se mg/kg)	G (Se mg/kg)	N
Hupeh beautyberry	0.14	0.23	0.18 ± 0.03	0.18	4
Agry wormwood	0.26	5.72	1.68 ± 1.27	1.39	28
Corn	0.17	4.82	1.48 ± 1.41	0.91	20
Bracken fern	0.053	11.61	0.63 ± 1.61	0.25	57
Central China dryoathyrium	0.086	3.16	0.48 ± 0.72	0.26	39
Soil, total	0.10	42.3	4.75 ± 7.43	2.41	150

N: number of samples; A: arithmetic mean; S.D.: arithmetic standard deviation. G = geometric mean.

(0.26 ~ 5.72 mg/kg; $n=30$, excluding two samples collected from the discarded coal spoil, in which Se content was 247 and 260 mg/kg, respectively); *Bracken fern*, 0.63 ± 1.61 mg/kg (0.07 ~ 11.6 mg/kg; $n=57$); and *Central China dryoathyrium*, 0.48 ± 0.72 mg/kg (0.09 ~ 3.16 mg/kg; $n=39$) and *Hupeh beautyberry*, 0.19 ± 0.03 mg/kg(0.14 ~ 0.23 mg/kg; $n=5$). No primary or secondary Se indicator plants as defined by Emerick and DeMarco's (1991) categories were found in the present study. The higher concentrations of Se in *agry wormwood* was grown in northwest and Shangba cropland areas, while the higher Se content in *Central China dryoathyrium* and *Bracken fern* are also mainly distributed in northwest and some locations of cropland in Yutangba (Fig. 3). The geometric mean of Se concentration (0.91 mg/kg) in corn growing in Yutangba cropland is slightly less than that in grain from HT (1.38 mg/kg) and almost 5 times greater than that in grain from HN (0.198 mg/kg) (Fordyce et al., 2000), and is 31 and 36 times greater than that in average corn from China (0.029 mg/kg, $n=726$) (Su, 1985) and Se-sufficient areas of China (0.025 ± 0.016 mg/kg, $n=14$)(Tan and Huang 1991), respectively. But it is lower than the values (3.85 mg/kg, $n=130$) reported by Zhu et al. (2001).

The spatial distribution of Se in these plant species is also significantly uneven. For example, in corn growing in soil near the riverbank (stream) in the center of Xiaba of Yutangba, the Se concentration is significantly higher than that in soil far away from the stream (Fig. 3). The Se concentration in agry wormwood growing in abandoned stone coal spoils was more than 200 mg/kg, which is significantly greater than that in other locations.

3.3. *Distribution of selenium in stream water and sediment*

Previous studies documented that SO_4^{2-} and HCO_3^- anions were prevalent in spring water in Enshi Prefecture (Fordyce et al., 2000) and were thought to be associated with the sulphide-rich carbonaceous shales and limestone of the HN and HT villages. In Yutangba stream water, the present study showed that HCO_3^- is the dominant anion, and pH similar to the value reported by Fordyce et al. (2000) and Zhang et al. (1998) vary from 6.2 to 6.6 between the upper and lower reaches of the stream. The average of Selenium concentrations in stream water is 58.4 ± 16.8 μg/L ($n=12$) with a range from 40.0 μg/L to 94.1 μg/L, which is greater than that in HT, 330 times greater than that in LK (Fordyce et al., 2000), and approximately 6 times greater than the drinking-water maximum concentration of 10 μg/L recommended by the World Health organization (WHO) and US Environmental Protection Agency (Presser, 1994). Higher Se concentrations in stream water are found at locations where stone coal outcrops and when the water flows through the abandoned stone coal spoils. The content of Se in water is higher in the upper reach of the stream than the low reaches.

Channel bed sediment in the stream is comprised mostly of debris from the carbonaceous rocks. The concentrations of Se in stream sediment range from 8.28 to 82.9 mg/kg with an average of 26.6 ± 26.8 mg/kg ($n=11$), which is greater than Se (3.5–7.1 mg/kg) in the bottom sediment from US Department of the Interior Reconnaissance Areas and approximately 19 times greater than the upper limit (1.4 mg/kg) of the expected 95% baseline range for Se in soils of the western United States (Presser, 1994; Presser et al., 1994). Selenium in stream sediment from upper to lower reaches of the stream is relatively uneven, reflecting the variable Se levels in those areas where the different rocks exposed.

4. Discussion

4.1. *Transport of selenium*

Yutangba lies in the middle part of the Shuanghe syncline. The arrangement of rock units has created a long, narrow, almost closed valley surrounded by hills, with elevation decreasing toward the central area from both northwest and southeast (Fig. 2). These geomorphic features make Yutangba situated in an almost closed natural environment and have given Yutangba a geochemical landscape high in Se, which has been demonstrated by many previous studies (Yang et al., 1981, 1983; Mao et al., 1990; Zheng et al., 1992, 1993; Mao and Su, 1993; Mao et al., 1997; Zhang et al., 1998; Fordyce et al., 2000; Zhu et al., 2001). The Se-rich carbonaceous rocks of the Permian Maokou and Wujiaping Formation were regarded as the source of Se for soils and plants in Yutangba. However, the pathways of Se transport into Yutangba have not been investigated in detail.

As shown in Fig. 2, high-Se soil is principally distributed in northwest and croplands of Yutangba whereas soil Se concentration in undisturbed sites is relatively low with a geometric mean of 0.98 mg/kg. The Se-rich strata strike NEE and dip ESS with an approximately dip angle of 55° (Fig. 4), and underlie the northern and northwestern areas of the field area. In this area, extremely high-Se deposits were found near the water table (Song, 1989; Wang and Li, 1996), and the mean Se concentration reaches 1251 ± 1219 mg/kg ($n=23$) with a maximum of greater than 3% (Zhu et al., 2004). Selenium can be transported naturally in the forms of groundwater, surface runoff, stream sediment transport, and rock debris movement. It can also be transported anthropogenically during activities such as mining and redistribution by local villagers (Naftz and Rice, 1989). In the case of Se

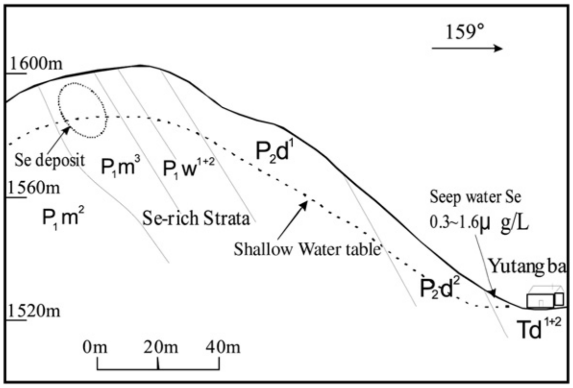

Fig. 4 – The map of geological cross section from Se-rich strata to the center of Yutangba.

in groundwater, although geomorphic characteristics facilitate the mobility of Se (Fig. 4), selenium in seep water collected from limestone at the foot of the hill is lower with ranges of 0.30–1.60 μg/L, indicating that the overlying muddy shale, mudstone and limestone of Dalong and Daye formations are a natural barrier to transport of Se in that direction. Therefore, small streams are the main natural pathway for Se from the Se-rich rocks in northwest Yutangba into the basin area. This is because the stream sediments consist mostly of Se-rich rocks debris in which Se concentration is still high with an average of 26.6± 26.8 mg/kg. However, the alluvium at the mouth of the stream valley covers only a small area, which is limited to the foot of the hill, so it is unlikely that this naturally transported material is the only source of Se in the basin.

The Se-rich carbonaceous rocks, known as stone coal locally, are very convenient for the local villagers to use as fuel for making lime. They also baked soil over stone coal fires or ground stone coal into powder as a fertilizer. Presently, many mined pits, spoils and waste residues up to several tens of meters high are found near the Se-rich carbonaceous strata. Additionally, villagers also discharged lime onto cropland to improve the soil during land clearing for agriculture or cultivation (Yang et al., 1983). The Se-rich carbonaceous rocks contain elemental Se (Zhu et al., 2004), and selenium associated with organic matter and selenium in sulfide/selenide minerals are the predominant Se forms (Zhu et al., 2006) During initial exposure of the Se-rich rocks, more rapid oxidation rates of elemental Se will occur followed by slower oxidation over a long time (Masscheleyn et al., 1990; Tokunaga et al., 1991; Huggins and Huffman, 1996; Séby et al., 2001; Zawislanski and Zavarin, 1996; Zawislanski et al., 2003), and organic-bounded and sulfide/selenide Se can also be oxidized. The added lime would increase the pH of soil facilitating the oxidation of reduced-type Se to selenate (Weres et al., 1989; Jayaweera and James, 1996). Local villagers did not realize that these processes can release a large amount of soluble Se into soil and supply much Se to their crop. At present, the past Se-mobilizing agricultural methods have ceased, but the incompletely weathered residue of lime mixed with stone coal debris or powder can still be found in soil vertical-sections in crop fields. These probably still act as a source of Se.

With the exception of northwest Yutangba where Se-rich carbonaceous strata are exposed, transport of Se in Yutangba is principally by means of the stream and anthropogenic transport. The latter appears to be the more important pathway because the 11 extremely Se-rich soil samples were found in different croplands of Yutangba, although these Se-rich soil samples should be conducted for further study.

4.2. *Trends in Se levels*

Despite the severity of human Se poisoning in the early 1960s in Enshi Prefecture, and concern over continued potential for Se poisoning, researchers in China have not selected a special site to monitor trends in Se levels over the long-term. Although comparisons of data from different studies using different analytical methods should be treated with caution, we compare the values obtained today to results reported over the last 40 years for Se in Yutangba. As shown in Table 3, Selenium concentrations in soil were almost unchanged over the past 40 years, and so was water Se. However, Se concentrations in corn have decreased gradually based on the sampling year (Table 3), even in such locations where the highest soil Se content was found and where the maximum Se in corn was collected (Zhu and Zheng, 2001). Nowadays it is impossible to find such corn samples that have Se of 44 mg/kg as reported by Yang et al. (1981), and it is also very uncommon to collect corn samples as high as the 16.9 mg/kg maximum found in 2001 (Zhu and Zheng, 2001). This indicates that Se availability to plants in Yutanba is gradually decreasing.

As the previous studies have shown, Se concentration in soil is not uniformly distributed in Yutangba (Fordyce et al., 2000; Zhu and Zheng, 2001). It was suggested that the microtopographic features and localized lithological variations in high-Se villages result in the considerable ranges in Se

Table 3 – The variation of Se in soil, corn and water in the past more than 30 years

Authors	Se in Soil (mg/kg)		Se in Corn (mg/kg)		Se in stream water (μg/L)		Sampling time (year)
	N	A (±S.D.)	N	A (±S.D.)	N	A (±S.D.)	
Mao et al. (1997)		6.83		33.47			1963
Yang et al. (1981)	6	7.86±0.69	5	14.6	4	139	1966
Mao et al. (1997)	4	3.45±1.53	4	14.07±7.26			1987
Zheng et al. (1993)	9	5.48±6.41					1989
Zhu et al. (2001)	28	4.06±1.24	130	6.47±4.29			1992
Fordyce et al. (1998)	5	4.99±2.38	5	3.24±1.54	1	40.4	1996
This Study	150	4.75±7.43	20	1.48±1.41	12	58.4±16.8	1999

N: number of samples; A: arithmetic mean; S.D.: arithmetic standard deviation. G = geometric mean.

concentration (Fordyce et al., 2000; Zhu and Zheng, 2001). However, anthropogenic factors were not examined in detail in these studies. Since 1964, local villagers have not used stone coal debris or powder as a fertilizer distributed over cropland in Yutangba, nor have they used lime. At the same time, selenium in soil should have undergone a natural process of depletion over the past 40 years owing to the loss of Se volatilization (Flury et al., 1997), but soil Se levels remain almost the same as before, indicating that the stone coal residues or powder added by local villagers into cropland have become the main source of Se in soil and kept it unchanged due to soluble Se released.

The Se content in stream water has decreased to 58.41± 16.82 μg/L from the initial 139 μg/L in 40 years ago, and has not changed greatly in recent years (Table 3). This data confirms our hypothesis that the strong Se releases observed in the past were dependent on human activities. Places where no villagers have disturbed the ground at the upper reaches of the stream, now release much less Se. The exposed Se-rich rocks and rock debris in stream sediment have become a stable Se source for the stream water. Because Se in seep water from limestone or mudstone (T_1d^1) is very low (0.30–1.60 μg/L), it cannot lead to the strong variation of Se content in the stream water. Higher Se concentration in water can be collected from certain restricted areas such as those near abandoned stone coal spoils. When the stream goes through them, water Se concentrations averaged 94 μg/L, approximately 1.6 times the average value (58.41 μg/L) of Se in all stream water samples. Even higher water Se concentrations can be found in certain samples collected in these places. Generally, the stream water has always been used as irrigation for cropland in Xiaba of Yutangba, and although the water Se concentration is much less than that in Se-rich rocks and soil, it is probably a source of Se in corn when they grow in these sites such as No. 38 and No. 39 near the riverbank (Fig. 3). Thus, Se in water would undoubtedly contribute to the uptake of Se by plants, indicating that the distribution of Se is related to the pathways of Se transportation.

The results for plant species are in agreement with the previous studies showing that Se uptake is related to plant species (Emerick and DeMarco, 1991; Maryland et al., 1991). Among samples taken at individual locations, selenium concentrations vary with the different plant species, although it is also dependent on the Se speciation, soil pH, Eh, organic matter and Se concentration (Johnsson, 1991; Arvy, 1992; Fordyce et al., 2000). Besides *corn* and *agry wormwood*, past data from other plant species are not available for comparison. Selenium in *agry wormwood* was 4.56 mg/kg in 1987 (Mao et al., 1997), whereas it is 1.68± 1.27 mg/kg in our study, obviously less than the Se level 19 years ago. This confirmed that both Se level in *corn* and *agry wormwood* are greatly decreased over the past 40 years. Similar results should also exist in other plant species. The relationship between soil Se, both total and extractable, and plant Se is generally strong, and there also has positive correlation between Se concentration in soil and that in corn (Zhu and Zheng, 2001). Thus, the comparison of current Se concentrations in plants with those of the 1960s, indicates that bioavailable Se in soil is becoming lower over time.

4.3. *Impact of human activities on selenium*

Many researchers have suggested that human Se poisoning occurred in Yutangba resulted from both anthropogenic (tree felling, mining coal, and burning coal) and natural factors (weathering and leaching of stone coal) (Mao et al., 1990, 1997; Zheng et al., 1992; Mao and Su, 1993), but the extent of human activities was not well characterized. As shown in Fig. 2, the soil samples with higher Se concentration were mainly distributed in northwest part and cropland of Yutangba, where the soils were heavily disturbed by human activities, while soil Se in undisturbed places was relatively low. In particular, the 11 extremely Se-rich soil samples (346 to 2018 mg/kg) discussed above as outliers within the total of 161 samples were collected at sites far away from the riverbank (Fig. 2). Besides soil samples No.93 and No.132, which were taken from cropland near the exposed Se-rich rock or abandoned stone coal spoils, the remaining 9 samples were located in croplands where the underlying bedrock units are muddy shale or limestone in which Se is in general less than 0.5 mg/kg. This means more Se was introduced into croplands by human activities such as dispersal of baked soil or use of stone coal powder as a fertilizer. Thus, human activities were the main cause of high Se in cropland soil, and also are one of the probable reasons for the highly variable Se concentrations in soil.

Among 150 plant samples, almost all high-Se plant samples (>5 mg/kg) were taken from abandoned stone coal spoils, mining sites of Se-rich stone coal and cultivated areas in Yutangba (Fig. 4). Higher values were found especially in some new reclaimed soil near abandoned stone coal spoils, where Se concentrations in a *konjac* and *agry wormwood* samples were up to more than 460 mg/kg (wet weight) and 260 mg/kg (dry weight), respectively. This latter Se content is approximately 155 times greater than the average value (1.68±1.27 mg/kg) of Se in *agry wormwood* across the whole area. Among the *Bracken fern* or *Central China dryoathyrium samples*, those with higher Se concentration are also distributed in cultivated sites or cropland near abandoned stone coal spoils and mining sites such as No.93a and 130a (Fig. 4). Based on the similar distribution features of Se in different plant species, we can infer that Se content in plants growing in human-disturbed land is generally greater than that in undisturbed land. This demonstrates that human activities such as tillage can affect the transformation of Se and its availability to plants. Thus, during human activities such as land clearing for agriculture, tillage and reclamation, large amounts of Se will be introduced into the soil, resulting in the further accumulation of Se in food chains to some extent.

In recent years, with increasing economic development and fuel/fertilizer needs, some local habitants have begun privately to mine stone coal again as a fuel to make lime and also as a fertilizer to improve cropland. Some of them even burn vegetation to clear land for agriculture. Once the mined Se-rich stone coal is exposed to the air or freely spread around, and abandoned stone coal spoils are again reclaimed for cropland, the original environmental equilibrium for Se-rich carbonaceous rocks is disprupted and large amounts of bioavailable Se could be released. The Se concentration of 460 mg/kg (wet weight) in a *konjac* sample collected from reclaimed soil near Se-rich stone coal has shown bioavailable Se was released and was assimilated by plants. So, although the existence of Se-rich stone coal strata is a necessary condition for incidence of Se poisoning, human activities such as certain crop cultivating methods, and mining of stone coal as a fuel or fertilizer provide the conditions for the transport and transformation of Se, along with increases in its availability to plants. As bioavailable Se is formed under suitable environmental conditions, Yutangba is still a high risk area where Se poisoning will occur again.

5. Conclusions

Since local residents in Yutangba were forced to evacuate their home 40 years ago, selenium concentration in soil remains unchanged substantially. The geometric mean of Se in soil is not extremely high, at 2.89 mg/kg. This is 2 times greater than the United States Geological Survey upper limit (1.4 mg/kg) of the expected 95% baseline range for soil of the western USA. But the distribution of Se in soil is highly uneven. The high-Se soil is mainly distributed in the northwest and cropland of Yutangba. Soil Se in northwest, cropland (disturbed areas) and undisturbed areas decreases in the order: northwest (15.0±11.7 mg/kg) >croplands(3.37±1.74 mg/kg)> undisturbed areas (1.14±0.65 mg/kg). High-Se plants also occur in the abandoned Se-rich stone coal spoils, mining sites of stone coal and crop cultivation sites such as in Shangba, Xiaba and the northwest areas, which were heavily disturbed by human activities. Unlike the stable Se concentrations in soils over the past years, the concentrations of Se in corn seeds have been decreasing, indicating that bioavailable Se in soil is decreasing. Selenium content in stream water has decreased in comparison with that 40 years ago, but is almost unchanged over past 10 years. This observation shows that a dynamic equilibrium between water and Se-rich rocks has been reached, and the latter provide a stable source for Se in the streams. It also confirmed our observation that no human disturbance or mining activities occurred near the upper reaches of the stream.

The distribution of Se in Yutangba, besides the localized lithological variations and micro-topographical features, is also related to the pathways of Se transport. The exposure of Se-rich carbonaceous strata in northwest Yutangba is necessary, but not sufficient condition for high-Se area of Yutangba to be developed. Human activities, such as stone coal transport by local villagers, mining of stone coal as a fuel or fertilizer, dispersal of stone coal baked fertilizer and discharge of lime into cropland to improve soil, were the main reason for Se deposition in cropland soil, and also are a probable reason for the observed extreme variability in Se concentrations in some cropland soils. Human activities played an important role in the distribution and transportation of Se and its bioavailability in Yutangba.

With the economical development and increased fuel and fertilizer needs in recent years, some local inhabitants have begun covertly to mine stone coal again. There is potential that more water-soluble Se could be produced and released into the surrounding soil under the suitable environmental conditions. If the local government cannot hold a prudent attitude to utilize Se resources and rationally manage the mining of Se-rich stone coal strata and abandoned stone coal spoils, Yutangba is still a high risk area where Se poisoning may occur again. This conclusion also applies to all high-Se areas in Enshi Prefecture.

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