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The bioavailability of selenium and risk assessment for human selenium poisoning in high-Se areas, China

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ABSTRACT

Enshi prefecture of Hubei Province is well known for human selenium (Se) poisoning in the early 1960s in China. Sporadic cases of Se poisoning in livestocks are still being found. In this study, Se levels in water, cropland soils and various crops from high-Se areas of Enshi were measured to investigate the distribution and bioavailability of Se in the environments, as well as probable daily intake (PDI) of Se for local residents. The total Se in surface water ranged from 2.0 to 519.3 μg/L with a geometric mean of 46.0 ± 127.8 μg/L ($n = 48$), 70.5–99.5% of which was present in the form of Se(VI). The soil Se concentration varied from 2.89 to 87.3 μg/g with a geometric mean of 9.36 ± 18.6 μg/g ($n = 45$), and most of Se was associated with organic matter (OM-Se). The total Se in rice, corn, and vegetable samples were 2.11 ± 2.87 μg/g ($n = 21$), 3.76 ± 11.6 μg/g ($n = 16$), and 2.09 ± 3.38 μg/g ($n = 25$), respectively. Stream water Se is likely leached from carbonaceous shale and mine wastes, leading to Se accumulation in paddy soils. OM-Se may play an important role in Se uptake by rice plant in high-Se area of Enshi.

The PDI of Se is approximately 2144 μg/day, and Se concentration in blood is estimated at about 3248 μg/L, posing a potential chronic Se poisoning risk to local residents. Cereal consumption (48.5%) makes a great contribution to human daily Se intake, followed by vegetables (36.6%), meats (8.5%), and drinking water (6.4%). However, when assessing health risk on human in high-Se areas, the contribution of drinking water to daily Se intake cannot be ignored due to high Se content and dominant Se(VI) species. Local inhabitants should be advised not to grow crops in high-Se lands or irrigate using high-Se water. If possible, they should drink pipe water and consume foods mixed with those from outside the high-Se areas.

1. Introduction

Selenium (Se) is of great concern because of its narrow range between dietary essentiality and toxicity for human beings. The recommended dietary allowance (RDA) of Se for an adult human is 55 μg/day based on the maximization of glutathione (GSH-Px) enzyme activity (U.S. IOM, 2000), whereas the upper tolerable nutrient level (UL) for adult is set at 400 μg/day (U.S. IOM, 2000; WHO and FAO, 2004). Insufficient intake of Se in humans has been proven to be linked to “Keshan disease” and “White muscle disease” (Fordyce, 2005; Wang and Gao, 2001). However, excessive Se intake could result in adverse health problems, including symptoms such as loss of hair and nails, skin lesions, and nervous system disorders, even paralysis and death (Bajaj et al., 2011; Fordyce, 2005; Hira et al., 2004; Lemire et al., 2012; Yang et al., 1983; Zheng et al., 1999). Recent studies suggested that increased Se intake might increase the risk of adverse type-2 diabetes and cardiovascular disease (Stranges et al., 2010, 2011). Additionally, Se can moderate mercury (Hg) toxicity in plant, fish, human and other organisms in fairly complicated ways, which have been observed both in numerous laboratory and field studies (Nascimento Pinheiro et al., 2009; Sørmo et al., 2011; Yang et al., 2008; Zhang et al., 2012). As a consequence, Se has attracted considerable attentions from a toxicological point of view.

Selenium status in general population is highly dependent on diet, which is the primary exposure pathway to Se (CCME, 2009). Previous studies have assessed Se status for inhabitants living in UK (Barclay et al., 1995), Suzhou of China (Gao et al., 2011), Korea (Choi et al., 2009), rural coastal community in Japan (Miyazaki et al., 2002), West Greenland (Hansen et al., 2004), USA (Longnecker et al., 1991), high and low-Se areas of Punjab, India (Hira et al., 2004) by estimating daily dietary Se intake, whose values are 34, 43.9, 57.5, 127.5, 235, 68–724, 52–65 and 475–632 μg/day, respectively. Obviously, a large variation in daily Se intake is observed in different geographical areas. This diversity of daily Se intake is mainly attributed to various eating habit, as well as Se content in consumed foods including crops, meats and fishes (CCME, 2009; Fordyce, 2005; Rayman, 2008; WHO and FAO, 2004). It is suggested that Se concentrations in crops

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and forages could be strongly controlled by bioavailable Se level in soils where they are grown (Fordyce, 2005; Frankanberger and Benson, 1994; Zhao et al., 2005). Water-soluble and exchangeable Se is generally considered to be directly taken up by plants (Chao and Sanzolone, 1989; Kulp and Pratt, 2004; Sharmasarkar and Vance, 1995), while part of Se associated with organic matter (OM-Se) could also act as the potential source for bioavailable Se (Abrams and Burau, 1989; Qin et al., 2012; Wang et al., 2012). Therefore, Se speciation in soils is of great importance to assess Se content in crops and human Se status.

Enshi prefecture of Hubei province is well-known for the outbreak of human Se poisoning in the early 1960s. In this area, there are approximately 477 cases of human selenosis over the past several decades, and sporadic cases of Se intoxication for local residents are still reported in recent years (Mao and Su, 1993; Zhu and Zheng, 2001; Zhu et al., 2008). A number of studies have been carried out in Enshi prefecture to investigate Se distribution and corresponding environmental effects. Yang et al. (1983) and Zheng et al. (1992) demonstrated that Se-rich carbonaceous rock (locally known as stone coal) is responsible for high-Se content in soils, crops, water and thus human Se poisoning. Fordyce et al. (2000) suggested that localized lithological variation lead to wide ranges of Se concentration in various samples in the high-Se villages. Zhu and coworkers (Zhu and Zheng, 2001; Zhu et al., 2008) studied the distribution and transport of Se in Yutangba of Enshi in detail, and emphasized on the roles of micro-topographic features and human activities. However, these studies didn't pay much attention to Se in water and corresponding impact on local soils and crops, as well as resident's health in high-Se areas of Enshi prefecture. Additionally, recent studies demonstrated that irrigation water with high Se content could result in remarkable Se accumulation in soils and crops in North-West India (Bajaj et al., 2011; Dhillon and Dhillon, 2003). In this study, we analyzed total Se content and Se speciation in water and soils, and measured Se level in foods from high-Se areas of Enshi for the following purposes: 1) investigate the sources of Se in water and their impact to Se accumulation in soils; 2) evaluate Se bioavailability in soils; and 3) estimate probable daily intake (PDI) of Se and assess potential health risk of Se poisoning for local residents.

2. Materials and methods

2.1. Study area

Enshi prefecture is in the southwestern of Hubei Province, and has a sub-tropical, humid climate characterized by abundant rainfall and mild temperatures. The annual mean precipitation is about 1600 mm, and the annual mean temperature is 16 °C.

Previous epidemiological investigations have identified the areas of low-Se with Keshan Disease, high-Se without selenosis and high-Se with selenosis in Enshi prefecture (Fordyce et al., 2000). The high-Se areas are mainly located in Enshi City, and Jianshi County, where population is estimated to be 750, 000 and 410,000, respectively. Three high-Se areas, Anlejing (ALJ), Huabei (HB), and Yutangba (YTB) (Fig. 1), were selected to investigate Se speciation, bioavailability and human Se status. In these villages, most of the young people go out to do labor work in cities; the remaining residents mainly live on rice, corn and vegetables grown locally by themselves. The drinking water for local inhabitants is from the wellsprings and streams, which are also used as irrigation water for crops due to absence of large local reservoirs.

2.2. Sample collection and preparation

A total of 48 water samples were collected from wellsprings and streams in ALJ ($n = 18$), YTB ($n = 23$), and HB ($n = 7$) villages in August 2010 and August 2011. Water samples were filtered in situ through a 0.45 μm filter, and then were preserved in the cooler (4 °C). Total Se concentration and Se speciation in water were measured within 7 days to avoid Se loss and speciation transformation.

Twenty-one, fifteen, and nine soil (0–30 cm) samples were collected from ALJ, YTB, and HB village during above sampling period, which include 16 paddy and 29 upland soil samples. The distance between sampling site and stream, and soils with or without irrigation was considered to evaluate the impact of water to Se accumulation in soils. Freeze-dried soil samples were ground in an agate mortar, passed through a 150-mesh sieve, and stored in air-tight plastic containers for chemical analysis.

The main crop plants including rice (*Oryza sativa* L., $n = 21$) and corn (*Zea mays* L., $n = 16$) were collected from the fields in three villages. We also collected 25 vegetable samples, including potato (*Solanum tuberosum* L., $n = 6$), radish leaves (*Raphanus sativus* L., $n = 6$), Chinese cabbage (*B. campestris* L., $n = 6$), carrot (*Daucus carota* L., $n = 4$), and kidney bean (*Phaseolus vulgaris* L., $n = 3$) in our study areas. The meat samples ($n = 3$) were obtained from local markets. Seven whole rice plants and corresponding soils were collected to investigate Se distribution in different parts of rice plant (root, straw, leaf, grain and hull) and the relationship with Se in paddy soil. All rice and corn samples were washed with deionized water and then freeze-dried. Rice grain samples were firstly dehulled to separate hull and wholegrain (brown rice) using a pestle and mortar, and then parts of wholegrain samples were polished to get bran and polished rice (white rice), following methods described in Sun et al. (2010). All cereal plant samples were crushed and ground by a grinder that was cleaned using quartz sand and ethanol after each sample to avoid cross-contamination. All vegetable and meat samples were only washed by deionized water since Se concentrations were obtained based on their wet weight.

2.3. Analytical methods

For total Se analysis, water samples were digested in PFA beaker using a mixture of concentrated HNO_3 and H_2O_2 (30%) on a hot plate; soil samples were decomposed in a Parr bomb with the mixture of concentrated HNO_3 and HF in an oven at 150 °C for 16 h, while plant and meat samples were digested with concentrated HNO_3 at 150 °C for 6 h. The total Se concentration was determined using hydride generation atomic fluorescence spectrometry (HG-AFS) after Se was reduced to Se(IV) by 5 M HCl following the methods described in our previous studies (Qin et al., 2012; Zhu et al., 2008).

The methods for Se speciation proposed by Kulp and Pratt (2004) were partly modified to quantify Se speciation in water samples. Briefly, Se(IV) concentration was directly measured by HG-AFS, Se(VI) content was calculated as the difference between that of Se(IV) and the sum of Se(IV) and Se(VI), which was determined after reducing Se(VI) to Se(IV) with 5 M HCl (95–100 °C). The organic Se (Org-Se) content was estimated as the difference between the sum of Se(IV) and Se(VI) and the total amount of Se in water.

For Se fractions in soil samples, the methods described in previous researches (Kulp and Pratt, 2004; Qin et al., 2012) are followed. Briefly, Milli-Q water, 0.1 M KH_2PO_4-K_2HPO_4 (P-buffer, pH = 7.0), and 0.1 M NaOH were used to sequentially extract water-soluble, ligand-exchangeable Se, and OM-Se in soils, respectively. Selenium concentration in each extract was digested and measured using HG-AFS method (Qin et al., 2012).

2.4. PDI calculation of Se

On the basis of consumed amount and Se concentration of food and drinking water, the PDI of Se was calculated for the general adult population according to the following equation:

$$PDI = \sum \left(C_{Se}^{i} \times IR \right) \qquad (1)$$

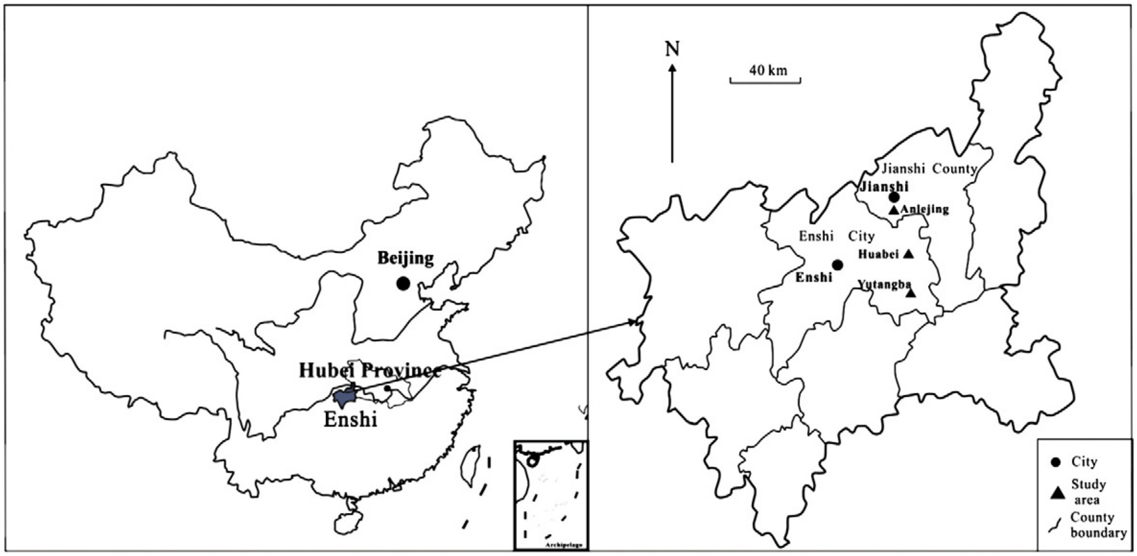

Fig. 1. The study areas in Enshi prefecture, Hubei Province, China.

where PDI is the probable daily intake of Se for a human; i is the kind of exposed medium, including drinking water, rice, corn, vegetable, and meat, etc.; C and IR are Se concentration and intake rate for each medium, respectively.

Sun et al. (1995) reported that atmospheric Se level in one selenosis area of Enshi was 39.5 ng/m^3. If local population inhales 20 m^3/day (WHO, 1986), the daily intake of Se through inhalation route was calculated to be 0.79 µg/day, which should be much lower at present due to less burning of high-Se coal (Liu et al., 2007; Zheng et al., 1999). Additionally, cooking oil, salt, milk and fruit usually come from the outside, and thus have low Se concentration and little consumption (Gao et al., 2011). Hence, we didn't consider Se intake through inhalation, oil, milk, and fruit in the PDI calculation for residents in high-Se areas of Enshi because of their very low contributions.

The intake rates of different food for the adult populations were based on the Hubei Statistical Yearbook edited by BHS (2010), and water consumption of 3 L was used according to the previous studies (Fordyce et al., 1998; Yang et al., 1989). The daily diet of the local inhabitants is comprised mainly of rice, corn and vegetables grown on their own land, while meat is rarely consumed and usually bought from markets.

2.5. Quality control

Quality control of Se analysis was assessed using duplicates, method blanks, matrix spikes and certified reference materials. The measured Se values in soil standard GBW07405 and GBW07406 were 1.63 ± 0.09 µg/g ($n = 11$) and 1.32 ± 0.18 µg/g ($n = 5$), which are consistent with the certified values of 1.60 ± 0.20 µg/g and 1.34 ± 0.17 µg/g. The average Se concentrations in standard GBW07602 (plant leaf) and GBW10010 (rice grain) were determined to be 0.185 ± 0.01 µg/g ($n = 11$) and 0.062 ± 0.02 µg/g ($n = 5$), which are comparable to certified concentration of 0.184 ± 0.01 µg/g and 0.061 ± 0.015 µg/g. The relative standard deviation for analysis of duplicate sample was less than 8%.

3. Results

3.1. Selenium in water

The total Se concentration in surface water samples collected from wellsprings and streams in three high-Se areas of Enshi widely varied from 2.0 to 519.3 µg/L, with a geometric mean of 46.0 ± 127.8 µg/L ($n = 48$) (Table 1). Elevated Se was observed in water from ALJ (geometric mean: 69.8 ± 168 µg/L, $n = 18$) comparing to YTB (geometric mean: 51.1 ± 35.0 µg/L, $n = 23$) and HB village (geometric mean: 11.2 ± 9.8 µg/L, $n = 7$). Similarly spatial distribution pattern for Se was found in all streams, higher Se content was generally observed in the upper reach of stream, and markedly elevated Se concentration was found at sites where water flows through the abandoned stone coal dumps (Fig. 2).

Se(VI) was the predominant Se species, accounting for 70.5 to 99.5% of total Se in water from three villages. Higher ratio of Se(VI) to total Se was usually observed in water with higher Se content. The percentage of Org-Se, and Se(IV) varied from 0.39 to 27.6%, and 0.03 to 23.5%, respectively.

3.2. Selenium in soil

The geometric mean of Se concentrations in soil samples was 9.36 ± 18.6 µg/g ($n = 45$), ranging from 2.89 to 87.3 µg/g (Table 1). The distribution of Se in soils is significantly uneven, and elevated Se content was observed in soils near the stream or with irrigation of high-Se water.

Table 2 shows the Se fractions in paddy (P-1 to P-7) and upland (U-3) soils. For paddy soils except sample P-7, water-soluble and ligand-exchangeable Se accounted for 1.58–5.62% (with a mean of 3.08%) and 4.22–10.4% (with a mean of 7.25%) of the total Se content, respectively. Most of Se is present as OM-Se fraction, accounting for 55.7–69.6% (with a mean of 62.2%) of total Se in paddy soils. The unextractable Se fraction, including Se associated with silicates, elemental Se, selenides, and others, was a relatively small part (19.9–36.6%, with a mean of 28.4%). In contrast, relatively lower

Table 1
Selenium concentration in the main exposure media in high-Se areas of Enshi.

Medium	Min	Max	Mean	SD	N	Distribution pattern
Water (µg/L)	2.00	519.3	46.0[a]	127.8	48	Log-normal
Polished rice (µg/g, DW)	0.16	10.2	2.11[a]	2.87	21	Log-normal
Corn (µg/g, DW)	0.39	37.2	3.76[a]	11.6	16	Log-normal
Vegetable (µg/g, WW)	0.25	13.0	2.09[a]	3.38	24	Log-normal
Meat (µg/g, WW)	1.20	4.80	2.90	1.81	3	

[a] Geometric mean; SD, standard deviation; N, number; DW, dry weight; WW, wet weight.

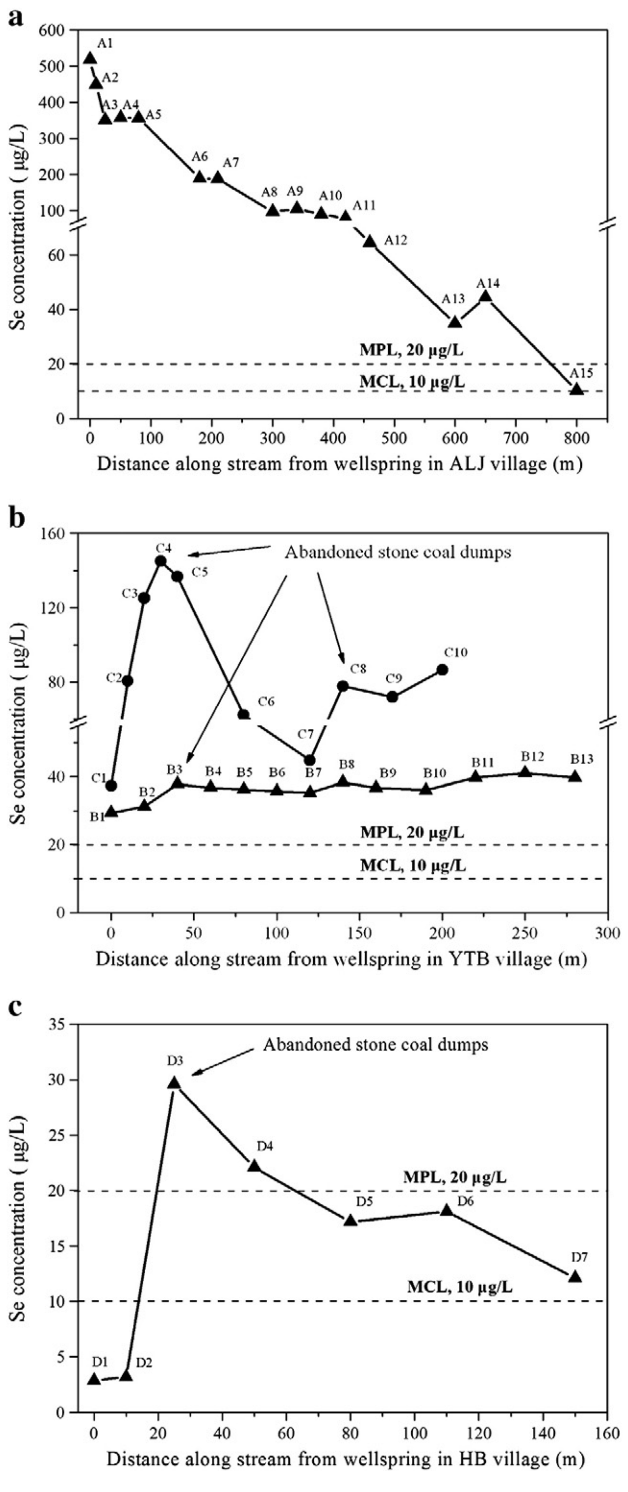

Fig. 2. Selenium distribution in streams at ALJ (a), YTB (b), and HB (c) villages.

OM-Se (35.5%) and higher unextractable Se (59.6%) was observed in the upland soil (U-3, the same location as P-3).

3.3. Selenium in plant and meat

Table 2
Se fractions in paddy and upland soils from high-Se areas of Enshi (μg/g).

Sample	W-Se	E-Se	OM-Se	U-Se	Total Se
P-1	0.66 (1.58)	2.59 (6.16)	23.5 (55.7)	15.4 (36.6)	42.1
P-2	1.18 (1.82)	6.55 (10.4)	42.3 (67.9)	12.9 (19.9)	63.0
P-3	1.08 (3.61)	2.11 (7.06)	18.5 (62.1)	8.10 (27.2)	29.8
P-4	1.02 (2.28)	2.85 (6.35)	31.1 (69.6)	10.4 (21.8)	45.4
P-5	1.58 (3.61)	4.11 (9.39)	25.1 (57.4)	13.0 (29.6)	43.8
P-6	1.26 (5.62)	0.95 (4.22)	13.7 (60.7)	6.62 (29.5)	22.5
P-7	0.08 (0.87)	0.86 (8.99)	3.44 (36.1)	4.38 (54.0)	9.52
U-3	0.17 (2.09)	0.24 (2.87)	2.93 (35.5)	4.93 (59.6)	8.27

W-Se, water-soluble Se; E-Se, ligand-exchangeable Se; U-Se, unextractable Se.
Value in parentheses indicates the relative percentage of each fraction (%).

The total Se content in polished rice ranged from 0.16 to 10.2 μg/g, with a geometric mean of 2.11 ± 2.87 μg/g ($n = 21$) (Table 1). Total Se content in tissues of selected rice plants and grain fractions exhibited the following distribution patterns: root > leaf > straw > bran > brown rice > polished rice > husk (Table 3). The geometric mean of Se content in corn grain was 3.76 ± 11.6 μg/g (0.39–37.2 μg/g, $n = 16$), which is much greater than that in rice (ANOVA, $p < 0.05$).

Selenium content in vegetables widely ranged from 0.25 to 13.0 μg/g, with a geometric mean of 2.09 ± 3.38 μg/g ($n = 25$). However, different Se concentration can be observed in different vegetable species, even the same vegetable species at different sites. The average Se content in potato, Chinese cabbage, radish, carrot, and kidney bean was 0.82 ± 0.81 μg/g (0.25–2.31 μg/g; $n = 6$), 2.25 ± 1.78 μg/g (0.69–5.26 μg/g; $n = 6$), 1.95 ± 4.74 μg/g (0.71–13.0 μg/g; $n = 6$), 5.37 ± 3.34 μg/g (3.22–10.7 μg/g; $n = 4$), and 3.84 ± 2.60 μg/g (3.12–7.29 μg/g; $n = 3$), respectively. The average Se in meat was 2.90 ± 1.81 μg/g ($n = 3$), varying from 1.2 to 4.8 μg/g.

3.4. PDI level of Se

The calculated PDI of Se for human in high-Se areas of Enshi was 2144 μg/day (Table 4). Cereal (rice and corn) and vegetable consumption were the major pathways of daily Se intake for local residents, accounting for 48.5% and 36.6% of PDI of Se, respectively. The meat (8.5%) and drinking water (6.4%) contributed very little to PDI of Se (Fig. 3).

4. Discussion

4.1. Selenium levels in water, soil, and plant

The geometric mean (46.0 ± 127.8 μg/L; $n = 48$) of total Se in surface water is much higher than that in other rivers (Conde and Alaejos, 1997; Fordyce, 2005; Robberecht and Van Grieken, 1982), which greatly exceeds not only the maximum contamination level (MCL, 10 μg/L) for drinking water, but also the maximum permissible level (MPL, 20 μg/L) for irrigation purpose (NAC-NAE, 1972; WHO, 1996). In comparison with previous investigations in high-Se toxicity areas of Enshi, average Se content in stream water is much lower than 139 μg/L (n = 4) Se reported by Yang et al. (1983), and is comparable with the values published in rencent studies (Fordyce et al., 2000; Zhu et al., 2008) (Table 5). This may be due to large Se release to stream by human activities in the past relative to present (Zhu et

Table 3
Se concentration in various parts of rice plant (μg/g).

Sample	Root	Straw	Leaf	Husk	Brown grain	Bran	Polished rice
Rice1	9.16	6.77	9.61	3.24	7.31	10.78	7.00
Rice2	17.12	9.75	10.89	3.98	10.21	14.61	10.17
Rice3	9.37	7.48	8.11	1.71	6.21	8.91	6.10
Rice4	15.29	8.35	11.74	2.23	7.12	9.11	6.81
Rice5	11.28	2.93	5.30	1.65	5.62	8.51	5.50
Rice6	9.25	5.61	8.74	0.97	3.11	4.21	3.09
Rice7	3.84	1.66	2.78	0.29	0.93	1.86	0.92
Mean[a]	9.85	5.27	7.46	1.56	4.74	7.03	4.64
SD	8.16	4.49	6.27	1.50	4.25	6.09	4.42

[a] Geometric mean; SD: standard deviation.

Table 4
The PDI of Se through all main routes for general adults in high-Se areas of Enshi.

Medium	Intake rate	Se concentration	PDI (μg/day)
Water	3 L/day	46.0 μg/L	138
Rice	425 g/day	2.11 μg/g	897
Corn	38 g/day	3.76 μg/g	143
Vegetable	375 g/day	2.09 μg/g	784
Meat	63 g/day	2.90 μg/g	183
Total			2144

Table 5
The comparison of Se concentration in surface water from different high-Se areas.

Location	Se concentration (μg/L)	References
California, USA	<1–269	Tracy et al., 1990
Šobov, Slovakia	0.12–32.2	Bujdoš et al., 2005
Punjab, Indian	0.25–69.5	Dhillon and Dhillon, 2003
High-Se toxicity areas, Enshi,	117–159	Yang et al., 1983
High-Se toxicity areas, Enshi	7.3–275	Fordyce et al., 2000
YTB, Enshi, China	40.0–94.1	Zhu et al., 2008
High-Se areas, Enshi, China	2.0–519.3	This study

al., 2008). However, water Se in Enshi is higher than that in other high-Se area like Punjab of Indian, and Šobov of Slovakia (Table 5).

Se contents in almost all soils from study areas are also higher than that in Se-excessive areas (3 μg/g, Tan and Huang, 1991). The geometric mean of soil Se is approximately 54 and 23 times greater than that in soils from China (0.173 μg/g, Tan et al., 2002) and world (0.40 μg/g, Fordyce, 2005), respectively. Compared with other areas, soil Se content in our study areas is higher (Table 6), likely contribtuted by high-Se stream water.

Se concentration in polished rice in this study is comparable to those (0.33–8.44 μg/g) in high-Se areas of Enshi in a recent study (Sun et al., 2010), but is lower than reported value (0.3–20 μg/g) 30 years ago (Yang et al., 1983). The geometric mean of Se content in polished rice is approximately 84 and 22 folds higher than Se content of regular polished rice in China (0.025 μg/g, Chen et al., 2002) and in the world (0.095 μg/g, Williams et al., 2009), respectively. Moreover, leaf, straw, and husk of rice plant is usually used as the fodder for cattle and swine in southern China, so it is expected that rice plant may pose potential Se poisoning risk on local populations and livestock in high-Se areas of Enshi. Corn grain is another staple food in Enshi Prefecture. Previous studies reported corn Se concentration in high-Se areas of Enshi ranged from 0.8 to 28.5 μg/g with an average of 8.1 μg/g 30 years ago (Yang et al., 1983), and ranged from 0.3 to16.9 μg/g with an average of 8.07 μg/g 10 years ago (Zhu and Zheng, 2001).Thus, Se levels in current cereal are becoming lower over time, which may be dependent on soil Se speciation, soil physical and chemical properties (Fordyce, 2005; Zhu et al., 2008).

4.2. Source of Se in water and its impact on soil Se

It is suggested that the composition of certain types of geological formations determine Se content in groundwater. Water derived from cretaceous geological zones may contain Se content as much as 1000 μg/L (Mayland et al., 1989), while Se concentration in seep water from limestone at YTB is very low in the range of 0.30–1.60 μg/L (Zhu et al., 2008). In our study areas, the total Se content in wellsprings is generally greater than 30 μg/L except wellspring D1, in which the maximum Se concentration is 519.3 μg/L from wellspring A1 in ALJ village (Fig. 2). Considering the fact that (i) total Se concentration (3.42 ± 0.57 μg/L ($n = 3$)) in rain samples, and the seep water from limestone and other rock is relatively low (Zhu et al., 2008), and (ii) carbonaceous shale (stone coal) contains high Se content, and mean Se concentration in certain stone coal layers in YTB reaches 1251 ± 1219 μg/g ($n = 23$) with a maximum of greater than 84,123 μg/g (Yang et al., 1983; Zheng et al., 1999; Zhu et al., 2007), it is reasonable to conclude that Se in wellspring water initially originate from the leaching of carbonaceous shales in high-Se areas of Enshi.

As shown in Fig. 2a, a significant decrease was observed in total Se in stream water with the distance from wellsprings. This could be explained by the fact that Se leached from carbonaceous shales is adsorbed by suspended solid and/or precipitated, and especially diluted by other tributaries with low Se content through upstream to downstream. However, elevated Se concentration in stream water was also observed when the stream flows through the mine waste dumps (Fig. 2b and c), which is in accordance with a previous study (Zhu et al., 2008). Taking stream C in YTB village for an example, Se concentrations raises up to 145 μg/L (C4 site of stream) from 37.3 μg/L (C1 site of wellspring) after stream goes through abandoned stone coal dumps. Streams B and D showed a similar pattern for total Se distribution. These observations indicate that the leaching of mine wastes should be another important Se source to stream water.

Many studies have demonstrated that Se(VI) can be preferentially released into water due to its high solubility during the process of rock weathering and leaching (Bujdoš et al., 2005; Kulp and Pratt, 2004; Martens and Suarez, 1997). In high-Se areas of Enshi, Se(VI) was predominant (70.5–99.5%) in high-Se water. On the contrary, most of Se (67.1%) was present as Se(IV) in the rain water, only 29.1% of Se was in the form of Se(VI). Therefore, the results on Se speciation confirm that Se source in high-Se water is mainly derived from the leaching of carbonaceous shale and mine wastes, while the rain makes an insignificant contribution to the Se content in water in high-Se areas of Enshi.

The total Se concentration (U-3: 8.27 μg/g) in upland soil without irrigation was much lower than in paddy soil (P-3: 29.8 μg/g) collected from the same area (Table 2). Se concentrations in paddy soils tend to be low with the decrease of Se level in corresponding irrigation water (Fig. 2). These suggest that irrigation with high-Se stream water probably make a great contribution to the formation of high-Se soils in these areas. Dhillon and Dhillon (2003) have demonstrated that the range of 240 to 5560 g/ha Se (depending on requirements of water and Se adsorption capacity for different crops) could be accumulated in soil within only 20 years of irrigation with water

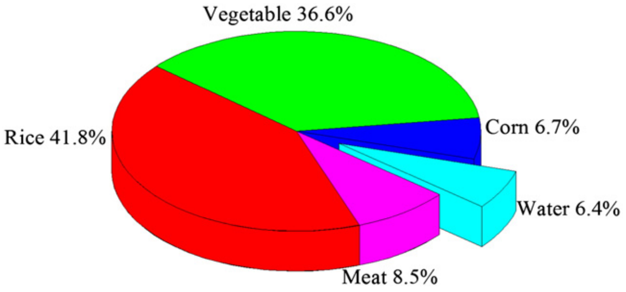

Fig. 3. Food Contribution to daily Se intake for residents in high-Se areas of Enshi.

Table 6
The comparison of Se concentration in soils from different sites.

Location	Se concentration (μg/g)	References
Kesterson reservoir, USA	4–25	Tokunaga et al., 1994
Punjab, Indian	0.23–4.55	Dhillon et al., 1992
Šobov, Slovakia	0.44–4.25	Bujdoš et al., 2005
Xuzhou, China	0.21–4.08	Huang et al., 2009
High-Se toxicity areas, Enshi	2.74–27.5	Fordyce et al., 2000
YTB, Enshi, China	1.40–6.91	Zhu and Zheng, 2001
Enshi, China	0.41–42.3	Zhu et al., 2008
Enshi, China	0.48–47.8	Sun et al., 2010
High-Se areas, Enshi, China	2.7–87.3	This study

containing the MPL for Se (20 μg/L) under different cropping sequences. In our study areas, stream water containing high Se level is used as the major irrigation water for local crops. Since paddy rice is the staple crop and needs more water irrigation, it should be expected that more Se would be enriched in paddy soils in the future.

Additionally, a larger proportion of Se can be extracted by water, P-buffer and NaOH solution for paddy soils than upland soil, indicating more bioavailable Se in paddy soils. Moreover, the addition of Se(VI) to aerobic soil could effectively increase Se concentration in rice grain (Li et al., 2010). The fact that Se(VI) is predominant Se form in irrigation water in high-Se areas of Enshi implies that more Se could be accumulated in rice grain and thereby pose a serious health risk for local populations and livestock.

4.3. Selenium speciation in soil and its relationship to rice plant

There was no significantly positive correlation between concentration of water-soluble Se and total Se in paddy soils (Table 7), which was consistent with the previous study on Chinese paddy soils (Tan et al., 2002). Concentration of ligand-exchangeable Se and OM-Se were significantly positive correlated with total Se in paddy soils. Moreover, more than 63.4% of Se in paddy soils (except P-7) can be extracted by water, P-buffer and NaOH solution, whereas these Se fractions were only 30.6% for the upland soil (Table 2). This could be explained by the fact that more mobile Se added through irrigation water is absorbed onto organic matter, oxide minerals and clay particles of paddy soil (Bajaj et al., 2011), and thus result in elevated total Se content in paddy soils. A previous study suggested that the forms of Se source can lead to distinct disparity of Se speciation in soils (Tokunaga et al., 1991). Most of Se was extractable in Kesterson soils, since Se was introduced to soils through drainage water (Se(VI)-dominant). However, Se in Californian agricultural soil was mainly derived from Se-bearing sulfide minerals, which resulted in more refractory and unextractable Se fractions (Tokunaga et al., 1991). In addition, other factors including irrigation, tilling, fertilization, plant growth etc., which also can affect the transformation of Se speciation, cannot be excluded.

There were significantly positive correlations between total Se content in paddy soils and Se concentration in rice tissues (Table 7), implying that soil Se is the major source of Se in rice plant. However, soil Se concentration was observed to be weakly and positively correlated with Se in straw and leaf of rice plant (Table 7). This is because Se in the aerial parts of rice plants could be affected by the deposition of atmospheric Se besides soil Se. Although Sun et al. (2010) reported that Se in rice stalk was significantly correlated with soil Se, further research is required to identify the contribution of atmospheric Se to plants in high-Se areas of Enshi.

Selenium uptake and accumulation by plants depend not only on the total Se content but also on Se speciation in the soil (Cao et al., 2001; Fordyce, 2005; Frankanberger and Benson, 1994). The correlations between different Se fractions in paddy soil and Se concentration in various tissues of rice plant were shown in Table 7. Content of water-soluble Se in soils had no significant correlation with Se in all parts of rice plant, implying that water-soluble Se is not a good index to predict Se in the rice plant in high-Se areas of Enshi. This observation was distinctly different from the similar study carried out in the Se-deficient area of Yangtze River Delta in which content of water-soluble Se has been reported to correlate with abundance of Se in the paddy soil and rice plant (Cao et al., 2001). This disparity is probably a consequence of irrigation water with different Se concentration in above two areas. However, relatively higher correlation coefficient ($r > 0.80$, $p < 0.05$) was observed between Se extracted by P-buffer solution and Se in rice root and all parts of grain. This is in agreement with the study of Zhao et al. (2005), whose results showed that phosphate extractable Se in soils could reflect the available Se to plants. Similarly, there was a significantly positive correlation ($r > 0.89$, $p < 0.01$) between OM-Se in paddy soil and Se in rice root and different fractions of grain. This may be well explained by the fact that part of OM-Se (i.e. weakly bound FA-Se) could act as the potential source of bioavailable Se in Enshi, which can be directly and indirectly taken up by plant (Qin et al., 2012; Wang et al., 2012). Considering OM-Se is the dominant fraction in paddy soils, OM-Se may play a very important role in Se uptake by rice plant in high-Se areas of Enshi. However, it is still difficult to find a reasonable consensus on which Se forms in soils can be used to evaluate Se level in plants. One reason is that extracting method for Se fraction is various (Chao and Sanzolone, 1989; Dhillon et al., 2005; Kulp and Pratt, 2004; Sharmasarkar and Vance, 1995; Zhao et al., 2005). The most possible explanation may be ascribed to different soil properties including pH, Eh, mineralogy, and organic matter that affect Se forms in soils (Chen et al., 2010; Fordyce, 2005; Frankanberger and Benson, 1994). In addition, every plant species has different Se uptake ability (Dhillon et al., 2010; Terry et al., 2000; Zhu et al., 2009). Therefore, more studies should be carried out to interpret the linkage between plant uptake of Se and Se in soils in different areas.

4.4. Source contributions to human Se intake

Yang et al. (1989) reported that 65–85% of daily Se intake for populations came from cereal consumption in Enshi, while PDI of Se from cereal is 48.5% in our study. This disparity could be ascribed to the change in consumption habit. With the economical development and improvement of living conditions, local inhabitants now eat more rice grain than corn, and consume more protein foods (BHS, 2010). Since corn usually contains higher Se level than rice and other food (Fordyce et al., 1998; Yang et al., 1983), the contribution of cereal to daily Se intake for local residents become less in the present. The local vegetable rather than meat is another staple foodstuff, and it

Table 7
Pearson's correlation matrix among the Se levels in tissues of rice plant and paddy soils.

	Se_{tot}	W-Se	E-Se	OM-Se	Root	Straw	Leaf	Husk	Brown grain	Bran	Polished rice
Se_{tot}	1										
W-Se	0.55	1									
E-Se	0.92**	0.48	1								
OM-Se	0.99**	0.55	0.91**	1							
Root	0.91**	0.62	0.81*	0.96**	1						
Straw	0.70	0.32	0.52	0.77*	0.79*	1					
Leaf	0.69	0.38	0.42	0.75	0.80*	0.94**	1				
Husk	0.91**	0.28	0.80*	0.89**	0.75	0.78*	0.73	1			
Brown grain	0.95**	0.46	0.84*	0.95**	0.86*	0.84*	0.77*	0.95**	1		
Bran	0.95**	0.44	0.87*	0.93**	0.81*	0.78*	0.70	0.96**	0.99**	1	
Polished rice	0.96**	0.47	0.86*	0.95**	0.87*	0.84*	0.76	0.95**	0.99**	0.99**	1

Se_{tot}, total Se in soil; W-Se, water-soluble Se; E-Se, ligand-exchangeable Se.
**Correlation is significant at the 0.01 level (2-tailed). *Correlation is significant at the 0.05 level (2-tailed).

makes a considerable contribution to daily Se intake for residents (Fig. 3). This is in accordance with the previous view that a great proportion of vegetable intake is one of the important reasons for sudden incidence of human selenosis in Enshi (Yang et al., 1983).

In previous studies conducted on daily Se intake for populations, the contribution of drinking water was usually neglected (Dhillon and Dhillon, 2003; Emmanuelle et al., 2012; Robberecht et al., 1983; WHO, 1996). Although the proportion (6.4%) of drinking water to PDI was relatively small, it is noted that daily Se intake via drinking water was up to 138 μg/day for local residents in this study, accounting for 34.5% of 400 μg/day of UL for Se. In particular, a wellspring contains Se concentration as high as 519.3 μg/L, this means daily Se intake could reach 1558 μg/day just through drinking water, which is approximately 3.9 folds higher than recommended UL for Se. Moreover, recent research found that inorganic Se intake via drinking water containing Se$\geq$1 μg/L could increase the risk for amyotrophic lateral sclerosis (Vinceti et al., 2010a, b). Therefore, drinking water with higher Se content in high-Se area of Enshi would pose a more serious health risk to local dwellers. It should not ignore the contribution of drinking water to daily Se intake, when assessing the health risk for residents in high-Se areas.

Various features for daily Se intake by humans can be found in different areas. In Suzhou of China, cereal, pork, and vegetable contributed 22.6%, 24.7%, and 9.3% to daily Se intake for local populations, respectively (Gao et al., 2011). Similar results were reported for Korean people, where 34%, 20% and 4.7% of Se intake derived from cereal, meat and vegetable (Choi et al., 2009). However, for Japanese people, daily Se intake was mainly from fish and shellfish (57%), followed by cereal (28%), meat (9%) and others (Hirai et al., 1996), and the greater contribution (68.7%) of fish to daily Se intake was reported for people living in a rural coastal community due to higher consumption of fish (Miyazaki et al., 2002). These difference in daily Se intake and corresponding food contribution were mainly because i) various eating habit, e.g., rice is the staple food and less fish is eaten in inland china (BHS, 2010), whereas fish and seafood is usually consumed in Japan (Hirai et al., 1996; Miyazaki et al., 2002) and Taiwan (Chien et al., 2003); ii) different Se content in food, e.g., meat and fish generally contains higher Se concentration than cereal and vegetable, though Se content in crops is dependent on the soils in which they are grown (Fordyce, 2005; WHO, 1986; WHO and FAO, 2004).

4.5. Potential risk assessment for human Se poisoning

The calculated PDI of Se for human in high-Se areas is considerably higher than 400 μg/day of UL, and approximately 39 times greater than 55 μg/day of recommended RDA (U.S. IOM, 2000; WHO and FAO, 2004). In comparison with the cases in other countries, the PDI of Se was remarkably greater than that of the UK, Greece, Korea, Japan, even high-Se areas in India (Fig. 4). Thirty years ago, Yang et al. (1983) reported that daily Se intake ranged from 3200 to 6690 μg/day, with an average of 4990 μg/day in Se poisoning areas of Enshi. After the prevalence of endemic Se intoxication subsided, our current results indicate a remarkable decrease in daily Se intakes for human in high-Se areas of Enshi. However, this still poses a high risk for chronic Se poisoning to residents.

Selenium in whole blood can be used as a favored biomarker to evaluate Se adverse health effects on people with high Se intake (Hansen et al., 2004; Lemire et al., 2006, 2012). In the present study, Se level in blood cannot be determined without official permission. However, it is possible to predict by using two well-documented equations. The first one is Eq. (2) based on an empirical linear relationship between human Se intake and Se concentration in blood (Ma and Zhang, 2000):

$$logBSe = 0.767 * logISe - 2.046 \tag{2}$$

where BSe is Se concentration in blood (μg/mL), and ISe is the daily Se intake (μg/day). Using this equation, Se level in blood was calculated at 3229 μg/L.

The second one is Eq. (3) of pharmacokinetic model proposed by Chien et al. (2003) and Mahapatra et al. (2001):

$$\tau = CV/IF \tag{3}$$

where τ is the turnover time of Se (17 days); C is the steady state concentration of Se in blood (μg/L); V is the apparent volume of blood in the body (5.5 L); I is daily Se intake (μg/day); and F is the uptake fraction into the blood through ingestion (50%). Based on the pharmacokinetic model, Se level in blood was estimated at 3267 μg/L, which is very similar to the calculated value by Eq. (2). The predicted blood Se concentration is significantly higher than 76 μg/L for Czech Republic adults (Benes et al., 2000), 224 μg/L for Taiwanese adult with a high seafood diet (Chien et al., 2003), 142–2447 μg/L for residents from Tapajós River region of the Brazilian Amazon (Lemire et al., 2006, 2012), and the maximal value of 1818 μg/L for people living in Greenland (Hansen et al., 2004), respectively. The estimated blood Se level is in excess of the toxic concentration for Se in whole blood of 1000 μg/L set by U.S. EPA (2002), and falls in the range of 1300–7500 μg/L for residents living in high Se areas of chronic selenosis (Yang et al., 1983).

However, in recent years, few cases of human selenosis and extremely severe symptom of Se poisoning for resident were reported in Enshi. This may be explained by at least three reasons.

Firstly, daily Se intake for residents has decreased because of the change in consumption pattern and Se concentration in the food in high-Se areas of Enshi. Moreover, not only the amount of Se intake, but also Se species is important to human health, though there are few species-specific research on the toxicity of Se for humans and none relating to dose and upper limits of particular Se species (Rayman, 2008; Rayman et al., 2008). In general, inorganic Se is more acutely toxic than organic Se forms (Barceloux, 1999; Rayman et al., 2008). The selenomethionine (SeMet) and Se(VI) have the absorption of more than 90% for human, while the absorption of Se(IV) is much lower (about 60%) (Thomson and Robinson, 1986, 1993). In Enshi, Se in rice grain is dominated by SeMet with less methylselenocysteine (SeMeSeCys) and inorganic Se (Li et al., 2010; Sun et al., 2010; Zhu et al., 2009), while Se in drinking water mainly occurs in the form of Se(VI). These limited data on Se speciation in food and water indicate that Se is easy to be absorbed by the human body in high-Se area of Enshi, but the toxicity is unclear. Hence, it is of great importance to know Se species in food and its nutrient and toxic function to further evaluate Se health risk for human beings.

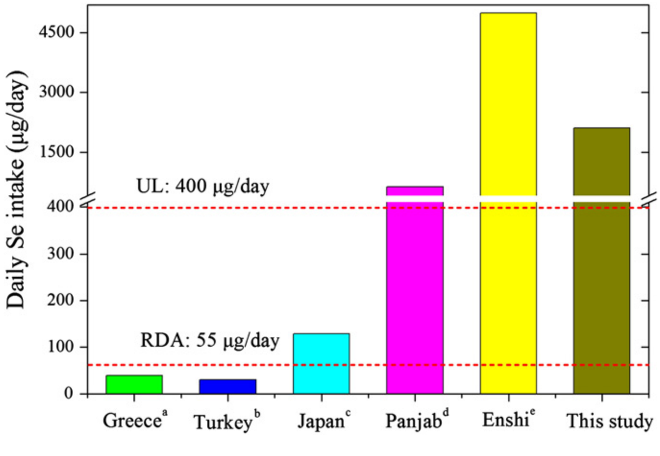

Fig. 4. Daily Se intake for population in different areas ([a]Pappa et al., 2006; [b]Foster and Sumar, 1997; [c]Hirai et al., 1996; [d]Hira et al., 2004; [e]Yang et al., 1983).

Secondly, Se toxicity may be offset by other trace elements (Pb, Cd, As, Hg, etc.) due to their interactions (Rosen and Liu, 2009). For example, Se can protect against the toxic effect of Hg in the brain and nervous system (Lemire et al., 2012), and thus Se toxicity may be reduced due to its interaction with Hg (Sørmo et al., 2011). Considering the accumulation of trace element in black shales and adjacent soils (Fan et al., 2008; Fang et al., 2002; Kim and Thornton, 1993), it is possible that the interactions between Se and other elements can decrease Se toxicity in high-Se areas of Enshi. However, severely combined toxicity of various elements to local residents cannot be ruled out.

Thirdly, local populations may have adapted and even developed the antagonism mechanisms to high Se intake in the long term life in high-Se areas of Enshi (Lemire et al., 2012; Mattson, 2008).

In order to avoid the potential health risk of Se poisoning, a local villager is not recommended to drink stream water with high Se content, and piped water should be supplied from elsewhere. The crop plants should be advised not to grow in the land irrigated with high Se water. However, since low-Se farmland is not sufficient, it is better to encourage local population to exchange produced foods with those produced outside of the high Se areas. This measurement could significantly reduce Se intake for local residents and improve Se level in lower Se areas.

5. Conclusions

Elevated Se content was found in water, soils and crops in high-Se areas of Enshi. Se in water may be mainly derived from leaching of carbonaceous shales and mine waste dumps. Irrigation with high-Se water can lead to Se accumlation and its speciation variation in paddy soils in the study areas. The Se level in rice plant is significantly correlated with OM-Se, suggesting that OM-Se may play an important role in Se uptake by rice plant in high-Se areas of Enshi.

The PDI of Se is approximately 2144 μg/day for residents in high-Se areas in Enshi, and Se concentration in blood is estimated at about 3248 μg/L, posing a serious health risk of chronic Se poisoning to populations in this areas. Cereal consumption is the major pathway of Se intake for local residents, followed by vegetables, meats, and drinking water. The contribution of drinking water to daily Se intake should not be ignored due to its high Se concentration and dominant Se(VI) species. In the high-Se areas of Enshi, villagers are advised to avoid growing crops in land with high Se content or irrigated by high Se water. In particular, they should be advised not to drink high-Se water and consume solely foods from their own lands.

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