Chapter 2
Selenium in Plants and Soils, and Selenosis in Enshi, China: Implications for Selenium Biofortification

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Abstract The total selenium (Se) content of soils in Enshi, China, the so-called "World Capital of Selenium", is concentrated in a range of 20–60 mg/kg DW which is approximately 150–500 times greater than the average Se content (0.125 mg/kg DW) in Se-deficient areas and approximately 50–150 times greater than that (0.40 mg/kg DW) in Se-enriches areas in China, respectively. However, the distribution of Se in soils is greatly uneven with some exceptionally high contents of more than 100 mg/kg DW, which is very likely caused by the micro-topographical features and leaching conditions. Among the 14 plant species in Enshi, *Adenocaulon himalaicum* has the highest contents of Se from 299 to 2,278 (mean 760) mg/kg DW in the leaf, from 268 to 1,612 (mean 580) mg/kg DW in the stem, from 227 to 8,391 (mean 1,744) mg/kg DW in the root, and therefore was identified as a secondary Se-accumulating plant. Furthermore, the SeCys2 fraction was predominant in the tissues with a proportion of 70–98 %, which is quite different from other Se-accumulating plants, e.g., garlic, onion, and broccoli. Although the Se concentration in resident foods and the daily Se intake decreased significantly from 1963 to 2010 in Enshi, the present daily Se intake (575 μg/d) is still above the recommended maximum safe intake of 550 μg/d, which indicates that there may be potential risk for selenosis in Enshi. Both Se distributions in soils

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and plants and human daily Se intakes obviously indicate that Enshi, China should be Se-phytoremediated to decrease the risk for selenosis there. Fortunately, Se-biofortification was taken as an effective method to overcome this problem. Hopefully, Enshi, China is moving on a natural field-scale trial for integration of Se-phytoremediation and Se-biofortification.

Keywords Selenium · Enshi, China · Soil · Plant · Selenium intake

2.1 Introduction

Selenium (Se), discovered by the Swedish chemist Jakob Berzelius in 1817, is a metalloid and states in group VIA with an atomic weight of 78.96. Selenium has five valence states in nature, including selenide (2−), elemental Se (0), thioselenate (2+), selenite (4+), and selenate (6+). Selenium is an essential nutrient for humans and animals to form important selenoproteins, including glutathione peroxide, thioredoxin reductase (Terry et al. 2000; Zhu et al. 2009). In 1973, Se was found to be involved in forming the active center of glutathione peroxidase and thioredoxin reductase enzymes; these enzymes play important roles in reducing certain oxidized molecules in animals (Liu et al. 2010).

The range between the beneficial and harmful concentrations of Se is quite narrow; the minimal Se nutrition levels for animals is about 0.05–0.10 mg/kg dry forage feed, while the toxic exposure level is 2–5 mg/kg dry forage (Wilber 1980; Wu et al. 1996). The World Health Organization (WHO) recommended the required dietary intake of Se to be 50–200 μg/day for adults (WHO 1987). Two well-known endemic diseases, Keshan Disease (a degenerative heart disease bursting out in Kesha, Heilongjiang, China) and Kaschin-Beck Disease (an osteoarthropathy which causes deformity of the affected joints) were linked to soil Se-deficiency and low Se daily intake (Tan and Huang 1991; Tan et al. 2002). However, because of long-term exposure to high levels of Se, Se toxicological symptoms, including hair and nail loss and nervous system disorders, extensively occurred in inhabitants in two notable Se-enriched areas, Enshi, Hubei, China and Ziyang, Shanxi, China (Yang et al. 1981a, b, 1983; Mei 1985; Li et al. 2011).

2.2 Enshi, the World Capital of Selenium

Enshi (E 108°23′12″–110°38′08″, N 29°07′10″–31°24′13″) is a national minority autonomous prefecture located in Northwestern Hubei Province, China (Fig. 2.1). From early 1930 to 1960, people living in Yutangba, Huabei, and Shadi villages of Enshi, experienced loss of hair and nails, showing the typical symptoms of Se toxicity (Zhang et al. 1998). For instance, 19 of 23 local inhabitants in Yutangba showed visible Se poisoning symptoms and all livestock in the village died in 1963. Subsequently, villagers were evacuated from their homes in Yutangba (Mao et al. 1990, 1997). After the occurrence of the incident, selenosis has become a matter of concern for local governments, scientists, and Se endemic disease investigators (Tan and Huang 1991; Zhang et al. 1998; Wang and Gao 2001; Tan et al. 2002). Among the studies carried out in Enshi, Yu (1993) reported the discovery of Se mines in Yutangba village, with a high Se content of 8,500 mg/kg. The Se mines were formed in Maokou, in the late Permian period with a thickness of 13 m, which were the "culprits" for the selenosis observed in the Yutangba village (Fig. 2.1).

2.3 Selenium in Plants

To investigate the characteristics of Se pollution in the seleniferous areas in Enshi, the dominant plants and their underlying soils were collected in Yutangba, including 14 species and 8 classes (Table 2.1).

The plant samples were rinsed in deionized water, and most of the plants were separated into root, stem, and leaf for Se content analysis, except for *Adenocaulon himalaicum, Elsholtzia splendens, Trifolium repens, Lycodium clavaturn, Polygonum hydropiper,* and *Rumex japonicas* that do not have true stems and were separated only into roots and shoots. The Se content in *Mosla dianthera* seed was also determined.

Our results showed that *Adenocaulon himalaicum* had exceptional high concentrations of Se with 563.60 mg/kg DW in the root and 1,317.46 mg/kg DW in the leaf, followed by *Medicago sativa* that accumulated Se concentrations of 150.96, 154.40, and 168.14 mg/kg DW in root, stem, and leaf, respectively. Furthermore, the leaves of *Sedum sarmentosum, Trifolium repens,* and *Mosla dianthera* had relatively higher concentrations of Se, compared with the Se contents in roots. The Se translocation factor (i.e., the ratios of shoot to root Se concentrations) of 4.5 was the highest in *Trifolium repens*, while the Se concentration in the root was only 17.65 mg/kg DW. For *Mosla dianthera* and *Sedum sarmentosum,* the Se translocation factor was greater than 2.

2.4 Selenium in Soils

The sequential chemical-extraction technique is a conventional method to evaluate the geochemical behavior of trace elements in soil (Sharmasarkar and Vance 1995; Mao and Xing 1999; Zhang et al. 2002). Se has several chemical forms in soil, such as Se^0, $SeO_3{}^{2-}$, SeO_4^{2-}, and organic Se. In the sequential chemical extraction, the fraction by water-extraction is called the water-soluble Se (Fraction 1), the fraction by KH_2PO_4–K_2HPO_4-extraction is called the exchangeable Se (Fraction 2), the fraction by HCl-extraction is called the acid-soluble Se (Fraction 3), the fraction

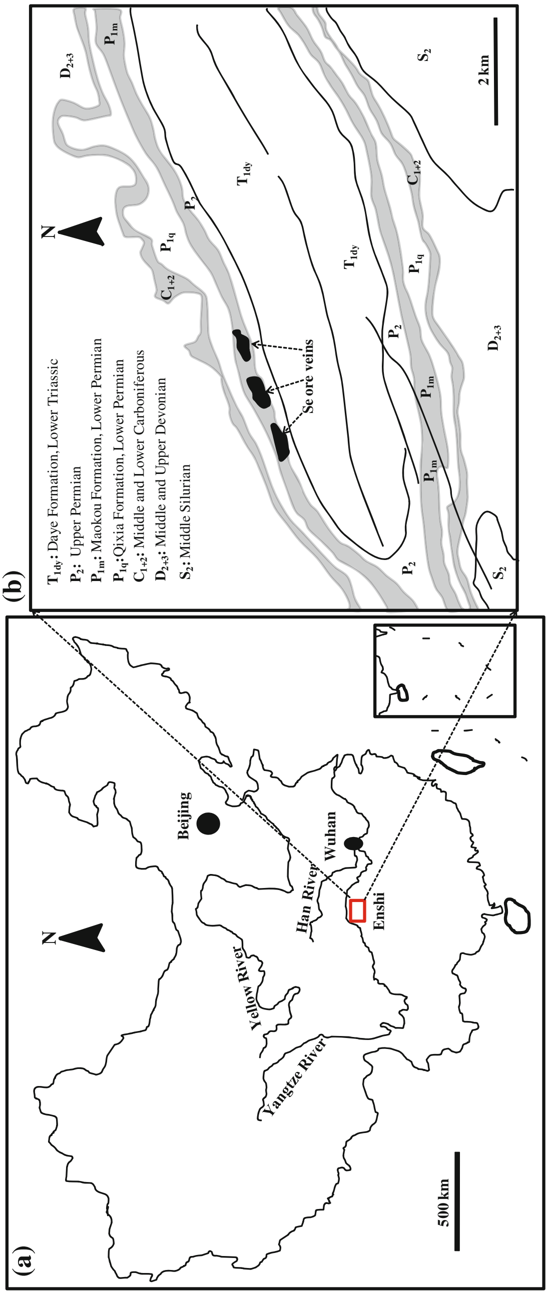

Fig. 2.1 Sketch map showing the location of Enshi, China (**a**) and the sketch geological map of Yutangba, Enshi, and the Se ore vents were marked (**b**)

by $K_2S_2O_8$-extraction is called the organic-bound Se (Fraction 4), and the remaining fraction is called the residue Se (Fraction 5). Among those fractions, the water-soluble Se and the exchangeable Se are considered as bioavailable Se, the

Table 2.1 The concentrations of Se in roots, stems, and leaves of plants from Enshi (mg/kg DW) and the ratio between the calculated shoot (Stem + Leaf) and the root

No.	Latin name	Class	Root	Stem	Leaf	Shoot/Root
1	*Adenocaulon himalaicum*	Asteraceae	563.60	/	1,317.46	2.34
2	*Siegesbeckia orientalis*	Compositae	112.29	84.61	4.92	0.80
3	*Erigeron annuus*	Compositae	18.03	14.83	13.56	1.57
4	*Artemisia lavandulaefolia*	Compositae	1.62	0.39	1.10	0.92
5	*Sedum sarmentosum*	Crassulaceae	43.12	19.94	99.22	2.76
6	*Miscanthus sinensis*	Gramineae	24.64	14.79	25.44	1.63
7	*Miscanthus purpurascens*	Gramineae	123.88	25.56	62.64	0.71
8	*Mosla dianthera*	Labiatae	8.91	7.24	12.84(Seed)	2.25
9	*Elsholtzia splendens*	Labiatae	19.86	/	11.83	0.60
10	*Trifolium repens*	Leguminosae	17.65	/	79.36	4.50
11	*Medicago sativa*	Leguminosae	150.96	154.40	168.14	2.14
12	*Lycodium clavaturn*	Lycopodiaceae	1.48	/	1.73	1.17
13	*Polygonum hydropiper*	Polygonaceae	21.33	/	27.57	1.29
14	*Rumex japonicus*	Polygonaceae	18.55	/	31.66	1.71

HCl-soluble Se and the organic-bound Se are regarded as the transferable Se, and the residue Se are regarded as the un-bioavailable Se. Overall, the bioavailable Se content in soil is the key factor for the Se accumulation in plant, and the transferable Se content in soil provides a potential Se source for plant uptake (Zhao et al. 2005; Zhu et al. 2008a).

The results of the total Se and the fractions of sequential chemical-extraction on Se in soils are shown in Table 2.2. The total Se contents varied from 3 to 4 mg/kg DW in the underlying soils of *Lycodium clavaturn* and *Artemisia lavandulaefolia* to 100–436 mg/kg DW in the underlying soil of *Miscanthus sinensis, Sedum sarmentosum,* and *Miscanthus purpurascens*. But the total Se concentrations in most of the soil samples collected in Yutangba contained 20–60 mg/kg DW, which is approximately 150–500 times greater than the average soil Se content (about 0.125 mg/kg DW) in Se-deficient areas (Tan and Huang 1991; Tan et al. 2002). When compared with the total soil Se concentrations in other Se-enriched areas worldwide, such as 3 mg/kg DW in China and 2.41 mg/kg DW in the western U.S., the soil total Se concentrations in Yutangba of Enshi was 10–30 times higher (Presser et al. 1994). It should be pointed out that the soil samples containing very high Se concentrations, such as the underlying soils of *Sedum sarmentosu* and *Miscanthus purpurascens,* were collected from the discarded Se-coal spoils. Although the local lithological differences could result in considerable variation in soil Se distribution (Fordyce et al. 2000), it is likely that micro-topographical features and hydrological conditions were the primary factors affecting the soil Se content and distribution in the study area (Zhu and Zheng 2001).

The fractionation analysis of Se in the vegetated soils revealed that the total Se concentration in the fraction 1 ranged from 1 to 2 mg/kg DW with lower concentrations in the underlying soils of *Lycodium clavaturn* (0.30 mg/kg DW) and *Adenocaulon himalaicum* (0.45 mg/kg DW), and with a higher concentration

Table 2.2 Fractional partitioning of Se in the underlying soils (mg/kg DW)

No.	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Fraction 5	Total Se
1	0.45	1.81	8.44	9.13	/	19.82
2	1.28	1.58	6.31	6.46	29.70	45.33
3	0.91	1.20	7.03	8.87	24.02	42.03
4	0.64	0.82	0.92	1.17	0.21	3.76
5	1.04	3.51	12.70	10.41	111.24	138.90
6	2.30	1.77	9.86	14.49	72.38	100.80
7	6.85	15.41	82.52	62.22	268.70	435.70
8	1.35	1.42	2.91	4.59	17.84	28.11
9	0.98	2.79	4.12	5.16	5.09	18.14
10	1.09	0.91	2.28	4.17	37.17	45.62
11	1.81	1.84	3.23	3.79	32.95	43.62
12	0.30	0.66	0.77	0.99	0.46	3.18
13	0.87	2.32	12.13	8.32	37.07	60.71
14	1.19	2.18	13.30	10.94	51.47	79.08

in the underlying soil of *Miscanthus purpurascens* (6.85 mg/kg DW). The Se in the fraction 2 was in a range of 1–3 mg/kg DW, with a low value in the underlying soil of *Lycodium clavaturn* (0.66 mg/kg DW) and a high value in the underlying soil of *Miscanthus purpurascens* (15.41 mg/kg DW). The Se distribution in fractions 3 (1–4 mg/kg DW) and 4 (1–5 mg/kg DW) were different compared with the Se distribution in other fractions. Relatively low concentrations of Se in fractions 3 and 4 were found in the underlying soils of *Artemisia lavandulaefolia, Mosla dianthera, Elsholtzia splendens, Trifolium repens, Medicago sativa,* and *Lycodium clavaturn*. In contrast, higher concentrations of Se in fractions 3 (7–13 mg/kg DW) and 4 (6.5–14.5 mg/kg DW) were observed in the underlying soils of *Adenocaulon himalaicum, Siegesbeckia orientalis, Erigeron annuus, Sedum sarmentosum, Miscanthus sinensis, Polygonum hydropiper,* and *Rumex japonicas*. Very high Se concentrations of 382.52 mg/kg DW in fraction 3 and of 62.22 mg/kg DW in fraction 4 were determined in the underlying soil of *Miscanthus purpurascens*. For fraction 5, Se concentrations were very low in the underlying soils of *Artemisia lavandulaefolia* (0.21 mg/kg DW), *Lycodium clavaturn* (0.46 mg/kg DW), and *Elsholtzia splendens* (5.09 mg/kg DW). Concentrations of Sein fraction 5 ranged from 20 to 70 mg/kg DW, with an exception in the underlying soils of *Sedum sarmentosum* (111.24 mg/kg DW) and *Miscanthus purpurascens* (268.70 mg/kg DW).

The percentages of Se distribution among different fractions in the underlying soils are shown in Fig. 2.2. Overall, Se in fraction 5 accounted for 40–80 % of the total Se, 10–20 % in fractions 3 and 4, and less than 3 % in fractions 1 and 2. Therefore, the proportion of bioavailable Se was <5 % in the underlying soils in Enshi. However, the proportion of transferable Se was relatively high (20–40 %), which could be used by plants for uptake. As for fraction 5, un-bioavailable Se was predominant in the vegetated soils.

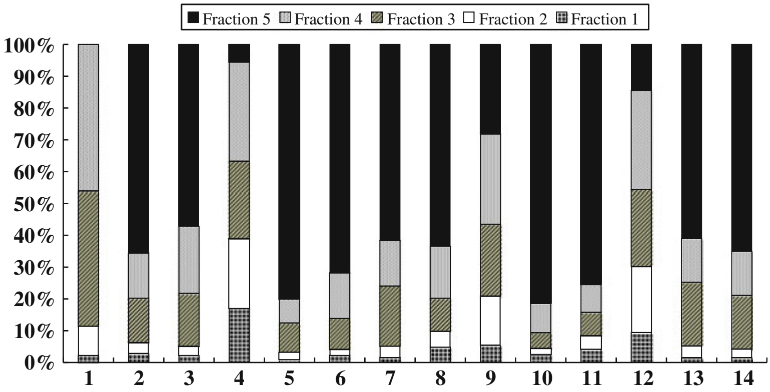

Fig. 2.2 The percentage of the fractional partitioning of Se in the underlying soils

Table 2.3 Variations of Se concentrations in soil and stream water in Enshi during 1963–2010

Se in soil (mg/kg dry weight) mean (min–max)	Se in stream water (μg/L) mean (min–max)	Sampling time (year)	References
6.83	/	1963	Mao et al. (1997)
9.68 (0.08–45.5)	56 (0–158)	1966	Yang et al. (1981a, b)
3.45 (1.92–4.98)	/	1987	Mao et al. (1997)
5.48 (0–11.89)	/	1989	Zheng et al. (1993)
4.06 (2.82–5.30)	/	1992	Zhu and Zheng (2001)
4.99 (2.61–7.37)	40.4	1996	Fordyce et al. (2000)
4.75 (0–12.18)	58.4 (41.6–75.2)	1999	Zhu et al. (2008b)
27.81 (3.76–79.08)	52.66 (15.13–192.70)	2010	This study

In comparing with other total soil Se concentrations reported previously by other researchers from the same research areas in Yutangba village, the temporal variation of soil Se concentration is shown for the time period from 1963 to 2010 in Table 2.3. The soil Se concentration in Yutangba was 6.83 mg/kg DW in 1963 (Mao et al. 1997) and 9.68 mg/kg DW, with a range of 45.42 mg/kg in 1966 (Yang et al. 1981a, b). During the time period from 1987 to 1999, the soil Se concentrations were from 3.5 to 5 mg/kg DW. However, in a recent study conducted in 2010, Yin and his colleagues reported that the soil Se concentrations in Yutangba varied from 3.76 to 79.08 mg/kg DW, with an average of 27.81 mg/kg. Based on these Se concentrations in the soil samples collected from 1963 to 2010 by different research groups, the soil Se concentrations in Yutangba were high in 1963 and 1966, low and relatively stable from 1987 to 1999, and then were higher again in 2010. Overall, the total Se content in soils in Enshi generally varied from 4 to 25 mg/kg DW which were approximately 30–200 times greater than the average Se content (0.125 mg/kg DW) in Se-deficient areas (Fordyce et al. 2000).

The Se concentrations in stream water were 40–60 μg/L, which is approximately 4–6 times greater than the drinking water maximum concentration of 10 μg/L recommended by the World Health Organization (WHO) and the US Environmental Protection Agency (Presser et al. 1994).

2.5 Plant Uptake of Selenium from Seleniferous Soil in Enshi

To estimate the ability of plants to take up Se from soil, the root bioconcentration factors (BCF = $[Se]_{plant\ root}/[Se]_{soil}$) were calculated for the plant species tested in the present study (Table 2.4). *Adenocaulon himalaicum, Medicago sativa,* and *Siegesbeckia orientalis* showed relatively high root BCFs of 28.44, 3.46, and 2.48, respectively. For stem tissues, *Medicago sativa* had the highest stem BCF with 3.54, 42.30, and 14.47 for S/T ($[Se]_{plant\ stem}/[Se]_{soil}$), S/B ($[Se]_{plant\ stem}/[Se]_{bioavailable\ in\ soil}$), and S/(B + Tr) ($[Se]_{plant\ stem}/[Se]_{bioavailable\ plus\ transferable\ in\ soil}$), respectively. The stem of *Siegesbeckia orientalis* also apparently accumulated Se from the underlying soil with BCFs more than 1. Although most of the ratios of S/B were more than 1 in the other plant species, the ratios of S/T and S/(B + Tr) on them were lower than 0.3 for S/T and 0.8 for S/(B + Tr). For leaf tissues, *Adenocaulon himalaicum* and *Medicago sativa* apparently accumulated Se from the underlying soil with the ratios of L/T ($[Se]_{plant\ leaf}/[Se]_{soil}$) of 66.47 and 3.85, respectively, which displayed more transportation efficiency than that in the root and the stem, especially for *Adenocaulon himalaicum.* It should be pointed out that the leaf of *Siegesbeckia orientalis* had a very low ratio of L/T. In contrast, the leaf of *Trifolium repens* could accumulate Se from the underlying soil with a ratio of L/T of 1.74, although its root did not display this feature. The other plant species had the ratios of L/T of less than 0.5, which revealed that those plants did not prefer Se. Similar trends were found in the ratios of L/B ($[Se]_{plant\ leaf}/[Se]_{bioavailable\ in\ soil}$) and L/(B + Tr) ($[Se]_{plant\ stem}/[Se]_{bioavailable\ plus\ transferable\ in\ soil}$).

Overall, *Adenocaulon himalaicum* displayed the exceptional ability to accumulate Se in its root, stem, and leaf tissues. *Medicago sativa* was also a good Se-accumulator. *Trifolium repens* accumulates Se in its leaf part, but not in other parts.

The relationships between plant selenium accumulation and the extracted fractions in vegetated soils, and Se concentrations in different plant tissues are compiled in Fig. 2.3. The results show that the Se concentration in root significantly correlated with ($R^2 = 0.81$, $P < 0.05$) the total Se content in the soil. The sum of bioavailable and transferable Se, not total Se in the underlying soil dominated the Se content in the plant stem and the plant leaf with a high positive correlation coefficient of 0.87 and 0.81, respectively, which is different from that in plant root (Fig. 2.3).

Table 2.4 The bioconcentration factors (BCF) of root (R), stem (S), and leaf (L) compared with the total Se content (T), the bioavailable Se content (B), and the transferable Se content (Tr) of underlying soils, respectively

No.	Latin name	Root (R)			Stem (S)			Leaf (L)		
		R/T	R/B	R/(B + Tr)	S/T	S/B	S/(B + Tr)	L/T	L/B	L/(B + Tr)
1	*Adenocaulon himalaicum*	28.44	249.38	28.42	/	/	/	66.47	582.95	66.44
2	*Siegesbeckia orientalis*	2.48	39.26	7.18	1.87	29.58	5.41	0.11	1.72	0.31
3	*Erigeron annuus*	0.43	8.55	1.00	0.35	7.03	0.82	0.32	6.43	0.75
4	*Artemisia lavandulaefolia*	0.43	1.11	0.46	0.10	0.27	0.11	0.29	0.75	0.31
5	*Sedum sarmentosum*	0.31	9.48	1.56	0.14	4.38	0.72	0.71	21.81	3.59
6	*Miscanthus sinensis*	0.24	6.05	0.87	0.15	3.63	0.52	0.25	6.25	0.90
7	*Miscanthus purpurascens*	0.28	5.57	0.74	0.06	1.15	0.15	0.14	2.81	0.38
8	*Mosla dianthera*	0.32	3.22	0.87	0.26	2.61	0.70	0.46	4.64	1.25
9	*Elsholtzia splendens*	1.09	5.27	1.52	/	/	/	0.65	3.14	0.91
10	*Trifolium repens*	0.39	8.83	2.09	/	/	/	1.74	39.68	9.39
11	*Medicago sativa*	3.46	41.36	14.15	3.54	42.30	14.47	3.85	46.07	15.76
12	*Lycodium clavaturn*	0.47	1.54	0.54	/	/	/	0.54	1.80	0.64
13	*Polygonum hydropiper*	0.35	6.69	0.90	/	/	/	0.45	8.64	1.17
14	*Rumex japonicus*	0.23	5.50	0.67	/	/	/	0.40	9.39	1.15

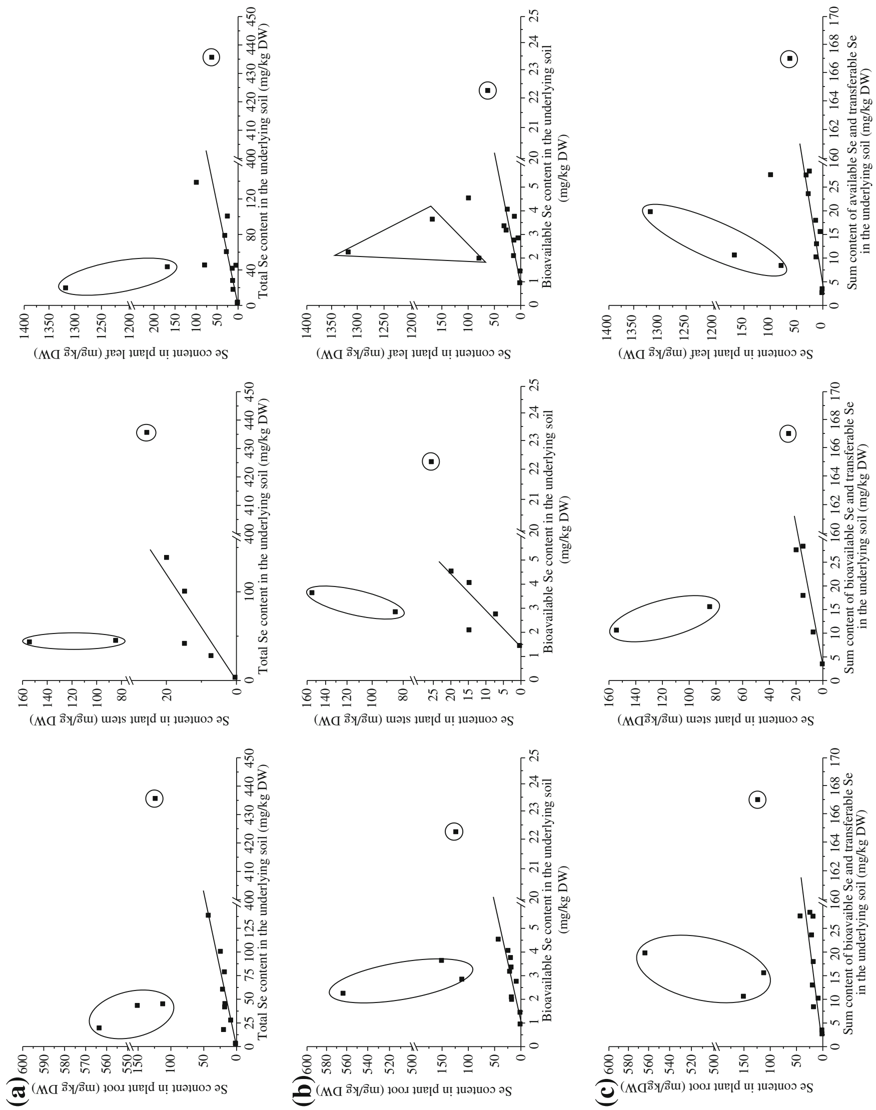

Fig. 2.3 The relationship between the Se content of extracted fraction in the underlying soil and the Se content of plant tissue. (**a**) The total Se content of underlying soil versus the Se content of plant root, plant stem, and plant leaf, respectively; (**b**) The bioavailable Se content of underlying soil versus the Se content of plant root, plant stem, and plant leaf, respectively; (**c**) The sum content of bioavailable Se and transferable Se in underlying soil versus the Se content of plant root, plant stem, and plant leaf, respectively

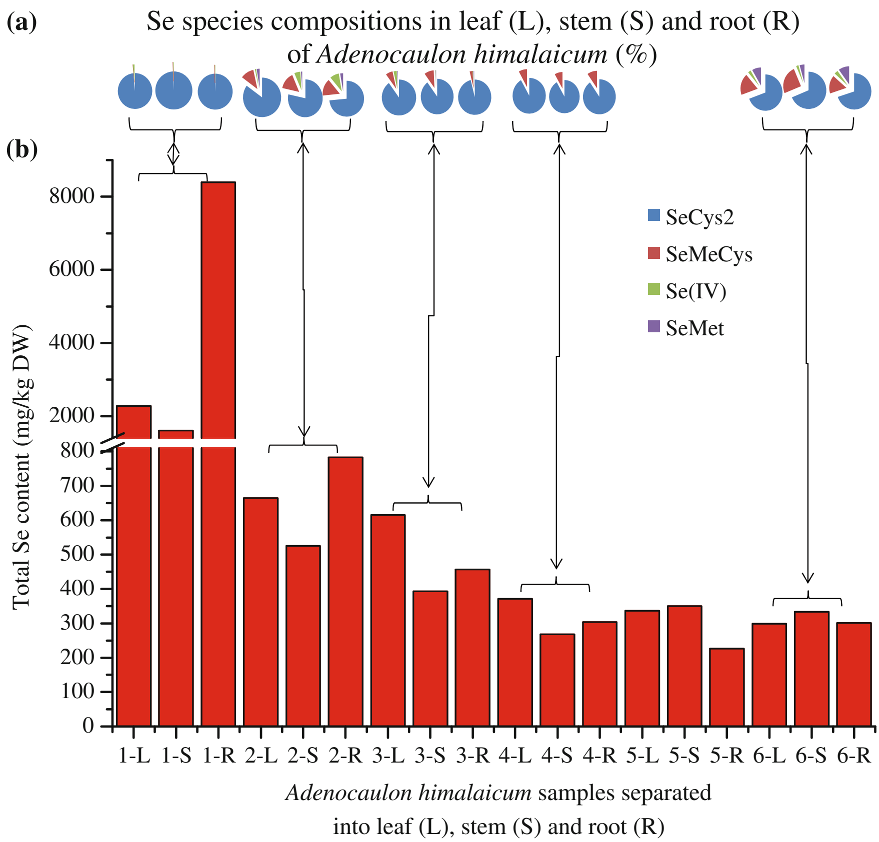

Fig. 2.4 The Se species compositions (**a**) and the contents of total Se (**b**) in leaves, stems, and roots of *Adenocaulon himalaicum* from Enshi

2.6 Selenium Hyperaccumulating Plant and its Implications

Generally, Se concentrations in plants in Se-enriched soils were less than 25 mg/kg DW (Bell, Parker and Page 1992), except for a few Se-hyperaccumulator species containing over 1,000 mg/kg (Ellis and Salt 2003). Our current study shows that *Adenocaulon himalaicum* could be classified as a secondary Se-accumulating species. Figure 2.4b shows the concentrations of total Se, Selenocystine (SeCys2), Se-Methylselenocysteine (SeMeCys), and Selenomethionine (SeMet) in the leaves, stems, and roots of *Adenocaulon himalaicum*. The total Se concentrations were 760 ± 692 mg/kg DW in the leaf, 580 ± 468 mg/kg DW in the stem, and 1744 ± 2978 mg/kg DW in the root. Selenium speciation analysis indicated that $SeCys_2$, SeMeCys, and SeMet accounted for 70–98, 7–19, and 3–11 %, respectively, of the total Se accumulated in *Adenocaulon himalaicum* leaves (Fig. 2.4a). A similar pattern occurred in the stem and the root tissues. The proportion of $SeCys_2$ in *Adenocaulon himalaicum* increases with increasing the accumulation of total Se in the plant tissues.

In the literature, *Arabidopsis thaliana* and *B. juncea* accumulate Se mainly in the chemical form of selenate. However, when soils were supplied with selenate, garlic (*Allium sativum*), onion (*Allium cepa*), leek (*Allium ampeloprasum*), and broccoli (*Brassica oleracea*) accumulate Se primarily as SeMeCys (Beilstein et al. 1991; Kahakachchi et al. 2004; Pilon-Smits and Quinn 2010). SeMet is a common dominant Se species in most grains, such as wheat, barley, and rye (Stadlober et al. 2001). However, to the best of our knowledge, this is the first time that SeCys2 is identified as the dominant Se chemical species in higher plants. This finding will provide important insight into Se-metabolism pathways for Se hyperaccumulator species. Moreover, if this Se-hyperaccumulating plant species could be cultivated and planted widely in Enshi, it could be a good Se-supplement source for animals or humans.

Generally, nonhyperaccumulating plants use Se through S pathways. However, recent studies suggest that Se might be essential for Se hyperaccumulator species and present specialized Se-specific transporters which are separate from S movement (Feist and Parker 2001; Galeas et al. 2007). Even in a different Se hyperaccumulator species (*Stanleya pinnata*), up to 90 % of the total Se accumulated in plant tissues is in the chemical form of MeSeCys (Freeman et al. 2006).

2.7 Selenium Distribution in Staple Crops and Selenosis in Enshi

The toxic effects of Se on human health are not commonly observed in natural environments worldwide. However, there are 477 cases of human selenosis reported between 1923 and 1988 in Enshi, China. In 1963, there were 283 people suffering from loss of hair and nail due to selenosis in the region. There are no human selenosis incidents reported in recent years, although the Se toxicity to livestock has been occasionally observed in the villages, showing hoof and hair loss (Fordyce et al. 2000).

To investigate the important factors that control human selenosis, a change in dietary Se intake in the past 50 years (1963–2010) was explored. The local daily dietary Se intake primarily depends on Se concentrations in foodstuff and the amounts of different types of food consumed. Yin and colleagues recently estimated that the food sources of daily dietary Se intake for residents in the Enshi region include cereals (50.7 %), vegetables (17.1 %), meat (15.7 %), tuber (13.5 %), bean (0.2 %), and others (2.8 %).

Maize is the most important cereal crop in Enshi, and the Se content in maize in Enshi had the highest Se concentration of 33.47 mg/kg DW in 1963 (Table 2.5). The average Se concentration in maize significantly decreased to 8.66 mg/kg DW 3 years later in 1966 (Yang et al. 1981a, b). While in the 1980s, the maize Se concentrations varied from 4.17 to 14.07 mg/kg DW (Zheng et al. 1993; Mao et al. 1997). During the early 1990s, maize had stable but low Se concentrations within a

Table 2.5 Variations on Se contents of food for residents in Enshi during 1963–2010

Food Source	Se content (mg/kg dry weight) mean (min–max)	Sampling time (year)	References
Maize	33.47	1963	Mao et al. (1997)
	8.66 (0.5–44.0)	1966	Yang et al. (1981a, b)
	14.07	1987	Mao et al. (1997)
	4.17 (0.77–7.57)	1989	Zheng et al. (1993)
	6.47 (2.18–10.76)	1992	Zhu and Zheng (2001)
	5.95 (4.40–7.50)	1995	Yin et al. (1996)
	1.38 (0.182–5.60)	1996	Fordyce et al. (2000)
	1.48 (0.07–2.89)	1999	Zhu et al. (2008a, b)
	0.37 (0–0.79)	2010	This study
Rice	3.96 (0.3–20.2)	1966	Yang et al. (1981a, b)
	1.26 (0.83–1.68)	1995	Yin et al. (1996)
	1.04 (0.34–1.74)	2010	This study
Bean	11.86 (5.0–22.2)	1966	Yang et al. (1981a, b)
	0.71 (0.46–1.37)	2010	This study
Carrot	11.84	1966	Yang et al. (1981a, b)
	0.23 (0.07–1.60)	2010	This study
Garlic	44.80 (8.30; 87.37)	1966	Yang et al. (1981a, b)
	0.53 (0.33–1.08)	2010	This study
Hyacinth bean	37.23	1966	Yang et al. (1981a, b)
	0.57 (0.11–3.75)	2010	This study
Chinese cabbage	36.42 (5.77–72.17)	1966	Yang et al. (1981a, b)
	0.72 (0.31–2.73)	2010	This study
Pumpkin	33.20 (6.28; 60.02)	1966	Yang et al. (1981a, b)
	0.76 (0.31–3.22)	2010	This study
Eggplant	38.30	1966	Yang et al. (1981a, b)
	1.04 (0.43–3.21)	2010	This study
Kidney bean	28.17	1966	Yang et al. (1981a, b)
	1.57 (0.41–4.14)	2010	This study
Potato	9.20 (3.17; 15.13)	1966	Yang et al. (1981a, b)
	0.28 (0.04–1.07)	2010	This study

range from 5.95 to 6.47 mg/kg DW (Yin et al. 1996; Zhu and Zheng 2001). However, the Se concentration in maize continued to decrease to 1.38–1.48 mg/kg DW during the late 1990s (Fordyce et al. 2000; Zhu et al. 2008b). Till 2010, the maximum Se concentration of maize was only 0.79 mg/kg DW, while 44.0 mg/kg in maize in 1963. Similar trends were found in rice, bean, carrot, garlic, hyacinth bean, Chinese cabbage, pumpkin, eggplant, kidney bean, and potato (Table 2.5). Concentrations of Se in blood or plasma are common indicators of Se status in the human body (Harrison et al. 1996). However, previous studies revealed that Se concentrations in the muscle and whole blood, red blood cells, blood plasma, hair, and toenails were significantly correlated with each other. In particular, human hair samples have been considered as a good bioindicator for the Se level in the human body (Tan and Huang 1991; Wietecha et al. 2005; Behne et al. 2010).

Table 2.6 Variations on Se contents of hairs and Se daily dietary intakes for residents in Enshi during 1966–2010

Se in hair (mg/kg dry weight) mean (min–max)	Se daily dietary intake (μg/d) mean (min–max)	Sampling time (year)	References
32.2 (4.1–100)	4,990 (3,200–6,690)	1966	Yang et al. (1981a, b)
/	1,338	1985	Yin et al. (1996)
26.4 (1.832–141)	/	1996	Fordyce et al. (2000)
17.49 (9.53–32.82)	575 (369; 526; 830)	2010	This study

In this study, we collected available data on Se contents of human hairs from Enshi region (Table 2.6). In 1966, the mean Se content in human hair was as high as 32.4 mg/kg DW, which was correspondent to selenosis there. After 30 years, the determined hair Se concentration was lower than that in 1966 and the value was 26.4 mg/kg DW, showing a decrease of 20 %. In this study, we also collected some hair samples from Enshi and the Se content was 17.94 mg/kg DW. Overall, the Se contents in human hair continued to decrease from 32.4 to 17.49 mg/kg DW during the past 45 years, which indicated that the Se level in the human body went down since selenosis occurred in the 1960s.

The adult daily dietary Se intake rates in different countries are compiled in Table 2.7, showing that the Se daily intake varied from 7 to 11 μg d^{-1} in the Keshan disease area to 600–5,000 μg d^{-1} in the selenosis areas in Enshi. The recommended dietary allowance (RDA) of Se for humans varied from country, region, age, and sex. In 1980, the estimated safe and adequate daily Se dietary intake for adults was 50–250 μg d^{-1}, and in 1989, the RDA value was established as 77 and 55 μg d^{-1} of Se for men and women, respectively (Pedrero and Madrid 2009). However, the WHO-recommended-RDA value for adults is 55 μg d^{-1} for both male and female (National Research Council 2000), and the tolerable upper Se intake level for adults is 400 μg d^{-1} (Food and Nutrition Board USA Institute of Medicine 2000). Yang et al. (1989) reported that Se homeostasis was disturbed at the Se intake of 750 μg d^{-1} or above, and the symptoms of selenosis occurred at the dietary Se intake level of >910 μg d^{-1}. It was also recommended that 550 μg Se d^{-1} was the maximum safe intake of Se for adults in high Se areas, such as Yutangba.

Based on our collected data, the daily Se intake was as high as 4,990 μg d^{-1} in 1966, much higher than the recommended maximum safe intake by Yang et al. (1989). But the daily Se intake for residents in Enshi continued to decrease from 4,990 μg d^{-1} in 1966 to 1,338 μg d^{-1} in 1985. Although the Se intake in 2010 was significantly lower compared with those in 1966 and 1985, the daily Se intake value still exceeded the recommended maximum safe intake of 550 μg Se d^{-1} (Yang et al. 1989; Yang and Xia 1995), indicating that there may be potential risk for selenosis currently in high Se areas in Enshi.

The Se-enriched coal stone was utilized as fuel materials for cooking and making lime by the villagers in Enshi, and they were also ground into powder as an

Table 7 A summary on Se intakes from different countries/regions modified from Rayman (2004) and Gao et al. (2011)

	Country/Region	Se intake (μg/person per day)	References
1	Keshan disease area (China)	7	Yang (1990)
	Saudi Arabia	15	Al-Salehet al. (1997)
	Czech Republic	10–25	Kvicala et al. (1996)
	Burundi (Africa)	17	Benemariya et al. (1993)
	New Guinea	20	Donovan et al. (1992)
	Nepal	23	Moser et al. (1988)
	China (except Keshan disease area and selenosis)	26–32	Chen et al. (2002)
	Croatia	27	Klapec et al. (1998)
	Egypt	29	Reilly (1996)
2	India	27–48	Mahalingam et al. (1997)
	Belgium	28–61	Robberecht and Deelstra (1994)
	Brazil	28–37	Maihara et al. (2004)
	UK	29–39	Ministry of Agriculture, Fisheries and Food (1997)
	France	29–43	Lamand et al. (1994)
	Serbia	30	Djujic et al. (1995)
	Slovenia	30	Pokorn et al. (1998)
	Turkey	30–36.5	Giray and Hincal (2004)
	Poland	30–40	Wasowicz et al. (2003)
	Sweden	31–38	Becker (1989)
	Germany	35	Alfthan and Neve (1996)
	Spain	35	Diaz-Alarcon et al. (1996)
	Portugal	37	Reis et al. (1990)
	Denmark	38-47	Danish Governmental Food Agency (1995)
	Slovakia	38	Kadrabova et al. (1998)
	Greece	39	Pappa et al. (2006)
	Netherlands	39–67	Kumpulainen (1993;) van Dokkum (1995)
	Italy	43	Allegrini et al. (1985)
	Suzhou (China)	44	Gao et al. (2011)
	Austria	48	Sima and Pfannhauser (1998)
	Ireland	50	Murphy et al. (2002)
3	Korea	58	Choi et al. (2009)
	Australia	57–87	Fardy et al. (1989)
	New Zealand	55–80	Vannoort et al. (2000)
	Switzerland	70	Kumpulainen (1993)
	Finland	80	Hartikainen (2005)
4	Japan	104–199	Rayman (2004)
	USA	94–134	Longnecker et al. (1991)
	Canada	98–224	Gissel-Nielsen (1998)
5	Venezuela	200–350	Combs and Combs (1986)
6	Selenosis area (China)	575–4,990	The present study

Note 1—Se deficiency area; 2—Se low-deficiency area; 3—Se adequate-low area; 4—Se high-adequate area; 5—Se high area; 6—Selenosis area agricultural fertilizer (Zhu et al. 2008b). Moreover, villagers in Enshi also discharged lime onto cropland to improve the soil quality during land clearing for agriculture or cultivation (Yang et al. 1983). These anthropogenic activities accelerated the release and transport of Se from coal stone into the food chain and very likely caused the Se poisoning in Enshi (Zhu et al. 2008b).

2.8 Selenium-Biofortified Agricultural Products in Enshi

Several earlier clinical trials have suggested that some organic forms of Se could lower the risk of certain types of cancer (Clark et al. 1996; Reid et al. 2008; Wallace et al. 2009).

Se daily intake data from the world are compiled in Table 2.7, which displays the intake of Se varying considerably between countries/regions. Keshan disease area (China), Saudi Arabia, Czech Republic, Burundi (Africa), New Guinea, Nepal, China (except KD and selenosis), Croatia, and Egypt were identified as Se-deficiency countries/regions because the levels of Se daily intake were below 30 μg/d; India, Belgium, Brazil, UK, France, Serbia, Slovenia, Turkey, Poland, Sweden, Germany, Spain, Portugal, Denmark, Slovakia, Greece, Netherlands, Italy, Suzhou (China), Austria, Ireland were identified as Se-low to Se deficiency area because the levels of Se daily intake were below the WHO recommended amount, 55 μg/d; Korea, Australia, New Zealand, Switzerland, and Finland were identified as Se-adequate to Se-low areas because of the levels of Se daily intake were in a range of 55–100 μg/d; Japan, USA, and Canada were recognized as Se-high to Se-adequate countries with the Se daily intake of 100–200 μg/d. It is quite a high level of Se intake in Venezuela with 200–350 μg/d; if the residents took more than 550 μg/d Se, it would cause selenosis symptoms, such as in Enshi, China. Overall, there are about 76 % (28/35) of countries located in Se-low areas with the Se daily intake level less than 55 μg/d. Especially in China, the Se daily intake varied considerably from toxic in Enshi, through low in Suzhou, to deficient in Keshan disease areas.

Soil Se distribution varied significantly in the world. More than 40 countries lack Se resources, while about 80 % of the world's total reserves of Se are located in Chile, the United States, Canada, China, Zambia, Zaire, Peru, Philippines, Australia, and Papua New Guinea (Liu et al. 2010). Although China is ranked fourth in Se reserves worldwide, after Canada, the United States, and Belgium, Se-deficiency occurs in a geographic low-Se belt stretching from Heilonjiang Province in the northeast to Yunnan Province in the southwest, affecting 71.2 % of Chinese land (Zhu et al. 2009). Therefore, Se food supplement is needed for many Chinese people. Till date, plant-based Se intake has been the only means for humans and animals in Se-deficient areas. Wheat, rice, and vegetables are usually Se-biofortificated to provide organic and safe Se compounds (Zhu et al. 2009; Liu et al. 2010).

2.8.1 Selenium Biofortification Strategy

Biofortification is a biological strategy, which aims to increase micronutrient contents in the edible parts of plants, animals, or microorganisms, via breeding or the use of biotechnology. It is considered to be a safe and effective way to alleviate micronutrient malnutrition in many micronutrient deficient/low areas or countries (Nestel et al. 2006; Mayer et al. 2008; Zhao and McGrath 2009). Generally, plant-based biofortification is the most effective and worldwide used strategy, especially on staple crops, because it is the best solution for improving the lack of nutritional trace elements in the world (White and Broadley 2009).

However, Se is not an essential micronutrition for higher plants, and Se will be transported via S-transportation pathway into plant tissues (Terry et al. 2000). In fact, the ability to absorb and accumulate Se is different in different plant species. Therefore, it is important to select special plant species which can accumulate Se in their edible parts for biofortification. Then, the biofortification strategies are used on these selected plants to increase the Se concentrations in the edible parts, which can be consumed by populations in Se malnutrition status. Furthermore, plants accumulating Se are useful as a "Se-delivery system" to supplement Se in the mammalian diet in many Se-deficient countries or areas, and these Se-biofortificated meat could be another important source for dietary Se intake. In addition, the un-edible parts of biofortified plants and the excrements of fortified animals could also be used as (organic) Se-enriched fertilizers for staple crops.

There are two strategies currently for Se-biofortification, agronomic approaches and genetic approaches.

(1) Agronomic biofortification strategies

Agronomic biofortification strategies are based on application of mineral fertilizers to improve the solubilization and mobilization of Se in the soil (White and Broadley 2009). The different forms of Se supplied for biofortification could be different in the Se accumulation of higher plants. Selenate is transported much more easily than selenite, or organic Se, and plant leaves could accumulate substantial amounts of selenate but much less selenite or SeMet (De Souza et al. 1998; Zayed et al. 1999). In addition, the mixture of organic acids with Se-mineral fertilizers were used to chelate Se, which could obviously improve the acquisition of Se and elevate the utilization efficiency of Se fertilizers (Morgan et al. 2005; Lynch 2007). It is also an effective approach to develop a more extensive root system, with longer, thinner roots with more root hairs, and by proliferating lateral roots in mineral-rich patches (White and Broadley 2005; Lynch 2007; Kirkby and Johnston 2008; White and Hammond 2008). Moreover, the rhizosphere microorganisms played an important role in phytoavailability of Se by plants (Morgan et al. 2005; Lynch 2007; Kirkby and Johnston 2008). It should be pointed out that the agronomic Se-biofortification strategies to increase crop Se contents by using inorganic Se fertilizers were very successful in Finland and New Zealand (Lyons et al. 2003; Hartikainen 2005). Clearly, it is promising to use the Se-enriched plants, crops, or agricultural products grown on naturally seleniferous soils, for example, in Enshi of China, as a natural Se supplement for people in areas with inadequate soil Se concentrations (Terry et al. 2000).

(2) Genetic engineering for biofortification

Genetic biofortification strategies are based on genetic variations or transgenic technology to increase abilities to acquire the objective micronutrient elements and accumulate them in edible parts of plants (White and Broadley 2009). Additionally, it is known that so-called "promoter" substances, such as ascorbate, β-carotene, and cysteine-rich polypeptides, could accelerate the absorption of micronutrient elements in plants, and it is possible to increase the concentrations of mineral elements in plants by increasing the contents of "promoter" substances in genetic ways. It is the reverse with "antinutrient" substances, such as oxalate, polyphenolics, or phytate (White and Broadley 2009). There is genetic variation in the concentrations of mineral elements in the grains of most cereal species. Some researches indicate that concentrations of Fe and Zn in cereal grain vary 1.5- to 4-fold among genotypes depending on the genetic diversity of the material tested (Cakmak 2008; Tiwari et al. 2008). Generally, the Se levels in different plants are as follows: brassica > bean > cereal (Liu et al. 2010). As for transgenic approaches, the selenocysteine methyltransferase gene of *Astragalus bisulcatus* (two-grooved poison vetch) was introduced into *Arabidopsis thaliana* (Thale cress) to overexpress Se-methylselenocysteine and γ-glutamylmethylselenocysteine in shoots (Ellis et al. 2004; Sors et al. 2005; Pilon-Smits and LeDuc 2009).

2.8.2 Selenium Biofortification in China

Considering that there are so many Se-deficient regions in the world, it is promising to take advantage of Se-enriched plants and crops in Enshi as a natural and green Se resource for animals and human beings.

One option is to add the Se-enriched plants in Enshi to soils in other Se-deficient areas as a source of organic Se fertilizer supporting forage crops. Proper amounts of this organic fertilizer can improve the Se status in the local soil as well as provide the crops with Se and other nutrition. Second, it is a good solution to use Se-enriched plant materials in Enshi as forage for animals in other Se-deficiency areas. Third, the Se-enriched staple crops in Enshi could be regarded as naturally Se-biofortified products, and those Se-enriched products could be consumed by populations in Se-deficiency areas as Se food supplement sources. The local business in Enshi has developed some Se-enriched products, such as tea, rice, maize, herb, and drinks.

The development of Se-biofortification has been ongoing for decades in China (Yang et al. 2007). Generally, Se biofortification approaches in China can be divided into three different categories:

(1) Selective Se-accumulated crop species

The black rice Jinlong No.1, cultivated by Jilin Academy of Agricultural Sciences, could accumulate Se with a content of 6.5 μg/g DW. Jiangsu Academy of Agricultural Sciences cultivated an Se-enriched rice species, named Longqing No.4, which was optimized from Suzi No.4 in Yunnan province. Shanxi Academy of Agricultural Sciences bred a new black wheat variety with Se concentration 112.8 % higher than the ordinary one. Furthermore, the selected Se-accumulated species, e.g., black rice, red rice, could significantly increase the content of Se in the edible parts. It is possible to mutagenize the Se-related genes in *Arabidopsis thaliana* to improve the efficiency of breeding Se-enriched crops at molecular level (Liu et al. 2010).

(2) Foliar application of Se fertilizer

Foliar spray with Se fertilizer is a practical way to improve the Se content of staple crops in China, and it played an important role in producing Se-enriched foods. Under the optimal application condition, Se contents of rice could be significantly increased by 194 % and reached over 120 μg/kg (DW) without reducing grain yields and protein/ash contents (Fang et al. 2008). Chen et al. (2002) also found that the Se contents of rice were significantly increased to 0.471–0.640 μg/g by foliar application of Se-fertilizer at a rate of 20 g Se/ha in the forms of sodium selenite and sodium selenate. At present, Se-enriched rice is available in the market and contributes significantly to consumers by improving their Se dietary intake since rice is one of the major staple foods in China. Tea is another popular Se biofortified product in China. Besides the Se contents of tea leaves being increased, the number of sprouts, the yield, the amino acid contents, the vitamin C contents as well as the sweetness and aroma of tea leaves could be significantly increased because of the implementation of the Se biofortification strategy (Hu et al. 2003).

(3) Application of soil Se fertilizers

This approach is to apply Se fertilizers around plant root zone to increase the total Se content and bioavailable Se in the rhizosphere environment. Compared with natural biofortification and foliar spray approaches, the application of soil Se fertilizers has the following advantages: (1) it breaks down the geological limitations for Se biofortification, compared with the natural biofortification in seleniferous areas; (2) the Se chemical forms and contents in Se-biofortified products would be much safer than those via foliar spray; and (3) it could largely reduce the deviation of Se contents in the biofortified products to ensure high quality on Se-enriched products in future.

Generally, fruits and vegetables in China contain less than 3 μg/kg Se (wet weight) while rice less than 50 μg/kg, and tea less than 250 μg/kg (Yin and Li 2011). However, the use of soil Se fertilizers could improve the Se contents in the products by several hundred times, and it was performed on various cereals, fruits, and vegetables (Liu et al. 2010; Yin and Li 2011). In recent years, the Se fertilizer application strategy was commonly used in Chinese agricultural production and produced safe and green Se-enriched foods in the market, such as fruits, vegetables, rice, and tea. Indeed, the novel concept of functional agriculture had been adopted by Chinese scientists and it has received more and more recognition from growers to consumers (Zhao and Huang 2010).

2.9 Summary and Outlooks

Selenium is an essential mineral nutrient for humans and animals. Selenium is needed for the formation of several proteins such as glutathione peroxide and thioredoxin reductase. However, the gap between the beneficial and harmful levels of Se is quite narrow. The Keshan disease and the Kaschin-Beck disease caused by Se deficiency occurred in Heilongjiang, China, with a daily Se intake less than 11 μg/d and the loss of hair and nail caused by Se poisoning occurred in Enshi, central China, with a daily Se intake more than 575 μg/d. Therefore, the concurrent endemic diseases of Se-deficiency and selenosis that happened in China indicated the greatly uneven distribution of Se resources in China.

Although the Se concentration in resident foods and the daily Se intake decreased significantly from 1963 to 2010 in Enshi, the present daily Se intake (575 μg/d) is still above the recommended maximum safe intake with 550 μg/d, which indicates there may be potential risk for selenosis in Enshi. Moreover, the total soil Se content in Enshi concentrated in a range from 20 to 60 mg/kg DW which was approximately 150–500 times greater than the average Se content (0.125 mg/kg DW) in Se-deficient areas and approximately 50–150 times greater than that (0.40 mg/kg DW) in Se-riches areas in China, respectively.

In contrast, there are about 76 % countries located in Se-deficiency areas with the Se daily intake level less than 55 μg/d for adults. Especially in China, Se-deficiency occurs in a geographic low-Se belt stretching from Heilonjiang Province in the northeast to Yunnan Province in the southwest, covering about 70 % of Chinese land.

Therefore, it is promising to take Se-biofortification naturally in Enshi. Se-enriched plants or crops in Enshi could be taken as a source of Se-organic fertilizer to increase the Se contents of staple crops, or as a source of Se-organic forage to support the Se-deficiency livestock in Se-deficient areas. Se-enriched crops, such as rice, maize, could be consumed by the population as a safe Se-supplement in Se deficiency areas. Furthermore, an Se-hyperaccumulating plant, *Adenocaulon himalaicum,* could be planted widely in Enshi to gain high-Se materials, and it could also be biofortified in Se deficiency areas as a selective species.

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