Distribution and geological sources of selenium in environmental materials in Taoyuan County, Hunan Province, China

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Abstract The selenium (Se) distribution and geological sources in Taoyuan County, China, were determined by using hydride generation atomic fluorescence spectrometry on rock, soil, and food crop samples collected from various geological regions within the county. The results show Se contents of 0.02–223.85, 0.18–7.05, and 0.006–5.374 mg/kg in the rock, soil, and food crops in Taoyuan County, respectively. The region showing the highest Se content is western Taoyuan County amid the Lower Cambrian and Ediacaran black rock series outcrop, which has banding distributed west to east. A relatively high-Se environment is found in the central and southern areas of Taoyuan County, where Quaternary Limnetic sedimentary facies and Neoproterozoic metamorphic volcanic rocks outcrop, respectively. A

relatively low-Se environment includes the central and northern areas of Taoyuan County, where Middle and Upper Cambrian and Ordovician carbonate rocks and Cretaceous sandstones and conglomerates outcrop. These results indicate that Se distribution in Taoyuan County varies markedly and is controlled by the Se content of the bedrock. The Se-enriched Lower Cambrian and Ediacaran black rock series is the primary source of the seleniferous environment observed in Taoyuan County. Potential seleniferous environments are likely to be found near outcrops of the Lower Cambrian and Ediacaran black rock series in southern China.

Keywords Selenium distribution · Selenium geological sources · Taoyuan County

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Introduction

Selenium (Se) is an essential element for both animals and humans; both its deficiency and excess can lead to Se-related diseases (Fordyce 2013). For example, Keshan disease and Kaschin–Beck disease (KBD) are both related to an environmental Se deficiency (Tan et al. 2002); human and animal selenosis has been reported from Enshi County, China, as a result of high level of Se in the environment (Fordyce et al. 2000). Combs (2001) has summarized that food system need to provide at least 40 µg Se/day (per adult), and a provisionally upper tolerable nutrient intake level for

Se was set at 400 µg/day for adults (FAO and WHO 2001). Therefore, the content and distribution of Se in environmental materials such as soil and food crops has received significant attention (Fordyce 2013; Duntas and Benvenega 2014; Johnson et al. 2000; Wang et al. 2013). Moreover, geochemical surveys of soil Se have been conducted worldwide (CCME 2009; Tan et al. 2002; US Geological Survey 2008; Yamada et al. 2009; Rawlins et al. 2012).

With regard to the distribution of soil Se, values in the USA range from 0.1 to 5.32 mg/kg (US Geological Survey 2008), with the highest concentrations found in the soils of the Great Plains and the most deficient soils found in the Pacific Northwest, northeastern USA, and the Southeastern Seaboard states (Kubota et al. 1967). In England and Wales, soil Se values range from 0 to 7 mg/kg (Rawlins et al. 2012). In Japan, the Se content of agricultural soils ranges from 0.05 to 2.80 mg/kg, with soils in the Kanto, Tohoku, Hokkaido, and Kyushu regions having the highest concentrations (Yamada et al. 2009). Thus, the Se content in soils varies markedly, and its distribution is extremely uneven.

With regard to the sources of Se in soils, particularly in the USA, seleniferous soils are related to Se-enriched Permian shales and Cretaceous rocks (Moxon 1937). In England and Wales, seleniferous soils are associated with organic matter and Lower Liassic (Jurassic) black shales (Rawlins et al. 2012). In Japan, seleniferous soils are related to organic-rich sediments and volcanic materials (Yamada et al. 2009).

With regard to plants, Se concentrations are generally relatively low at less than 0.1 mg/kg (Plant et al. 2014), although certain plants such as *Cardamine hupingshanensis* can accumulate high Se concentrations of up to 8000 mg/kg (Yuan et al. 2013). The Se content in plants is influenced by the Se content and speciation in the soil and the species of the plant. However, several factors require further study: the effects of the rock type and rock Se content on the content and distribution of Se in soil; the reason for the variance in Se content in identical plant species depending on the different geological stratum in their growth area is unknown.

Several studies have investigated the Se content and distribution patterns in soils, feed, and food for human consumption in China. For example, Liu et al. (1985) discussed the Se contents and distribution in forage

feed. Samples were collected to represent a variety of terrains, soil types, and agricultural zones. In total, they analyzed 11,467 samples from 1782 sampling sites across 1103 counties, including one to two sampling sites per county. The results showed that the Se contents in the forage feed of 790 counties, ~71.6 % of those investigated, were <0.05 mg/kg, suggesting that most forage feed in China is Se deficient.

The Endemic Disease Research Group at the Institute of Geographic Sciences and Natural Resources Research (IGSNRR) created a “Selenium Ecological Landscape Map of China” based on ~2000 soil samples (personal communication with Mr. Tan, the author of “Selenium Ecological Landscape Map of China”) in which a grading system for soil Se content was proposed. In this scale, ≥ 3.0 mg/kg is excessive; 0.40–3.0 mg/kg is high; 0.175–0.40 mg/kg is moderate; 0.125–0.175 mg/kg is marginal; and <0.125 mg/kg is deficient (Tan 1989). This map, which shows the macroscopic distribution pattern of Se in Chinese soils, contains fundamental data important for all subsequent research in this area. However, certain limitations remain.

China covers a vast geographical area; most of its counties are large with relatively complex geology. Furthermore, the Se contents of soils and plants vary greatly across Chinese counties. For example, soils with high Se concentrations (16–36 mg/kg) in the two areas with the most cases of selenosis (Ziyang County, Shaanxi, and Enshi County, Hubei Province) are locally distributed (Luo et al. 2004; Fordyce et al. 2000). These two selenosis areas are small, at about 0.5 and 0.42 km², respectively. The Se concentrations in the soils adjacent to these selenosis areas are significantly lower, at 0.034–0.288 mg/kg (Fordyce et al. 2000). Therefore, data from just one or two sampling sites per county are not necessarily representative of the actual Se contents and distribution patterns. Increasing the number of samples is necessary in general; gaining an in-depth understanding of the distribution and geological sources of Se in specific areas requires detailed investigation.

In addition, because the endemic disease research group at IGSNRR focused on Se deficiency, data were collected in areas of relatively low Se content, including areas with high rates of Keshan disease and KBD. Probable areas of high Se were outside of the group’s consideration.

Moreover, the average Se content of soil from a specific area was generally calculated as an arithmetic value based on the available samples from that area. However, the relative proportion of areas with different Se contents was not considered. Further, China has 2853 counties, many of which still require Se investigations. Therefore, the distribution and sources of Se in a specific area, such as a county, still require detailed investigation.

In summary, Se distribution in the environment is extremely uneven, and soil origin material such as bedrock, volcanic materials, and soil components such as organic matter and oxides affect Se distribution in soil and plants. Further survey is needed because the details of existing investigations are insufficient for reflecting Se levels in a relatively small area such as a county.

Taoyuan County has the largest cultivated land area in Hunan Province and is one of China's important agricultural bases for rice and its by-products. For many years, Se levels in Taoyuan County have been considered deficient. In response, the "selenium supplement program" was instigated in December 2006. The purpose of this program was to improve human dietary Se intake by developing, producing, and consuming Se-enriched agricultural and sideline products. However, some studies have found that not all areas have a Se deficiency; some Taoyuan County soils have relatively high Se concentrations (Ge et al. 1996). Thus, Se content and distribution patterns for the entire county are poorly understood.

The objectives of the present study are to investigate the concentrations and distribution patterns of Se in environmental materials such as bedrock, soil, and food crops in Taoyuan County and to discuss the geological sources of Se in soils and food crops in this county.

Geological and geographical setting

Taoyuan County is located in the northwest region of Hunan Province, China (longitude: 110°50'36"E–110°36'32"E; latitude: 28°24'30"N–29°24'13"N). Taoyuan is bordered by Shimen County to the north; Anhua to the south; Yuanling, Cili, and Yongding to the west; and Linli and Dingcheng to the east (Fig. 1).

Geologically, Taoyuan is located in the northeast region of the Xuefeng and Wuling uplifts and

southwest of the western Dongting depression. The earliest stratigraphic unit in Taoyuan is the Neoproterozoic Lengjiaxi Group. Stratigraphic development of the Upper Proterozoic and Lower Paleozoic deposits is complete, with the exceptions of missing upper Silurian strata; most of the Upper Paleozoic strata are also missing. The stratigraphic distribution within Taoyuan County is well defined with the Neoproterozoic Lengjiaxi Group slates outcropping mainly in the south, Neoproterozoic Banxi Group slates and sandstones present in the south and west, Neoproterozoic Ediacaran black siliceous rocks and Cambrian black shales and limestones present in the west, Ordovician limestones present in the northeast and northwest, Silurian siltstones present in the north, and Cretaceous sandstones and mudstones present in the central region. Paleogene mudstones and Quaternary limnetic sedimentary facies outcrop along the Yuanjiang River (Fig. 1).

Materials and methods

A total of 385 samples were collected from various geological regions of the county. The rock samples were collected from outcrops with fresh, unaltered faces. Following collection, all samples were washed with tap water and then with deionized water before being dried in a laboratory at room temperature. The soil samples were collected from cultivated farmland and were dried in a laboratory at room temperature. Branches, leaves, grass roots, and stones found within soil samples were removed with plastic tweezers. The dried rocks and soil samples were crushed until they were able to pass through a 100-mesh sieve and were stored in sealed plastic bags. Food crop samples were collected from the areas in which the soil samples were collected, washed with tap water followed by deionized water, and dried at 60 °C. The dried crop samples were also crushed to 100 mesh and were stored in sealed plastic bags.

The rock, soil, and crop samples were digested with a mixture of HNO₃ and HClO₄ acids. Se concentration was then determined by using hydride generation atomic fluorescence spectrometry (HG-AFS; AFS-9780, Beijing Kechuang Haiguang Instrument Co., Ltd, Beijing, China). For quality control during the chemical analyses, the following Chinese certified reference materials were randomly analyzed with each

Fig. 1 Geological map of Taoyuan County. *Shaded area* in the thumbnail (*left*) shows the location of Taoyuan County in China; *black dots* in geological map (*right*) show the sampling sites of this study

batch of rock, soil, and crop samples: soil: GBW07401, GBW07403, and GBW07406; rock: GBW07112; and crop: GBW10010, GBW10014, and GBW10016. In all Se analyses, the relative standard deviation was <10 %.

For extraction of water-soluble Se (W-Se) in the rocks and soils, such samples were treated twice with 25 mL deionized (DI) water and were shaken at 170 rpm for 2 h. After centrifugation, the supernatants were mixed carefully and were digested with a (5:1) mixed acid of HNO₃ and HClO₄. Se⁶⁺ was reduced to Se⁴⁺ with 6 M HCl, and the Se content in the digestion solution was then measured by using HG-AFS. Details of this method have been published elsewhere (Kulp and Pratt 2004).

Results

Se in rocks

The Se content in the rocks of Taoyuan County varies greatly, from 0.02 to 223.85 mg/kg, according to the type and age of the rock (Table 1). Lower Cambrian black shales contain the highest Se content at 21.59 ± 46.92 mg/kg, followed by Ediacaran black siliceous rocks at 2.91 ± 1.52 mg/kg and Middle and Upper Cambrian limestones at 0.68 ± 0.13 mg/kg. Very little difference, approximately 0.20 mg/kg, was found in the Se content of Ordovician limestones, Proterozoic Lengjiaxi and Banxi group slates, Cretaceous sandstones and mudstones, and Paleocene

Table 1 Selenium content in bedrock, soil, rice, corn, and beans in Taoyuan County (mg/kg)

Stratum	Lithology	Relative area (%)	Rock	Soil	Rice	Corn	Beans
Neoproterozoic Lengjiayi Group	Slate	14	0.11–0.28	0.50–1.03		0.026–0.042	
			0.18 ± 0.06	0.71 ± 0.21		0.034 ± 0.012	
			$n = 6$	$n = 4$		$n = 2$	
Neoproterozoic Banxi Group	Slate	16	0.08–0.33	0.43–0.67	0.047–0.135	0.032–0.081	0.062–0.157
			0.15 ± 0.07	0.53 ± 0.09	0.097 ± 0.036	0.055 ± 0.022	0.103 ± 0.041
			$n = 10$	$n = 4$	$n = 6$	$n = 6$	$n = 4$
Ediacaran	Black siliceous rock	2	0.92–6.38	1.41–1.52		0.051–0.064	0.053–0.234
			2.91 ± 1.52	1.48 ± 0.05	0.115	0.058 ± 0.010	0.143 ± 0.128
			$n = 24$	$n = 3$	$n = 1$	$n = 2$	$n = 2$
Lower Cambrian	Black shale	2	2.13–223.85	0.99–7.05	0.139–4.780	0.215–1.283	0.131–0.334
			21.59 ± 46.92	3.18 ± 1.95	1.040 ± 1.840	0.749 ± 0.755	0.225 ± 0.102
			$n = 27$	$n = 10$	$n = 6$	$n = 2$	$n = 3$
Middle and Upper Cambrian	Limestone	9	0.48–0.87	0.33–0.36		0.044–0.060	
			0.68 ± 0.13	0.34 ± 0.01	0.06	0.052 ± 0.011	0.108
			$n = 7$	$n = 2$	$n = 1$	$n = 2$	$n = 1$
Ordovician	Limestone	2	0.23–0.24	0.51–0.65			
			0.23 ± 0.004	0.60 ± 0.06			
			$n = 3$	$n = 4$			
Silurian	Siltstone	4	0.02–0.19	0.18–0.72	0.036–0.063		
			0.07 ± 0.05	0.45 ± 0.17	0.050 ± 0.019		
			$n = 21$	$n = 6$	$n = 2$		
Cretaceous	Mudstone Sandstone	34	0.09–0.45	0.20–0.68	0.040–0.391	0.038–0.088	0.052–0.245
			0.20 ± 0.12	0.41 ± 0.12	0.093 ± 0.085	0.060 ± 0.026	0.109 ± 0.050
			$n = 6$	$n = 32$	$n = 17$	$n = 3$	$n = 18$
Paleocene	Mudstone	3	0.13–0.22	0.35–0.80	0.006–0.098		0.083–0.135
			0.18 ± 0.02	0.60 ± 0.14	0.061 ± 0.036	0.044	0.107 ± 0.026
			$n = 11$	$n = 6$	$n = 6$	$n = 1$	$n = 3$
Quaternary	Limnetic facies sediment	14		0.31–0.80	0.047–0.151	0.026–0.183	0.065–0.423
				0.51 ± 0.13	0.089 ± 0.030	0.077 ± 0.058	0.160 ± 0.098
				$n = 40$	$n = 15$	$n = 6$	$n = 15$

mudstones. The Silurian siltstones contained the lowest concentration of Se at 0.07 ± 0.05 mg/kg.

Se in soil

The Se contents in the soils of Taoyuan County range from 0.18 to 7.05 mg/kg (Table 1), with an arithmetic mean value of 0.76 mg/kg. Soil samples with relatively low (<0.4 mg/kg), moderate 0.4–1.0 mg/kg, and high (>1.0 mg/kg) Se concentrations account for 6, 82, and 12 % of the total soil samples, respectively.

Because each soil sample represents a different soil area, an arithmetic mean value might mask the actual distribution of soil Se concentration. Therefore, the relative proportion of each geological area sampled in Taoyuan was used as weighting value for calculation of the weighted average for Se soil concentration (0.57 mg/kg).

The mean concentration of Se in the soils of various stratum outcrop areas decreased in the following order: Lower Cambrian (3.18 ± 1.95 mg/kg) > Ediacaran (1.48 ± 0.05 mg/kg) > Neoproterozoic Lengjiayi

group (0.71 ± 0.21 mg/kg) > Ordovician (0.60 ± 0.06 mg/kg), Paleogene (0.60 ± 0.14 mg/kg) > Neoproterozoic Banxi group (0.53 ± 0.09 mg/kg) > Quaternary (0.51 ± 0.13 mg/kg) > Silurian (0.45 ± 0.17 mg/kg) > Cretaceous (0.41 ± 0.12 mg/kg) > Middle and Upper Cambrian (0.34 ± 0.01 mg/kg).

Se geochemical trends are considered to be influenced by natural processes rather than by county or other political borders. Large counties almost always span several heterogeneous geological provinces; thus, a countywide average for an element may not actually be representative of any specific point in that county. Therefore, a distribution map was selected to more accurately represent the Se concentration in soils across the entire county. In general, interpolation methods are used for the prediction of Se content in unknown areas. However, this method is suitable only for areas with approximately homogeneous geological backgrounds. For areas containing complex geology, predicting Se distribution in soil using Kriging interpolation will likely produce a poor approximation of the actual concentrations (Fig. 2a). Therefore, a predictive soil Se distribution map was created by using the average soil Se values for each of the various geological units (Fig. 2b). As expected, this map (Fig. 2b) provided a better approximation of the actual soil Se geochemical trends.

The highest Se concentrations in Taoyuan County soils occur in the west, where the Lower Cambrian and Ediacaran black rocks series outcrops. These outcrops exhibit banding distributed west to east. Relatively large Se concentrations occur in central and south areas, where Quaternary limnetic sedimentary facies and Neoproterozoic metamorphic volcanic rocks outcrop, respectively. Soils with relatively low Se concentrations are distributed in the central and northern areas, where Middle and Upper Cambrian and Ordovician carbonate rocks and Mesozoic Cretaceous sandstones and conglomerates outcrop.

Water-soluble Se in rocks and soils

The W-Se content in selected rocks and soils is summarized in Table 2. W-Se in rocks from various strata ranged from 1.37 to 1022.55 μ g/kg. Among all rock samples, Lower Cambrian black shale and Ediacaran black siliceous rock contained the highest amount of W-Se, at 197.81–1022.55 and 101.46–247.86 μ g/kg, respectively, whereas that of other rocks was relatively

low at 1.37–18.47 μ g/kg. The W-Se in the Lower Cambrian black shale and Ediacaran black siliceous rock accounted for 2.35–5.19 and 1.83–4.42 % of the total Se, respectively, although that in other rocks showed little difference at 0.90–8.36 %, with an average of 3.76 ± 2.64 %. The proportions of W-Se in high-Se rocks in Taoyuan, including the Lower Cambrian black shale and Ediacaran black siliceous rock, are similar to those in previous research of Se-enriched strata in South China that showed averages of 5.04 and 7.32 % in black shale and cherts, respectively (Fan et al. 2011).

The W-Se content in soils derived from various strata ranged from 1.60 to 1103.86 μ g/kg, with a geometric mean of 28.34 μ g/kg. Soils derived from Lower Cambrian black shale contained the highest amount of W-Se, at 294.45–1103.86 μ g/kg. However, the W-Se content in soils derived from Ediacaran black siliceous rocks, at 46.29–70.58 μ g/kg, was slightly higher than that in other soils, at 1.60–47.68 μ g/kg with an average of 22.27 ± 11.48 μ g/kg. The W-Se in the soil of Taoyuan was higher than that in soils of the KBD area; that in the Tibetan Plateau is 5.7–10.9 μ g/kg with an average of 7.6 μ g/kg (Wang et al. 2013).

Se in food crops

The Se content in food crops in Taoyuan County ranged from 0.006 to 5.374 mg/kg (Tables 1, 3). The Se contents in rice, corn, and beans were 0.006–4.780 mg/kg (mean: 0.190 ± 0.632 mg/kg), 0.026–1.283 mg/kg (mean: 0.118 ± 0.253 mg/kg), and 0.052–0.413 mg/kg (mean: 0.133 ± 0.077 mg/kg), respectively (Table 1). The Se in peanuts was 0.010–0.150 mg/kg (mean: 0.075 ± 0.035 mg/kg), and that for tea was 0.127–0.174 mg/kg (mean: 0.156 ± 0.020 mg/kg). In other food crops, the Se concentrations ranged from 0.006 to 5.374 mg/kg (Table 3). Se concentration in the same types of food crops but from different strata outcrop areas varied markedly.

The Se content in food crops grown in the soils of different strata outcrop areas also varied greatly. In general, the rice, corn, and beans grown in the Lower Cambrian black shale outcrop area contained the highest concentrations of Se; that in the rice, corn, and beans from the other strata outcrop areas was relatively low. For other food crops, those grown in Lower Cambrian black shale and Ediacaran black

Fig. 2 Soil Se distribution map of Taoyuan County. Map **a** (left) was finished by using ArcGIS 10.0 (Kriging interpolation was applied); map **b** was drawn manually based on the average

siliceous rock outcrop areas also contained significantly high Se (Table 3). For example, the Se contents in the leaves and stalk of asparagus were 3.084 and 5.374 mg/kg, respectively, which is significantly higher than their commonly occurring values of 0.2–0.8 mg/kg (Sirichakwal et al. 2005).

Discussion

Se levels in Taoyuan County

The weighted mean Se contents (0.57 mg/kg) of soils from Taoyuan County were 1.43 and 1.97 times higher than the mean soil Se values worldwide (0.4 mg/kg) and in China (0.29 mg/kg), respectively (Plant et al. 2014). These values are also higher than the mean soil Se values for the USA (0.26 mg/kg) (US Geological Survey 2008), Canada (0.3 mg/kg) (CCME 2009), and Japan (0.51 mg/kg) (Yamada et al. 2009). Se contents

soil Se values for each of the different geological units. Red dots with different radius refers to soil Se content of this site

in the soils of Taoyuan County were higher than the mean soil Se values in Ziyang County at 0.094–23.530 mg/kg with a mean of 0.323 mg/kg (Zhao et al. 1993); however, the values were significantly lower than those in Ziyang County, at 16–36 mg/kg in Naore village (Luo et al. 2004).

Statistical analysis showed that the Se contents in soils from Se-deficient, Se-moderate, and selenosis areas in China were 0.004–0.48, 0.73–5.7, and 1.49–59 mg/kg, respectively (Plant et al. 2014). Therefore, the soil Se content in Taoyuan County is closest to the moderate Se concentrations, with only a few soil samples containing Se concentrations beyond the moderate range. Furthermore, the arithmetic and weighted mean values of Se concentrations in the soils of Taoyuan County were both higher than the upper limit value for Se-deficient areas in China. The mean values of Se concentration in the main food crops of rice, corn, and beans were also higher than the mean values in moderate Se concentration areas but were

Table 2 Water-soluble Se content in selected rock and soil samples from different stratum

Stratum	Rock					Soil			
	Sample ID	Lithology	W-Se ($\mu\text{g/kg}$)	Se _{tot} ($\mu\text{g/g}$)	W-Se/ Se _{tot} (%)	Sample ID	W-Se ($\mu\text{g/kg}$)	Se _{tot} ($\mu\text{g/g}$)	W-Se/ Se _{tot} (%)
Neoproterozoic Lengjiayi Group	TY3Y-1	Slate	5.55	0.16	3.42	TY3T-2	30.15	1.51	1.99
	THYY-1	Slate	7.17	0.17	4.32	THYT-1	9.72	0.50	1.93
Neoproterozoic Banxi Group	SPY-1	Slate	1.87	0.21	0.90	SPT-2	38.56	0.43	8.89
	TY-27	Slate	5.95	0.08	7.58	TT-26	1.60	0.28	0.57
Ediacaran	JJS-7	Black siliceous rock	247.86	5.61	4.42	TT-43	70.58	1.52	4.64
	JJS-9	Black siliceous rock	101.46	5.56	1.83	TT-44	46.29	1.41	3.28
Lower Cambrian	GYSM-34	Black shale	197.81	8.43	2.35	GY2T-3	1103.86	4.26	25.94
	TY3Y-6	Black shale	1022.55	19.72	5.19	TY3T-6	294.45	6.36	4.63
Middle and Upper Cambrian	TY3Y-8	Limestone	4.11	0.26	1.56	TY3T-8	37.37	0.39	9.52
Ordovician	HPY-1	Limestone	3.99	0.24	1.68	HPT-1	18.46	0.63	2.93
	HSY-1	Limestone	18.47	0.23	8.09	HST-1	29.50	0.37	7.90
Silurian	RSY-1	Siltstone	4.25	0.08	5.48	RST-1	21.09	0.59	3.57
	RSY-22	Siltstone	11.79	0.14	8.36	RST-5	47.68	0.72	6.60
Cretaceous	TY-11	Mudstone	2.10	0.18	1.14	TT-11	13.37	0.29	4.61
	TY-12	Sandstone	1.37	0.09	1.52	TT-12	14.10	0.35	4.05
	LTY-1	Mudstone	3.34	0.15	2.17	LTT-4	11.65	0.45	2.60
Paleocene	JSY-11	Mudstone	5.83	0.22	2.67	JST-1	20.31	0.57	3.53
Quaternary						QH2T-1	20.44	0.63	3.27
						QH2T-2	30.31	0.80	3.78

Se_{tot} total Se in rock or soil samples, W-Se water-soluble Se

lower than those in selenosis areas (Yang et al. 1983; Fordyce 2013). The Se concentration in Taoyuan County teas was lower than that in regulated Se-enriched teas (0.25–4.00 mg/kg, NY/T 600–2002) and in teas (0.6 ± 0.6 mg/kg) from Ziyang County (Cheng et al. 1991).

Therefore, the Se levels in the environmental materials of Taoyuan County can be categorized as moderate according to the Chinese scale, which is in contrast to previous determinations of Se deficiency in the area.

Source of Se in Taoyuan County

The Se concentrations in the soil and food crops varied greatly, in which the highest value was hundreds of times greater than the lowest value. Furthermore, soils and food crops contain high Se values when the bedrock also contains high Se values (Fig. 3). An exponential relationship was found between the average Se contents in bedrock and those in soil and food

crops (Fig. 4). This indicates that the Se content of the bedrock controls the Se concentrations in soils and food crops.

Naore Village, Ziyang County, Shannxi Province, is a selenosis area of China. In this area, Luo et al. (2004) performed a detailed study of the Se content, distribution pattern, and sources of Se. The soil was found to be derived from high-Se, pyritic, black carbonaceous slate and volcanic tuff of the Lujiaping Formation, which is early Cambrian and late Neoproterozoic in age and is exposed in this area. The authors deduced that this series of Se-enriched rocks also occurs in other parts of the Daba region of South Qinling Mountain. In addition, Se-enriched black carbonaceous shales of early Cambrian age occur in several other provinces of South China. The Lower Cambrian and Ediacaran black rock series is widely distributed in the Niuchehe, Zhongjiapu, Ligonggang, and Guanyinsi villages of Taoyuan County, and the strata age and rock type are the same as those in Naore Village. Soil and crop samples containing high Se

Table 3 Selenium content in vegetables and teas in Taoyuan County (mg/kg)

Crops	Stratum	Bedrock	Se content
Peanut	Lower Cambrian	Black shale	0.150 ($n = 1$)
	Middle and Upper Cambrian	Limestone	0.048 ($n = 1$)
	Cretaceous	Mudstone and sandstone	0.069 ± 0.015 ($n = 6$)
	Paleocene	Mudstone	0.066 ($n = 1$)
	Quaternary	Limnetic facies sediment	0.075 ± 0.046 ($n = 4$)
Garlic	Neoproterozoic Banxi Group	Slate	0.435 ($n = 1$)
	Cretaceous	Mudstone and sandstone	0.102 ($n = 1$)
Garlic sprout	Neoproterozoic Banxi Group	Slate	0.197 ($n = 1$)
	Cretaceous	Mudstone and sandstone	0.060 ($n = 1$)
Chili	Neoproterozoic Lenjiaxi Group	Slate	0.143 ($n = 1$)
	Ediacaran	Black siliceous rock	0.605 ($n = 1$)
	Middle and Upper Cambrian	Limestone	0.035 ($n = 1$)
	Cretaceous	Mudstone and sandstone	0.045 ($n = 1$)
	Quaternary	Limnetic facies sediment	0.088 ($n = 1$)
Pumpkin	Neoproterozoic Banxi Group	Slate	0.046 ($n = 1$)
Asparagus leaves	Lower Cambrian	Black shale	5.374 ($n = 1$)
Asparagus stalk	Lower Cambrian	Black shale	3.084 ($n = 1$)
Apium	Neoproterozoic Lenjiaxi Group	Slate	0.125 ($n = 1$)
Houttuynia	Neoproterozoic Lenjiaxi Group	Slate	0.071 ($n = 1$)
Fiddlehead	Neoproterozoic Lenjiaxi Group	Slate	0.179 ($n = 1$)
Sweet potato	Neoproterozoic Banxi Group	Slate	0.049 ± 0.014 ($n = 2$)
	Middle and Upper Cambrian	Limestone	0.044 ($n = 1$)
Camellia seed	Quaternary	Limnetic facies sediment	0.013 ($n = 1$)
Tea	Neoproterozoic Lengjiaxi Group	Slate	0.174 ($n = 1$)
	Cretaceous	Mudstone and sandstone	0.147 ± 0.019 ($n = 2$)

concentrations were collected from all of the aforementioned villages. On this basis, it can be concluded that the Se-enriched Lower Cambrian and Ediacaran black rocks series is the source of the seleniferous soils in Taoyuan County.

Effect of Se in rocks on soil and crop Se distribution

In general, Se in rock is relatively low, with 0.05 mg/kg measured in the Earth's crust. As given in Table 1, the Se content in slate, limestone, siltstone mudstone, and sandstone is 0.02–0.87 mg/kg. Very high Se concentrations were found in some black rock series including black shale and cherts (Feng et al. 2010). Similarly, the Se contents in Lower Cambrian black shale and Ediacaran black siliceous rocks were significantly higher than those in the other rocks of

Taoyuan County. Se in rock is the most important natural source of Se in the environment. High-Se rocks such as the Lower Cambrian–Ediacaran black rock series act as sinks for the seleniferous environment, whereas low-Se rocks exposed in the middle and north regions of Taoyuan County are likely responsible for the development of the low-Se environment.

Se concentrations in soils derived from the Lower Cambrian–Ediacaran black rock series were significantly lower than those in their origin materials (Tables 1, 2). However, soils derived from the other strata contained higher Se than their origin materials (Tables 1, 2). This result indicates that other factors affect Se distribution in soil. Johnson et al. (2000) suggested that organic-rich soils may have higher Se in Zhangjiakou District and the seleniferous soils are related to organic matter and volcanic materials in Japan (Yamada et al. 2009). Additional, Se(IV) is

Fig. 3 Effects of selenium content in bedrocks on selenium content in soil and food crops

Fig. 4 Relationship between selenium content in bedrocks and in soil and food crops

strongly absorbed in iron oxides in acidic soils (Plant et al. 2014). These findings suggest that factors other than Se in rock are responsible for the relatively low-Se environment in Taoyuan County.

Bioavailable Se plays a more important role than total Se in soil in Se uptake by plants. W-Se is the major form of bioavailable Se. As given in Tables 1 and 2, W-Se in the Lower Cambrian–Ediacaran black rocks series and their derived soils is significantly higher than that in the other rocks and soils, respectively. This indicates that the high-Se Lower Cambrian–Ediacaran black rocks series can provide significantly more W-Se than the other rocks. Therefore, food crops planted on the Lower Cambrian–Ediacaran black rocks series outcrop areas have more available W-Se. The accumulation of heavy metals in the environment to toxic concentrations may lead to ecological damage (Ashraf et al. 2011a, b; Abu Bakar et al. 2013). Excessive amounts of W-Se in the soil lead to toxic amounts of Se in edible parts of food crops, which can lead to Se poisoning in animals and human. Therefore, the Lower Cambrian–Ediacaran black rocks series outcrop areas are potential areas of Se poisoning.

Conclusions

This study has determined that the Se contents in bedrock, soil, and food crops in Taoyuan County, China, vary greatly at 0.02–223.85, 0.18–7.05, and 0.006–5.374 mg/kg, respectively. The Se distribution in Taoyuan County is extremely variable, with the highest Se concentrations occurring in Lower Cambrian and Ediacaran strata outcrop areas. Relatively high Se concentrations occur in Quaternary, Neoproterozoic strata outcrop areas, whereas relatively low Se concentrations occur in Middle and Upper Cambrian, Ordovician, and Mesozoic strata outcrop areas. The Se content in bedrock is the main controlling factor for the Se concentrations in soil and food crops. The seleniferous environment in Taoyuan County shows a banding west–east distribution. Its source is the Se-enriched Lower Cambrian–Ediacaran black rocks series, which is widespread in the Yangtze Platform in South China. The Se contents in these rocks, including the Lower Cambrian Niutitang Formation black shale and Ediacaran Liuchapo Formation cherts, are significantly higher

than those in other rocks. Therefore, we conclude that potential environments of Se poisoning are distributed in areas in which the Lower Cambrian–Ediacaran black rock series outcrops. Thus, caution should be heeded if these areas are cultivated.

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