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Geochemical characteristics and ecological effects of Se and Zn in topsoil in Western Fuling of Chongqing

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Abstract: A large area of soil in China is deficient in selenium (Se) and zinc (Zn)， meanwhile, Se and Zn are essential trace elements for human body, so it is of great significance to find Se and Zn rich soil to cultivate crops. Based on the data of Se and Zn in topsoil, crops and root soil obtained from 1:50000 land quality geochemical survey, this paper taking the western area of Fuling in Chongqing as the research area, studies the content and spatial distribution characteristics of Se and Zn in soil and crops, and analyzes the enrichment law of Se and Zn in agricultural crops. The results show that the average values of Se and Zn in the topsoil of the study area are 0.265mg/kg and 77.56mg/kg respectively. There are some differences in the contents of Se and Zn in different geological backgrounds, soil parent materials and soil types. The high value areas of Se and Zn are mainly distributed in the exposed areas of Triassic carbonate; in the study area, the average contents of Se and Zn in maize seeds are 0.029mg/kg and 20.752mg/kg respectively, and the enrichment rates are 96% and 82% respectively. The average contents of Se and Zn in rice seeds are 0.032mg/kg and 11.463mg/kg respectively, and the enrichment rates are 13.3% and 5% respectively. The bioaccumulation coefficients of Se and Zn in maize are higher than that in rice, and the availability of Se and Zn elements in maize root soil is higher.The results can provide geochemical basis for developing characteristic land resources, functional agriculture and promoting rural revitalization in Fuling District.

Key words: Fuling; Soil; Crops; Se; Zn; Ecological Effect

1. Introduction

At present, China's agriculture has developed into the third stage of functional agriculture after high-yield agriculture and green agriculture, which has been written into the document on Rural Revitalization of the State Council and the rural industry revitalization of the Ministry of agriculture and rural areas, and has become an important direction for developing high-quality agriculture, health leading agriculture and promoting the strategy of healthy China (Zhao Qiguo et al., 2018; Zhang Junling et al., 2020). Functional agriculture solves the health problem of “invisible hunger” caused by the lack of micronutrients. Selenium (Se) and zinc (Zn), as essential trace elements for human body to maintain normal metabolism, lacking or excessing will endanger human health (Kao Xibin et al., 2007; Hu Yan et al., 2011; Zhang Ling et al., 2013; Weekly and Harris, 2013; Hosnedlova et al., 2017). In the biosphere, human beings obtain Se, Zn and other trace elements mainly through the food chain “soil-plant-human” or “soil-plant-animal-human”. Soil is the main source, and plants absorbing the content of Se, Zn and other elements in soil is the key. The distribution of soil Se and Zn is extremely uneven all over the world. About 72% of the soil in China is varying degrees deficient in Se, and there is a low Se belt from northeast to southwest (Wang et al., 2017; Dinh et al., 2018a). Chongqing is also deficient in Se (China environmental monitoring station, 1990). At the same time, it is a large area of Zn deficiency in the soil of in in the north and central southern China such as Hunan, Anhui, Jiangsu, Sichuan and other provinces (Alina k p et al., 1996; Hu Xueyu, 1999), and local residents are facing a certain degree of “hidden hunger” health risk. Therefore, it is of great significance to find out the distribution, development and utilization potential of Se and Zn rich soils and crops in an area for promoting Rural Revitalization and high-quality development of local economy and society based on local characteristic and advantageous resources.

Based on the content data of Se, Zn and other elements in topsoil, rice, maize and corresponding root soil obtained from the 1:50000 land quality geological survey, this paper taking the western area of Fuling in Chongqing as the research area, studies the distribution characteristics, migration and transformation laws and influencing factors

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of Se and Zn elements in soil and crops, and evaluates the ecological effects of Se and Zn rich land resources. It provides geochemical basis for the rational and effective development and utilization of Se and Zn rich characteristic land resources and the development of characteristic and efficient agriculture in Fuling area.

2. Overview of the study area

The study area is located in the hinterland of Chongqing and the Three Gorges Reservoir area, at the junction of Chengdu Chongqing egion, the junction of the twin city economic circle and the Yangtze River economic belt. The geographical coordinates between 106°56′-107°43′E and 29°21′-30°01′N. It is the transitional zone between Sichuan Basin and basin edge mountains. The landform types in the area are diverse, mainly hills and platforms, followed by low mountains, middle mountains and flat dams. The ridge shaped anticline low mountains and the wide and gentle syncline valley bottom are arranged alternately and orderly, mainly belonging to the Jiangnan area which is crossed by the Yangtze River and Wujiang River valley into the east of the Yangtze River, the north of the Yangtze River and the south of the Yangtze River (Fig.1). The climate belongs to the humid monsoon climate zone in the middle subtropical zone, and the three-dimensional climate is obvious. Rivers are developed in the area, mainly including Wujiang River, Lixiangxi River, Longtan River, Youjiang River, etc. Sedimentary rocks are widely developed, and Mesozoic Jurassic strata are exposed in a large area, mainly including Zhenzhuchong Formation (J1z), Ziliujing Formation (J1zl), Xintiangou Formation (J2x), Shaximiao Formation (J2s), Suining Formation (J3sn) and Penglaizhen Formation (J3p), and the lithology is mainly quartz sandstone, mudstone and siltstone, while only exposed in a small area on the east and west sides of the study area with Mesozoic Triassic Daye Formation (T1d) limestone mixed with mudstone and shale, Jialingjiang Formation (T1j) limestone and dolomite mixed with a small amount of salt soluble breccia, Badong Formation (T2b) dolomite, argillaceous dolomite and shale, Xujiahe Formation (T3xj) siltstone and feldspathic quartz sandstone mixed with mudstone, carbonaceous shale and coal cuttings. The land use types in the area mainly include paddy field, dry land, orchard, forest land and idle land. The soil types are mainly paddy soil, purple soil, yellow soil and yellow cinnamon soil, and the main bulk crops are rice and maize.

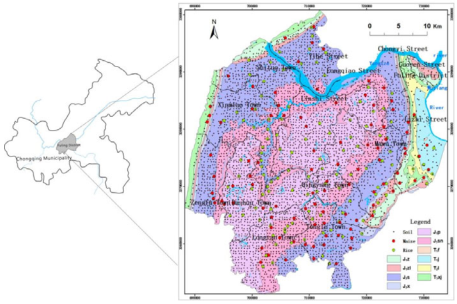

Figure 1 Schematic diagram of study area location and sampling points

3. Sample collection and analysis

3.1 Sample collection

In accordance with the specifications for geochemical evaluation of land quality (DZ/T 0295-2016) and the technical requirements for geochemical evaluation of land quality (Trial) (DD2008-06), a 1:50000 geochemical survey of land quality was carried out in the west of Fuling in 2020. 4372 surface soil samples were collected by grid and speckle method, with a sampling density of 4~6 points/km2, and the sampling depth is 0~20cm, and the newly transported accumulated soil and obvious pollution area shall be avoided during sampling.Around each sample point, which is composed of 4~5 sub samples within 50m. The collected samples shall be dried in the air, and the broken samples shall be sieved through 10 meshes. After the shrinkage method, 200 grams shall be weighed and bagged and sent to the laboratory for test and analysis. 120 samples of rice seeds and corresponding root soil and 100 samples of corn seeds and corresponding root soil were collected in August 2020. Rice (maize) seed samples are washed with distilled water, dried and shelled (manual threshing), and then sent to the laboratory for further processing and testing.

3.2 Analysis and test

Topsoil, crop seed and root soil samples are analyzed by Chongqing mineral resources supervision and testing center of the Ministry of natural resources. The soil samples are tested for pH, Corg.、Zn、Se and other 54 indicators, and 9 indexes such as heavy metal plus Se in crop seed test. PH was determined by ion electrode method (ISE), Corg. was determined by oxidation-reduction volumetric method (VOL), the contents of Zn, SiO2, Al2O3, TFe2O3、CaO、Na2O were determined by X-ray fluorescence spectrometry (XRF), Ce、Ni、Ba、Cu were determined by inductively coupled plasma spectrometry (ICP-AES), and Se and Ge were determined by atomic fluorescence spectrometry (AFS) in soil samples. As, CD, Cr, Pb, Zn, Cu and Ni were determined by plasma mass spectrometry, Se by atomic fluorescence method and Hg by cold atomic fluorescence method in crop seed samples. The test process shall be carried out in strict accordance with the relevant provisions of DZ/T0295-2016 code for geochemical evaluation of land quality, and the combination of external quality monitoring and internal quality monitoring is used to control the quality of sample analysis.

4. Results and discussion

4.1 Soil Se and Zn content and spatial distribution characteristics

The contents of Se and Zn in the surface soil of the study area are statistically analyzed, and the arithmetic average value after the cyclic elimination of three times of dispersion data is taken as the soil background value of the study area. The results are shown in Table1. The contents of Se and Zn in the topsoil of the study area are

0.06~19.9mg/kg and 21.4~950mg/kg respectively, with average values of 0.265mg/kg and 77.56mg/kg respectively, and background values of 0.26mg/kg and 76.95mg/kg respectively, which are higher than the background values of 0.126mg/kg and 72.965mg/kg of Chongqing riverside economic belt (Tang Jiang et al., 2006), close to the background values of 0.290mg/kg and 74.2mg/kg of Chinese soil (Wei Fusheng et al., 1991). The coefficients of variation were 31.06% and 31.82% respectively, belonging to the medium variation level, indicating that the spatial distribution of Se and Zn in the soil in the study area is relatively uniform.

Table 1 Contents and characteristic parameters of Zn and Se in soil (mg/kg)

element	minimum value	Maximum	average value	Coefficient of variation	Background value
Se	0.06	19.9	0.265	31.06%	0.26
Zn	21.4	950	77.56	31.82%	76.95

According to the specification for geochemical evaluation of land quality (DZ/T0295-2016), the contents of Se and Zn in the topsoil of the study area are evaluated. The results are shown in Table2. The content of soil Se in the study area is mainly distributed in the moderate amount of Se, 0.175~0.4mg/kg, with an area of 1233.57km2, accounting for 88.34% of the whole study area. The area with high Se is 44.4km2, accounting for 3.18%; the content of soil Zn is mainly concentrated in 71~200mg/kg, accounting for 71.17% of the whole study area, of which the Zn rich area is 528.98km2, accounting for 37.88%; the area relatively rich in Zn is 464.87km2, accounting for 33.29%. In addition, the content of Zn and Se in some soils exceeds the higher limit, which may cause pollution risk. While due to the small area, it has little impact on the overall environment.

Table 2 Statistical results of Se and Zn abundance and deficiency classification in the study area

Zn	Abundance and deficiency level	Unit	First (rich)	Second (relatively rich)	Third (medium)	Grade 4(relatively deficient)	Grade 5(deficient)	Higher limit value
	Rating criteria	Content (mg/kg)	>84	71 ~ 84	62 ~ 71	50 ~ 62	≤50	≥200
	Evaluation results	Area (km^2)	528.98	464.87	189.07	133.9	79.14	0.05
		Proportion(%)	37.88	33.29	13.54	9.59	5.67	0.04
Se	Abundance and deficiency level	Unit	Surplus	High	Moderate	Marginal	Deficient	
	Rating criteria	Content (mg/kg)	>3.0	0.40 ~ 3.0	0.175 ~ 0.40	0.125 ~ 0.175	≤0.125	
	Evaluation results	Area (km^2)	0.77	106.47	1233.57	44.4	11.24	
		Ratio (%)	0.06	7.62	88.34	3.18	0.81	

The evaluation map of soil Se and Zn abundance and deficiency (Fig.2) shows that there are some differences between soil Se and Zn in spatial distribution. Moderate Se soil is widely distributed in the whole region, and high Se soil is mainly distributed in the area of lizhi Street-Guoren Street-Chongyi Street-Longqiao street along the Wujiang River and the Yangtze River in the east of the study area and the western area of Xinmiao town in the West. Zn deficient and relatively deficient soils are mainly distributed in Linshi town-Mawu town-Qingyang Town. Zn rich and relatively rich soils are widely distributed in other areas. In general, in the study area, the area of high Se and moderate Se soil,and the area of Zn rich and Zn relatively rich soil are more, and which is distributed continuously, and has the potential to develop Se and Zn rich land resources and crops.

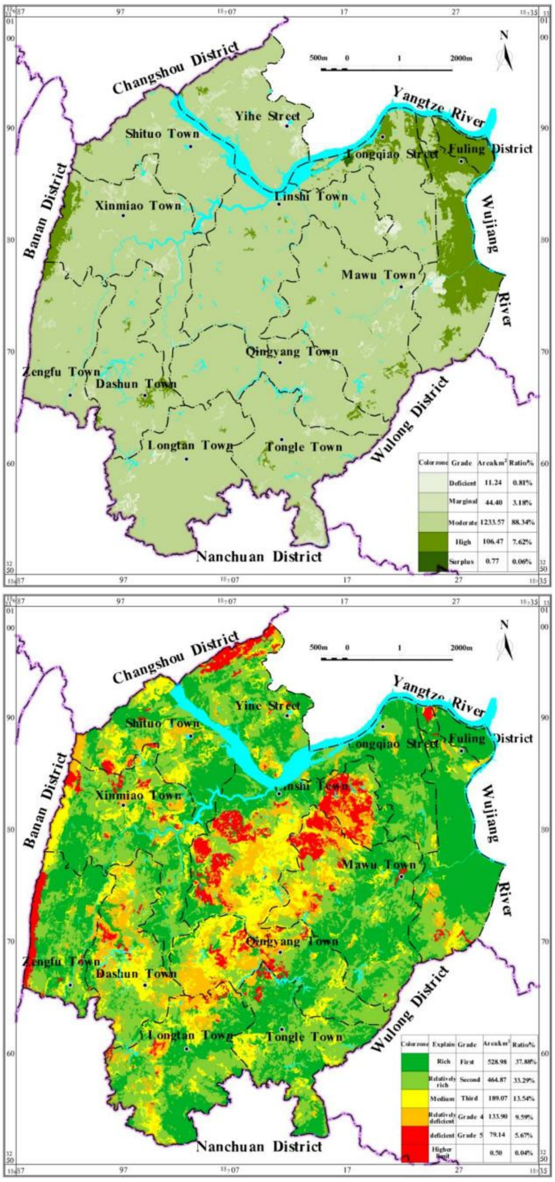

Figure 2 Evaluation map of Se and Zn abundance and deficiency in topsoil of the study area

4.2 Influencing factors of soil Se and Zn content

According to the research results of many scholars for many years, factors such as soil parent material and soil type are the main influencing factors of Se and Zn content in soil (Wang Meizhu et al., 1996; Mast et al., 2014; Liu Daorong et al., 2021; Ji Huawei et al., 2021; Xu et al., 2021). By comparing the stratigraphic (Fig.1) and lithologic distribution of the study area, it can be seen that the spatial distribution of Se and Zn elements in the soil of the study area is controlled by the lithology and structural pattern of the soil forming parent material to a certain extent. The Se and Zn rich soil is mainly distributed in the Triassic strata of the anticline on the East and west sides of the study area, especially in the limestone distribution area (Fig.2), and the average contents of Se and Zn in the soil of limestone parent material area are 0.4mg/kg and 103.45mg/kg respectively, which is significantly higher than that of sandstone and mudstone areas such as Jurassic Penglaizhen Formation in the central inclined Valley (Table3), reaching the standard of Se and Zn rich soil. Limestone is prone to secondary enrichment of trace elements such as Zn and Se in the process of leaching and acid insoluble matter accumulation (Chen Wu et al., 2010; Guo Chao et al., 2019; Ma Xudong et al., 2021), this is consistent with the conclusion that the soil in the Triassic limestone area of Chongqing inherits the high Se content of the parent material and the high enrichment of Se in the soil (Yan Mingshu, 2014). Paddy soil, purple soil and yellow soil formed by weathering of sandstone and shale in the study area are the main planting soils in the study area, inheriting the characteristics of relatively low content of Zn and Se in soil forming parent material.

Table 3 Statistical table of soil Se and Zn contents in different soil types and soil forming parent material areas

Serial number	type	Se				Zn			
		minimum value	maximum	mean value	coefficient of variation (%)	minimum value	maximum	mean value	coefficient of variation (%)
1	mudstone area	0.087	1.07	0.26	29.09	26.3	950	79.27	31.23
2	sandstone area	0.064	19.9	0.28	37.7	21.4	261	68.12	31.44
3	limestone area	0.22	0.54	0.4	18.71	49.1	165	103.45	22.42
4	shale area	0.089	0.29	0.21	40.86	60	88	77.53	15.67
5	paddy soil	0.088	1.01	0.26	25.36	26.5	950	74.00	0.34
6	Purple Soil	0.084	19.09	0.266	34.56	29.4	200	85.59	24.85
7	yellow soil	0.064	1.21	0.31	40.36	21.4	179	74.06	33.33

4.3 Ecological effects of Se and Zn

4.3.1 Contents of Se and Zn in crop seeds and root soil

The contents of Se and Zn in rice, maize seeds and root soil in the study area are shown in Table4. The contents of Se and Zn in maize seeds ranged from 0.013mg/kg to 0.042mg/kg and 13.601mg/kg to 37.522mg/kg respectively, with average values of 0.029mg/kg and 20.752mg/kg respectively; the contents of Se and Zn in rice seeds ranged from 0.013mg/kg to 0.191mg/kg and 4.407mg/kg to 19.745mg/kg respectively, with average values of 0.032mg/kg and 11.463mg/kg respectively. The variation coefficients of Se and Zn in rice and maize seeds were 19.76% and 18.57% respectively, and the degree of variation was low and the distribution was uniform.

The contents of Se and Zn in maize root soil ranged from 0.1mg/kg to 0.69mg/kg and 35.2mg/kg to 187mg/kg respectively, with an average of 0.241mg/kg and 81.53mg/kg respectively; the contents of Se and Zn in rice root soil ranged from 0.15mg/kg to 0.49mg/kg and 36.5mg/kg to 117mg/kg respectively, and the average values were 0.253mg/kg and 75.253mg/kg respectively. The Se content in maize root soil is slightly lower than that in rice, and the Zn content is slightly higher than that in rice, with a small variation range.

According to “Se enriched rice” (GB/T22499-2008) and Chongqing local standard “Se enriched agricultural products” (DB50T705-2016), Se≥0.40mg/kg and Se≥0.02mg/kg are used as Se enriched standards for rice and maize seeds respectively. Since there is no relevant standard for Zn rich crops at home and abroad, this paper takes Zn≥14.60mg/kg and Zn≥17mg/kg as Zn rich standards for rice and maize respectively according to the Chinese food composition table (Yang Yuexin et al., 2018) and existing studies (MA Xudong et al., 2021). As shown in Table4, the Se and Zn enrichment rates of rice seeds in the study area are 13.33% and 5% respectively, and the Se and Zn enrichment rates of maize seeds are as high as 96% and 82% respectively.

Table 4 Statistics of Se and Zn contents in crop seed and root soil (mg/kg)

element	type		Number of samples	minimum value	Maximum	average value	standard deviation	coefficient of variation (%)	enrichment rate (%)
Se	Rice	seed	120	0.013	0.191	0.032	0.018	58.38	13.33
		root soil		0.15	0.49	0.253	0.063	24.78	
		enrichment factor		0.047	0.578	0.127	0.062	48.85	
	Maize	seed	100	0.013	0.042	0.029	0.006	19.67	96
		root soil		0.1	0.69	0.241	0.099	41.17	
		enrichment factor		0.032	0.352	0.14	0.064	45.73	
Zn	Rice	seed	120	4.407	19.745	11.463	2.18	19.01	5
		root soil		36.5	117	75.253	18.087	24.04	
		enrichment factor		0.042	0.342	0.163	0.056	34.25	
	Maize	seed	100	13.601	37.522	20.752	3.854	18.57	82
		root soil		35.2	187	81.53	21.695	26.61	
		enrichment factor		0.143	0.642	0.272	0.094	34.64	

Note: enrichment rate= (number of Se or Zn rich crop samples/number of crop samples) ×100%

4.3.2 Enrichment law of Se and Zn in crops

The element enrichment coefficient can characterize the absorption and enrichment of trace elements in soil by crops. It is the ratio of element content in crops to element content in corresponding root soil. The greater the enrichment coefficient, the stronger the enrichment ability of crops to elements in soil (Liao Qilin et al., 2013). It is showing that the average enrichment coefficients of rice Se and Zn in the study area are 0.127 and 0.163 respectively in Table4, and that of maize Se and Zn are 0.14 and 0.272 respectively. The enrichment coefficients of maize Se and Zn are slightly higher than that of rice, indicating that the absorption and enrichment ability of Maize to Se and Zn elements in the study area is higher than that of paddy rice. Predecessors used the standard of Se enrichment in rice and the enrichment coefficient of Se in rice to estimate the minimum standard value of soil Se in the producing area of Se rich rice C=standard value of rice Se enrichment/enrichment coefficient) (Liu Jian et al., 2021). In this paper, the same method is used to draw the following conclusions: the soil Se and Zn contents of maize in the study area that meet the Se and Zn enrichment standards are 0.143mg/kg and 62.5mg/kg respectively, which is far lower than the average content of Se and Zn in the soil in the study area; the soil Se and Zn contents of rice in the study area that meet the Se and Zn enrichment standards are 0.315mg/kg and 89mg/kg respectively, which is higher than the average content of Se and Zn in the soil in the study area, and is consistent with the phenomenon of producing Se and Zn rich maize in the non Se and Zn rich soil area of the study area.

Previous studies have shown that the absorption process of trace elements such as Se and Zn by crops is very complex, which is not only related to the content of trace elements in soil and the types of crops, but also related to the occurrence form, bioavailability, soil physical and chemical properties, interaction between elements and human activities (Lin qintie et al., 2013; Xu Cong, 2018; Ma Xudong, 2021). The minimum standard value of soil that meets the requirements of Se and Zn rich crops obtained here is only a rough reference value. When developing and utilizing Se and Zn rich characteristic land resources for cultivating Se and Zn rich crops in the field, other influencing factors need to be comprehensively considered for further research and analysis.

5. Conclusion

(1)The average contents of Se and Zn in the topsoil of the study area are 0.265mg/kg and 77.56mg/kg respectively, and the background values are 0.26mg/kg and 76.95mg/kg respectively, which are higher than the background values of Chongqing riverside economic belt of 0.126mg/kg and 72.965mg/kg, close to the background values of China's topsoil of 0.290mg/kg and 74.2mg/kg. The distribution of Se and Zn contents in the soil is controlled by the soil forming parent material and structural pattern. The high value area is mainly distributed in the exposed area of Triassic carbonate rocks of anticline on both sides of the study area, and the low value area is mainly distributed in the sand mudstone areas such as Jurassic Penglaizhen Formation in the central inclined valley.

(2) The content of Se in the soil of the whole region is generally at the appropriate level of Se, with an area of 1233.57 km2, accounting for 88.34% of the total area, and an area rich in Se of 44.4 km2, accounting for 3.18% of the total area; the content of Zn element is generally at the Zn rich level. The first-grade Zn rich area is 528.98km2, accounting for 37.88% of the total area, and the second-grade Zn rich area is 464.87km2, accounting for 33.29% of the total area.

(3) The average contents of Se and Zn in maize seeds in the study area are 0.029mg/kg and 20.752mg/kg respectively, the average enrichment coefficient is 0.140 and 0.272 respectively, and the Se enrichment rate and Zn enrichment rate are 96% and 82% respectively; the average contents of Se and Zn in rice seeds were 0.032mg/kg and 11.463mg/kg respectively, the average enrichment coefficient was 0.127 and 0.163 respectively, and the Se and Zn enrichment rate were 13.33% and 5% respectively. The ability of Maize to absorb and enrich Se and Zn elements is significantly higher than that of rice. It is easy to cultivate Se and Zn rich functional maize for human absorption and health promotion.

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