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ORIGINAL PAPER

Characteristics and the possible origins of selenium in surface soil in Lanling County, Shandong Province, China

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Abstract

Soil selenium (Se) levels deeply affect the Se intake in the human body, and the origins of soil Se are significant for the utilization of Se-rich soils and local human health. The Se origins of Se-rich soils were detected by comparing surface soil Se levels and exogenous soil Se fluxes in two areas with different parent rocks. Soil Se levels in Kuangkeng Town (0.095–0.631 mg/kg) are higher than those in the Cangshan Subdistrict (0.044–0.526 mg/kg). However, the net flux of exogenous soil Se in Cangshan Subdistrict (0.793 g/ha/y) is observed to be 2.7 times that in Kuangkeng Town (0.294 g/ha/y). The geological background of Ordovician carbonate in Kuangkeng is confirmed to be responsible for the Se-rich soil. Se enriches in soil with the leaching of numerous $CaMg(CO_3)_2$ in Ordovician carbonates during weathering, which is the important Se origin of Se-rich soil. Soil Se levels overlying Ordovician are also significantly higher than those overlying Cambrian and Quaternary strata, and the geostatistical analysis also indicates a dominating Se source of parent rocks. The geochemical cycles of soil Se are forwarded. Therefore, Ordovician carbonates should be of concern for Se-rich soils although they have low-Se levels.

Keywords Soil Se · Geochemical cycles · Origin · Lanling County

Introduction

Selenium (Se) is an essential trace element for human health. Se is an important component of many enzymes in the body such as glutathione peroxidase (GSH-Px) (Foster and Sumar 1995). The appropriate intake of Se has been linked to anticancer, antioxidant, suppressor mutation, prevention of heart disease and improving immunity functions. However, excessive intake of Se may cause lower reproduction rate, hair loss, nail loss and neurological disorders (Rotruck 1973). The effective scope between Se deficiency and toxicity in humans is very narrow, with a recommended daily Se intake of 60–400 μg per day for adults (CNS 2000). Especially, cardiovascular diseases and diabetes are documented to be related to Se deficiency in the body. Keshan disease and Kashin-Beck disease occur when Se levels in the body are severely deficient (Shen et al. 2021). Therefore, Se levels in the environment are of great importance for human health.

The atmosphere, soil, water bodies, plants and food are all reservoirs of Se in nature. Se in soils can enter the atmosphere, water, plants and humans through volatilization, water–rock interactions, plant metabolism and food chain. Soil Se levels become the key to Se geochemical cycle (Eurola et al. 2005).

However, Se is very uneven in the earth's crust. Although Se-rich soils are documented in some local areas, such as Enshi City of Hubei, Ziyang City of Shaanxi (Tian et al. 2017), Chizhou City of Anhui (Liang et al. 2022), Yongchun County of Fujian (Lin 2019) and Puning City of Guangdong (Jiang et al. 2019), China is generally characterized by Se-deficient soils. The investigation indicated about 72% of areas in China are Se deficient, and more than 700 million people are involved (Ma 2010). The surface soil in China has average Se level of 0.29 mg/kg (range of 0.06–0.32 mg/kg), which is significantly lower than that in the USA

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(0.39 mg/kg), Europe (0.4 mg/kg), Japan (0.51 mg/kg), India (0.53 mg/kg) and the world average of 0.4 mg/kg (Dhillon and Dhillon 2014; Chi 2007; Yamada et al. 2009). Soil Se background level in Shandong Province is only 0.13 mg/kg, which is less than half of that in China (Wang 2020). Therefore, the study of characteristics and origins of soil Se in Shandong Province is of great importance for regional human health and scientific land use.

The origins of soil Se are relatively complex. Se levels in rocks profoundly determine soil Se levels (Liu and Jiao 2021), and some high-Se rocks are often considered to be Se origins of Se-rich soil, such as black shale, carbonaceous rock, slate and stone coal (Tuttle et al. 2014; Parnell et al. 2016; Tian et al. 2016; Zhao et al. 2020). Atmospheric deposition and volcanic eruptions are other important natural sources of soil Se (Floor and Román-Ross 2012; Sun et al. 2016). The study in Norway confirmed that the contribution of Se in the ocean to soil Se is not negligible, atmospheric deposition amounts of soil Se gradually decrease from the coast to inland under the influence of the monsoon (Lag and Steinnes 1978). Sun et al. (2016) even observed the low-Se zone in China has a non-negligible relationship with atmospheric Se deposition. Floor and Román-Ross (2012) argued that Se from volcanic eruption was adsorbed on the ash surface and entered the soil during the ash weathering process. Therefore, volcanic eruptions are considered as one of the origins of soil Se. Additionally, numerous studies have revealed anthropogenic activities are important origins of soil Se, such as fertilization, irrigation, grain harvest, fossil fuel combustion, mining, effluent discharge, copper and aluminum industries, shale gas exploitation and others (Foster and Sumar 1995; Xu and Tao 2004; Fordyce 2013; Yu et al. 2014; Vriens et al. 2015; Wei et al. 2016; Etteieb et al. 2021; Parnell et al. 2016). The soil Se has multiple and complex origins of natural and anthropogenic. Therefore, defining the contributions of different origins of soil Se and the geochemical cycle processes is significant for clarifying the cause of Se-rich soils, planning the Se-rich land and improving regional economic development. A series of researchers has tried to analyze the origins and contribution rates of soil Se based on different methods. Yu et al. (2014) used element correlations and elemental mass balance analysis and concluded that different human activities are important processes of the soil Se cycle in Mianyang City. Song et al. (2020) used geostatistical analysis and elemental geochemical analysis and found that soil Se levels in Sanjiang Plain are controlled by both natural factors (such as soil-forming parent material) and anthropogenic activities. It seems to be difficult to distinguish one origin from others and to define the contributions of each origin, especially the natural from the anthropogenic.

The soil Se levels in Lanling County, in the southwestern part of Linyi City, Shandong Province, are very uneven. However, there is no detailed information about the characteristics of soil Se levels in this region and its origins and influencing factors remain unknown. Two areas (Kuangkeng Town and Cangshan Subdistrict) with different parent rocks in Lanling County were studied, and surface soil, atmospheric deposition, irrigation water, fertilizer application and crops were systematically collected and analyzed to detect the possible origins and geochemical cycling processes of soil Se. The objectives are: (1) to characterize the Se levels in the soil, spatial distribution and the influencing factors; (2) to reveal the soil Se fluxes of different origins and define their contributions to soil Se levels in the two areas; (3) to forward geochemical cycle pattern and discuss the main Se origins by comparing the soil Se characteristics and fluxes in the two areas.

Materials and methods

Study area

Lanling County is located in the southwest of Linyi City, Shandong Province, China (Fig. 1). The county has an area of 773km^2, with geographical coordinates of 117° 40′ 39″–118° 08′ 26″ (E) and 34° 48′ 44″–35° 05′ 51″ (N). The area is in the warm temperate monsoon zone and has a semi-humid continental climate, with an average temperature of 13.2 °C and an average annual precipitation of 881.1 mm. The landform types mainly are low mountains, low hills and intermountain plains. Soil types include brown soil, cinnamon soil, tidal soil and sandy black soil.

Kuangkeng Town is located in the northernmost part of Lanling County, with geographical coordinates of 117° 59′ 18″ to 118° 05′ 47″ (E), 35° 01′ 12″ to 35° 05′ 10″ (N). The town is adjacent to Fei County and Lanshan District in the north and Zhongcun Town in the south. The town has an area of 86 km^2. The strata in Kuangkeng Town are mainly lower-middle Ordovician, including Sanshanzi Formation (O_1s), the Fenghuangshan Formation (O_2d), the Beianzhuang Formation (O_2b), the Tuyu Formation (O_2t) and the Wudangshan Formation (O_2w), from oldest to newest. The lithology of lower-middle Ordovician is mostly constituted of dolomite and limestone. The Ordovician strata cover more than 70% of the total area (Fig. 1).

Cangshan Subdistrict is located in the northern part of Lanling County, with geographical coordinates of 118° 0′ 10″ to 118° 05′ 15″ (E), 34° 48′ 40″ to 34° 58′ 25″ (N). The area is bordered by Chewang Town and Zhongcun

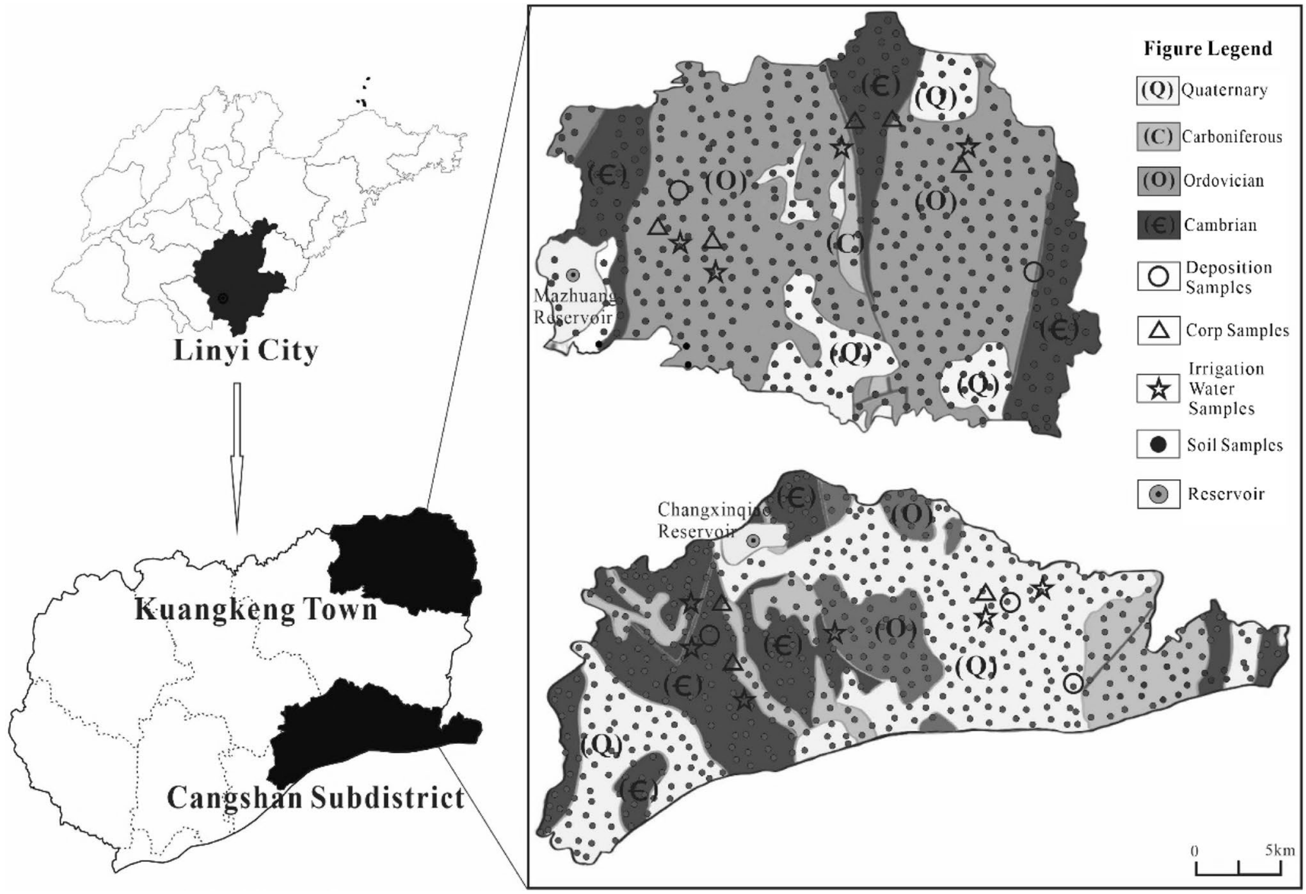

Fig. 1 Sampling locations in Kuangkeng Town and Cangshan Subdistrict

Town to the north and Xiangcheng Town and Bianka Subdistrict to the south. The area is about 101 km^2. The main strata in Cangshan Subdistrict is middle-upper Cambrian and Quaternary. The Cambrian strata include the Mantou Formation (Є$_{2\text{-}3}m^1$), the Zhangxia Formation (Є$_3z$), the Gushan Formation (Є$_{3\text{-}4}g$) and the Cambrian lithology is mainly shale, mudstone, clay and limestone. The Quaternary is mainly constituted of loose sediments. The Ordovician is sporadically exposed, with the proportion of less than 10% (Fig. 1).

Sample collection

Soil samples were collected at depths of 0–20 cm, with a density of 4 samples/km^2. In total, 511 samples from Kuangkeng Town and 471 samples from Cangshan Subdistrict were collected. About 1 kg of soil sample was placed in sampling bags after the impurities were removed. Two samples of atmospheric deposition in Kuangkeng Town and three in Cangshan Subdistrict were collected. The atmospheric deposition was collected in dust catcher cylinders of 89.5 cm × 5489.5 cm × 60.8 cm size from September of 2018 to September of 2019. Considering maize and wheat are the prevailing crops in this area, five maize samples and five wheat samples in Kuangkeng Town, and one maize sample and four wheat samples in Cangshan Subdistrict were collected. Irrigation water was gathered from the water system or underground irrigation area, and 4 samples in Kuangkeng Town and 6 samples in Cangshan Subdistrict were collected. The detailed locations of the samples are shown in Fig. 1. Compound fertilizer, ammonium bicarbonate, phosphate fertilizer and organic fertilizer are the main fertilizers according to our investigation to large grain production households in Lanling County, and 355.05 kg/ha compound fertilizer, 311.25 kg/ha ammonium bicarbonate, 26.4 kg/ha phosphate fertilizer and 29.25 kg/ha organic fertilizer were used per year.

Analyzing method

The soil samples were air-dried, and ground into less than 0.25 mm in agate jars for the determination of soil organic carbon (SOC) levels. The soils were ground into less than 0.074 mm for other element analysis. Cd and I levels were determined by inductively coupled plasma-mass spectrometry (ICP-MS). Cr, Ni, Pb, SiO_2, S, Cu, Zn and Al_2O_3 levels were measured by X-ray fluorescence spectrometry (XRF). Se, Hg and As levels were determined by hydride generation-atomic fluorescence spectrometry (HG-AFS). Mn levels in the soil samples was measured by an inductively coupled plasma-optical emission spectrometer (ICP-OES). SOC levels were measured by volatile organic compounds (VOL). After calibration of the pH meter with standard solutions of pH = 4.01, 6.86 and 9.18, the soil pH was determined using a PH-3C pH meter with a water to soil ratio of 1:2.5. The crops were dried and ground to less than 60 mesh using a cyclone mill, and Se levels in crops, irrigation water and atmospheric wet deposition were analyzed using hydride generation-atomic fluorescence spectrometry (HG-AFS). The blank samples, parallel samples and standard samples were used for quality control, and the relative errors were less than 10%.

Results and discussion

Soil Se levels in Kuangkeng Town and Cangshan Subdistrict

The soil Se levels in Kuangkeng Town and Cangshan Subdistrict are illustrated in Fig. 2a, b, respectively. The soil Se levels in Kuangkeng Town range from 0.1 to 1.1 mg/kg, with an average Se level of 0.38 mg/kg. The soils in Cangshan Subdistrict have Se levels of 0.04–0.73 mg/kg, with a mean of 0.27 mg/kg. The average soil Se level in Kuangkeng Town is 1.4 times higher than that in Cangshan Subdistrict, indicating that the surface soils in Kuangkeng Town are relatively richer in Se levels when compared to Cangshan Subdistrict. The world average soil Se level is 0.4 mg/kg (Wang and Gao 2001). Dinh et al. (2018) reported an average Se level of 0.38 mg/kg in the A-layer soil in the USA. The soils in the two regions have lower Se levels than those in the world and USA. The average surface soil Se level in China is 0.29 mg/kg (Chen et al. 1991). The average soil Se level in Kuangkeng Town was higher than the average in China, but in Cangshan Subdistrict, it was equal to or even slightly lower than that of China's. Chi (2007) and Wang (2020) recorded an average Se level of 0.13 mg/kg in the soils of Shandong Province. Kuangkeng Town has an average soil Se level of 2.9 times that of Shandong Province, and Cangshan Subdistrict has 2.1 times that of Shandong Province. Such facts indicate Se in the two regions is relatively enriched in soil Se-deficient Shandong Province.

According to the classification criteria of soil Se levels, the soils can be divided into the following: Se deficient (< 0.125 mg/kg), potentially Se deficient (0.125–0.175 mg/

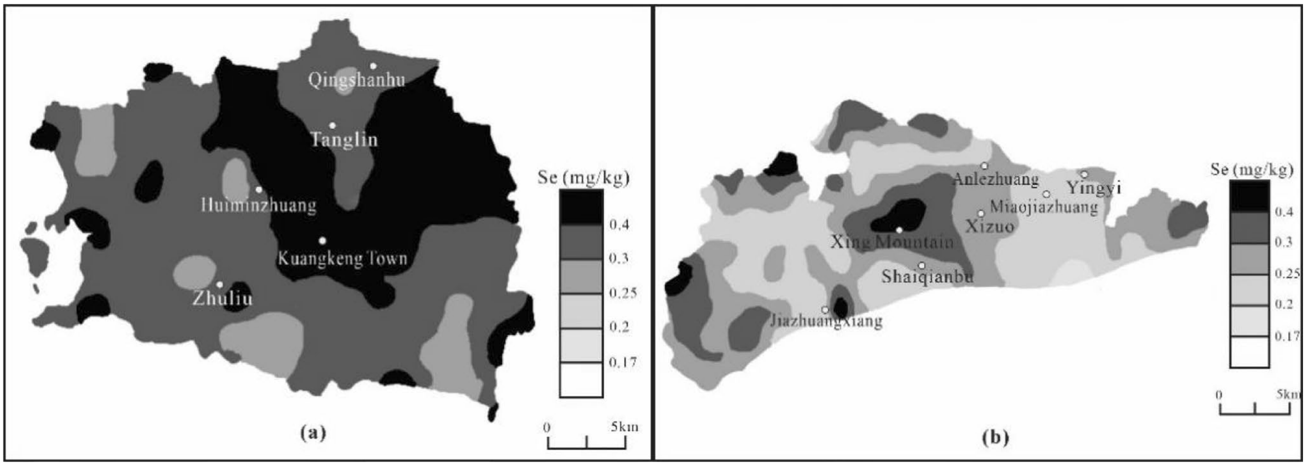

Fig. 2 Soil Se levels and the distribution in Kuangkeng Town (**a**) and Cangshan Subdistrict (**b**)

kg), sufficient Se (0.175–0.4 mg/kg), Se-rich (0.4–3.0 mg/kg) and Se poisoning (> 3.0 mg/kg) (Tan 1989). Of the samples in Kuangkeng Town, 63.49% and 34.05% belong to sufficient Se and Se-rich, respectively. 88.44% and 7.02% of the total samples in Cangshan Subdistrict are sufficient Se and Se-rich, respectively. The both areas are dominated by sufficient Se and Se-rich areas, and the soil areas of Kuangkeng Town and Cangshan Subdistrict meeting the Se-sufficient standard (> 0.175 mg/kg) were 98% and 95%, respectively. The Se-rich area (0.4–3.0 mg/kg) in Kuangkeng Town occupied 23.09% of the total area, mainly distributed in the central and eastern parts. However, the Se-rich area (0.4–3.0 mg/kg) in Cangshan Subdistrict is only sporadically distributed in the central part near Xingshan, but occupies a small ratio of 4.67%. The strata in Kuangkeng Town and Cangshan Subdistrict are distinctly different. Kuangkeng Town is dominated by Ordovician strata, and Cangshan Subdistrict is dominated by Cambrian and Quaternary strata. The Ordovician lithology is mainly constituted of carbonates, including dolomite and limestone. The lithology of Cambrian is mainly composed of shale, mudstone, sandstone and limestone. The Quaternary is mainly loose sediments, and the main sediments of the Yihe Group are gray-yellow gravel and sand layers. The Shanqian Formation is mainly residual slope deposits. In fact, the Se-rich areas in Kuangkeng Town are associated with the distribution of Ordovician carbonates, and those in Cangshan Town mainly also distribute where Ordovician carbonates sporadically occur.

The soil Se levels on different stratigraphic units are counted and shown in Table 1. The average soil levels in the Quaternary, Ordovician and Cambrian strata are 0.23–0.25 mg/kg, 0.33–0.59 mg/kg and 0.24–0.39 mg/kg, with an average of 0.24 mg/kg, 0.42 mg/kg and 0.33 mg/kg respectively. Specifically, the soils overlying the Tuyu Formation, Wudangshan Formation and Guzhuang Formation have Se levels exceeding the Se-rich criteria (> 0.4 mg/kg). Therefore, the widely distributed carbonates in the Ordovician strata in Kuangkeng Town should be responsible for the higher soil Se levels than found in Cangshan Subdistrict, and the Ordovician carbonates may be the potential origins of Se-rich soils. Moreover, the distribution of the Ordovician strata and Se-rich soil are not completely uniform, which indicates not all the rocks of the Ordovician strata contribute to Se-rich soil.

The Se levels in rocks are in the range of 0.02–0.06 mg/kg in this region, with an average of 0.03 mg/kg (Table 1). The Ordovician carbonates have no obviously high-Se levels although their overlying soils are rich in Se levels. Contrarily, the rocks of Gushan Formation and Zhangxia Formation have relatively higher Se levels. So, the Se levels in rocks themselves cannot well explain the high-Se soils.

Table 1 Average Se levels in soils and rocks on different stratigraphic units

Geochron stratigraphy	Lithologic stratigraphy		Soil Se levels (mg/kg)	Se levels in rocks (mg/kg)
Quaternary		Yihe formation (Qh*y*)	0.25	–
		Shanqian formation (Q*s*)	0.23	–
Ordovician	Majiagou group ($\mathrm{O}_{2\text{-}3}M$)	Gezhuang formation (O_2g)	0.59	0.03
		Wudangshan formation (O_2w)	0.41	0.03
		Tuyu formation (O_2t)	0.44	0.02
		Bian zhuang formation (O_2b)	0.37	0.03
		Fenghuangshan formation (O_2d)	0.33	0.02
	Jiulong group (Є$_2$-O_1J)	Sanshanzi formation (O_1s)	0.38	0.03
Cambrian		Conidia formation (Є$_4c$)	0.39	0.02
		Gushan formation (Є$_{3\text{–}4}$g)	0.32	0.05
		Zhangxia formation (Є$_3z$)	0.29	0.06
		Mantou formation (Є$_{2\text{-}3}m$)	0.24	0.03

Table 2 The correlations of soil Se levels with other properties in Kuangkeng Town and Cangshan Subdistrict

Areas	Cr	Ni	Pb	As	Cd	Hg	Al_2O_3	SiO_2	S	SOC
Kuangkeng Town	0.344**	0.431**	0.440**	0.556**	0.108*	0.066*	0.054	− 0.351**	0.368**	0.441**
Cangshan Subdistrict	0.238**	0.269**	0.456**	0.476**	0.305**	0.222*	0.171*	− 0.348**	0.544**	0.526**

Geostatistical analysis

Table 2 shows the correlations between soil Se and other geochemical properties in the two areas. Se is a sulfophilic element, S^{2-} and Se^{2-} have similar radii and electronegativity and Se is easily isomorphic with S (Sharma and Chang 1996; Yu et al. 2018). The vast majority of Se is dispersed into the lattices of sulfide minerals, and Se has a significant correlation with S (Yu et al. 2018). There also exist significant positive correlations of soil Se and S, with $R^2 = 0.504$ in Kuangkeng Town and $R^2 = 0.624$, respectively. Cr, Ni, Pb, As, Cd and Hg are commonly in the form of sulfide in rocks, and Se is easily combined with these elements (Wang et al. 2002). Soil Se levels are observed to be positively correlated in the two areas, with $R^2 = 0.305$(Cr), 0.389(Ni), 0.595(Pb), As(0.548), Cd(0.199) and Hg(0.096) in Kuangkeng Town, and $R^2 = 0.162$(Cr), 0.153(Ni), 0.529(Pb), As(0.468), Cd(0.376) and Hg(0.111) in Cangshan Subdistrict. The high levels of hydroxy-estrogen or carboxyl in SOC facilitate the complexation with Se (Zhai 2021). Large amounts of functional groups such as amidogen, carboxyl and oxhydryl provide sorption sites to adsorb soil Se (Johnsson 1991; Kausch et al. 2012). A series of researches argued SOC profoundly governed soil Se levels (Tolu et al. 2014; Meng et al. 2021). Soil Se levels were significantly positively correlated with SOC, with $R^2 = 0.441$ in Kuangkeng Town and $R^2 = 0.526$ in Cangshan Subdistrict, respectively. In addition, soil SiO_2 was significantly negatively correlated with soil Se levels, with $R^2 = -0.351$ in Kuangkeng Town and $R^2 = -0.348$ in Cangshan Subdistrict respectively, and Al_2O_3 was negatively correlated with soil Se levels in Cangshan Subdistrict, with $R^2 = 0.171$. This implies Se accumulates in the soil during weathering because there are more SiO_2 and Al_2O_3 residues in the soil with an increase in leaching of other substances, which is consistent with the previous studies (Gong et al. 2022).

Principal component analysis (PCA) was widely used to detect the origins of soil elements, and the results are shown in Table 3. The four biggest powers of exponent rotation in Kuangkeng Town were selected. A Kaiser–Meyer–Olkin value of 0.747 (> 0.6) and a Bartlett significance value of 0 (< 0.005) validate the analysis. Four rotated principal components with eigenvalue > 1 were extracted, and the cumulative variance was 75.650. Ni(0.864), As(0.853), Cr(0.746), Pb(0.713), Se(0.703) and SiO_2(0.569) fall in PC1, suggesting that the source of parent rocks, Se and these elements synchronously entered the soil during the weathering of rocks (Xu and Tao 2004). Thus, PC1 was defined as the parent material. Al_2O_3 and Mn have the highest loadings for PC2, with loadings of 0.704 and 0.597, respectively, with a contribution rate of 14.353%. PC2 is defined as a soil-forming process since Al_2O_3 is the indicator of soil-forming processes (Huang and Gong 2000). Cd and Hg have loadings of 0.571 and 0.731, respectively and are defined as PC3, contributing 12.516%. PC3 possibly represents anthropogenic activities since Hg and Cd is largely governed by human inputs. The element of I was defined as PC4, with a contribution rate of 9.841% and a loading of 0.663. PC4 indicates an atmospheric source because soil I is mainly derived from atmospheric deposition (Junior et al. 2022).

Table 3 The principal component analysis of soil elements

Element	Principal components						
	Kuangkeng Town				Cangshan Subdistrict		
	1	2	3	4	1	2	3
Se	0.703	0.415	0.296	−0.104	0.605	0.360	0.193
Cr	0.746	0.174	−0.361	0.164	0.802	−0.308	0.048
Ni	0.850	−0.061	−0.317	0.187	0.821	−0.409	0.045
As	0.691	0.459	−0.102	−0.302	0.582	0.529	−0.404
Cd	0.570	0.183	0.571	0.015	0.521	0.312	0.426
Mn	0.520	0.597	−0.303	0.311	0.482	0.560	−0.279
Hg	0.016	0.058	0.731	0.251	0.072	0.374	0.787
Al_2O_3	0.576	−0.704	−0.170	0.032	0.674	−0.552	−0.025
SiO_2	−0.569	0.432	−0.018	0.459	−0.753	0.450	0.012
Cu	0.690	−0.370	−0.041	0.306	/	/	/
Zn	0.639	−0.305	0.413	0.335	/	/	/
I	0.537	−0.001	0.138	−0.663	/	/	/
Pb	/	/	/	/	0.443	0.705	−0.161

The Kaiser–Meyer–Olkin value of 0.745 (> 0.6) and the Bartlett significance value of 0 (< 0.05) validate the PCA for Cangshan Subdistrict. Three rotated principal components with eigenvalue > 1 were extracted, and the total cumulative variance was 70.793. The contribution of PC1 was 37.404%, and the higher loadings of Cr, Ni, As, Cd, Se, Al_2O_3 and SiO_2 were 0.802, 0.821, 0.582, 0.512, 0.605, 0.674 and 0.753, respectively. PC1 is also defined as a natural factor and is mainly controlled by the soil-forming parent material. PC2 contributes 22.279% and has higher loadings of Mn and Pb at 0.560 and 0.705, respectively. PC2 is probably related to industrial activities. Hg falls in PC3, indicating a source of agricultural activities. Generally, the soil Se in the two areas indicates a dominating natural source of parent rocks.

The semi-variance function is used to describe the spatial variation of soil, and the parent material often has an important influence on the variation of soil properties (Okuda et al. 1995). GS + 9.0 was used to simulate the soil Se elemental semi-variance functions, and the results are illustrated in Table 4 and Fig. 3. The model plot of the optimal semi-variance function for Se elements in both Kuangkeng Town and Cangshan Subdistrict are consistent with the exponential model. Usually, $C_0/C+C_0$ is used to represent the degree of spatial correlation of variables. < 25% indicates strong spatial correlation, 25–75% has moderate spatial correlation and > 75% has weak spatial correlation (Cambardella et al. 1994). The ratio of the nugget variance (C_0) to the structural variance sill ($C+C_0$) was 19.52% and 13.51% (less than 25%) for Kuangkeng Town and Cangshan Subdistrict, respectively. External anthropogenic variables such as fertilization and irrigation may control the variability of these weakly spatially correlated parameters. Therefore, the soil Se levels in Kuangkeng Town and Cangshan Subdistrict are little influenced by human activities (Cambardella et al. 1994). Such facts also confirm that the spatial variability of Se levels is mainly structural variability with strong spatial correlation (Liu et al. 2019), and natural factors play an important role in determining the soil Se levels in the two areas.

Soil Se geochemical cycles

Soil Se input fluxes

Atmospheric deposition includes dry deposition and wet deposition. Considering dry deposition has little effect on soil Se input (Sun et al. 2017), only wet deposition Se input flux is calculated as follows:

$$S_P = C_P \times V_P/100 \tag{1}$$

where S_p is the input flux of soil Se from atmospheric precipitation (g/ha/y); C_p is the Se level in precipitation (μg/L), which is 0.127 μg/L for Kuangkeng Town and 0.167 μg/L for

Table 4 Se elemental semi-variance functions in the soils of Kuangkeng Town and Cangshan Subdistrict

Se	Model type	Nugget variance (C_0)	Structural variance sill ($C+C_0$)	$C_0/(C+C_0)$
Kuangkeng Town	Exponential	1.39×10^{-3}	7.12×10^{-3}	0.1952
Cangshan Subdistrict	Exponential	7.00×10^{-4}	5.18×10^{-3}	0.1351

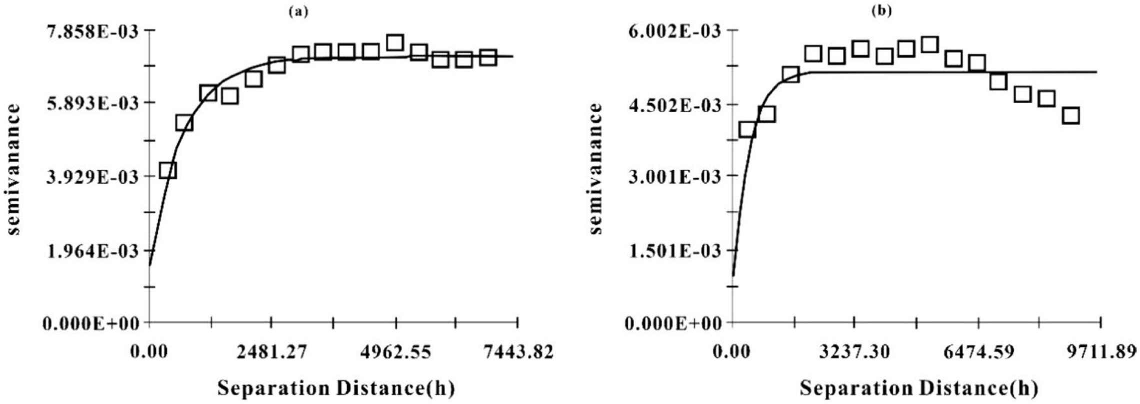

Fig. 3 Se elemental semi-variance functions in the soils of Kuangkeng Town (**a**) and Cangshan Subdistrict (**b**)

Cangshan Subdistrict; V_{p} is the average annual precipitation (mm), and 881.1 mm was used as a reference; 100 is the unit conversion coefficient.

The calculated results indicate the Se input flux of atmospheric wet deposition of 1.119 g/ha/y for Kuangkeng Town and 1.471 g/ha/y for Cangshan Subdistrict.

The Se input flux for irrigation water is estimated as follows:

$$S_{\mathrm{IR}} = C_{\mathrm{IR}} \times V_{\mathrm{IR}} / 1000 \tag{2}$$

where S_{IR} is the input flux of soil Se for irrigation water (g/ha/y); C_{IR} is the Se level in irrigation water (μg/L), which is 0.102 μg/L for Kuangkeng Town and 0.124 μg/L for Cangshan Subdistrict; V_{IR} is the average annual irrigation water volume (m^3/ha) and 4500 m^3/ha was used as a reference in this research considering maize and wheat are the dominating crops in this region; 100 is the unit conversion coefficient.

Consequently, the soil Se input fluxes for irrigation water in Kuangkeng Town and Cangshan Subdistrict are 0.459 g/ha/y and 0.558 g/ha/y, respectively.

The Se input flux from fertilization is evaluated using the following equation:

$$S_{\mathrm{F}} = \sum_{j=1}^{n} c_j \cdot q_j / 1000 \tag{3}$$

where S_{F} is the soil Se input flux from fertilization (g/ha/y); c_j is the Se level in fertilizer (mg/kg); q_j is the annual fertilizer use (kg/ha); n is the number of fertilizer types, and 1000 is the unit conversion coefficient.

According to our investigation, there are four types of fertilizers mainly used in the region, including compound fertilizer, ammonium bicarbonate, phosphate fertilizer and organic fertilizer. The applications of compound fertilizer, ammonium bicarbonate, phosphate fertilizer and organic fertilizer are 323.13 kg/ha, 310.08 kg/ha, 30.8 kg/ha and 25.35 kg/ha in Kuangkeng Town, and 355.05 kg/ha, 311.25 kg/ha, 26.4 kg/ha and 29.25 kg/ha, respectively. The Se levels in compound fertilizer, ammonium bicarbonate, phosphate fertilizer and organic fertilizer are 0.3 mg/kg, 0.24 mg/kg, 1.39 mg/kg and 1.0 mg/kg, respectively.

The input flux of soil Se from fertilizer application was 0.239 g/ha/y in Kuangkeng Town and 0.247 g/ha/y in Cangshan Subdistrict, respectively.

Soil Se output fluxes

The infiltration-induced soil Se output flux is an important part of the Se geochemical cycle and it can be calculated using the following equation:

$$S_{\mathrm{I}} = C_{\mathrm{I}} \times V_{\mathrm{I}} / 100 \tag{4}$$

This can be seen through soil leaching experiments, the percentages of Se after infiltration fraction accounted for 34.41% and 31.12% of the total Se, respectively. C_{I} is the Se level leached by rainfall during some time (mg/L); S_{I} is the infiltration-induced soil Se output flux (g/ha/y); V_{I} is the annual rainfall in the study area (mm), C_{I} is 0.0437 μg/L in Kuangkeng Town and 0.0528 μg/L in Cangshan Subdistrict, respectively.

Based on the above, the infiltration-induced soil Se output fluxes were 0.385 g/ha/y in Kuangkeng Town and 0.465 g/ha/y in Cangshan Subdistrict, respectively.

Crop harvest is the main pathway of the soil Se biogeochemical cycle. Maize and wheat are the main crops in this region, with total annual yields of 6531.8 kg/ha/y and 6433.2 kg/ha/y, respectively.

The Se output fluxes for crop harvest were achieved using the following equation:

$$S_{\mathrm{grain,CH}} = 1000 \times \left(C_{\mathrm{CH1}} \times Y_{\mathrm{CH1}} + C_{\mathrm{CH2}} \times Y_{\mathrm{CH2}} \right) \tag{5}$$

where $S_{\mathrm{grain,CH}}$ is the annual harvest-induced soil Se output flux (g/ha/y); C_{CH1} and C_{CH2} are Se levels in maize and wheat (mg/kg); Y_{CH1} and Y_{CH2} are yields per hectare (kg/ha/y) derived from maize and wheat yields, respectively, and 1000 is the unit conversion coefficient.

Accordingly, the harvest-induced soil Se output fluxes were estimated to be 0.655 g/ha/y in Kuangkeng Town and 0.675 g/ha/y in Cangshan Subdistrict.

Se volatilization is closely related to the level of soil organic matter (Sun and Zhang 2022). The levels of soil organic matters in Kuangkeng Town and Cangshan Subdistrict was 1.989% and 1.996%, respectively, both less than 5%. Previous studies by Johnsson (1997) showed that when soil organic matter level was low ($<5\%$), soil organic matter played a good role in fixing soil Se by providing adsorption sites, thus reducing the volatilization of soil Se. Referencing to the previous information, soil Se volatilization is approximately 0.001–0.092% of total soil Se (Wang 1993). In this research, the volatilization of Se was selected as 0.024%. The formula is as follows:

$$S_{\mathrm{v}} = 5.3 \times 10^{6} \times C_{\mathrm{a}} \times 0.024\% \tag{6}$$

Table 5 Exogenous soil Se budget for the input and output in Kuangkeng Town and Cangshan Subdistrict

	Precipitation g/ha/y	Irrigation g/ha/y	Fertilizer g/ha/y	Infiltration g/ha/y	Harvest g/ha/y	Volatilization g/ha/y	S_{in} g/ha/y	S_{out} g/ha/y	ΔS g/ha/y
Kuangkeng Town	1.119	0.459	0.239	0.385	0.655	0.483	1.817	1.523	0.294
Cangshan Subdistrict	1.471	0.558	0.247	0.465	0.675	0.343	2.276	1.483	0.793

S_v is the soil Se output flux (g/ha/y) for volatilization; a soil density of 2.65×10^3 kg/m^3 is used as a reference in this region and C_a is the Se levels in the topsoil (< 20 cm).

The output flux of soil Se volatilization was estimated to be 0.483 g/ha/y in Kuangkeng Town and 0.343 g/ha/y in Cangshan Subdistrict.

Net flux of exogenous soil Se

The source of soil Se is influenced by the input flux and output flux of exogenous Se, and the net flux of soil Se can be expressed as follows:

The total soil Se input flux: $S_{in} = S_P + S_{IR} + S_F$;
The total soil Se output flux: $S_{out} = S_I + S_{grain,CH} + S_V$,
The net flux of exogenous soil Se: $\Delta S = S_{in} - S_{out}$.

The annual input and output fluxes of soil Se in the two areas are listed in Table 5. The annual net flux of soil Se in Kuangkeng Town was calculated to be 0.294 g/ha/y, while in Cangshan Subdistrict, it was 0.793 g/ha/y. The annual net flux of exogenous soil Se in Cangshan Subdistrict was about 2.7 times that in Kuangkeng Town although Kuangkeng Town has higher soil Se levels.

Geochemical cycle pattern and the possible origin of soil Se

Exogenous input and output are important sources of soil Se. Atmospheric deposition, irrigation and fertilization are important and main forms of soil Se input, and infiltration, volatilization and crop harvest are the main forms of soil Se output. Among these, atmospheric deposition is the most dominant Se input flux. The research in Mianyang City and Sanjiang Plain concluded wet deposition Se input accounts for 89% and 84.9% of the total input flux (Yu et al. 2014; Song et al. 2020). The wet deposition Se input fluxes in Kuangkeng Town and Cangshan Subdistrict accounted for 81.1% and 84.9% of the total input fluxes, respectively. The global annual atmospheric wet deposition of Se is approximately 3.6×10^9–10.0×10^9 g/y (Amouroux et al. 2001). Atmospheric wet deposition Se fluxes in the two areas were significantly lower than global Se deposition. The reason may be that this region is on land and the atmospheric wet deposition Se input fluxes are less influenced by the monsoon compared to the ocean (Sun and Zhang 2022). The wet deposition Se inputs in this research were lower than those in Mianyang (5.4 g/ha/y) and Sanjiang Plain (2.08 g/ha/y) (Yu et al. 2014; Song et al. 2020), probably because this region is far from industrial activity. However, the atmospheric wet deposition input fluxes in this research were roughly equal to those in French forests and mainland China (Pisarek et al. 2021; Sun et al. 2016). Irrigation-induced Se input

Table 6 Comparison of Se input and output fluxes in this region with others (g/ha/y)

Areas	Precipitation	Irrigation	Fertilizer	Infiltration	Harvest	Volatilization	References
Global	$3.6–10 \times 10^9$(g/y)	/	/	/	/	/	Amouroux et al. (2001)
French forests	0.44	/	/	/	/	/	Pisarek et al. (2021)
Mainland China	0.8–1.6	/	/	/	1.0–2.0	/	Sun et al. (2016)
Shandong	/	0.56–10.36	0.1–0.59	/	/	0.85	Wang (2020)
Mianyang	5.4	5.27	0.23	2.0	0.105	0.24–19.51	Yu et al. (2014)
Sanjiang Plant	2.08	0.36	0.01	2.24	0.24	0.54	Song et al. (2020)
Fengqiu	/	/	0.57	/	/	/	Wang et al. (2016)
Kuangkeng Town	1.06	0.459	0.239	0.385	0.483	0.655	This work
Cangshan Subdistrict	1.39	0.558	0.247	0.465	0.343	0.675	This work

fluxes in this region were slightly lower than those in other areas, which may be related to the lower soil Se levels in Shandong Province. Fertilizer-induced Se input fluxes in this region were roughly equivalent to those in Shandong Province (0.1–0.59 g/ha/y) and Mianyang City (0.23 g/ha/y) (Yu et al. 2014), but were different from those in Sanjiang Plain (0.01 g/ha/y) and Fengqiu City (0.57 g/ha/y) (Song et al. 2020; Wei et al. 2016) because different regions have different farming structures and fertilizer types. The volatile and crop-harvested Se output fluxes in this region were slightly higher than those in Mianyang and Sanjiang Plain, but the volatilization-induced Se output flux was lower than mainland China and the crop-harvested Se output flux in this region was slightly lower than in Shandong Province (Sun et al. 2016) (Table 6). The volatilization-induced or crop-harvested Se output flux is closely associated with rainfall and soil properties (Dong et al. 2002).

The net flux of exogenous soil Se in Cangshan Subdistrict was observed to be about 2.7 times that in Kuangkeng Town. However, the average soil Se level in Kuangkeng Town was about 1.4 times that in Cangshan Subdistrict. The Se-rich soil area in Kuangkeng Town was also about 5.2 times that in Cangshan Subdistrict. Therefore, the external Se input and output fluxes cannot better explain the difference in soil Se levels in the two areas, and such difference mainly contributes to the different soil-forming parent material in the two areas. The geostatistical analysis above also resulted in a dominating natural source of parent material in this region. The strata in Kuangkeng Town are mainly Ordovician strata, characterized by the lithology of pure limestone and dolomite. While the underlying strata of the soil in Cangshan Subdistrict are mainly Cambrian and Quaternary. Thus, the Ordovician carbonate rocks are responsible for the higher soil Se levels in Kuangkeng Town than in Cangshan Subdistrict (Fig. 4). The statistical average soil Se levels on different stratigraphic units also support such ideas.

Parent rocks largely determine soil Se levels, and some high-Se rocks are often considered to be the main Se source in Se-rich soils (Fordyce 2013). Particularly, Se-rich coals and black rocks are widely mentioned (Li et al. 2004; Ren

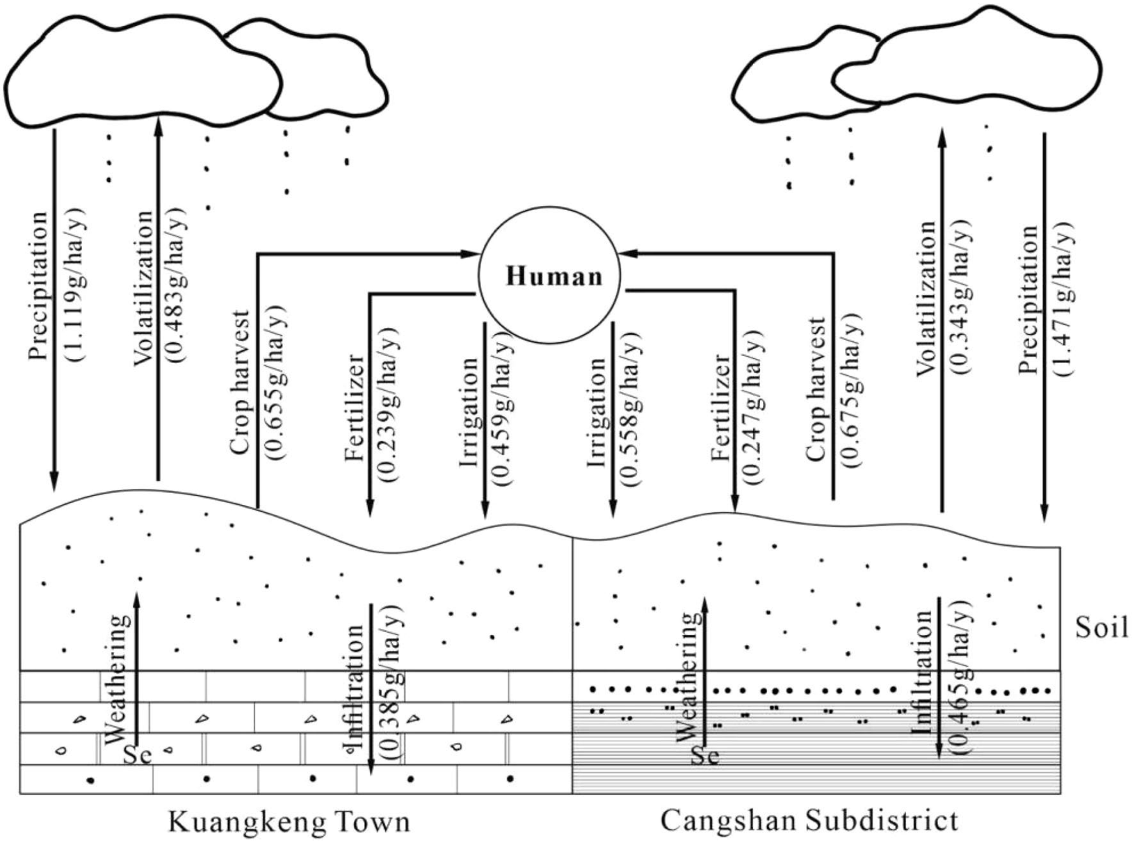

Fig. 4 Soil Se geochemical cycle pattern

et al. 2012; Cheng et al. 2021; Wang 2022). The Se levels of siliceous shale in the Enshi Yutangba area reach up to 8390 mg/kg (Feng et al. 2021). The black carbonaceous slate in the Daba region of South Qinling Mountain has an average Se level of 22 mg/kg (Luo et al. 2004). The black shales of the Great Plains in the USA have abnormal Se levels and cause Se-rich soils or even selenosis (Fordyce 2013; Jaime and Michael 2018; Parnell et al. 2016). Xu and Tao (2004) and Tian et al. (2017) documented the high-Se soils in southern Shaanxi and the Guangning District of Guangdong Province are derived from early Cambrian black shales. Additionally, other high-Se rocks are also reported to cause high-Se soils, such as volcanic tuffs (Jaime and Michael 2018; Luo et al. 2004), coal (Wang 2022), marine or black shale (Liao et al. 2016), basalt (Gong et al. 2022), etc.

However, carbonates have low-Se levels because of the numerous Ca(Mg)CO_3 (Fordyce 2013), and which is in agreement with this research (Table 1). Yang et al. (2020) reported an average level of 0.122 mg/kg in limestone in western Sichuan, Li et al. (2005) recorded an average level of 0.166 mg/kg in muddy limestone and 0.099 mg/kg in limestone in Zhejiang. Luo et al. (2004) documented an average level of 0.14 mg/kg in limestone in the Daba Mountains. The low-Se carbonates are always ignored when the origins of high-Se soil are discussed. However, massive $CaMg(CO_3)_2$ and other soluble materials run off during the soil-forming process of carbonates, which greatly distinguishes it from the soil-forming process of other rocks. The soluble materials were estimated to be more than 90% in carbonates (Wang et al. 1999) and even Li et al. (2006) estimated an average acid insoluble level of about 1% in limestone (Li et al. 2006). Naturally and logically, Se can accumulate in residuals during the weathering of carbonates, forming high-Se soil. Li et al. (2017) found that Ca in the soil overlying carbonate rocks (especially limestone) determines the SOC levels. Ca plays a non-negligible role in the retention of SOC because the erosion rate of carbonate is fast, and Ca can be supplemented. Therefore, the carbonate weathering process can indirectly affect soil Se levels by Ca leaching.

The high-Se soil overlying carbonate rocks has also been widely documented. The average soil Se levels overlying Cambrian muddy limestone and Ordovician limestone in Changshan Country, Zhejiang Province are 1.24 mg/kg and 1.19 mg/kg, respectively (Wang 2022). The average soil Se level overlying Cambrian–Ordovician limestone and muddy limestone in Chizhou, Anhui Province reaches 1.106 mg/kg (Liang et al. 2022). The soils overlying Cambrian dolomite and dolomitic limestone in Fenggang County, Guizhou Province have an average Se level of 1.22 mg/kg (Liu et al. 2012). Zhang et al. (2005) reported an average Se level of 0.87 mg/kg in soil overlying limestone in Hong Kong. 92.3% of soils overlying carbonate rocks have an average Se level of 0.56 mg/kg in Guizhou Province (Yao et al. 2020). The overlying soils of the Cambrian–Ordovician carbonates in Shiquan County, Shaanxi Province were found to be significantly enriched in Se, with an average Se level of 1.798 mg/kg (Zheng et al. 2022).

To summarize, Se gradually enriches in residue during the weathering of the Ordovician carbonates in this region, and Se-rich soils form with the leaching of numerous $CaMg(CO_3)_2$ and other soluble materials. Although the net flux of exogenous soil Se in Kuangkeng Town is lower than that of Cangshan Subdistrict, Kuangkeng Town has higher soil Se levels and larger areas of Se-rich soils than Cangshan Subdistrict because Kuangkeng Town is mainly dominated by Ordovician carbonates. Therefore, the special soil-forming process of the Ordovician carbonates is an important factor for soil Se enrichment, and the low-Se carbonates should be of concern when the Se origins are discussed in this region.

Conclusion

The soil Se levels and Se geochemical cycles were compared in Kuangkeng Town and Cangshan Subdistrict of Lanling County, Shandong Province, China. The two areas have different geological backgrounds. Kuangkeng Town is characterized by lower-middle Ordovician carbonates, and Cangshan Subdistrict by shale, mudstone, sandstone, limestone of Cambrian and loose sediments of Quaternary. Kuangkeng Town has soil Se levels of 0.095–0.631 mg/kg, with a mean of 0.38 mg/kg, and Cangshan Subdistrict has those of 0.044–0.526 mg/kg, with an average of 0.27 mg/kg. Kuangkeng Town has higher Se levels and a larger Se-rich area. Geostatistical analysis indicates parent materials play an important role in determining soil Se levels in the two areas. Geochemical cycles of soil Se show the net flux of exogenous soil Se in Cangshan Subdistrict is 0.793 g/ha/y, which is 2.7 times that in Kuangkeng Town (0.294 g/ha/y). The exogenous flux does not adequately explain the difference in soil Se levels in the two areas. The Se enriches in soil when numerous $CaMg(CO_3)_2$ in carbonates of lower-middle Ordovician leaches during weathering, which is the important forming factor of Se-rich soil in Kuangkeng Town. Thus, the lower-middle Ordovician carbonates should be of concern when the Se-rich soils are discussed.

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Author contributions QD and QC conceived and designed the experiments. QC, YZ, and XW contributed reagents/materials/analysis tools. SL, YZ, QM, FL, and HG performed the experiments. QC and YZ analyzed the data. YZ and QC writing—original draft. QD and FL review, and editing.

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Data availability The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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