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Selenium speciation and characteristics of selenium-enriched crops in Guiyang seleniferous soil, southwestern China

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Environmental context. Elemental selenium plays an important role in maintaining human health and the growth of plants and animals. We studied the availability of selenium in soils and agricultural crops in Guiyang City, China, and found that the soil is selenium-rich and the crops are selenium-enriched. These results can help to understand and improve the development of mountain agriculture and rural revitalisation.

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ABSTRACT

Rationale. Selenium (Se) is a critical element for both maintaining human health and the growth of plants and animals. The content of Se in crops is primarily determined by its speciation in soil. Therefore, the investigation of soil Se and its speciation has become a key focus of current research. **Methodology.** In this study, taking a typical seleniferous area in Guiyang City as the study area, we investigated selenium speciation in Se-rich soil and its distribution characteristics in both soil and crops using atomic fluorescence spectroscopy (AFS) and a five-step extraction processing methods. Moreover, we further explored the key factors that affect the distribution of Se in soil. **Results.** The findings are summarised as follows: (1) the Se content in all investigated samples met the standards of selenium-rich soil (0.40 mg/kg). The Se content in the soil surrounding crop roots ranged from 0.96 to 4.29 mg/kg, with an average value of 2.18 mg/kg. (2) Soil Se primarily existed in organic, residual, and iron and manganese oxide-binding species. The organic, sulfide-binding, and elemental Se species were the major contributors, accounting for an average of 47.00%, while the content of water-soluble, exchangeable, and carbonate-binding Se species was significantly lower. (3) Almost all crops, regardless of their types, were found Se-enriched, accounting for approximately 89.47% of the total crops in the study area. The average Se content was 0.35, 0.12, and 0.026 mg/kg in tea, rice, and corn, respectively. **Discussion.** Varying soil physical–chemical properties, such as the content of soil organic matter content and pH levels, etc. can impact the distribution of Se in soil differently. These findings can serve as a scientific foundation for the effective utilisation of selenium-rich land resources in Guiyang city. They can also support and facilitate the development of modern specialty and high-efficiency mountain agriculture, ultimately contributing to rural revitalisation and the national implementation of the Big Ecology Strategy.

Keywords: bio-availability, efficient use of land resources, guiyang city, influencing factors, seleniferous soil, selenium-enriched crops, selenium-rich soil, speciation.

Introduction

Selenium (Se) is a typical dispersed element commonly found in the Earth's curst at a concentration of 0.05–0.09 mg/kg (Liu *et al.* 1984). Despite this, it is an essential trace element necessary for the healthy growth of humans and animals. Se can enhance animal immune function, antagonise the toxicity of heavy metals, and improve the human body's anti-cancer and anti-aging ability (Heath *et al.* 2010; Ben Amara *et al.* 2011; Jarzyńska and Falandysz 2011; Kolachi *et al.* 2011). Insufficient Se intake can result in many Se deficiency diseases, such as Keshan disease, Kaschin-Beck disease, and white muscle disease, in both humans and animals (Zhang *et al.* 1990; Tan 1996), while excessive Se consumption can cause potential Se toxicity, leading to hair loss, nail discolouration, and staggering disease in animals and local humans living in high-seleniferous area (Ellis and Salt 2003; Thomson 2004; Ben Amara *et al.* 2011; Xue *et al.* 2011; Natasha *et al.* 2018). Therefore, the World Health Organization (WHO) recommends a Se intake of 40–400 μg/day for adults (World Health Organization 1996; Dinh *et al.* 2018). However, approximately 20% of the world's land is affected by a deficiency of Se. Se deficiency had been frequently reported in countries such as New Zealand, Finland, the United States, and the United Kingdom (Fordyce 2013). China is also one of the countries suffering Se deficiency, with about 51% of its land affected by Se scarcity (Dinh *et al.* 2018). In China, the discovery of many Se-rich land resources during the Multi-target Regional Geochemical Survey (1:250 000) in 1999 led to the identification of 35 thousand square kilometers of green Se-rich cultivated land by 2015 in a survey area of 1.5 million square kilometers (Zhou 2020). A survey in the Guiyang area, Guizhou province, found that 96% of the total survey area had Se-rich soil, with an average Se content in the topsoil of 0.70 mg/kg, 2.4 times the national soil (Layer A) background value (0.29 mg/kg) (Guizhou Academy of Geological Survey 2012). Similar information was found in the 2017 Geochemical Survey and Evaluation of Cultivated Land Quality in Guizhou Province. This survey revealed that cultivated land in the Guiyang area had a soil Se content ranging from 0.08 to 8.96 mg/kg with an average value of 0.62 mg/kg. Furthermore, the survey identified that the overall area of Se-rich cultivated land exceeds 2000 km^2, accounting for more than 80% of the total surveyed cultivated land area. This indicates a significant potential for the development of a Se-rich agricultural product industry. However, many previous studies have found that the Se content in crops, vegetables, and other plants is not solely associated with the total Se content present in soil, but also with its chemical forms and valence states, between which the latter was believed to be of much more importance (Yang 2000; Qin *et al.* 2017). These varying chemical forms can impact the geochemical behaviours of Se, including activation, migration, transformation, and enrichment of Se, and thus play a vital role in improving aspects such as the bioavailability of Se and human health (Thiry *et al.* 2012; Kieliszek and Błażejak 2013). The four valence states of Se in soil are organic selenide (Se^{2-}), elemental selenium (Se^0), selenite (SeO_3^{2-}), and selenate (SeO_4^{2-}) (Kulp and Pratt 2004; Favorito *et al.* 2017), which can be divided into five fractions according to the chemical extraction method: soluble Se (SOL-Se), exchangeable and carbonate-bound Se (EX-Se), Fe–Mn oxide-bound Se (FMO-Se), organic matter-bound Se (OM-Se), and residual Se (RES-Se).

Our study area was the Lindong-Jiu'an Country, located in Guiyang city, that has long been known to have abnormal soil Se content. However, there is currently a lack of reports on clarification of Se content, speciation, and characteristics in the soils of this area. The primary objective of this study is to investigate and determine the chemical speciation of soil Se and the characteristics of Se-enriched crops in this typical seleniferous area. The results of our research can offer a scientific foundation for understanding and making informed decisions about current Se-rich land resources, facilitating the development of modern specialty and high-efficiency mountain agriculture, and ultimately serving and supporting rural revitalisation and the national policy of Big Ecology Strategy.

Experimental

Overview of the study area

This study was conducted in Guanshan Lake and Huaxi administrative districts (26°27′8″–26°35′38″N, 106°31′19″–106°38′25″E) in the southwest of Guiyang city. The soils in the Guiyang area of Guizhou Province, China, have been identified as anomalous in terms of Se content through the Multi-targeted Regional Geochemical Survey Project. The landform in this area is highly dynamic, with hills comprising 50% of the region, followed by mountains and flat dams together accounting for the remaining 50%. Soil types are primarily yellow and yellow-brown soil. Previously, this area was a major coal industrial base of Guiyang city, but with most coal mines closed, rice, corn, tea, vegetables, fruit trees, and other economic crops have been planted. For example, the tea industry is the leading sector in Jiu'an county, with the most well-known 10 000 mu ecological tea garden in the Jiulong Mountain area.

The primary rock strata found in the area consist of formations from the Permian and Triassic systems. Specifically, the Maokou, Longtan, and Changxing Formations belong to the Permian System, while the Shabaowan, Daye, Anshun, and Songzikan Formations belong to the Triassic System. Within the Permian strata, the sedimentary facies are mainly platform and lagoon tidal flat facies. The middle series of the Permian System primarily consists of limestone from the Maokou Formation, while the upper series comprises coal-bearing clastic rocks from the Longtan Formation. On the other hand, the Triassic strata primarily exhibit platform facies, with the lower series consisting of limestone from the Daye Formation and dolomite from the Anshun Formation. The main mineral resource found in the area is coal.

The anomalous area spans 98 km^2, with soil Se content ranging from 0.77 to 2.89 mg/kg. The coefficient of variation is 34.87%, and the average value is 1.56 mg/kg. This average value is 5.4 times and 7.8 times higher than the national average value of Layer A soil and the global soil background value, respectively. These numbers suggest that the area has abundant selenium-rich soil resources, which can serve as a natural foundation for developing industries that leverage this characteristic. This can potentially increase farmers' income and contribute to rural revitalisation.

Sampling and data processing

The Guiyang area is rich in soil Se, which is mainly concentrated in coal measure strata. Given that tea and rice are the primary crops grown in this area, we selected and allocated the sampling sites primarily in tea plantations and rice fields. Specifically, we collected samples from cultivated land area, including Jiulongshan Tea Garden, Dashan Tea Garden, and other representative farmland areas. Fig. 1 shows a detailed spatial distribution of all sampling locations in this study. At each sampling spot, we collected soil samples and corresponding crop samples for further analysis.

Soil samples

To ensure the representativeness and accuracy of the samples, a quincunx points distribution method for sample collection was used. First, using GPS for positioning, 3–5 separate samples of equal quantity were collected in the central point of a 50 m radius area and its surrounding area, then these samples were mixed into one sample. The sampling soil depth was required to be within 0–20 cm, and each sample mass was no less than 1500 g. Following sample collection, the impurities such as plant residues and stones were removed in the laboratory and the samples were dried naturally under cool indoor conditions. The samples were crushed with a wooden hammer or stick and each smashed soil sample was passed through a 20-mesh nylon screen. Finally, the quartering method was used to reduce sample mass to 500 g and samples were stored in Teflon bottles for subsequent analysis.

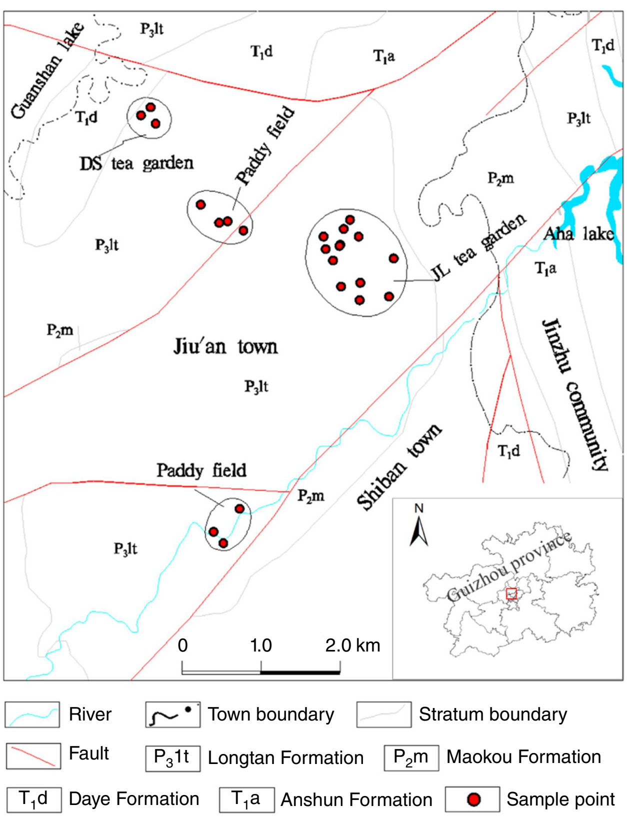

Fig. 1. Schematic diagram of study area and sampling positions.

Crop samples

Crop samples were collected from the main soil sampling points following the strict sampling methods and technical requirements specified in DZ/T0295-2016 *Specification of Geochemical Assessment of Land Quality*, ensuring the representativeness and quality control of the samples. For tea samples, the 'quincunx' method was used to collect the old, middle, and young tea leaves from 3 to 5 soil sampling points, with each sample mass being greater than 300 g. The rice sample collection method was roughly the same as that of tea. However, as there were few corn crops planted locally, 2–3 corns in the corn planting plot were randomly collected as samples.

The crop samples were washed three times with tap water and then three times with distilled water. After drying at room temperature, they were crushed in a plant sample crusher, passed through a 60-mesh (0.280 mm) plastic sieve, and sealed and stored in a polyethylene plastic bag for further analysis.

In total, 25 soil samples and 19 crop samples were collected during this study, including 12 tea samples, 5 rice samples, and 2 corn samples.

Sample analysis

Sample analysis was performed at the Central Laboratory of Bureau of Geology and Mineral Exploration and Development Guizhou Province. The detailed analytical procedures used are described by Zheng *et al.* (2005). The measurement of Se was conducted using an atomic fluorescence spectroscopy (AFS) method (AFS2300E), with the furnace temperature set at 200°C, a carrier gas flow rate of 400 mL min^{-1}, shielding gas flow rate of 900 mL min^{-1}, lamp current of 45 mA, and negative voltage at 280 V. Organic matter was measured using the potassium dichromate volumetric method, pH was determined using the potential method, nitrogen (N) was measured using the Kjeldahl distillation–volumetric method, and phosphorus (P) was measured using an inductively coupled plasma–atomic emission spectroscopy (ICP-AES) method (Icap6300), with the RF power set at 1.15 kW, an atomising gas flow rate of 0.7 L min^{-1}, auxiliary gas flow rate of 0.5 L min^{-1}, cooling gas flow rate of 15 L min^{-1}, and analysis pump speed of 50 r min^{-1}. For analysing soil morphology, we employed a five-step extraction processing method (Qu *et al.* 1997). Qu Jianguo *et al.* (1998) proposed a classification and treatment method for identifying soil Se speciation. According to this method, soil Se can be briefly divided into five forms, namely, water-soluble (SOL-Se), exchangeable and carbonate-binding (EXC-Se), iron and manganese oxide-binding (FMO-Se), organic matter and sulfide-binding and elemental (OM-Se), and residual Se (RES-Se) in soils (Qu *et al.* 1998).

The analysis quality was strictly regulated according to the requirements of the multi-target regional geochemical survey specifications, the accuracy and precision was monitored using the national Level-1 reference material of soil (GBW Series). Moreover, the analysis quality was monitored by rechecking the abnormal points and repeating the analysis by more than 10%. For the morphological analysis of soil Se, parallel analysis was carried out and the national Level-1 soil standard samples were inserted for quality control.

Data processing and graph generation

The primary software tools utilised for statistical analysis of geochemical parameters were EXCEL and SPSS 26. Meanwhile, Mapgis6.7 was employed to generate maps.

Results and discussion

Distribution characteristics of soil selenium

Fig. 2 illustrates the distribution of Se content in 25 soil samples. Our analysis revealed significant variation in Se content in soil, ranging from 0.96 to 4.29 mg/kg, with an average value of 2.18 mg/kg and a coefficient of variation of 0.94. Based on Tan Jianan's classification method for selenium-rich soil, which considers soil Se content equal to or greater than 0.4 mg/kg (Tan 1996), the Se content in soil and mean soil Se content around the roots in the study area were 2.4–10.7 times and 5.5 times the standard of selenium-rich soil, respectively, meeting the standard of selenium-rich soil. However, the soil Se content at four sampling points exceeded 3.00 mg/kg, indicating excessive Se content in this area. This may pose a risk to human health. Results from the multi-target regional geochemical survey showed that the soil Se content varied greatly among different geological units. The highest content was found in the Longtan Formation and Changxing Formation, where the soil Se content was above 1.57 mg/kg. The Daye Formation, Songzikan Formation, and Shabaowan Formation had relatively high Se content ranging from 0.75 to 0.93 mg/kg. These findings suggest that the high Se content in the study area's soil may be related to the coal-bearing clastic rock stratum of the Longtan Formation of the Permian System, which is mainly caused by the natural geological background.

Morphological distribution characteristics of soil selenium

Qu *et al.* (1998) proposed a classification and treatment method for Se forms in soils, which categorises soil Se into five forms: water-soluble (SOL-Se), exchangeable and carbonate-binding (EXC-Se), iron and manganese oxide-binding (FMO-Se), organic matter and sulfide-binding and elemental (OM-Se), and residual (RES-Se) soil Se. SOL-Se and EXC-Se are generally considered effective states that can be directly or easily absorbed and utilised by plants. FMO-Se and OM-Se cannot be directly absorbed and utilised by plants, but they can be transformed into effective states under certain physicochemical conditions. However, RES-Se is mainly found in the crystal lattice of some crystalline solids such as sulfide and silicate, which are difficult to break down. As a result, RES-Se is generally not available for uptake by most crops, and therefore is usually considered an unusable form.

In this study, we analysed the morphological characteristics of soil Se for 10 soil samples. Our results showed that among all forms of soil Se, OM-Se had the highest content of 0.49–1.80 mg/kg with an average value of 1.07 mg/kg. This was followed by FMO-Se, which had a content of 0.24–0.63 mg/kg with an average value of 0.39 mg/kg. SOL-Se, on the other hand, had an extremely low content, ranging from 0.0001 to 0.0023 mg/kg with an average value of 0.0004 mg/kg (Table 1). The content of RES-Se was found to be between 0.21 and 1.46 mg/kg, with an average value of 0.72 mg/kg. Based on the distribution characteristics of different forms of soil Se (Fig. 3), we found that SOL-Se had a very low proportion and a mean value of only 0.03%. EXC-Se accounted for 1.31–7.12% with an average of 4.40%,

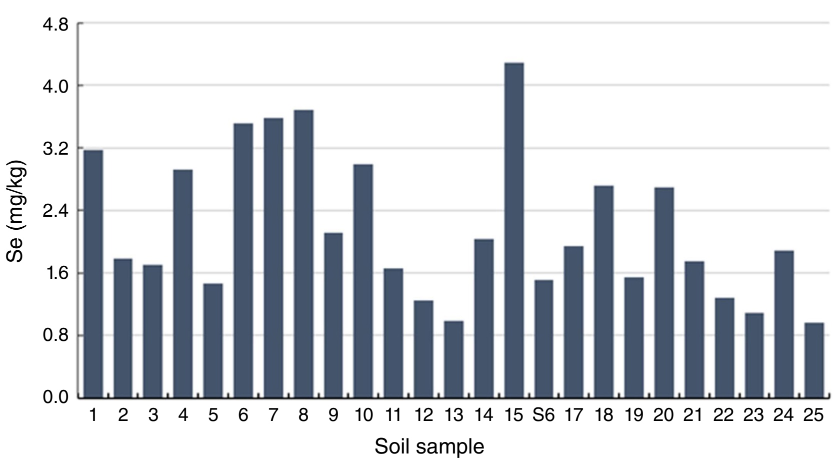

Fig. 2. Distribution of selenium content in soil samples.

Table 1. Form analysis and characteristic statistics of soil selenium.

Sample no.	SOL-Se		EXC-Se		FMO-Se		OM-Se		RES-Se		Se_{tol}(mg/kg)
	Content (mg/kg)	%	Content (mg/kg)	%	Content (mg/kg)	%	Content (mg/kg)	%	Content (mg/kg)	%	
S01	0.0001	0.003	0.04	1.31	0.28	9.48	1.10	36.52	1.46	48.69	3.00
S06	0.0005	0.014	0.22	6.27	0.63	17.88	1.54	43.62	1.10	31.32	3.52
S04	0.0012	0.040	0.13	4.35	0.31	10.38	1.70	56.82	0.82	27.38	2.99
S09	0.0001	0.005	0.15	7.12	0.29	13.19	1.04	48.11	0.62	28.76	2.16
S11	0.0004	0.025	0.08	4.77	0.32	19.59	0.69	41.97	0.50	30.73	1.63
S13	0.0001	0.010	0.03	2.90	0.24	24.20	0.49	49.99	0.26	26.06	0.99
S15	0.0001	0.003	0.12	3.17	0.60	15.54	1.80	46.78	1.31	33.87	3.86
S17	0.0001	0.005	0.09	4.43	0.45	23.03	0.91	46.75	0.45	22.99	1.96
S19	0.0001	0.006	0.05	3.18	0.40	24.10	0.81	48.72	0.43	25.83	1.67
S22	0.0023	0.180	0.08	6.53	0.35	27.17	0.65	50.75	0.21	16.36	1.29
Mean	0.0004	0.03	0.100	4.44	0.387	18.63	1.074	47.44	0.72	29.47	2.18

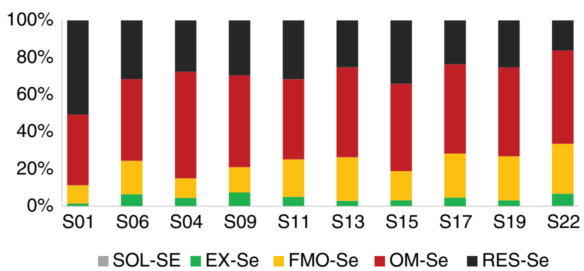

Fig. 3. Distribution characteristics of selenium forms in soil samples.

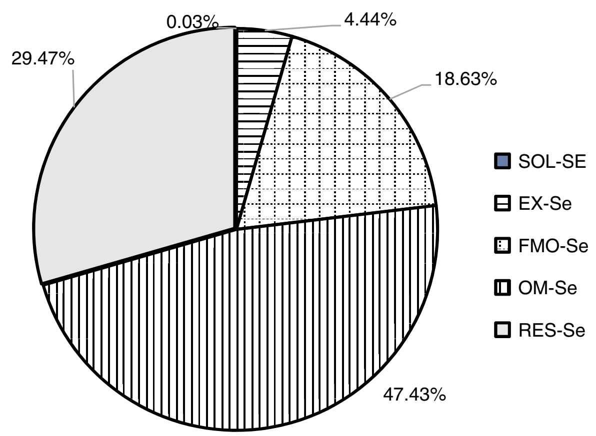

Fig. 4. Distribution of average proportion of various forms of soil selenium.

while FMO-Se had a proportion of 9.48–27.17% with an average of 18.63%. The highest proportion was found in OM-Se, which ranged from 36.52 to 56.82% with an average of 47.44%, and RES-Se had a proportion of 16.36–48.68% with an average of 29.47%. In addition, we also found that the distribution characteristics of different forms of soil Se in the study area tended to have a clear pattern of OM-Se > RES-Se > FMO-Se > EXC-Se > SOL-Se (Figs 3, 4). The content of soil OM-Se is similar to that found in Se-rich soils in Ping'an-Qinghai, Yutangba-Hubei, and Ankang-Shaanxi areas, and many other places (Pyrzyńska 2002; Zhu *et al.* 2008; Song *et al.* 2017; Wang *et al.* 2022). However, findings from Sharmasarkar and Vance's study (1995) on soils with high Se content in pastoral areas and mining areas of varying characteristics in the United States demonstrated that RES-Se is the primary form of Se in the soil. This suggests that the morphological distribution of soil Se is influenced by factors such as soil parent material, as well as its physical and chemical properties. We also found that the content of soil SOL-Se and EXC-Se in the study area was remarkably low, with the combined average proportion of the two forms less than 5%, particularly for SOL-Se (< 0.1%). This finding contrasts with the results of other studies (Chang *et al.* 2019; Zhang *et al.* 2021; Wang *et al.* 2022) and could be attributed to the low migration ability of Se in strongly acidic soils with a pH less than 5. This leads to the easy absorption of Se by iron and aluminium oxides or complex reaction with organic matter.

Distribution characteristics of selenium in crops

In this study, we collected a total of 19 crop samples consisting of 12 tea samples, 5 rice samples, and 2 corn samples. Our results showed that the content of Se in all crop samples ranged from 0.057 to 0.56 mg/kg, with an average value of 0.26 mg/kg, except for one sample that could not be detected for unknown reasons (Table 2). As for Se content in tea, we found that the values ranged from 0.24 to 0.56 mg/kg, with an average value of 0.35 mg/kg. Based on the Se-enriched Tea Standard for Agricultural Sector (NY/T 600-2002), 11 out of the 12 tea samples collected

Table 2. Summary of the statistics for selenium (Se) content, enrichment coefficient, and Se-rich status by crop type.

Sample no.	Crop	Crop Se (mg/kg)	Root soil Se (mg/kg)	Content coefficient of crops	Se-rich status	Se-rich Standard (Se) (mg/kg)
Z01	Rice	0.083	2.92	0.028	Yes	GB/T22499-2008 (Se-rich rice: 0.04–0.30) (Standardization Administration of China 2008)
Z02	Rice	0.100	1.47	0.068	Yes	
Z04	Rice	0.178	3.52	0.016	Yes	
Z05	Rice	0.118	3.58	0.050	Yes	
Z06	Rice	0.113	3.69	0.032	Yes	
Z03	Corn	0.057	2.12	0.053	Yes	DB50/T 705-2016 (Se-rich corn: 0.02–0.3) (Chongqing Bureau of Quality and Technical Supervision 2016)
Z07	Corn	ND	2.99	0	No	
Z08	Tea	0.366	1.66	0.220	Yes	NY/T 600-2002 (Se-rich tea: 0.25–4.0) (The Ministry of Agriculture of the People's Republic of China 2002)
Z09	Tea	0.368	1.25	0.294	Yes	
Z10	Tea	0.296	0.99	0.299	Yes	
Z11	Tea	0.402	2.04	0.197	Yes	
Z12	Tea	0.341	4.29	0.079	Yes	
Z13	Tea	0.306	1.51	0.203	Yes	
Z14	Tea	0.328	1.94	0.169	Yes	
Z15	Tea	0.240	2.72	0.088	No	
Z16	Tea	0.560	1.55	0.361	Yes	
Z17	Tea	0.448	2.69	0.167	Yes	
Z18	Tea	0.301	1.75	0.172	Yes	
Z19	Tea	0.280	1.28	0.219	Yes	

from the study area met the standard making the Se enrichment rate in tea up to 91.7%. Meanwhile, the Se content in non-Se-enriched tea samples (0.24 mg/kg) was found close to the standard. As for Se content in rice, we found that the values ranged from 0.083 to 0.18 mg/kg, with an average value of 0.12 mg/kg. Based on the National Se-enriched Rice Standard (GB/T22499-2008), all samples met the standard making its Se enrichment rate up to 100%. Comparably, only half of the corn samples met the Se-enriched corn standard specified in Chongqing Se-enriched Agricultural Products Standard (DB50/T705-2016), thus yielding a Se enrichment rate of 50%. Overall, 17 out of 19 samples met the above Se-enriched crop standards, indicating an 89.47% Se-enriched crops ratio in the study area, regardless of crop type.

The ratio of Se content in crops and soil, known as the enrichment factor, indicates the ability of crops to absorb and utilise selenium from soil. Table 1 shows that different crops vary greatly in selenium absorption from soil. Tea, rice, and corn, for example, had enrichment coefficients of 0.079–0.361 (average 0.206), 0.028–0.068 (average 0.046), and only 0.016, respectively. The order of crops with the highest to lowest Se enrichment ability is tea > rice > corn. Furthermore, the enrichment coefficient of Se in tea is 4.5 times and 12.9 times higher than that of rice and corn, respectively.

Factors affecting the distribution of Se Speciation

Previous studies have established a close relationship between the accumulation of Se in plants and the total Se of soil, as well as its distribution form (Yang 2000; Li *et al.* 2017; Wang *et al.* 2022). The physical and chemical conditions of soil partly regulate the level of Se enrichment of soil and the mutual transformation between different forms of Se (Li *et al.* 2017; Wang *et al.* 2022). Therefore, it is necessary to explore the effects of the total Se of soil and physical and chemical properties of soil on the occurrence form of soil Se. Table 3 shows the analysis results of the total Se content of soil and related physical and chemical indicators in soils.

Effects of total soil Se on Se speciation

Although the total Se content of soil does not directly reflect the amount of available Se for crops, it serves as the storage source for different forms of Se in the soil and impacts the distribution of various Se forms to some extent. Based on the results of the correlation analysis between soil Se content of various forms and the total Se content in the soil, significant positive correlations were found between FMO-Se, OM-Se, and RES-Se with the total Se content of various forms in the soil, with a correlation coefficient (R) of 0.642, 0.946, and 0.912, respectively (Table 4). Among them,

Table 3. The total Se content and physicochemical parameters in soils.

Sample No.	Se (mg/kg)	pH	OM (%)	CEC (cmol/kg)	N (mg/kg)	P (mg/kg)
S01	3.17	4.21	3.52	27.3	1982	915
S04	2.92	5.66	14.26	22.3	3690	1311
S06	3.52	4.41	10.34	27.6	3603	1428
S09	2.12	4.98	7.8	32	3469	1223
S11	1.66	4.82	4.59	29.2	2342	793
S13	0.99	4.42	2.85	26.3	1635	1192
S15	4.29	4.48	3.54	29.1	1467	708
S17	1.94	4.21	3.08	38.5	1194	636
S19	1.55	4.31	4.49	28.5	1701	907
S22	1.28	4.30	4.42	35.8	1957	858

Note: OM and CEC stand for organic matter and cation exchange capacity of soil, respectively.

Table 4. Correlation between selenium speciation and organic matter.

R	SOL-Se	EXC-Se	FMO-Se	OM-Se	RES-Se	Tol-Se	OM.
SOL-Se	1						
EXC-Se	0.117	1					
FMO-Se	−0.090	0.625	1				
OM-Se	−0.045	0.660*	0.600	1			
RES-Se	−0.310	0.328	0.416	0.760*	1		
Tol-Se	−0.177	0.608	0.642*	0.946**	0.912**	1	
OM.	0.325	0.685*	0.087	0.591	0.188	0.416	1

Note: *Significantly correlated at the level of 0.05 (double tail).
**Significantly correlated at the level of 0.01 (double tail).

OM-Se and RES-Se exhibited a strong correlation with the total Se content in the soil, followed by FMO-Se ($R = 0.608$) and EXC-Se ($R = 0.608$). In contrast to a previous study (Wang *et al.* 2018), our correlation analysis revealed a slight negative correlation (-0.177) between SOL-Se and the total Se content in the soil, which could be attributed to the extremely low soil SOL-Se content in the study area.

Physical and chemical properties of soil

The study of Shao *et al.* (2018) found that there was a clear positive correlation between Se content and soil physiochemical properties such as organic matter, while Se content exhibited a negative correlation with pH. Therefore, the physical and chemical properties of soil and nutrient content have some impact on the morphological distribution of soil Se. This paper mainly focuses on exploring the impacts of organic matter, pH, cation exchange capacity (CEC), and nitrogen and phosphorus nutrients on the patterns of soil Se morphological changes.

Effects of organic matter. Our analysis revealed that the study area had a high soil organic matter content, ranging from 2.85 to 14.26%, with an average value of 5.89%. Moreover, the correlation analysis between the content of various Se forms and organic matter indicated that there was a strong positive correlation between organic matter and total soil Se ($R = 0.416$) (Table 4). However, the correlation between various Se forms and organic matter was not consistently predictable. Specifically, weak or no correlation was observed between soil organic matter content and RES-Se ($R = 0.188$) and FMO-Se ($R = 0.087$), while strong positive correlations were found between organic matter and EXC-Se ($R = 0.685$; $P < 0.05$), OM-Se ($R = 0.59$), and SOL-Se ($R = 0.325$). These findings are consistent with previous studies (Tang *et al.* 2010; Liu *et al.* 2021*a*; Liu *et al.* 2021*b*; Wang *et al.* 2022) that reported a significant positive correlation between soil available Se (or EXC-Se) and soil organic matter, both of which increase as soil organic matter content increases. Additionally, we also found extremely strong correlations between EXC-Se and OM-Se ($R = 0.660$) and FMO-Se ($R = 0.625$), indicating that the transformation of the latter two Se forms into EXC-Se is likely to occur under certain conditions, leading to an increase in Se bioavailability in soils.

In the study area, EXC-Se, as an essential component of the effective state, exhibited the strongest correlation with soil organic matter. This may be due to the fact that the decomposition of soil organic matter can release some of the bound Se and, meanwhile, generate some intermediate products that promote the activation of Se (Tang *et al*. 2010). As a result, soil organic matter affects the contents of various Se forms mostly by affecting the content of organic Se and second absorbing inorganic Se.

Soil pH value. pH plays a crucial role in regulating the chemical speciation and bioavailability of soil Se by affecting the valency of soil Se and the formation and hydrolysis of metal oxides such as iron, manganese, calcium, and magnesium (Shaheen *et al.* 2018). In acidic soils, Se mostly exists in the form of Se^{IV}, which has a weak migration ability and can be easily absorbed by iron and aluminium oxides or react with organic matter in a complex way. As a result, the chemical speciation of Se in such soil mostly exist as oxides of iron and manganese or organic binding species (Shaheen *et al.* 2014; Antoniadis *et al*. 2017; Natasha *et al*. 2018). In contrast, in neutral or alkaline soils, the decrease in positive charges on the surface of hydroxides and clay minerals weakens a soil's ability to absorb Se. Thus, Se in these soils mainly exist as Se^{VI} species, which are generally SOL-Se or EXC-Se and can be easily absorbed by plants (Rovira *et al*. 2008; Antoniadis *et al.* 2017). Yan *et al*.'s (2019) study also demonstrated a positive correlation between available Se content and pH. Soils in the study area are considered acidic, as the pH ranges from 4.21 to 5.66. Correlation analysis between soil pH and various Se speciation showed that the SOL-Se ($R = 0.212$), EXC-Se ($R = 0.343$), and OM-Se ($R = 0.399$) contents in the soil were positively correlated with soil pH (Table 5). These findings are consistent with previous studies conducted by Zhang *et al.* (2002) and Yan *et al*. (2019).

Furthermore, we also found a negative correlation between soil pH and FMO-Se content ($R = -0.279$), while the RES-Se content appeared to be independent of soil pH. Interestingly, a previous study conducted by Qu *et al.* (1998) found a negative correlation between soil pH and both EXC-Se and FMO-Se, whereas Gong *et al.* (2015) drew contrary conclusions that the pH was positively correlated with FMO-Se content and negatively correlated with high OM-Se content. These indicate that the influence of pH on Se speciation in the soil varies greatly among different geographical regions, possibly due to differences in soil composition such as parent material, soil type, and organic matter.

Effects of CEC. Soil CEC is a measure of the ability of soil colloids to absorb cations in soil by electrostatic attraction. It is an important parameter for evaluating buffering capacity, fertility retention capacity, and soil improvement (Zhang *et al*. 2005). Correlation analysis between various soil Se speciation and CEC showed that SOL-Se ($R = 0.127$) and FMO-Se ($R = 0.143$) were slightly positively correlated with CEC, while RES-Se ($R = -0.397$) and OM-Se ($R = -0.397$) showed opposite correlations with CEC. EXC-Se showed no sign of correlation with CEC in the soil (Table 5). These results indicate that as soil CEC increases, the capacity of negatively charged soil colloids to absorb Se in a free ionic state, such as Se^{IV}, Se^{VI}, etc. decreases, leading to an increase in Se content in soil solutions.

Nitrogen and phosphorus nutrients. We conducted correlation analysis between Se speciation and two key soil nutrients, nitrogen (N) and phosphorus (P), and found that all Se speciation, except for FMO-Se, were positively correlated with the two nutrients. Among the Se speciation types, EXC-Se exhibited the strongest positive correlation, with an extremely significant correlation with N ($R = 0.721$; $P < 0.05$), followed by OM-Se ($R = 0.433$), SOL-Se ($R = 0.238$), and RES-Se ($R = 0.198$). FMO-Se showed only slight correlation with the soil nutrients.

It is evident that the physical and chemical properties and the nutrient content of soil can indirectly affect the bioavailability of soil selenium by altering the content of different forms of Se in the soil, which, in turn, can affect the Se content in rice seeds.

Conclusion

We conducted a study on Se speciation in the soil, and the selenium enrichment status of crops, in a typical selenium-rich soil (abnormal selenium) area of Guiyang. The key findings are as follows:

(1) The Se content in the soil surrounding crop roots ranges from 0.96 to 4.29 mg/kg with an average of 2.18 mg/kg.

Table 5. Correlation analysis between Se speciation and pH, CEC, N, P, and other indicators.

R	SOL-Se	EXC-Se	FMO-Se	OM-Se	RES-Se	TSe
pH	0.212	0.343	−0.279	0.399	0.007	0.173
CEC	0.127	−0.053	0.143	−0.397	−0.397	−0.344
N	0.238	0.721*	−0.015	0.433	0.198	0.340
P	0.103	0.516	−0.085	0.253	0.085	0.169

Note: *Significantly correlated at the level of 0.05 (double tail).
**Significantly correlated at the level of 0.01 (double tail).

All the sampling points meet the standard for selenium-rich soil.
(2) OM-Se, RES-Se, and FMO-Se are the primary forms of soil Se, with OM-Se having the highest concentration and SOL-Se and EXC-Se being relatively rare.
(3) The distribution of Se speciation is affected by the total Se content of soil and the soil's physiochemical indicators such as OM, pH, and CEC. OM is strongly and positively correlated with EXC-Se, OM-Se, and SOL-Se, while slightly, positively correlated with RES-Se and FMO-Se. Soil pH is positively correlated with EXC-Se, OM-Se, and SOL-Se, but negatively correlated with FMO-Se.
(4) The Se content of crops in the area ranges from 0.057 to 0.56 mg/kg with an average of 0.26 mg/kg. The crops in this area are highly enriched in selenium, with a total Se enrichment rate of 89.47%.

Overall, our study shows that the selenium-rich soil in Guiyang is wide-spread and has high selenium enrichment intensity. The crops can absorb Se in the soil and crops in this area are generally selenium-enriched, indicating a great potential for developing a selenium-rich characteristic agriculture in this region.

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Data availability. The data that support this study will be shared upon reasonable request to the corresponding author.

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