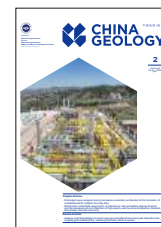




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Distributions and influencing factors of selenium in soils and edible wild mushrooms and the development and utilization of high-quality wild mushrooms (*Boletus*, *Ramaria botrytoides*, *Russula virescens*)

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ABSTRACT

Selenium (Se) serves as a trace element essential for the human body owing to its significant physiological functions and extensive pharmacological effects. The Se required by the human body is primarily obtained from soil-derived foods. This study revealed Se-rich soils covering a certain area and Se-rich edible wild mushrooms with high Se accumulation rates in Chuxiong, central Yunnan Province, China through a geochemical survey of soil quality. Furthermore, this study investigated the Se migration and transformation mechanisms in the soil-wild mushroom system, aiming to provide a scientific basis for the development and planning of Se-rich green foods in the study area. Using the geochemical data of samples collected from topsoils, deep soils, and wild mushrooms and their root soils in Nanhua County, Chuxiong, this study analyzed the Se contents in soils and wild mushrooms and their root soils and explored the mechanisms and influencing factors of Se enrichment in wild mushrooms. The results indicate that the topsoils in the study area exhibit Se contents ranging from 0.07 mg/kg to 0.95 mg/kg, with an arithmetic average of 0.25 mg/kg. The Se-rich soils cover an area of 356 km², which accounts for 13.07% of the total topsoil area. The wild mushrooms in the study area display Se contents varying from 0.004 mg/kg to 47.10 mg/kg, with a median of 0.977 mg/kg. The analyses of Moran's index and semivariogram indicate that the Se content distributions in both topsoils and deep soils in the study area exhibit distinct spatial structures. Specifically, the semivariogram model for the Se content in the deep soils emerges as a Gaussian model, and the Se content exhibits a nugget-to-sill ratio of 21.72%, suggesting that the Se content in deep soils is primarily influenced by structural factors such as parent materials. Se in the soils originates primarily from soil-forming parent rocks, with the origin of the Se-rich soils closely related to Triassic black shales, thin coal seams, and metamorphic rocks in the Ailao Mountain area. The wild mushrooms in the study area enjoy significantly higher Se content than other reported naturally Se-rich agricultural products, with a Se accumulation rate of up to 92.31% and an overall over-limit ratio of Pb and Cd of merely 11.54%, suggesting that the study area has substantial potential for the development of naturally Se-rich green foods. The wild mushrooms in the study area exhibit bioconcentration factors (BCFs) of Se ranging from 0.02 to 157.00 (median: 4.26), with Se bioavailability decreasing in the order of *Boletus edulis*, *Boletus aereus*, *Leccinum nigrescens*, *Ramaria botrytoides*, and *Russula virescens*. For the Se absorption and enrichment in the wild mushrooms, the primary controlling factor is identified as the wild mushroom species. Furthermore, they are significantly influenced by the Se content in soils but are minimally affected by the physicochemical indicators of soils.

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1. Introduction

Se serves as a trace element essential for human health (Sharma S et al., 2017). As a significant nutritional factor in the human body, Se fulfills multiple functions including oxidation resistance, cancer prevention, and immunity boosting (Feng CX et al., 2002; Chen XY et al., 2018).

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However, the human body cannot synthesize Se and primarily obtains it through food chains. To meet the requirement for Se of the human body, developing Se-rich agricultural products holds promising prospects and great economic significance (Zhou XW et al., 2021). Se-rich agricultural products are primarily produced from Se-rich soils, with the Se enrichment degree of soils determining whether the agricultural products are rich in Se (Huang CL et al., 2013). Therefore, the Se content in soils directly influences the Se levels in crops, further affecting human health.

The Se distribution in soils exhibits pronounced zoning. In China, soils in most regions are relatively depleted in Se, with topsoils exhibiting an average Se content of 0.22 mg/kg (Hou QY et al., 2020). Yunnan Province is identified as a primary region in China where Se-deficient soils are distributed, with topsoils featuring an average Se content of only 0.20 mg/kg (Hou QY et al., 2020). Presently, the identified Se-rich soils in Yunnan are mainly distributed in the Zhaotong, Wenshan, Xuanwei, and Yimen areas (Liu JP et al., 2020), with no report of such soils in other areas. Against the backdrop of general Se deficiency across the Yunnan Province, developing green foods in local areas with Se-rich soils provides a significant guarantee for the province to promote green food production and develop agriculture with plateau characteristics (Liao QL et al., 2007).

In recent years, the China Geological Survey has initiated numerous geochemical surveys of land quality, discovering Se-rich soils covering a certain area and wild mushrooms with high Se accumulation rates and BCFs in Nanhua, Chuxiong, central Yunnan. Yunnan is known for its abundant mushrooms, especially in Chuxiong, where Nanhua is renowned for its high-quality wild mushrooms. Focusing on the soils and wild mushrooms in the Nanhua area in central Yunnan, this study investigated the geochemical characteristics of Se in topsoils and deep soils, analyzed the distribution, migration, and transformation characteristics of Se in the soil-wild mushroom system, and explored the bioavailability of Se in wild mushrooms and its influencing factors. This study will provide a scientific basis for the development and planning of Se-rich land resources and green foods in the Nanhua area, thus facilitating the development of Yunnan's "green food brand" among its brands of green energy, green foods, and destination for healthy life, as well as the implementation of the rural revitalization strategy in the province.

2. Overview of the study area

The study area, located in Nanhua County, Chuxiong Yi Autonomous Prefecture, central Yunnan Province (Fig. 1a), resides within the Chuxiong Basin in the western Yunnan-Guizhou Plateau. This area exhibits elevations ranging from 963 m to 2861 m, high in the northwest and low in the southeast. Regarding the landscapes, this area is predominantly mountainous, with numerous mountains distributed throughout its southwestern part and wavy hills, interspersed with small plain areas, in its northeastern part.

With low latitudes and high elevations, the study area has a subtropical monsoon climate, characterized by mild weather and distinct seasons. The complex landforms and significantly different relief result in the occurrence of diverse climates ranging from subtropical to temperate ones, which form a multi-level climate where one can experience four seasons even in one mountain and distinct weather in valleys and on slopes. Nanhua County spans two major river basins, i.e., the Yangtze and Honghe river basins, and three major water systems, i.e., the Jinsha, Yuanhe, and Honghe river systems, with primary rivers including the Longchuan, Yupao, Lishe, Malong, and Tujie rivers. Nanhua County emerges as the most significant production area of wild mushrooms and the largest collection and distribution center of wild mushrooms in China. With over 290 species of known edible wild mushrooms, this county has earned titles such as "the wild mushroom kingdom of the world", "the county with gourmet wild mushrooms in China", and "the hometown of wild mushrooms in China". All these establish Nanhua County as an integral part of the urban agglomeration of central Yunnan.

The soil types within the study area exhibit a typical vertical zonation distribution due to the impacts of the vertical climate. The primary soil types include dry red soil, paddy soil, purple soil, red soil, yellow-brown soil, brown soil, and dark brown soil (Fig. 2). Among these, purple soils are the most widely distributed, red soils are primarily found in areas with sufficient heat and moisture, paddy soils predominantly occur in intermountain basins, and brown and dark brown soils are principally discovered in high-elevation regions. The primary land use types include paddy fields, arid lands, orchards, arbor forest lands, shrub forest lands, and grasslands, with forest lands covering the largest area, followed by arid lands.

The study area, located in the western part of the Yangtze paraplatform, exhibits exposed strata including the Proterozoic Ailaoshan Group (PtaI) and strata formed during the Permian (P), Upper Triassic (T₃), Jurassic (J), Cretaceous (K), Neogene (N₂), and Quaternary (Q), with Indosinian-Yanshanian intrusions sporadically visible. The strata and faults in the study area have a strike of northwest (Fig. 1b). The Lower Proterozoic strata, the Proterozoic Ailaoshan Group, and the Permian strata exposed in the study area consist primarily of metamorphic rocks, including slates, microcrystalline schists, gneisses, leptynites, and sandy slates. The upper part of the Permian outcrops is interbedded with siliceous rocks, biogenic limestones, and thin coal seams. The Upper Triassic outcrops principally include sandstones, gray limestones, and dark gray to grayish-black shales, with the upper part interbedded with thin coal seams. The Jurassic and Cretaceous strata exposed in the study area consist predominantly of purplish-red sandstones, siltstones, and mudstones. The Neogene strata exposed primarily comprise gray sandstones and sandy mudstones interbedded with coal seams. The Quaternary strata exposed are dominated by proluvium and alluvium. The study area enjoys abundant mineral resources, which display a distinct regional distribution pattern. Different types of minerals in the study

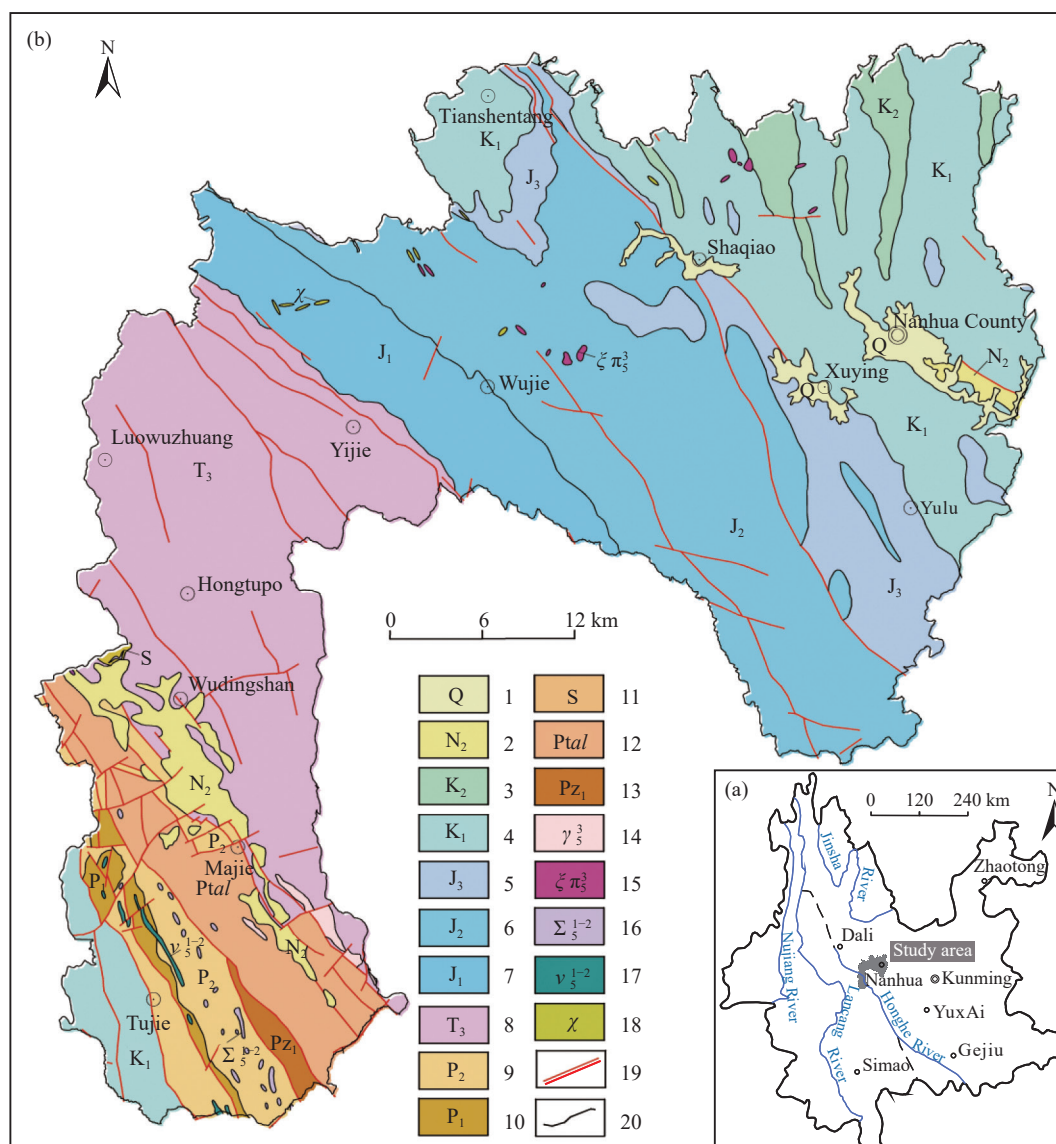


Fig. 1. Location (a) and geological map (b) of the study area. 1–Quaternary; 2–Neogene; 3–Upper Cretaceous; 4–Lower Cretaceous; 5–Upper Jurassic; 6–Middle Jurassic; 7–Lower Jurassic; 8–Upper Triassic; 9–Upper Permian; 10–Lower Permian; 11–Silurian; 12–Proterozoic Ailao-shan Group; 13–Lower Proterozoic; 14–Yanshanian granite; 15–orthophyre; 16–Indosinian-Yanshanian serpentinite and peridotite; 17–Indosinian-Yanshanian gabbro; 18–lamprophyre, kersantite dike; 19–fault; 20–geological boundary.

area are relatively intensively distributed. Specifically, lignite is primarily found in the Longchuan–Lvhe area in the eastern part of Nanhua County, while anthracite is distributed in the Yijie–Mila Mountain area in the western part. Noble minerals such as platinum, palladium, gold, lead, zinc, and copper, as well as non-ferrous metals, are concentrated in the Wudingshan–Tujie polymetallic metallogenic belt in the western part. Additionally, gypsum is found exclusively in the Wudingshan area, and sands, rocks, and soils are widely distributed. Existing mines are primarily identified in the northern and eastern parts of Nanhua County.

3. Materials and methods

3.1. Sample collection and processing

This study collected 571 topsoil samples, 142 deep soil samples, and 26 wild mushroom samples in accordance with

industry standard DZ/T 0295-2016 *Specification of Land Quality Geochemical Evaluation* (Fig. 3). The soil samples were taken using grid sampling on the principle of representativeness primarily considering uniformity and rationality. Given that the study area is largely hilly and mountainous, the samples were mostly collected from gentle slopes and intermountain plains where soils are prone to accumulate. The topsoil samples were collected without anthropogenic pollution factors. For each sampling site, samples from 3 to 5 sampling points within 100 m were combined. The topsoil samples were air dried and then sieved through a 20-mesh (0.8 mm) nylon sieve. These samples were collected at a density of 1 point/km², with those collected from 4 km² considered a unit of analytical samples. The deep soil samples were collected at a density of 16 points/km², with those collected from 16 km² considered a unit of analytical samples. For each unit, four soil samples were placed into a

clean polyethylene sample bottle after splitting and even mixing.

Wild mushroom samples were collected during their growing season in August, with 26 sets of samples of wild mushrooms and their root soils taken from both Se-rich and non-Se-rich soils. The wild mushroom samples collected included *Boletus edulis*, *Boletus aereus*, *Ramaria botrytoides*, *Leccinum nigrescens*, *Onion bacteria*, and *Russula virescens*, as illustrated (Fig. 4). Given the irregular growth patterns of wild mushrooms, 3–5 contiguous mushrooms of the same species were treated as a sample, weighing greater than 500 g. The samples, placed in preservation boxes, were immediately sent for laboratory analysis. Considering a small amount of root soils adhering to the mushrooms that were pulled out, the soils surrounding the mushroom roots were collected as root soils. After being air dried under ventilated and shaded conditions, these samples were sieved through a 10-mesh nylon sieve. Then, they were placed into sample bags after

being processed using the quartering method, with each weighing more than 2000 g.

3.2. Sample analysis and tests

The analysis and tests of the topsoil samples and root soil samples were conducted at the Kunming Natural Resources Comprehensive Survey Center, China Geological Survey. The indicators including the contents of Se, SiO₂, Al₂O₃, TFe₂O₃, Mn, pH, and organic carbon (C_{org}) in these samples were tested in accordance with industry standard DZ/T 0130–2006 *The Specification of Testing Quality Management for Geological Laboratories*. The analysis and tests of the wild mushroom samples were carried out at the Chengdu Comprehensive Rock and Mineral Testing Center of the Sichuan Bureau of Geology and Mineral Exploration and Development. Indicators such as the Se, Pb, and Cd contents in these samples were tested following industrial standard DD2005-03 *Technical Requirements for Sample Analysis for*

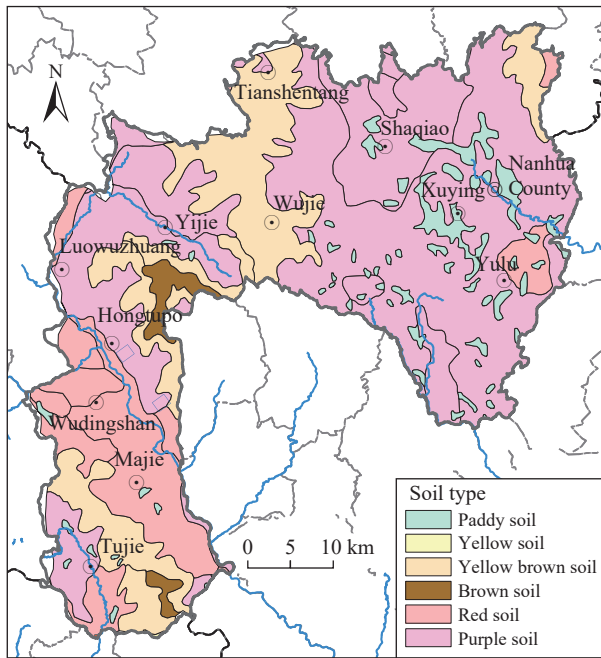


Fig. 2. Map showing the soil types in the study area.

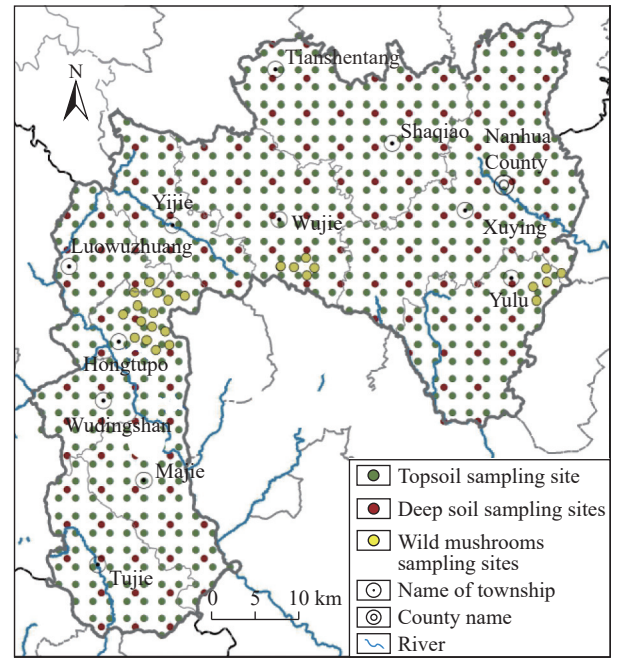


Fig. 3. Map of sampling points.

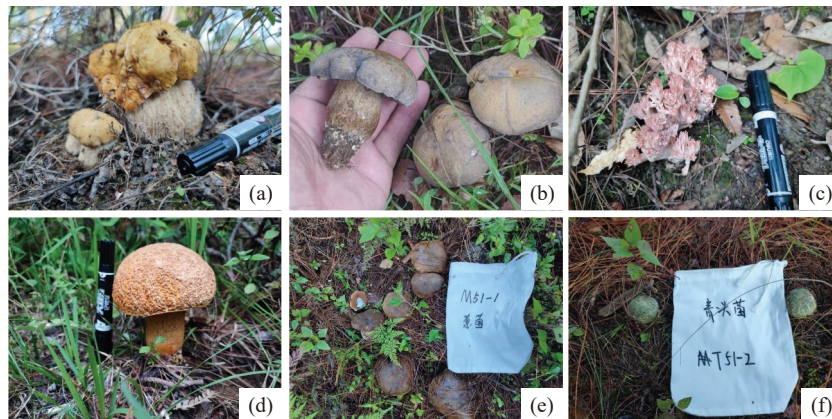


Fig. 4. Photographs of wild mushrooms samples. a–*Boletus edulis*; b–*Boletus aereus*; c–*Ramaria botrytoides*; d–*Leccinum nigrescens*; e–*Onion bacteria*; f–*Russula virescens*.

Ecological Geochemical Evaluation. Table 1 shows the relevant detection methods and detection limits of various indicators of the samples, with all the detection limits meeting the requirements of specified standards.

In the analysis of the soil samples, four national primary certified reference materials were inserted every 50 samples. For each indicator, the logarithmic error $\Delta \lg C$ (GBW) between the determined values and the standard value was calculated to control the analysis accuracy. Meanwhile, the standard deviation λ between the logarithmic differences of the four monitored samples was calculated to determine the analysis precision. A total of 17 national primary certified reference materials were inserted, with methods for analyzing the elements/indicators of the soil samples yielded qualified rates greater than 98%, exceeding 98%, and 92.7% in terms of precision, accuracy, and repeatability inspection. Besides, the certified reference materials yielded qualified rates greater than 98% in terms of accuracy. Therefore, all the methods meet the requirements of standard DZ/T 0130-2006. For the analysis of the wild mushroom samples, five GBW certified reference materials were inserted. Each sample was analyzed eight times, during which the relative error (RE) between the analysis-derived averages and the recommended value of the certified reference material was calculated to control the analysis accuracy and the relative standard deviation (RSD) derived from the eight analyses of a single sample was calculated to measure the analysis precision. The methods for analyzing the wild mushroom samples yielded qualified rates of 100% in terms of precision, accuracy, and repeatability inspection, complying with the requirements of standard DD2005-03.

3.3. Data analysis and processing

This study conducted statistical analyses of the element/indicator contents in soils and wild mushrooms and prepared scatter plots of relevant elements using Excel 2021, performed Pearson correlation and significance analyses using SPSS 24.0, and conducted spatial autocorrelation analysis using geostatistical analysis program GS+9.0. Additionally, it plotted geological sketch maps of the study area using MapGIS 10.7 and CorelDRAW 18.0 and prepared sampling

point maps and related geochemical maps using ArcGIS 10.8.

3.3.1. Semivariogram

The semivariogram, a key function for investigating soil variability in geostatistics, allows for the quantitative description of the spatial variation patterns of soil properties (Liu QQ et al., 2017; Shang BJ et al., 2021). The formula of semivariogram is as follows (Eq. 1):

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (1)$$

where $\gamma(h)$ is the semivariogram of sample point spacing, $N(h)$ is the calculated logarithm for spacing h , $Z(x_i)$ is the content of element i in soils at location x_i (mg/kg), and $Z(x_i + h)$ is the content of element i in soils at location $x_i + h$ (mg/kg). Primary theoretical models for the variogram include exponential, Gaussian, spherical, and linear models (Zheng F et al., 2022; Lu XH et al., 2022), with major parameters including nugget constant (C_0), sill ($C_0 + C$), range, coefficient of determination (R^2), and residual sum of squares (RSS) (Zuo XH et al., 2022). The analytical results of the semivariogram are primarily reflected by the nugget-to-sill ratio [$C_0/(C_0 + C)$]. Generally, a higher [$C_0/(C_0 + C)$] indicates a more dispersed scattered spatial distribution and a weaker correlation of corresponding physical quantities (Fu WJ et al., 2013; Wang M et al., 2021).

3.3.2. Moran's index

Moran's index I is used to characterize the spatial correlation of the same variable at different spatial locations (Ovenmars KP et al., 2003; Huo XN et al., 2009). The formula for Moran's index is:

$$I = \frac{n}{\sum_{i=1}^n \sum_{j=1}^n \omega_{ij}} \times \frac{\sum_{i=1}^n \sum_{j=1}^n \omega_{ij} (x_i - \bar{x})(x_j - \bar{x})}{\sum_{i=1}^n (x_i - \bar{x})^2} \quad (2)$$

where x_i represents the actual value of element x measured at location i , $\bar{x}$ is the average of element x , ω_{ij} is the spatial weight function, with the spatial correlation typically determined using the standard deviation Z -value under the assumption of approximate normal distribution in random conditions (Zhang CS et al., 2004, 2008). In the case of $Z >$

Table 1. Analytical methods and detection limits of indicators.

Sample	Element/indicator	Laboratory detection limit	Standard detection limit	Analytical testing methods
Soil	Se	0.01	0.01	Atomic fluorescence spectrometry (AFS)
	Mn	5	10	Inductively coupled plasma optical emission spectrometry (ICP-OES)
	SiO ₂ *	0.06	0.1	X-ray fluorescence spectroscopy (XRF)
	Al ₂ O ₃ *	0.03	0.05	
	TFe ₂ O ₃ *	0.01	0.05	
	Corg*	0.04	0.1	Volumetric analysis (Vap-Vol)
	pH**	0.1	0.1	Ion-selective electrode (ISE)
Wild mushroom	Se	0.007	0.01	AFS
	Pb	0.02	0.02	Inductively coupled plasma mass spectrometry (ICP-MS)
	Cd	0.002	0.002	

Notes: *denotes unit %, ** denotes a dimensionless unit, and the remaining units are mg/kg.

1.96 and $p < 0.05$, the null hypothesis is rejected. This case indicates a positive spatial autocorrelation, meaning that similar observations tend to cluster spatially. In the case of $-1.96 < Z < 1.96$, the null hypothesis is accepted, suggesting spatial randomness. When $Z < -1.96$ and $p < 0.05$, the null hypothesis is accepted. This case suggests a negative spatial autocorrelation, meaning that similar observations tend to be spatially isolated (Liu B et al., 2019; Liu ZY et al., 2021).

4. Results and discussion

4.1. Se content in soils

The statistical characteristics of Se contents in 571 topsoil samples and 142 deep soil samples from the study area are listed in Table 2. The topsoil samples from the study area exhibited Se contents ranging from 0.07 mg/kg to 0.95 mg/kg, with an arithmetic average of 0.25 mg/kg. Although the study area is located in a Se-deficient zone in China, the average Se content in its topsoil samples exceeds the background values of topsoils in Yunnan (0.20 mg/kg), southwestern China (0.21 mg/kg), and China (0.22 mg/kg) (Hou QY et al., 2020). The deep soil samples in the study area exhibited Se contents varying from 0.10 mg/kg to 0.68 mg/kg, with an arithmetic average of 0.24 mg/kg, which is slightly lower than that of the topsoil samples but significantly higher than the background values of deep soils in Yunnan (0.17 mg/kg), southwestern China (0.13 mg/kg), and China (0.13 mg/kg). The Se contents in the topsoil and deep soil samples displayed coefficients of variation (CVs) of 0.58 and 0.49, respectively. According to the CV ranking proposed by Wilding LP (1985), the Se contents in both the topsoil and deep soil samples were categorized as high variation ($CVs > 0.36$), indicating uneven spatial distributions and significant heterogeneity of Se in soils. However, the topsoil samples exhibit higher CVs of Se content than the deep soil samples. This finding suggests that Se has experienced secondary enrichment or migration-induced loss in the epigenetic process, leading to more significant spatial heterogeneity of Se content in the topsoils.

Based on the criteria for grading the Se content in soils

specified in DZ/T 0295-2016, the topsoils in the study area were graded (Table 3). The results indicate that the areas of topsoils with excessive, high, moderate, marginal, and deficient Se in the study area account for 0%, 13.07%, 44.2%, 27.31%, and 15.42%, respectively, of the total area of the topsoils. The Se-rich soils (Se content: > 0.4 mg/kg) cover an area of 356 km², which accounts for 13.07% of the total area of the topsoils, indicating generally abundant Se resources in soils in the study area.

4.2. Spatial variation and distribution of Se in soils

The K-S test indicates that the Se contents in both the topsoil and deep soil samples exhibited skewed distributions. After a logarithmic transformation, the Se content in the deep soil samples followed a normal distribution. However, the Se content in the topsoil samples failed to follow a normal distribution after common transformations (i.e., logarithmic, square root, and Box-Cox transformations). Therefore, semivariance was employed to analyze the spatial variation of the Se content in the deep soils in the study areas (Wang YH et al., 2012). The analytical results indicate that the semivariogram model for the Se content in the deep soils was a Gaussian model, exhibiting an effective range of 84.073 km, a coefficient of determination of 0.966 (Table 4), and residuals close to zero. These results indicate a high fitting degree of the model. The nugget-to-sill ratio can represent the spatial autocorrelation of a parameter, reflecting the effects of natural and anthropogenic factors (Wang QL et al., 2021). The Se content in deep soil samples in the study area exhibits a block-to-nugget ratio of 21.722%, less than 25%, indicating strong spatial autocorrelation. The Se content in deep soils is primarily influenced by structural factors such as soil-forming parent materials, with stochastic factors posing minor impacts.

Studies have revealed that the spatial autocorrelation analysis outperforms semivariogram analysis (Liu Q et al., 2011). To further investigate the spatial autocorrelation of the Se content in soils, this study calculated the Moran's indices of both the topsoil and deep soil samples (Table 5) and then determined the significance of the spatial autocorrelation

Table 2. Statistics of Se contents in soils (mg/kg).

Element	Sample type	Min.	Max.	Average	Standard deviation	CV	Skewness	Kurtosis	Yunnan	Southwestern China	China
Se	Topsoil	0.07	0.95	0.25	0.15	0.58	1.49	2.43	0.20	0.21	0.22
	Deep soil	0.10	0.68	0.24	0.12	0.49	1.32	1.46	0.17	0.13	0.13

Note: Background values of soil Se in Yunnan, southwestern China, and China are sourced from literature (after Hou QY et al., 2020).

Table 3. Grades of Se content in topsoils.

Grade	Excessive	High	Moderate	Marginal	Deficient
Criterion/(mg/kg)	> 3.0	0.4–3.0	0.175–0.4	0.125–0.175	≤ 0.125
Area/(mg/kg)	0	356	1204	744	420
Proportion/%	0	13.07	44.2	27.31	15.42

Table 4. Spatial semivariogram model of Se content in deep soils and its parameters.

Variable	Theoretical model	Nugget	Sill	Range/km	Nugget-to-sill ratio/%	Coefficient of determination/ R^2	RSS
Se	Gaussian model	0.087	0.400	84.073	21.722	0.966	9.953×10^{-4}

according to the Z-values. The Se contents in both the topsoil and the deep soil samples exhibited Z-values exceeding 1.96 and $P<0.05$, indicating significant positive spatial autocorrelation. This means that the Se content distributions in both topsoils and deep soils in the study area exhibit distinct spatial structures.

To analyze the spatial distribution and anomaly degrees of the Se contents in the soils in the study area more intuitively, this study prepared the maps showing the spatial distribution of Se contents in the topsoils and deep soils using the radial basis functions in ArcGIS 10.8 (Fig. 5). The maps indicate that the Se contents in the topsoils and the deep soils exhibit highly consistent spatial distributions. Furthermore, these distributions show a high degree of spatial coupling with the stratigraphic distribution in the study area (Fig. 1), indicating that the Se in the soils primarily originates from soil-forming parent rocks (materials), with its spatial distribution constrained by the parent materials. Zones with high and low Se contents in both the topsoils and the deep soils primarily show a NW-directed zonal distribution. Specifically, zones with high Se content are primarily distributed in the Hongtupo Town-Yijie Town area and the Ailao Mountain in the Majie Town-Tujie Town area, while zones with low Se contents are mainly found in the Shaqiao Town-Xuying Township-Dongchuan Town-Yulu Township area.

The primary strata in the zones with high Se content include the Triassic and Permian strata, as well as the Proterozoic metamorphic rock groups in the Ailao Mountain

area. The Triassic strata consist primarily of grayish-black shales, grayish-yellow shales, limestones, and sandstones, with the Upper Triassic strata frequently interbedded with thin coal seams. The Permian and Proterozoic strata are mainly composed of metamorphic rocks including leptynites, gneisses, and microcrystalline schists. The primary strata in the zones with low Se content encompass Jurassic, Cretaceous, and Quaternary strata, which consist primarily of Mesozoic purplish-red sandstones, siltstones, mudstones, and alluvium. Relevant studies indicate that black shales (Long J and Luo K, 2017), coal seams (Yang GQ et al., 1983), and metamorphic rocks (Tian H, 2017) typically exhibit high Se content, while Mesozoic sandstones and siltstones feature low Se content (Wu ZL et al., 2021). Therefore, the distribution of the Se content in soils in the study area is primarily governed by the geological background, with Se-rich soils closely associated with Triassic black shales, thin coal seams, and metamorphic rocks in the Ailao Mountain area.

To further investigate the extent to which the geological background controls the Se content in soils in the study area, this study analyzed the average content of heavy metals in the topsoils and deep soils across different strata (Fig. 6). Notably, each piece of data on deep soils, within a large grid, corresponds to the average value of all data on topsoils in the grid. The strata with high Se content include the Neogene, Triassic, Permian, and Proterozoic data, while those with low Se content consist of the Quaternary, Cretaceous, and Jurassic strata. There is a positive linear correlation, passing through

Table 5. Spatial autocorrelation analysis of Se elements in soils.

Oxides	Sample type	Variance	Z	P	Index
Se	Topsoil	0.0009	26.78	0.00	0.82
	Deep soil	0.0040	9.08	0.00	0.57

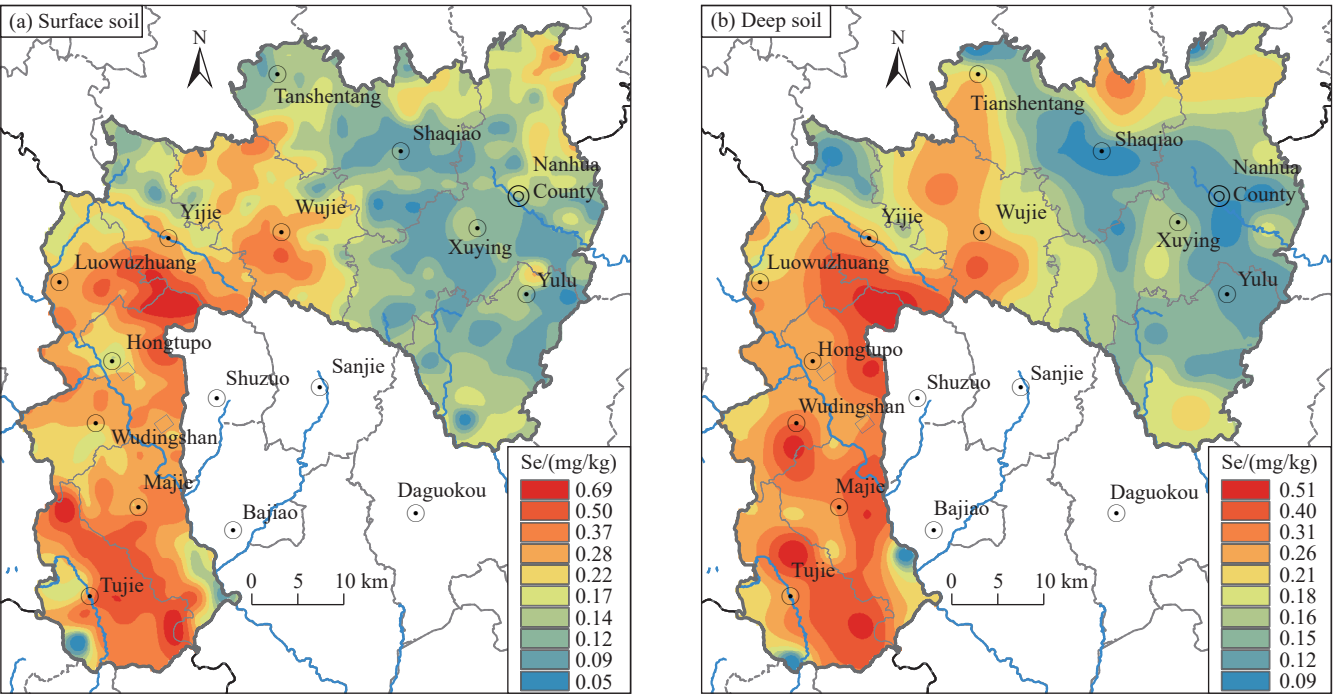


Fig. 5. Spatial distribution of Se contents in topsoils (a) and deep soils (b) in the study area.

the origin, between the Se contents in the topsoil and deep soil samples. This indicates that the Se in the soils is inherited from parent rocks and that the Se in the topsoils is inherited from the deep soils, with human activities posing minimal impact.

4.3. Se enrichment characteristics and heavy metal over-limit ratio of wild mushrooms

For Se-rich edible mushrooms, the reference value of Se content is ≥ 0.02 mg/kg, as specified by industry standard T/5115YBAPS 023.5-2020 *Selenium-Enriched Edible Fungi* and Chongqing local standard DB50T 705-2016 *Selenium-Enriched Agricultural Products*. For Se-rich soils, the reference value of Se content is ≥ 0.4 mg/kg as per DZ/T 0295-2016. The wild mushroom species analyzed in this study included *Boletus edulis*, *Boletus aereus*, onion bacteria, *Leccinum nigrescens*, *Russula virescens*, and *Ramaria botrytoides*, as well as *Russula grisea*, *Lactarius auranticus*,

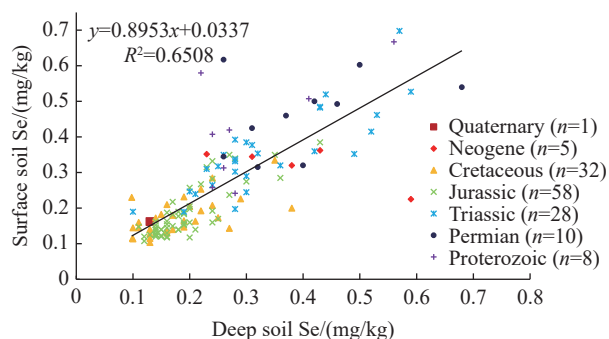


Fig. 6. Relationship between the Se contents in deep soils and topsoils across different strata in Se distribution areas.

Catathelasma ventricosum, and *Pseudohydnum gelatinosum* (also referred to as other types). Table 6 presents the statistics of the contents and enrichment characteristics of Se in 26 samples of wild mushrooms and their root soils from the study area. The wild mushroom samples exhibited Se contents ranging from 0.004 mg/kg to 47.10 mg/kg, with an average of 2.97 mg/kg and a median of 0.98 mg/kg. Among them, two samples yielded Se content below the detection limit (0.007 mg/kg), and their Se content was set at half the detection limit (0.0035 mg/kg) for ease of analysis. The remaining samples displayed Se content exceeding 0.02 mg/kg. Therefore, they were identified as Se-rich wild mushrooms, with an overall accumulation rate of 92.31%. Different types of wild mushroom samples manifested significantly different Se content, even the same type. Among other types, the *Pseudohydnum gelatinosum* samples displayed a Se content of up to 47.10 mg/kg. The root soil samples yielded Se contents varying from 0.12 mg/kg to 0.41 mg/kg and a Se accumulation rate of merely 3.85%, with only one sample identified as Se-rich soils.

Presently, the Se-rich foods in China can be classified into two categories according to their cultivation environments: Naturally Se-rich foods and artificially transformed Se-rich foods. Regions known for longevity, such as Enshi in Hubei and Ankang in Shaanxi, have developed extensive naturally Se-rich agricultural products such as Se-rich tea and fruits (Hu JL et al., 2018). For instance, high-Se rice and tea from Enshi exhibit total Se contents of up to 1.62 mg/kg and 1.12 mg/kg, respectively (Zhang X et al., 2013), and the eggplants and peppers from Ziyang County in Shaanxi Province also present high Se contents of 3.72 mg/kg and 1.32 mg/kg, respectively (Cui ZW, 2018). Liu JP et al. (2020) revealed that eight wild

Table 6. Se content, accumulation rates, and BCFs of wild mushrooms and their root soils.

Wild mushroom species	Type	Min./(mg/kg)	Max./(mg/kg)	Avg./(mg/kg)	Se accumulation rate of soils/%	Se accumulation rate of mushrooms/%
<i>Boletus edulis</i> (n=9)	Mushrooms	1.04	2.86	1.98	3.85	92.31
	Rhizosphere soil	0.15	0.41	0.27		
	BCF	4.48	9.96	7.47		
<i>Boletus aereus</i> (n=3)	Mushrooms	0.48	1.07	0.80		
	Rhizosphere soil	0.21	0.36	0.30		
	BCF	1.33	4.04	2.87		
Onion bacteria (n=3)	Mushrooms	0.77	6.31	2.71		
	Rhizosphere soil	0.12	0.39	0.21		
	BCF	5.91	16.18	10.28		
<i>Leccinum nigrescens</i> (n=3)	Mushrooms	0.32	0.35	0.33		
	Rhizosphere soil	0.12	0.27	0.20		
	BCF	1.20	2.67	1.84		
<i>Russula virescens</i> (n=2)	Mushrooms	0.004	0.15	0.08		
	Rhizosphere soil	0.13	0.20	0.17		
	BCF	0.03	0.73	0.38		
<i>Ramaria botrytoides</i> (n=2)	Mushrooms	0.04	0.15	0.10		
	Rhizosphere soil	0.18	0.34	0.26		
	BCF	0.13	0.82	0.47		
Other mushrooms (n=4)	Mushrooms	0.04	47.10	11.89		
	Rhizosphere soil	0.17	0.30	0.23		
	BCF	0.02	157.00	39.81		

mushroom samples from the Yimen area in central Yunnan yielded Se contents ranging from 0.05 mg/kg to 6.35 mg/kg, indicating that all the samples were Se-rich wild mushrooms. In contrast, the natural wild mushrooms in the study area exhibit a Se content of up to a maximum of 47.10 mg/kg, which is significantly higher than the reported Se contents of other naturally Se-rich agricultural products. Therefore, the study area has considerable potential for the development of naturally Se-rich wild mushrooms.

In this study, the *BCF* was employed to characterize the capacities of wild mushrooms to migrate Se from root soils and to be enriched in Se (Liao QL et al., 2013; Ma XD et al., 2022; Song B et al., 2022). A higher *BCF* value corresponds to a higher capacity of crops to be enriched in elements from soils (Shen TZ et al., 2014). The *BCF* can be used as follows:

$$BCF_i=C_{i\text{ wild mushrooms}}/C_{i\text{ root soils}} \tag{3}$$

where *BCF_i* is the bioconcentration factor of element *i*, *C_i* wild mushrooms is the content of element *i* in wild mushrooms, and *C_i* root soils is the content of element *i* in the root soil of wild mushrooms. Table 6 shows that the overall *BCFs* of Se in wild mushrooms in the study area range from 0.02 to 157.00, with an average of 10.50 and a median of 4.26, averaging 4.64 after the maximum value (*sarcodon imbricatus*) is excluded. Among the wild mushroom species investigated, *sarcodon imbricatus* exhibits the highest *BCF* (157.00). Gao W et al. (2022) found that *sarcodon imbricatus* shows a Se content of up to 251.29 mg/kg. This study revealed that the *BCFs* of the mushrooms decrease in the order of onion bacteria, *Boletus edulis*, *Boletus aereus*, *Leccinum nigrescens*, *Ramaria botrytoides*, and *Russula virescens*. Duan ZM et al. (2019) discovered that both *Hericium erinaceus* and *Boletus edulis* exhibit Se contents far greater than the average, indicating that both mushrooms have higher potential for Se-rich food development than other mushroom species.

Se tends to be associated with heavy metal elements (Geng JM et al., 2012; Fu TT et al., 2019). For instance, Se exhibits a strong association with Cd (Yu T et al., 2018). Therefore, this study assessed heavy metal elements Pb and Cd in wild mushrooms in accordance with national standard GB2762–2022 *National Food Safety Standard for Maximum Levels of Contaminants in Foods* (Table 7). Based on the criteria for categorizing edible mushrooms and their products specified in GB2762–2022, this study categorized the wild mushrooms into three groups: *Boletus* (i.e., *Boletus edulis*, *Boletus aereus*, *Leccinum nigrescens*, and onion bacteria), *Russula virescens*, and other mushrooms. Table 7 indicates that the wild mushroom samples exhibited Pb contents

ranging from 0.01 mg/kg to 0.108 mg/kg, with an over-limit ratio of 0. These samples displayed Cd contents ranging from 0.007 mg/kg to 0.676 mg/kg. Among them, one *amanita hemibapha* sample and two *Russula virescens* samples exhibited Cd content exceeding the limit, leading to an overall over-limit ratio of 11.54%. Additionally, the Cd content of all *Boletus* samples fell below the limit.

4.4. Factors influencing the *BCF* of Se in wild mushrooms

Crops’ absorption of beneficial elements such as Se in soils is closely related to factors such as crop type and variety, agricultural activities, and soils. As shown in Table 6, different types of wild mushrooms exhibit significantly different *BCFs*, indicating that the wild mushroom species emerges as a primary factor influencing wild mushrooms’ absorption and accumulation. Previous studies indicated that the presence of ionic groups, such as sulfur and amino groups, on cell walls allows bioadsorption to become a major cause of efficient Se enrichment in wild mushrooms (Zheng DX et al., 1986; Liu JP et al., 2020). Therefore, it can be inferred that the differences in cell wall structure are an inherent factor affecting the bioavailability of Se in different species of wild mushrooms.

The relationship between Se contents in wild mushrooms and root soils is illustrated in Fig. 7a. According to this figure, there is no distinct relationship between the Se contents in the wild mushrooms and root soils. However, after the maximum anomaly value (*sarcodon imbricatus*) is excluded, a certain linear positive correlation can be observed (Fig. 7b), with a correlation coefficient (*R*²) of 0.263. Furthermore, this correlation passes the significance test at a significance level of 0.01. Wang D et al. (2022) also revealed a positive correlation between the enrichment level of Se in crops and the Se content in soils. Therefore, the Se content in soils is identified as a factor influencing the Se enrichment in wild mushrooms.

The analyses of the relationships between the *BCF* of Se in wild mushrooms and the physicochemical indicators of root soils indicate that the *R*² values between the *BCF* and Al₂O₃, TF₂O₃, Mn, pH, SOM, and Si/Al are 0.001, 0, 0.019, 0.033, 0.003, and 0, respectively. None of these correlations pass the significance test at a significance level of 0.05, indicating that the bioavailability of Se in the wild mushrooms is minimally influenced by the physicochemical indicators of soils. However, extensive studies (Ma HH et al., 2020; Liu XJ et al., 2020; Tang ML et al., 2020) reveal that the physicochemical indicators of soils act as important factors affecting the migration, transformation, and bioavailability of elements in

Table 7. Over-limit ratios of heavy metals in wild mushrooms.

Indicator	Pb/(mg/kg)					Cd/(mg/kg)				
	Min.	Max.	Avg.	Limit	Over-limit number (over-limit ratio)	Min.	Max.	Avg.	Limit	Over-limit number (over-limit ratio)
<i>Boletus</i> (<i>n</i> = 18)	0.01	0.108	0.046	1	0(0)	0.007	0.336	0.128	1	3(11.54%)
<i>Russula virescens</i> (<i>n</i> = 2)	0.043	0.091	0.066	1		0.033	0.2	0.117	0.6	
Other mushrooms (<i>n</i> = 6)	0.021	0.052	0.035	0.5		0.013	0.676	0.276	0.2	

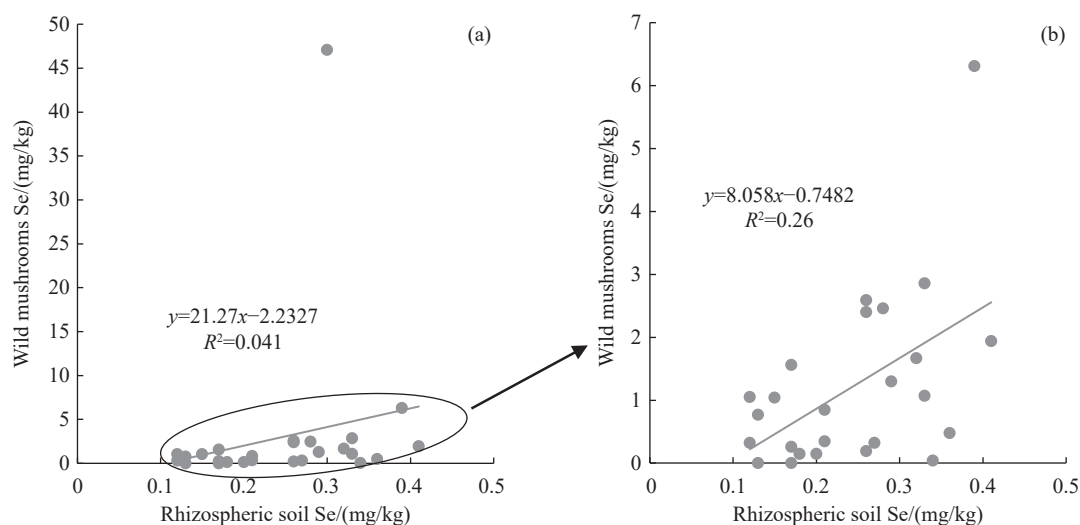


Fig. 7. Relationship between Se content between wild mushrooms and root soils.

the soil-crop system. Se exhibits different absorption and transport means in wild mushrooms and plants. For plants, Se is typically absorbed by their roots in the form of selenates, selenites, or organic Se such as selenocysteine (SeCys) and selenomethionine (SeMet) (Deng XF et al., 2020). For instance, selenates enter a plant body through high-affinity sulfate transporters in the plasma membrane of roots (Shinmachi F et al., 2010). For wild mushrooms, the presence of ionic groups, such as sulfur and amino groups, on the cell wall establishes bioadsorption as a highly efficient method for Se enrichment. Through the metabolic transformation of materials within hyphal cells, edible mushrooms absorb inorganic Se and combine it with macromolecular active materials (e.g., proteins and polysaccharides), with the inorganic Se ultimately existing as organic Se like selenoproteins and Se-polysaccharides (Ling HT et al., 2008). Therefore, it can be inferred that different Se enrichment mechanisms result in significant differences in Se bioavailability and influencing factors between wild mushrooms and plants.

4.5. Development and utilization of selenium-enriched wild mushrooms

Yunnan Province is renowned for its abundant resources of edible wild mushrooms. Among the 2166 known wild mushrooms species worldwide, 978 are found in Yunnan, accounting for 45% of the global total and 91% of China's total (Liu T, 2014). Among these, more than 600 species are edible, with over 70 being prized for their exceptional flavor and quality (Ding L, 2008). Yunnan's wild mushrooms are exported to over 20 countries and regions globally. Japan, the European Union, and the United States represent traditional markets, while ASEAN countries, Russia, Africa, and South America constitute emerging markets. Wild mushrooms have emerged as an export-oriented industry exceeding USD 150 million in annual turnover. Yunnan Province dominates the fresh *Tricholoma matsutake* export market, accounting for over 80% of national shipments, while dried *Boletus* slices

constitute 58% of the country's total export volume. According to relevant reports (Liu T, 2014), the total production of wild mushrooms in Yunnan Province reached 70000 t in 2013, generating an output value of 5.74×10^9 yuan. Wild mushrooms are increasingly favored by consumers owing to their natural growth environments and high nutritional value.

The study area is characterized by abundant soil selenium resources with strong spatial autocorrelation and stable distribution patterns, exhibiting minimal anthropogenic interference, which provides favorable geological conditions for the sustainable production of naturally selenium-enriched wild mushrooms. The overall selenium enrichment rate of wild mushrooms in the study area reaches 92.31%, with maximum selenium content of 47.10 mg/kg—substantially exceeding reported values for naturally selenium-enriched agricultural products documented to date, demonstrating significant potential for the development of naturally selenium-enriched wild mushroom resources. It is recommended to leverage this distinctive resource advantage by prioritizing the wild mushroom industry as a key development direction for regional characteristic selenium-enriched agriculture.

Due to species-specific selenium enrichment mechanisms, significant variations exist in selenium bioaccumulation capacity among different wild mushrooms taxa. *Pseudohydnum gelatinosum* and *Boletus* demonstrate pronounced selenium-enrichment characteristics. Furthermore, *Boletus* exhibit the advantage of non-exceedance in heavy metal concentrations, and this taxonomic group is abundantly produced in the study area. Therefore, *Boletus* are recommended as priority candidates for selenium-enriched food development, with the establishment of standardized industrial chains encompassing harvesting, processing, and marketing to create premium selenium-enriched wild mushroom brands. For species with weaker selenium enrichment capacity and potential cadmium contamination risks, such as *Russula virescens*, cautious development or

consumption restrictions are advised. The selenium bioavailability in wild mushrooms is minimally influenced by soil physicochemical properties, showing significant divergence from plant selenium enrichment mechanisms. This characteristic indicates that selenium enrichment capacity in wild mushrooms from the study area remains relatively stable and less susceptible to soil environmental fluctuations, conferring substantial potential for exploitation and utilization.

5. Conclusions

This study investigated the content, spatial distribution, and influencing factors of Se in the soil-wild mushroom system in Nanhua County. The findings lead to the following conclusions.

(i) The topsoils in the study area exhibit Se content ranging from 0.07 mg/kg to 0.95 mg/kg, with an arithmetic average of 0.25 mg/kg. Although the study area is located in a Se-deficient zone in China, the average Se content in its topsoils exceeds the background values of topsoils in Yunnan, southwestern China, and China. The Se-rich soils (Se content: > 0.4 mg/kg) cover an area of 356 km², which accounts for 13.07% of the total area of the topsoils, indicating generally abundant Se resources in soils in the study.

(ii) The analysis of Moran's index reveals that the Se content distributions in both topsoils and deep soils in the study area exhibit distinct spatial structures. The semivariogram model for the Se content in the deep soils emerges as a Gaussian model, exhibiting a high fitting degree. The Se content exhibits a nugget-to-sill ratio of 21.722%, indicating that the Se content in deep soils is primarily influenced by structural factors such as soil-forming parent materials. Furthermore, these distributions show a high degree of spatial coupling with the stratigraphic distribution. Therefore, the Se in the soils primarily originates from soil-forming parent rocks (materials), with its spatial distributions restricted by the parent materials. Specifically, the origin of the Se-rich soils is closely related to Triassic black shales, thin coal seams, and metamorphic rocks in the Ailao Mountain area.

(iii) The wild mushrooms in the study area exhibit Se contents ranging from 0.004 mg/kg to 47.10 mg/kg, with an average of 2.97 mg/kg and a median of 0.98 mg/kg, significantly higher than the reported Se contents of other naturally Se-rich agricultural products. Their Se accumulation rate reaches up to 92.31% and an overall over-limit ratio of Pb and Cd of merely 11.54%, suggesting the study area has considerable potential for the development of naturally Se-rich wild mushrooms. The wild mushrooms exhibit *BCFs* of Se varying from 0.02 to 157.00, with an average of 10.50 and a median of 4.26. The Se bioavailability of these wild mushrooms decreases in the order of *Boletus edulis*, *Boletus aereus*, *Leccinum nigrescens*, *Ramaria botrytoides*, and *Russula virescens*.

(iv) For the absorption and enrichment of Se in wild

mushrooms, the wild mushroom species is identified as the primary controlling factor influencing. Meanwhile, the degree of Se enrichment in wild mushrooms is significantly affected by the Se content in soils. However, unlike most crops, the Se absorption and enrichment in wild mushrooms are minimally influenced by the physicochemical indicators (Al₂O₃, TFe₂O₃, Mn, pH, SOM, and Si/Al) of soils.

CRedit authorship contribution statement

Lei Xu conceptualized the entire paper and prepared the manuscript. Meng-sheng Zhao and Yan-xun Cheng collected soil and wild mushroom samples. Yao-tang Zhang and Ji-yun Guan conducted the preliminary processing, shipping, and quality control of the samples. Fang-fang Lu and Chang-wei Linghu processed the geochemical data and plotted the illustrations. Yong-sheng Yuan supervised the work and contributed new findings. All authors discussed the results, drew conclusions, and contributed to the manuscript.

Declaration of competing interest

The authors declare no conflict of interest.

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