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Investigation into the Geological Origin and Influencing Factors of Selenium-Enriched Soil in Licheng, Jinan, Shandong Province

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Abstract: The geochemical classification of soils is crucial for the scientific development and utilization of land, particularly in the investigation of selenium-rich soils, which plays a guiding role in the cultivation layout of local selenium-rich agricultural products. This study involves the collection and analysis of over 6000 samples of soil, water quality, and crops from the entire area of Licheng District in Jinan City, Shandong Province. By analyzing the data in conjunction with the geochemical classification standards for soil nutrient levels, soil environmental geochemical levels, and comprehensive soil quality geochemical levels, we delineated a distribution area of selenium-rich soils covering 192.26 km^2 in Licheng District, providing a bibliographic basis for the scientific planning of agriculture and forestry in the region.

Keywords: selenium-rich soil; geochemical analysis; Shandong; ICP-OES; ICP-MS

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1. Introduction

In recent decades, with further research into selenium, it has been recognized as an essential trace element for humans and animals, with benefits such as enhancing immunity, preventing aging, and reducing the risk of cancer. Additionally, some cancers and regional thyroid disorders are closely related to low-selenium environments [1–4]. The biogeochemical processes of selenium in soil connect soil selenium with the selenium nutrition of plants and animals, ultimately linking to humans through the food chain [5–8].

Selenium-rich soils are often the weathering products of selenium-rich geological formations and represent a valuable soil resource for the development of agriculture, forestry, and horticulture [9]. The establishment of standards for selenium-rich soils is based on their geochemical background values [10]. Globally, the total selenium content in soils ranges from a minimum of approximately 0.01 mg/kg to a maximum of about 2.0 mg/kg, with the majority of soil samples exhibiting total selenium concentrations between 0.2 and 0.4 mg/kg. The distribution of selenium in the Earth's crust is closely related to the latitude of the crustal region. Soils with selenium concentrations greater than 0.4 mg/kg are classified as selenium-rich soils [11]. As a subject within agricultural geology, selenium-rich soils have become a research focus in many countries in recent years. For instance, selenium concentrations in Scottish soils range from 0.11 to 0.88 mg/kg [12], while in Spain, the range is from 0.01 to 2.70 mg/kg [13]. Additionally, several countries, including Japan, China, Europe, and the United States, have reported cases of selenium deficiency in animals or humans [14–16].

Research indicates that the average selenium content in surface soils in China is 0.20 mg/kg [17]. The distribution of selenium in Chinese soils exhibits a pattern of higher concentrations at the edges and lower concentrations in the central region, which features a low-selenium belt trending northeast to southwest, with relatively higher total selenium levels in the surrounding areas [18]. Approximately 22 provinces and municipalities in China are partially or predominantly selenium-deficient, covering about 70% of the country's total area, and the population in selenium-deficient regions constitutes roughly 50% of the national population [19].

Data from soil studies in Shandong Province indicate that the background value of selenium-rich elements in its soils is 0.18 mg/kg [20], which is below the national average. In Jinan City, the background value of selenium content in soils is 0.22 mg/kg, with industrial coal combustion identified as one of the sources of selenium in surface soils [21].

Research on selenium-rich soils not only enhances our understanding of the distribution and accumulation patterns of selenium in soils but also aids in the development and utilization of selenium-rich soil resources. This provides a scientific basis for the production and development of selenium-enriched agricultural products, which is significant for improving the quality and nutritional value of agricultural products, promoting the upgrading of the agricultural industry, and ensuring sustainable development [5,22–25]. This study systematically analyzes soil samples from Licheng District, delineates the distribution range of selenium-rich soils, investigates the geological genesis of selenium-rich strata in Jinan's Licheng District, and analyzes the influencing factors. The findings offer reference materials for similar regions and contribute to the advancement of high-quality agricultural production.

2. Geological Setting

The research area is located in Licheng District, Jinan City, China (Figure 1), in the southeast of Jinan City, with Mount Tai to the south, bordered by the Yellow River, Qihe County, and Jiyang County to the north, adjacent to Zhangqiu City to the east, and Changqing District to the west. It is situated at the junction of the southern hills and hills of central Shandong and the western plain of Shandong, with higher elevation in the south and lower elevation in the north. The terrain types mainly include mountains, hills, and plains from south to north, with elevations ranging from 20 to 975 m. The highest peak in the area is Mount Tizi with an elevation of 975 m, and the lowest point is Han Guanzhuang in Tangwang Town with an elevation of 20 m (Figure 2).

Figure 1. Location map of Licheng District, Jinan City.

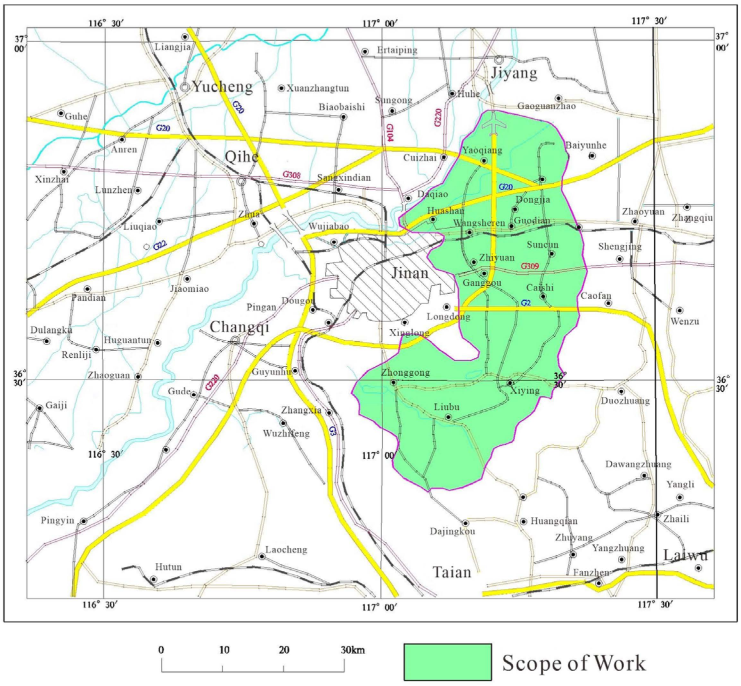

Figure 2. Traffic location map of Licheng District.

Licheng District, Jinan City, is located in the transitional zone between the western uplift and the northwestern depression of Shandong in terms of tectonics, characterized by a north-dipping monocline structure dominated by Paleozoic strata. Igneous rocks are mainly distributed in the northern part of Jinan City, also known as the "Jinan rock mass", with the main evaluation area located in the western Shandong block.

3. Samples and Analytical Methods

3.1. Sample Collection

This study collected a total of 6668 surface soil samples, with an average sampling density of 5 samples per square km. Additionally, 28 samples of reservoir and river sediment were collected, along with 22 samples of atmospheric dry and wet deposition. Irrigation water samples were collected at a density of 1 sampling point per 26 square km, with sampling conducted at the same locations during the abundant water period (May to September) and the dry period (December to February). A total of 100 irrigation water samples were collected during the abundant water and dry periods, with 82 samples from general areas (41 samples each from the abundant water and dry periods) and 150 sets of accompanying crop samples, of which are 16 sets of strawberry plant samples and their root soil; 16 sets of cherry plant samples and their root soil; 35 sets of wheat plant samples and their root soil; and 35 sets of maize samples and their root soil. A total of 150 sets of plant samples were collected from 16 sets of walnut, cabbage, lotus root, and root soil.

3.2. Analytical Methods

The analytical methods employed in this project mainly include inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), atomic fluorescence spectroscopy (AFS), alternating current arc-emission spectroscopy (ES), the ion-selective electrode method (ISE), the combustion-iodine titration method (IOD), volumetric method (VOL), the potentiometric method (ISE), and the catalytic spectrophotometry method (COL) for multi-element analysis (Table 1).

Table 1. Traffic location map of Licheng District.

Elements	Based on Criteria	Detection Method	Method Detection Limit
As	HJ 680-2013	AFS	0.2
B	DZ/T 0279.11-2016	ES	1
CaO	HJ 974-2018	ICP-OES	0.05*
Cd	HJ 803-2016	ICP-MS	0.021
Co	DZ/T 0279.3-2016	ICP-MS	0.2
Cr	DZ/T 0279.2-2016	ICP-OES	2
Cu	DZ/T 0279.2-2016	ICP-OES	1
F	DZ/T 0279.21-2016	ISE	100
Ge	DZ/T 0279.16-2016	ICP-MS	0.1
Hg	GB/T 17136-1997	AFS	0.0003
I	DZ/T 0279.24-2016	ICP-MS	0.2
K_2O	DZ/T 0279.2-2016	ICP-OES	0.02 *
Mn	HJ 974-2018	ICP-OES	5
Mo	HJ 803-2016	ICP-MS	0.2
N	DZ/T 0279.29-2016	VOL	10
Ni	DZ/T 0279.2-2016	ICP-OES	2
P	DZ/T 0279.2-2016	ICP-OES	5
Pb	DZ/T 0279.2-2016	ICP-OES	2
pH	HJ 962-2018	ISE	0.10 **
S	DZ/T 0279.28-2016	IOD	30
Se	HJ 680-2013	AFS	0.01
V	DZ/T 0279.2-2016	ICP-OES	5
Zn	DZ/T 0279.2-2016	ICP-OES	2
organic matter	GB/T 33469-2016	VOL	0.1 *

Note: Unit: mg/kg, mg/kg, "*" unit of measurement is %, "**" is dimensionless.

3.3. Quality Control

In order to enhance the reliability of data analysis, the units conducting the analytical tests strictly adhere to technical standards such as the "Specification for Geochemical Survey in Multiple Target Areas (1:250,000)" (DZ/T0258-2014), "Technical Requirements for Analysis of Ecological Geochemical Evaluation Samples" (DD2005-03), "Supplementary Provisions for Technical Requirements for Analysis of Samples in Regional Ecological Geochemical Evaluation", and the "Quality Management Specification for Geological Mineral Laboratory Testing" (DZ0130-2006) issued by the China Geological Survey [26,27].

4. Evaluation Level Classification

4.1. Evaluation Unit Assignment

The smallest spatial unit for the classification of soil nutrient geochemical grade, soil environmental geochemical grade, and soil quality geochemical composite grade is referred to as the evaluation unit.

First, the original data of each evaluation unit of mean, maximum, minimum, and standard deviation are gathered. The data with ±3 times the average deviation are used as the abnormal interval, and the data beyond the abnormal interval are verified. The verified data are compared with the soil data of adjacent plots in terms of the parent material type, soil type, land use status, etc., and the cause of the obviously unreasonable data needs to be found and adjusted [28].

4.2. Soil Nutrient Geochemical Level

The classification criteria refer to the “National Soil Survey Specification for the Second National Soil Survey.” The grading standards for the effective amount of trace elements in soil are combined with the research results of the agricultural production and cultivation levels in Shandong Province and the regional soil element abundance and deficiency standards. The grading evaluation standards for total and available organic matter, N, P, and K, as well as the nutrient element content of the soil, are established as the basis for this soil nutrient element content grading evaluation. The grading standards for calcium, magnesium, boron, molybdenum, manganese, sulfur, copper, and zinc in the soil are based on the “Land Quality Geochemical Evaluation Specification” (DZ/T0295-2016) [29], while the grading standards for selenium, iodine, and fluorine are illustrated in Table 2 [27].

Table 2. Standard values for soil selenium, iodine, and fluoride levels (mg/kg).

Level		Absence	Margin	Moderate	High	Excess
Selenium	Standard value	≤0.125	0.125~0.175	0.175~0.40	0.40~3.0	>3.0
	Colour					
	R:G:B	234:241:221	214:227:188	194:214:155	122:146:60	79:98:40
Iodine	Standard value	≤1	1~1.50	1.50~5	5~100	>100
	Colour					
	R:G:B	198:217:241	141:179:226	84:141:212	31:74:127	15:36:62
Fluorine	Standard value	≤400	400~500	500~550	550~700	>700
	Colour					
	R:G:B	253:233:217	251:212:180	250:191:143	227:108:10	152:72:6

4.3. Soil Environmental Geochemical Level

The environmental quality level classification criteria for arsenic, cadmium, chromium, lead, mercury, nickel, copper, and zinc in the soil evaluated at a scale of 1:50,000 follow the secondary standard values in the “Soil Environmental Quality Standards (GB15618-1995)” [30]. For multiple limit standards at different pH values, the “maximum restriction” principle is applied for determination (i.e., “strict rather than lenient”). The soil pH grading standards are shown in Table 3 [29], and based on the soil pH grading standard values in the table, the soil acidity and alkalinity environmental geochemical level is classified.

Table 3. Standard classification of soil pH levels.

pH	<5.0	5.0~6.5	6.5~7.5	7.5~8.5	>8.5
Level	Strongly acidity	Acidity	Neutral	Alkaline	Strongly alkaline
Colour					
R:G:B	192:0:0	227:108:10	255:255:192	0:176:240	0:112:192

Based on the division boundaries of the soil single pollution index geochemical environmental grades shown in Table 4 [31], a 1:50000 single index soil geochemical environmental grade division is carried out.

Table 4. Division boundaries for soil geochemical environmental grades.

Grades	Top-Grade	Second-Grade	Third-Grade	Fourth-Grade	Fifth-Grade
Soil environment	$P < 1$	$1 < P \leq 2$	$2 < P \leq 3$	$3 < P \leq 5$	$P \geq 5$
	Clean	Slight pollution	Mild pollution	Moderate pollution	Severe pollution
Colour					
R:G:B	0:176:80	146:208:80	255:255:0	255:192:0	255:0:0

On the basis of the single index soil geochemical environmental grade division, the comprehensive soil geochemical environmental grade division is carried out according to the following principles: the soil geochemical comprehensive grade of each evaluation unit is equivalent to the worst grade of the environmental grade divided by a single index [29]. For example, if the environmental geochemical grades divided by As, Cr, Cd, Cu, Hg, Pb, Ni, and Zn are grade 4, 2, 3, 2, 2, 3, 2, and 2, respectively, then the soil geochemical comprehensive grade of the evaluation unit is grade 4.

4.4. Soil Quality Geochemical Comprehensive Grade

The soil quality geochemical comprehensive grade is generated by overlaying the soil nutrient geochemical comprehensive grade of the evaluation unit with the soil geochemical comprehensive grade. The expression and meaning of the soil quality geochemical comprehensive grade are shown in Table 5 [29].

Table 5. Illustration and meaning of the comprehensive geochemical grade expression of soil quality.

	Clean	Slight Pollution	Mild Pollution	Moderate Pollution	Severe Pollution	Implication
Abundant	Grade 1 excellent	Grade 3 moderate	Grade 4 poor	Grade 5 inferior	Grade 5 inferior	**Grade 1 is excellent:** The soil environment is clean, and the soil nutrients are abundant to relatively abundant. **Grade 2 is good:** The soil environment is clean, and the soil nutrients are moderate. **Grade 3 is moderate:** The soil environment is clean, the soil nutrients are relatively lacking, or the soil environment is slightly polluted, ranging from abundant to relatively lacking in soil nutrients. **Grade 4 is poor:** The soil environment is clean or slightly polluted, the soil nutrients are lacking, or the soil environment is slightly polluted, ranging from abundant to lacking in soil nutrients, or the soil salinization level is severe. **Grade 5 is inferior:** The soil environment is moderately to heavily polluted, the soil nutrients range from abundant to lacking, or the soil salinization level is saline.
Relatively abundant	Grade 1 excellent	Grade 3 moderate	Grade 4 poor	Grade 5 inferior	Grade 5 inferior	
Moderate	Grade 2 good	Grade 3 moderate	Grade 4 poor	Grade 5 inferior	Grade 5 inferior	
Less absence	Grade 3 moderate	Grade 3 moderate	Grade 4 poor	Grade 5 inferior	Grade 5 inferior	
Absence	Grade 4 poor	Grade 4 poor	Grade 4 poor	Grade 5 inferior	Grade 5 inferior	

4.5. Land Quality Geochemical Grade

On the basis of the soil quality geochemical comprehensive grade, we overlay the atmospheric environmental geochemical comprehensive grade and irrigation water environmental geochemical comprehensive grade to form the land quality geochemical grade, as shown in Table 6 [29].

Table 6. Illustration and meaning of the geochemical grade of land quality.

Schema	R:G:B	Implication
22	255:0:0	The comprehensive geochemical grade of soil quality is Grade 5—inferior; the geochemical grades of atmospheric and irrigation water environments are Grade 2, indicating a relatively high deposition flux of dry and wet atmospheric substances and excessive irrigation water.
11	255:192:0	The comprehensive geochemical grade of soil quality is Grade 4—poor; the geochemical grades of atmospheric and irrigation water environments are Grade 1, indicating a relatively low deposition flux of dry and wet atmospheric substances and compliance with water quality standards for irrigation water.
20	255:255:0	The comprehensive geochemical grade of soil quality is Grade 3—moderate; the geochemical grade of the irrigation water environment is Grade 2, indicating excessive irrigation water; there were no samples for the dry and wet deposition flux of the atmosphere.

Table 6. *Cont.*

Schema	R:G:B	Implication
01	146:208:80	The comprehensive geochemical grade of soil quality is Grade 2—good; there were no samples for irrigation water; the geochemical grade of the atmospheric environment is Grade 1, indicating a relatively low deposition flux of dry and wet atmospheric substances.
10	0:176:80	The comprehensive geochemical grade of soil quality is Grade 1—excellent; the geochemical grade of the irrigation water environment is Grade 1, indicating compliance with irrigation water quality standards; there were no samples for the dry and wet deposition flux of the atmosphere.

5. Discussion

5.1. Study on the Geochemical Characteristics of the Study Area

5.1.1. Soil Geochemical Background Values of Elements

In this study, the soil element background values in Shandong Province were referenced from the data compiled by Pang Xugui, Dai Jieji, and others [32–35]. The statistical param of soil element geochemical background values are shown in Table 7. As shown in the table, the soil element geochemical background values in the Licheng District of Jinan City compared to the average values in Shandong Province exhibit the following characteristics (Figure 3).

Table 7. Statistical table of geochemical background values of soil elements.

Elements	Average	Statistics	Eliminated	Background Value	Coefficient of Variation (%)	Data Frequency Distribution Type	Shandong Soil Background Value	Specific Value (K)
As	9.913	6475	48	11.35	28.992	skewness	8.6	1.32
B	52.044	6208	315	52.044	28.591	normality	42.7	1.22
CaO	4.181	5971	552	4.181	52.779	normality	3.36	1.24
Cd	0.176	5982	541	0.176	32.055	normality	0.132	1.33
Co	13.31	6153	370	13.31	20.253	normality	11.9	1.12
Cr	71.38	5953	570	71.38	16.326	normality	62	1.15
Cu	25.651	6122	401	25.651	21.651	normality	22.6	1.14
F	581.375	6165	358	581.375	16.048	normality	521	1.12
Ge	1.311	6404	119	1.311	11.489	normality	1.3	1.01
Hg	0.041	6086	437	0.041	44.504	normality	0.031	1.32
I	2.405	5494	1029	2.405	38.013	normality	1.96	1.23
K_2O	2.212	6204	319	2.212	15.429	normality	2.47	0.9
Mn	611.628	6275	248	611.628	17.344	normality	576	1.06
Mo	0.566	6241	282	0.566	22.769	normality	0.58	0.98
N	1144.698	5744	779	1144.698	39.45	normality	890	1.29
Ni	30.426	6157	366	30.426	18.01	normality	27.1	1.12
P	779.737	6270	253	698.59	41.63	skewness	824	0.85
Pb	23.857	6229	294	23.857	24.685	normality	23.6	1.01
pH	8.192	5189	1334	8.192	38.471	normality	7.32	1.12
S	229.192	5897	626	206.33	39.899	skewness	211	0.98
Se	0.282	6021	502	0.282	38.526	normality	0.18	1.57
V	82.577	6197	326	82.577	15.313	normality	75.6	1.09
Zn	73.832	6189	334	73.832	17.622	normality	63.3	1.17
organic	1.959	5654	869	1.959	41.93	normality	1.36	1.44

Note: Organic matter (CaO, K_2O): %; pH: non-dimensional; remaining elements: μg/g.

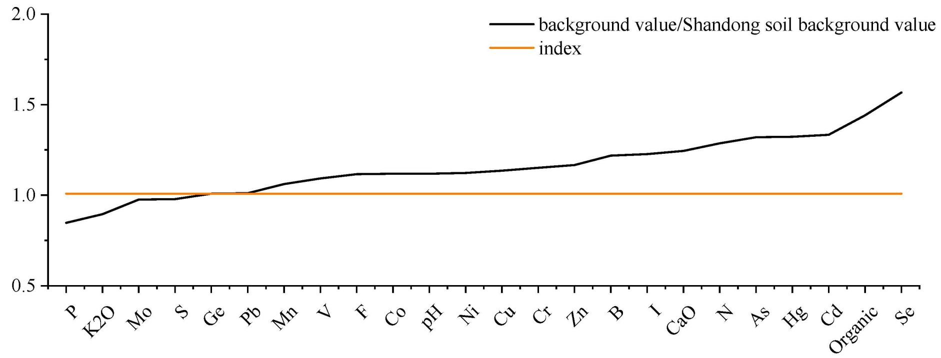

Figure 3. Ratio curve of background values of surface soil geochemistry of surface soil in Licheng District.

When comparing the Licheng District soil background values to those of Shandong Province, the background value ratio K values of elements range from 0.85 to 1.57. Elements with lower values ($0.8 < K \leq 0.9$) include P and K_2O, which are lower than the provincial background values and should be given attention in agricultural production. Elements with values close to one ($0.9 < K < 1.1$) include S, Mo, Ge, Pb, Mn, and V. Elements with higher values ($1.1 < K \leq 1.2$) include pH, Co, F, Ni, Cu, Cr, and Zn. Elements with significantly higher values ($K > 1.2$) include B, I, CaO, N, As, Hg, Cd, organic matter, and Se, with Se being particularly prominent, significantly higher than the soil Se element background values in Shandong Province.

5.1.2. Geochemical Regional Distribution Characteristics of Selenium in Soil

Through statistical analysis and processing of area-scale soil test data, selenium geochemical maps were compiled by plotting single-element or indicator contour lines (Figure 4). The selenium values are mainly distributed in the areas near Sijia in Tangwang Town, Hanjiazhuang West Village, Cuijiacun; Liu Jiazhuang in Wangsheren Town, Zhifang Village; Tianjingyu in Ganggou Town, Xilujia; Youlanyu in Caishi Town, Kangjing, Mengcun, and the area of Humeng-Daogou.

5.1.3. Soil Geochemical Zoning and Characteristics

According to the principles and methods of soil geochemical zoning, it was found that the results of soil zoning are sensitive to geological background or landform reflection. Therefore, the geochemical zones are mainly delineated based on geological boundaries, while sporadic geological background areas within each zone are omitted. The entire region is divided into three geochemical zones and seven geochemical subzones (Figure 5, Table 8). Among them, the three geochemical zones are the "Xiyin-Liubu-Huangchao Geochemical Zone"—an intrusive rock distribution area; the "Caishi-Zhonggong-Gaoer Geochemical Zone"—a limestone and dolomite area; and the "Tangwang-Yaoqiang-Suncun Geochemical Zone"—a Quaternary distribution area. The high background area of selenium elements is mainly concentrated in the Caishi-Gaoer geochemical subzone (II-1) and the Quanfu-Wangsherenzhen-Guodian geochemical subzone (III-3).

Xiying–Liubu–Huangchao Geochemical District (I)

This geochemical district is located southeast of Xiying–Liubu Town, characterized by a geological background primarily consisting of the black amphibolite of the Taishan Group, along with the presence of black schist, diorite, gabbro, monzogranite, and granitic gneiss from various geological periods. The parent material of the soil in this geochemical district is predominantly composed of weathered residuals from nearby rock formations, resulting in soil geochemical characteristics that generally reflect those of the underlying rocks. High background levels are observed for organic matter and cobalt (Co), while arsenic (As), boron (B), calcium oxide (CaO), pH, lead (Pb), potassium oxide (K_2O), mercury (Hg), cadmium (Cd), manganese (Mn), selenium (Se), germanium (Ge), molybdenum (Mo), and phosphorus (P) exhibit low background levels.

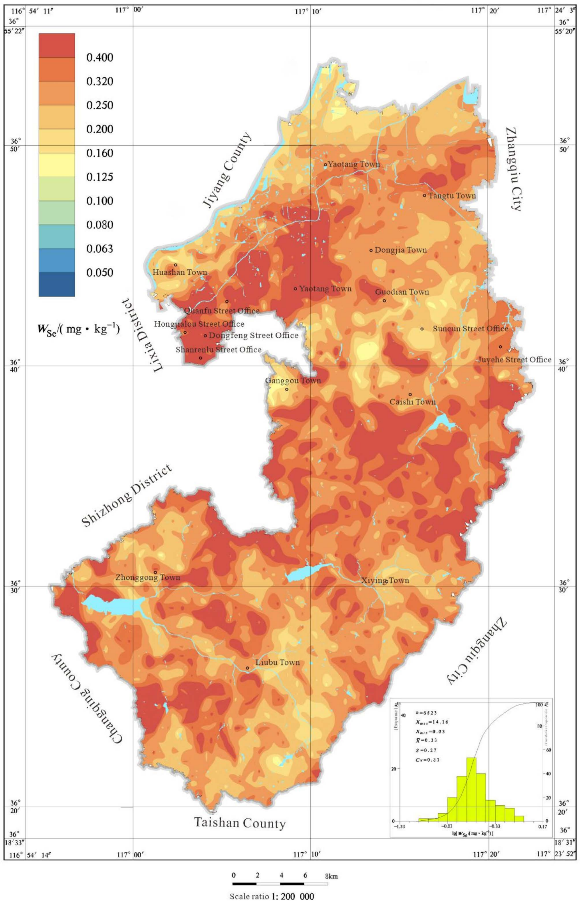

Figure 4. Geochemical map of selenium element in surface soil (logarithmic histogram in the lower right corner).

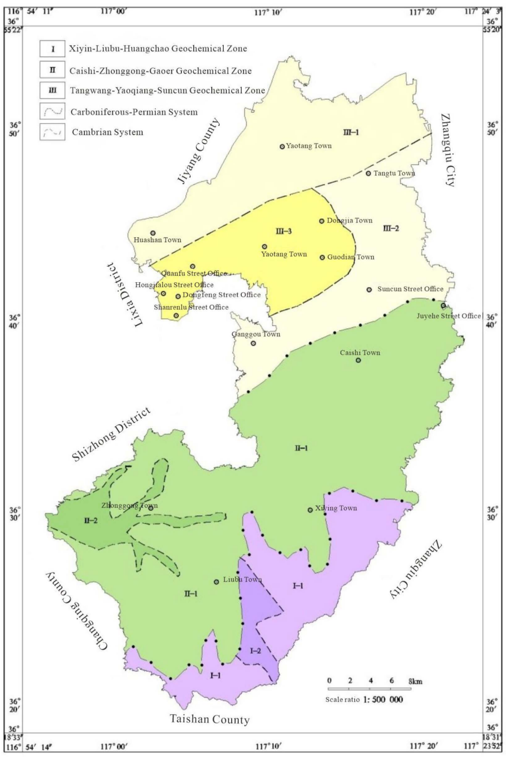

Figure 5. Geochemical zoning map of soil in Licheng District.

Table 8. Characteristics of geochemical zoning of soil in Licheng District, Shandong Province.

Partition Name		High Background Element or Indicator	Low Background Element or Indicator
Xiyin-Liubu-Huangchao Geochemical Zone	Xiyin-Huangchao Geochemical Subzone (I-1)	Organic matter, Co	As, B, CaO, pH, Pb, K_2O, Hg, Cd, Mn, Se, Ge, Mo, P
	Liubu Geochemical Subzone (I-2)	F	As, B, I, Hg
Caishi-Zhonggong-Gaoer Geochemical Zone	Caishi-Gaoer Geochemical Subzone (II-1)	Se, CaO, Organic matter, N, I, Cu, F, B, Cd, Co, S	No large area of low background elements
	Zhonggong Geochemical Subzone (II-2)	Ag, As, Au, Ba, Cd, Hg, Ni	Br, Cl, I, Ge, Li
Tangwang-Yaoqiang-Suncun Geochemical Zone	Huashan-Yaoqiang Geochemical Subzone (III-1)	S, CaO, P	Organic matter, N, I, Co
	Tangwang-Suncun Geochemical Subzone (III-2)	S, Hg	Organic matter, N, I, Co
	Quanfu-Wangsheren-Guodian Geochemical Subzone (III-3)	Cd, Zn, Se, Pb, Mo, CaO, Hg, S, Mn	Organic matter, N, I, B

Based on variations in geological background and elemental compositions, this area is divided into two geochemical subregions: the Xiying–Huangchao Geochemical Subregion (I-1) and the Liubu Geochemical Subregion (I-2). The characteristics of each subregion are as follows:

1. Xiying–Huangchao Geochemical Subregion (I-1)

The soil parent material primarily consists of weathered products from amphibolite and schist. The dominant soil types include brown soil, brown soil variants, and coarse calcareous soil, with localized development of podzolic soil and leached brown soil. High background levels are noted for organic matter and Co, while As, B, CaO, pH, Pb, K_2O, Hg, Cd, Mn, Se, Ge, Mo, and P show low background levels.

2. Liubu Geochemical Subregion (I-2)

The soil parent material is mainly composed of weathered products from monzogranite. The prevalent soil types include brown soil, brown soil variants, and coarse calcareous soil, with some localized development of podzolic soil. In this subregion, fluorine (F) exhibits high background levels, while As, B, iodine (I), and Hg show low background levels.

Caishi–Zhonggong–Gao'er Geochemical District (II)

This geochemical district is located in the Caishi–Zhonggong–Gao'er area, which occupies a significant proportion of the evaluation area. The geological background is primarily composed of Cambrian–Ordovician limestone and dolostone. The soil geochemical characteristics largely reflect those of the underlying rocks. High background levels are present for selenium (Se), CaO, organic matter, nitrogen (N), iodine (I), copper (Cu), fluorine (F), boron (B), cadmium (Cd), cobalt (Co), and sulfur (S), while the background values for most other elements are generally comparable to the overall district background.

This district is divided into two geochemical subregions based on geological background and elemental composition: the Caishi–Gao'er geochemical subregion (II-1) and the Zhonggong geochemical subregion (II-2). The characteristics of each subregion are as follows:

1. Caishi–Gao'er Geochemical Subregion (II-1)

This subregion is characterized by soil types predominantly consisting of podzolic soil and podzolic variants, with localized development of coarse calcareous soil and leached podzolic soil. High background levels are observed for Se, CaO, organic matter, N, I, Cu, F, B, Cd, Co, and S, while the background values of most other elements are comparable to the overall district background.

2. Zhonggong Geochemical Subregion (II-2)

This subregion is primarily characterized by podzolic soil, with As exhibiting low background levels, while Cd, Se, phosphorus (P), mercury (Hg), and sulfur (S) show high background levels.

Tangwang–Yaoqiang–Suncun Geochemical District (III)

This geochemical district is located in the Tangwang–Yaoqiang–Suncun area, characterized by a landscape of alluvial plains at the foothills and the Yellow River floodplain, with the geological background predominantly consisting of Quaternary deposits. High background levels are observed for sulfur (S) and phosphorus (P), while organic matter, N, I, and Co exhibit low background levels. The background values for most other elements are generally comparable to the overall district background.

Based on geological background and elemental composition, the study area is divided into three geochemical subregions: the Huashan-Yaoqiang geochemical subregion (III-1); the Tangwang-Suncun geochemical subregion (III-2); and the Quanfu-Wangshe Ren-Guodian geochemical subregion (III-3). The characteristics of each subregion are as follows:

1. Huashan-Yaoqiang Geochemical Subregion (III-1):

This geochemical subregion is primarily characterized by soil types such as fluvo-aquic soil, saline fluvo-aquic soil, and brown soil. Locally, there are also developed paddy soils. The soil exhibits high background values for sulfur (S), calcium oxide (CaO), and phosphorus (P), while organic matter, nitrogen (N), iodine (I), and cobalt (Co) show low background values. The background values of most other elements are roughly comparable to the overall regional background values.

2. Tangwang-Suncun Geochemical Subregion (III-2):

The predominant soil types in this geochemical subregion are brown soil and fluvo-brown soil, with local occurrences of saline fluvo-aquic soil and sandy black soil. The soil displays high background values for sulfur (S) and mercury (Hg), while organic matter, nitrogen (N), iodine (I), and cobalt (Co) exhibit low background values.

3. Quanfu-Wangshe Ren-Guodian Geochemical Subregion (III-3):

This geochemical subregion is primarily designated for urban use and contains numerous chemical plants and polluting enterprises. Elements such as cadmium (Cd), zinc (Zn), selenium (Se), lead (Pb), molybdenum (Mo), calcium oxide (CaO), mercury (Hg), sulfur (S), and manganese (Mn) show high background values, whereas organic matter, nitrogen (N), iodine (I), and boron (B) display low background values. The elevated background values are primarily influenced by anthropogenic activities.

5.2. Selenium Element Abundance and Deficiency in Different Regions

The evaluation of selenium in the Quaternary, Ordovician, and Cambrian exposed areas of the evaluation region show selenium levels are rich in these areas, while in other regions, the soil is mostly at adequate selenium levels. The area with rich selenium covers 264.37 km^2, accounting for 20.31% of the evaluation region's area; the area with adequate selenium covers 979.36 km^2, accounting for 75.27% of the evaluation region's area.

According to common classification standards: Se > 3.0 indicates selenium toxicity, 0.4–3.0 indicates selenium abundance, 0.175–0.4 indicates adequate selenium, 0.125–0.175 indicates potential selenium deficiency, and Se < 0.125 indicates selenium deficiency. The area of selenium toxicity in the evaluation region is small, only 0.26 km^2, accounting for 0.019% of the total area; the areas with potential selenium deficiency and selenium deficiency are limited, only covering 57.48 km^2, accounting for 4.42% of the total evaluation region's area, indicating an overall abundance of selenium in the evaluation region.

5.3. Sources of Soil Element Anomalies

The sources of surface soil anomalous elements are inherited from the parent material and influenced by human activities. Combining the actual situation in this region and based on the geochemical anomaly lower limit values of each element in the region, we delineate the anomalous areas and describe the sources of anomalies based on the geochemical maps of each element.

5.3.1. Geological Background Influence on Soil Element Anomalies

The geological background of the evaluation region is relatively simple, with the northern part dominated by the Quaternary, and the southern part characterized by extensive Mesozoic Cambrian-Ordovician strata. The southeastern part of the evaluation region is composed of Taishan Group black biotite gneiss, black phyllite, as well as various periods of diorite, diorite porphyry, syenogranite, granite gneiss, and other rocks.

High-value anomalies of elements Cr, Ni, Cu, Co, and V are associated with the exposure of fine-grained diorite porphyry group in the Songshan unit of Liubu Town, mainly related to primary anomalies associated with the geological background. The Cd element anomaly area in the limestone–dolomite exposure area is mainly due to primary anomalies related to the geological background. Anomalies of I, CaO, N, B, Mo, and organic matter in the southern part of the evaluation region coincide with the limestone–dolomite exposure area in the Caishi-Zhonggong area, primarily influenced by the geological background. The low anomaly areas of elements P, K_2O, B, Mn, I, F, Ge, As, Pb, and CaO match the distribution of old strata rocks in Xiyin-Liubu southeast, with the distribution of these elements mainly influenced by the geological background. The high-value area of element F is surrounded by faults, where fault structures may be the main factor influencing the high or low content of F.

5.3.2. Impact of Atmospheric Dry and Wet Deposition on Soil Element Anomalies

According to the "Technical Requirements for Geochemical Evaluation of 1:50,000 Land Quality Survey in Shandong Province" (Trial), the evaluation index for the geochemical classification of atmospheric dry and wet deposition is the annual deposition flux of Cd and Hg. Based on the classification of environmental geochemical grades for atmospheric dry and wet deposition as single indicators, the comprehensive grade of environmental geochemistry for atmospheric dry and wet deposition in each evaluation unit is equivalent to the lowest grade determined by the single indicator classification. The evaluation shows that the comprehensive environmental index of atmospheric dry and wet deposition in Licheng District is first-class, indicating that the impact of atmospheric dry and wet deposition on soil environmental quality in Licheng District is minimal.

5.3.3. Impact of Irrigation Water on Soil Element Anomalies

There are three instances of irrigation water exceeding standards in the evaluation area: the first instance is located west of Qinjiadaokou Village in Yaoqiang Town, where sample SY35 exceeds standards during both wet and dry seasons. The soil in this area is classified as a high fluoride zone, mainly distributed along the Yellow River sedimentary area. However, nearby water samples do not exceed fluoride levels, suggesting that the impact of irrigation water on soil geochemical quality in this area is minimal and the high fluoride zone in the soil is likely related to the sedimentary environment of the soil parent material. The second instance of exceeding standards is found in Fengjiazhuang in Yaoqiang Town, where chlorine (Cl^-) levels exceed standards. Testing during wet and dry seasons shows that only chlorine (Cl^-) levels exceed standards during the wet season. Since soil chlorine levels were not tested in this study, the impact of irrigation water on soil geochemical quality in this area cannot be evaluated. The third instance of exceeding standards is in Wangsheren Town, where total salt levels exceed standards. Testing during wet and dry seasons shows that only total salt levels exceed standards during the dry season. This water is used for shallow groundwater drinking and does not involve agricultural irrigation. The quality of water in this area has minimal impact on soil geochemical quality.

5.3.4. Influence of Surrounding Environmental Factors on Soil Element Anomalies

Under the influence of human activities, toxic elements such as Hg, As, Cd, S, and Cr, as well as agricultural nutrients such as N, P, K, Se, and organic matter, undergo changes in distribution and allocation in the soil. Human activities, including fertilization, pesticide use, residential living, and industrial waste emissions (such as anomalies of Cd, Zn, Se, Pb, Mo, CaO, Hg, S, Mn near the Jigang steel plant area), mainly store these substances in the surface soil. Therefore, the distribution patterns of harmful elements, especially heavy metals, in surface soil and changes in soil deposition columns can roughly reflect the degree and extent of human activity influence, leading to the enrichment of elements in the soil.

The analysis of the sources of soil element anomalies in the region is based on data from the current investigation. This analysis provides a comprehensive interpretation of the land quality and environmental conditions in the study area; however, it lacks universal applicability. Consequently, the findings of this research may not be broadly applicable to similar geological environments, but they can serve as a reference for future studies.

5.4. Factor Analysis of Surface Soil Elements

To explore the interrelationships among elements in surface soil, factor analysis was conducted on 24 elements using the factor analysis module of SPSS software. The characteristic roots and corresponding eigenvectors of the correlation matrix were calculated, and the cumulative percentage of variance contribution was determined based on the percentage of characteristic roots to identify the number of principal factors. The results indicated that the first seven factors accounted for 66.064% of the cumulative contribution of the 24 elements or indicators (Table 9). Therefore, these seven factors were regarded as the principal factors. An orthogonal rotation using the "varimax" method was applied to the initial factors, resulting in a rotated factor model (Table 10).

The purpose of factor analysis extends beyond merely identifying principal factors; it aims to elucidate the underlying meanings represented by each principal factor. Initially, the initial factor loading matrix was computed; however, the overall correlation among the initial factors was not very strong (the coefficients of the original variables showed minimal variation). To enhance the distinction among the coefficients of the original variables, a varimax rotation was applied to the orthogonal factor loading matrix, allowing for an analysis of the relationship between the 24 soil elements or indicators and the seven factors. This analysis aimed to identify which factors predominantly influence the regional distribution of different combinations of elements or indicators. The variables represented by each principal factor of the surface soil are as follows:

Table 9. Surface soil characteristic root and factor extraction results table.

Topsoil Characteristic Root			
No.	**Eigenvalue**	**Eigenvalue Percentage**	**Cumulative Percentage**
F1	3.713	15.469	15.469
F2	3.271	13.628	29.097
F3	2.371	9.878	38.974
F4	2.129	8.872	47.846
F5	1.686	7.026	54.872
F6	1.438	5.993	60.866
F7	1.247	5.198	66.064

Table 10. Rotational component matrix.

Elements	Factor Component						
	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**
Se	0.020	0.528	−0.098	0.535	0.170	0.165	0.003
N	−0.039	0.949	0.017	0.074	−0.027	−0.051	0.053
I	−0.029	0.755	0.168	−0.012	0.219	0.110	−0.164
S	−0.008	0.589	−0.135	0.339	0.195	0.014	0.159
Organic	−0.028	0.937	−0.056	0.154	0.002	−0.041	0.027
pH	−0.134	−0.225	0.465	0.010	0.499	0.446	0.034
B	−0.027	0.196	0.593	−0.079	0.190	0.280	−0.130
Co	0.890	0.031	0.126	−0.048	−0.153	0.079	−0.037
Cu	0.543	−0.014	0.158	0.346	−0.158	0.166	0.171
F	0.349	0.111	0.482	−0.020	−0.146	0.368	0.172
Ge	0.228	−0.113	0.719	0.127	0.108	−0.154	0.031
Mn	0.560	0.006	0.270	0.257	0.315	−0.117	0.009
Mo	0.121	0.158	−0.117	0.144	0.496	0.000	0.072
P	0.002	−0.094	0.112	0.228	−0.050	−0.027	0.754
V	0.798	−0.100	0.165	0.109	0.052	−0.124	−0.063
Zn	0.146	0.014	−0.047	0.784	0.141	−0.097	0.055
CaO	−0.077	0.039	−0.133	−0.001	−0.018	0.912	−0.046
K_2O	−0.101	−0.048	0.818	−0.050	−0.041	−0.193	0.022
Cd	−0.031	0.143	0.034	0.538	−0.115	0.057	0.137
Cr	0.852	−0.039	−0.174	0.008	0.122	−0.027	0.027
Ni	0.835	0.008	−0.165	−0.117	0.062	−0.055	−0.002
Pb	0.016	0.282	0.065	0.694	0.428	−0.091	−0.043
As	−0.022	0.135	0.254	0.029	0.741	−0.028	0.108
Hg	0.006	0.119	−0.097	−0.025	0.259	−0.001	0.705

Extraction method: principal component. a. Rotation converges after seven iterations.

Factor F1: This factor is composed of Co, Cr, Ni, V, Mn, and Cu. It accounts for 15.469% of the variance, representing a stable group of metals, with Co, Cr, and Ni having the most significant effects.

Factor F2: This factor includes N, organic matter, I, S, and Se, contributing 13.628% of the variance, with N and organic matter being the most influential.

Factor F3: This factor consists of K, Ge, B, F, and As, reflecting elements that are susceptible to the influence of soil parent material and human activities. It accounts for 9.878% of the variance, with K and Ge being the most significant contributors.

Factor F4: This factor comprises Zn, Pb, and Cd, also indicating elements affected by soil parent material and human activities. It contributes 8.872% of the variance, with Zn being the most influential.

Factor F5: This factor includes pH and Mo, contributing 7.026% of the variance, with pH being the most significant.

Factor F6: This factor represents the single-element principal factor CaO, accounting for 5.993% of the variance, indicating that the factors influencing the original data structure of CaO are characterized by multiple sources and relative independence.

Factor F7: This factor consists of P and Hg, contributing 5.198% of the variance, with P being the most significant.

5.5. Horizontal and Vertical Migration Characteristics of Soil Elements

In order to further verify the selenium enrichment status, clarify the rules of element migration and transformation in the vertical direction, and assess the geochemical quality of soil, three horizontal profiles (SP1 to SP3) and three vertical profiles (CP1 to CP3) were established. Among them, SP1 was set up in the selenium-rich area from Sijiazhuang in Tangwang Town to Cuijiazhuang, with an east–west orientation and a total length of 3.2 km, and a vertical profile CP1 was set up on this horizontal profile. SP3 was set up from Chuanliu Village to Liangsi Village, oriented east–west, and a vertical profile CP3 was set up on this horizontal profile. SP2 was only used to assess the anomalies and degrees of pollution for various elements in this study and will not be discussed further.

From the horizontal profiles of SP1 and SP3 (Figures 6 and 7), all points reached selenium concentrations, except for five points (SP1-4, SP1-29, SP3-122, SP3-133, SP3-143); most points along the profile lines reached selenium-rich concentrations, which is consistent with the selenium evaluation map.

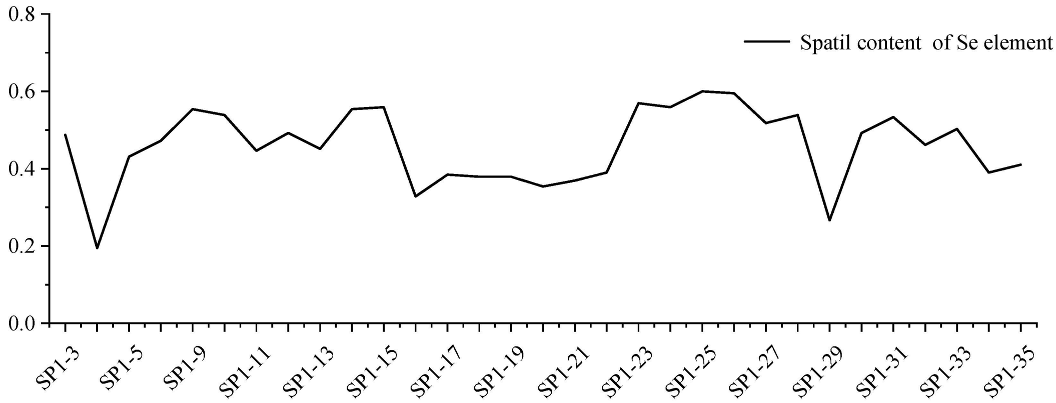

Figure 6. Spatial content change of Se element in horizontal profile SP1 (μg/g).

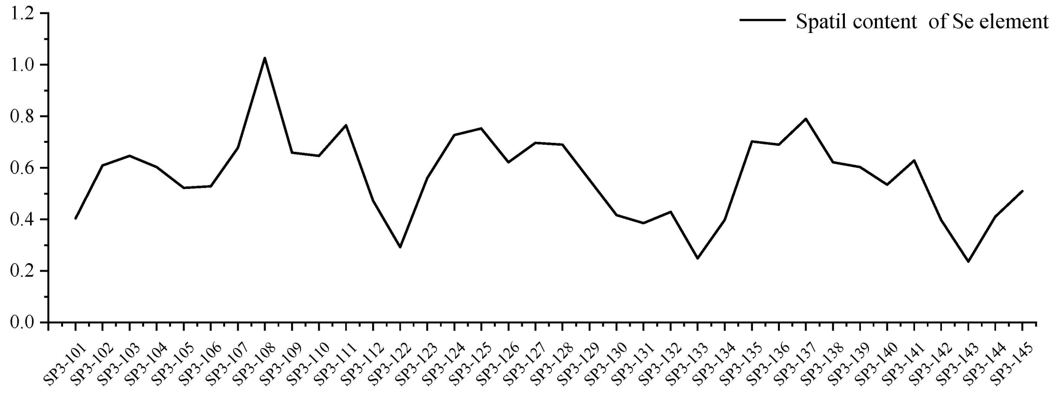

Figure 7. Spatial content change of Se element in horizontal profile SP1 (μg/g).

From the vertical profiles of CP1 and CP2 (Figures 8 and 9), the Se element showed a trend of decreasing content from top to bottom, with a stable layer from 60 to 200 cm, indicating that these elements are mainly enriched in the surface layer of the soil, possibly influenced by external sources rather than soil parent material.

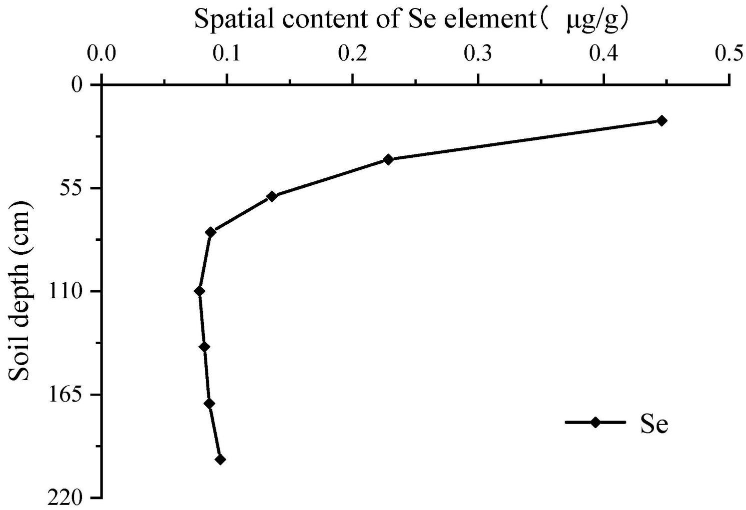

Figure 8. Spatial content change curve of Se element in vertical profile CP1 (μg/g).

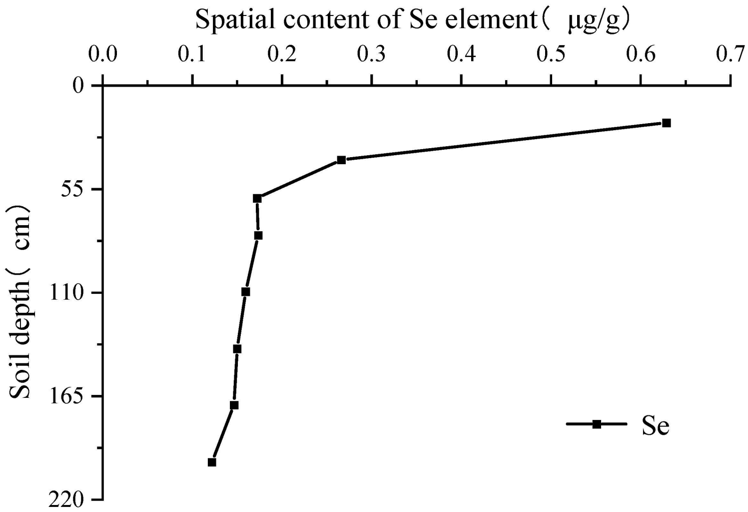

Figure 9. Spatial content change of Se element in vertical profile CP3 (μg/g).

6. Conclusions

Based on the concept of soil geochemical background values and established basic principles, the geochemical param of 24 soil elements or indicators were statistically analyzed according to geological background, soil type, landform units, etc., to evaluate the geochemical background characteristics of soil. Elements that are lower compared to the provincial soil background values include P and K_2O, which are below the provincial background values and should be given attention in agricultural production. Elements that are close to the background values include S, Mo, Ge, Pb, Mn, and V, while elements that are higher include pH, Co, F, Ni, Cu, Cr, and Zn. Elements that are significantly higher include B, I, CaO, N, As, Hg, Cd, organic matter, and Se. This indicates that the important elements for high-quality agricultural products in Licheng District are selenium-rich and mainly distributed near Sijia in Tangwang Town, Hanjiazhuang, Cuijiacun; Liujiazhuang in Wangsheren Town, Zhifangcun; Tianjingyu in Ganggou Town, Xilujia; Youlanyu in Caishi Town, Kangjing, Mengcun, Humeng, Daogou area; and Sunjiacun in Zhonggong Town, Beigaoer area.

The delineation of high-quality selenium-rich land in this study is based on the regional planning of high-quality selenium-rich land in selenium-rich soils, indicating that the land quality is geologically excellent, with sufficient nutrients and excellent environmental quality. The division also follows the principle of dividing areas that are relatively connected in terms of area and relatively concentrated in size, excluding temporarily small selenium-rich areas that are not conducive to overall development from the delineation of selenium-rich land [36].

According to the above definition, the delineation of selenium-rich land in the evaluation area is shown in Figure 10, with the following results: high-quality selenium-rich land is distributed in Tangwang Town, north of Wangsheren Town, south of Caishi, north of Zhonggong, and near Gaoercun, with an area of 192.26 km^2, of which the arable land area is 35.83 km^2. The soil in the high-quality selenium-rich land area is rich in nutrients, the soil environment is clean, and the selenium content is high. According to the land use, it is suitable for developing selenium-rich agriculture, selenium-rich secondary industries, and other industries. Additionally, the use of selenium-enriched fertilizers [37,38] can improve the surrounding soil environment suitable for cultivation, thereby enhancing the quality of local selenium-rich agricultural products. Furthermore, to advance the development of local selenium-rich agriculture, future research should consider the specific land quality conditions of the region. It is essential to propose scientifically sound and contextually appropriate agricultural and forestry planting layout designs, which can provide guiding recommendations for the development of local agricultural and forestry industries.

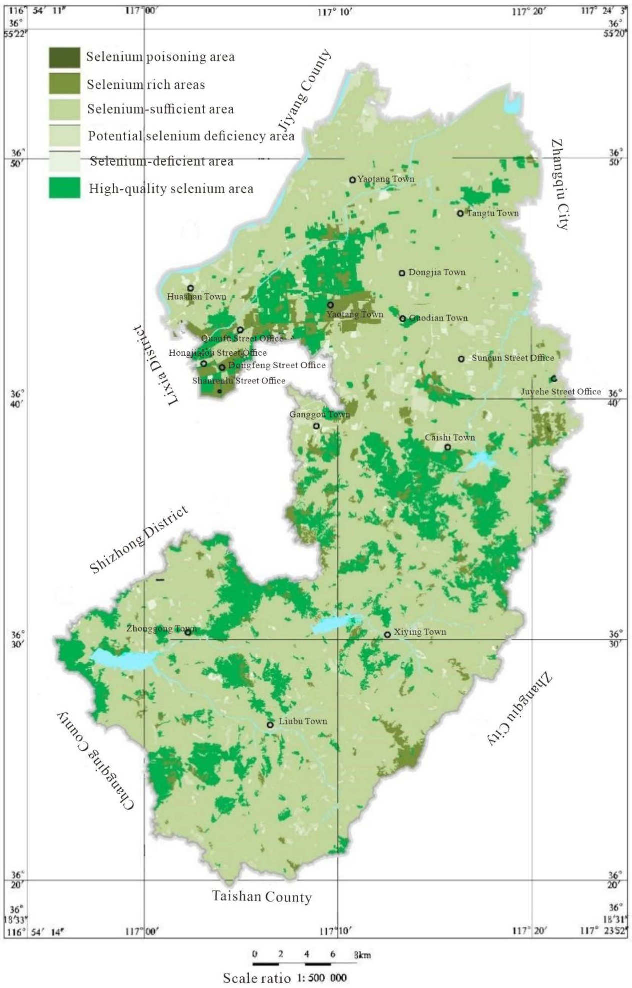

Figure 10. Planning map of high-quality selenium-rich areas.

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