

## Research Article

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# Assessment of Se, As, Cd, Cr, Hg, and Pb content status in Ankang tea plantations of China

<https://doi.org/10.1515/chem-2024-0054>

received February 29, 2024; accepted May 24, 2024

**Abstract:** Selenium (Se) is an essential trace element for humans. The Ankang tea plantation area in China is the best place for producing high-quality and Se-enriched organic tea. However, accumulation of potentially toxic elements (PTEs) in soil and tea leaves has attracted a lot of attention. Therefore, in this research, the content status of Se and five PTEs (As, Cd, Cr, Hg, and Pb) in soil and tea leaf samples collected from 88 Ankang tea plantations was studied. Results showed that the average Se content was  $0.17 \text{ mg kg}^{-1}$  and the Se-enrichment rate was 25% for the 88 tea leaf samples, and As, Cd, Cr, Hg, and Pb contents in all tea leaf samples met the Chinese standard for pollution-free tea except for 11.2% excess Cr in only one sample. Cd concentrations in 56.82% soil samples exceeded the Chinese risk screening value for soil contamination of the agricultural land, and therefore the pollution degree of Cd is high in these soil samples. Moreover, the Hakanson potential ecological risk assessment of soil As, Cd, Cr, Hg, and Pb indicated that the Ankang tea plantation area was at a medium potential ecological risk level. These results will provide theoretical support for ecological risk management and safe production of Se-enriched tea in Ankang Se-enriched tea plantations.

**Keywords:** selenium, potentially toxic elements, tea leaves, tea plantations, potential ecological risk

## 1 Introduction

Selenium (Se), which is called “life element,” is an essential trace element for humans and animals [1,2]. Studies have confirmed that Se has important roles in the treatment of Keshan disease, Kashin–Beck disease, prevention of cardiovascular and cerebrovascular diseases, scavenging free radicals in the body, preventing membrane lipid peroxidation, and as anti-cancer and anti-aging agents [2–5]. Therefore, Se supplements are extremely beneficial to people's health, especially in the low-Se zone. Moreover, developing Se-enriched foods is the most effective and safe means of Se supplementation [6,7], such as the successfully developed Se-enriched tea, garlic, and broccoli [8–11].

Like tea [12], Se-enriched tea also exhibits properties like anti-genotoxic, cancer chemopreventive, anti-inflammatory, and antioxidant properties [9,10]. China's tea culture has a long history, and tea is the most widely used daily drink in the world [13]. Therefore, Se-enriched tea can be used as a safe and effective means to improve Se deficiency in humans, and it will also be favored by consumers for its high quality and health care effect [9].

In China, the Ankang City, located in the Shaanxi Province and bordered by the Qinling-Bashan Mountains, is the largest natural Se-rich area at present. The area has ideal geological and geographical conditions for Se accumulation and utilization; the area is thick in strata and large in exposed area, and the soil area with a Se content above  $0.2 \text{ mg kg}^{-1}$  exceeds  $10,000 \text{ km}^2$ , forming a natural Se-rich belt covering the whole city with Ziyang County as the center [14,15]. The Ankang tea plantation area is mainly distributed in mountainous and hilly areas at higher altitudes in Ziyang, Pingli, Hanbin, Langao, and other counties, belonging to the high latitude tea area in the North of the Yangtze River. The climate, light, humidity, and Se-enriched soil in this area are recognized as the main reasons for high-quality Se-enriched organic tea in China and abroad [14,15].

Large quantities of potentially toxic elements (PTEs) are present in the environment due to the increased anthropogenic activities and natural processes, and accumulation of

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PTEs in soil and tea leaves has been a particular concern for tea consumers worldwide; moreover, there are still challenges in identifying the pollution characteristics of PTEs at the local scale [16–20]. Throughout the Ankang area, there are black shales which contain black shale, carbonaceous rocks, and coal in the Cambrian Donghe Formation, and thus it is very important to figure out the influence of black shales, enriched with trace elements, on soils and edible plants growing in the soils [14]. Therefore, in this study, 88 tea leaf samples and 88 soil samples from 88 tea plantations in 3 counties of the Ankang tea planting area in Shaanxi Province, China, were selected as the research objects, the content characteristics of Se and five PTEs (As, Cd, Cr, Hg, and Pb) in tea plantation soils and cultivated tea leaves were analyzed and studied, and the classical Lars Hakanson potential ecological risk index method was used to evaluate the potential ecological risk of As, Cd, Cr, Hg, and Pb in the soils of the tested tea plantations [19,21–23]. These study results will provide a scientific basis for pollution-free planting, ecological risk warning, and safe production of Se-enriched tea in Ankang Se-enriched tea plantations.

## 2 Experimental section

### 2.1 Materials

The tea plantation soil and tea leaves in Ziyang County, Hanyin County, and Pingli County, the main planting areas of Ankang Se-enriched tea, were selected as the investigation objects. A total of 88 tea plantations were randomly selected in the 3 tea planting counties, from which 88 fresh tea leaf samples and 88 corresponding root soil samples were collected (Figure 1). Fresh tea leaf samples were dried after fixation then they were ground, and passed through a 20-mesh nylon sieve for complete analysis of Se, As, Cd, Cr, Hg, and Pb. Soil mixed samples were naturally air-dried, ground, and then passed through a 100-mesh nylon sieve for the full analysis of Se, As, Cd, Cr, Hg, and Pb.

### 2.2 Method of elemental analysis and detection

Sample analysis and testing were undertaken by the Xi'an Mineral Resources Supervision and Testing Center of the Ministry of Land and Resources, China. To 0.5 g soil samples, 10 mL of nitric acid and 2 mL of hydrogen peroxide were added for digestion by a microwave system (ETHOS UP,

Milestone, Italy), then the resulting solution was diluted to a certain volume for determining the total Se content in soils. To 0.1 g soil samples, 5 mL of nitric acid, 2 mL of hydrofluoric acid, and 2 mL of hydrogen peroxide were added for digestion by the microwave system, then the resulting solution was diluted to a certain volume for determining the content of As, Cd, Cr, Hg, and Pb in soils. Tea leaf samples of 0.2–0.5 g (accurate to 0.001 g) weight were first soaked in 5–8 mL of nitric acid overnight, then put in the microwave for 3–4 h of digestion, and then diluted to a certain volume for analysis. Details of testing elements, methods, and main instruments for tea leaf and root soil samples are, respectively, shown in Tables 1 and 2. Moreover, operating conditions for inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7800 and XSERIES 2), inductively coupled plasma atomic emission spectrometry (ICP-AES; iCAP7400), hydride generation – atomic fluorescence spectrometry (AFS-8500), and vapor generation – cold atomic fluorescence spectrometry (XGY 1011A) are shown in Tables S1–S5. Selected isotopes, internal standard elements, and interference correction for the ICP-MS and elemental analysis line and background correction for the ICP-AES are shown in Tables S6–S8. During the test, national first-level standards were randomly added to control the analysis quality. The rate of all samples was reported to be 100%, and the qualification rate of accuracy and precision monitoring of samples were over 98%.

### 2.3 Evaluation method and evaluation standard of PTEs

In this study, to evaluate and analyze the contents of As, Cd, Cr, Hg, and Pb in soils and tea leaves, the soil background levels of As, Cd, Cr, Hg, and Pb in Shaanxi Province, China, were taken as the reference value, and standard values specified by the soil environmental quality risk control standard for soil contamination of agricultural land of China (GB15618-2018) [24] and the agricultural industry standards “Pollution-Free Food and Tea” (NY5244-2004) [25] and “Residue limits for chromium, cadmium, mercury, arsenic and fluoride in tea” (NY659-2003) [26] were also used for comparison.

Moreover, the classical Lars Hakanson potential ecological risk index method, which was characterized by comprehensive consideration of the concentration, toxicity, ecological sensitivity, and synergy of multiple elements, was used to evaluate the potential ecological risk of As, Cd, Cr, Hg, and Pb in the soils of the tested tea plantations [21]. Its calculation is shown in formulas (1)–(4) as follows



Figure 1: Sampling sites of tea leaves and root soils in Ankang.

Table 1: Testing elements, methods, and main instruments for tea leaf samples

Elements	Detection standard (method number and name)	Detection limit	Testing instruments and models	Environmental conditions	
				Temperature (°C)	Humidity (%)
As	GB 5009.268-2016 National food safety standard – Determination of many elements in food	0.0017 mg kg <sup>-1</sup>	Inductively coupled plasma mass spectrometry (Agilent 7800)	24	36
Cd		0.0019 mg kg <sup>-1</sup>		24	36
Cr		0.0472 mg kg <sup>-1</sup>		24	36
Pb		0.0174 mg kg <sup>-1</sup>		24	36
Se		0.005 mg kg <sup>-1</sup>		24	36
Hg	GB 5009.17-2021 National food safety standard – Determination of total mercury and organic mercury in food	0.0025 mg kg <sup>-1</sup>	Atomic fluorescence spectrometry (XGY 1011A)	24	30

**Table 2:** Testing elements, methods, and main instruments for root soil samples

Elements	Detection standard (method number and name)	Detection limit	Testing instruments and models	Environmental conditions	
				Temperature (°C)	Humidity (%)
Cd	DZ/T 0279.5-2016 Analysis methods for regional geochemical sample – Part 5: Determination of cadmium contents by inductively coupled plasma mass spectrometry	0.021 mg kg <sup>-1</sup>	Inductively coupled plasma mass spectrometry (XSERIES 2)	25	30
Pb	DZ/T 0279.3-2016 Analysis methods for regional geochemical sample – Part 3: Determination of 15 elements including barium, beryllium, bismuth etc. by inductively coupled plasma mass spectrometry	0.50 mg kg <sup>-1</sup>	Inductively coupled plasma mass spectrometry (XSERIES 2)	25	30
Cr	DZ/T 0279.2-2016 Analysis methods for regional geochemical sample – Part 2: Determination of 27 components including calcium oxide etc. by inductively coupled plasma atomic emission spectrometry	0.20 mg kg <sup>-1</sup>	Inductively coupled plasma atomic emission spectrometry (ICAP7400)	25	35
Se	DZ/T 0279.14-2016 Analysis methods for regional geochemical sample – Part 14: Determination of selenium contents by hydride generation – atomic fluorescence spectrometry	0.0096 mg kg <sup>-1</sup>	Atomic fluorescence spectrometry (AFS-8500)	23	40
Hg	DZ/T 0279.17-2016 Analysis methods for regional geochemical sample – Part 17: Determination of mercury by vapor generation – cold atomic fluorescence spectrometry	0.50 ng g <sup>-1</sup>	Atomic fluorescence spectrometry (XGY 1011A)	23	35
As	DZ/T 0279.13-2016 Analysis methods for regional geochemical sample – Part 13: Determination of arsenic, antimony and bismuth contents by hydride generation – atomic fluorescence spectrometry	0.20 mg kg <sup>-1</sup>	Atomic fluorescence spectrometry (2022E)	21	31

$$C_f^i = C_s^i / C_n^i, \quad (1)$$

$$C_d = \sum_{i=1}^7 C_f^i, \quad (2)$$

$$E_r^i = T_r^i C_f^i, \quad (3)$$

$$I_R = \sum_{i=1}^7 E_r^i, \quad (4)$$

where  $C_f^i$  is the single-factor pollution index of the  $i$ th element;  $C_s^i$  is the measured content of the  $i$ th element in the soil,  $\text{mg kg}^{-1}$ ;  $C_n^i$  is the background reference value of the  $i$ th element,  $\text{mg kg}^{-1}$ ;  $C_d$  is the sum of multiple element pollution indices;  $E_r^i$  is the potential ecological risk index of a single element;  $T_r^i$  is the toxicity response coefficient of element  $i$ , and the toxicity response coefficients of the five PTEs are  $\text{Hg}(40) > \text{Cd}(30) > \text{As}(10) > \text{Pb}(5) > \text{Cr}(2)$  [19]; and  $I_R$  is the comprehensive potential ecological risk index of various elements in the region. The evaluation standard of potential ecological risk indices is shown in Table 3.

## 2.4 Statistical analysis

ArcGIS 10.7 (ESRI, Inc., Redlands, CA, USA) was used to mapping and showing the sampling sites of tea leaves and root soils in Ankang, China. The data were the average of the measured results of parallel samples, and Microsoft Office Excel 2007 (Microsoft, Redmond, WA, USA) and IBM SPSS Statistics version 25 (IBM SPSS Inc., Chicago, IL, USA) were used for statistical analysis.

# 3 Results and discussion

## 3.1 Characteristics of Se content in tea leaves from different regions

The Se content of tea leaves in the tea plantations in the Ankang City ranged from 0.02 to  $1.64 \text{ mg kg}^{-1}$ , showing a

large spatial variation of Se content (Table 4). Moreover, the average Se content ( $0.17 \text{ mg kg}^{-1}$ ) of tea leaves in the Ankang tea plantations was higher than the Se content standard of Se-enriched tea ( $0.15 \text{ mg kg}^{-1}$ ), and the Se enrichment rate of tea leaves was 25% (Table 4). In different regions, the spatial variation of Se content data in Pingli tea plantations was larger than that in Hanyin and Ziyang; the average Se content of tea leaves in Pingli ( $0.27 \text{ mg kg}^{-1}$ ) was significantly higher than the Se content standard of Se-enriched tea ( $0.15 \text{ mg kg}^{-1}$ ), but the average Se content of tea leaves in both Hanyin ( $0.10 \text{ mg kg}^{-1}$ ) and Ziyang ( $0.11 \text{ mg kg}^{-1}$ ) was lower than the Se content standard of Se-enriched tea ( $0.15 \text{ mg kg}^{-1}$ ) (Table 4). In addition, the rate of Se enrichment of tea leaves in Pingli was higher than that of tea leaves in Hanyin and Ziyang (Table 4). Similar to some previously reported results, the Se content in green tea is generally not high (about  $0.1 \text{ mg kg}^{-1}$ ) [9]. The variation of Se content in tea leaves in this study should be caused by the variation of soil Se content for that tea leaves with high Se content ( $1.4 \text{ mg kg}^{-1}$ ) mainly grown in areas with high Se soil [9].

The total Se content of soil in Ankang tea plantations ranged from 0.05 to  $8.04 \text{ mg kg}^{-1}$ , with a large spatial variation of Se content and an average value of  $0.97 \text{ mg kg}^{-1}$  (Table 5). Moreover, according to the ecological landscape threshold of Se in topsoil in China [23], the Se content of 37.5% of the soil samples reached the Se-enriched level ( $0.40\text{--}3.00 \text{ mg kg}^{-1}$ ), and 6.82% of the soil samples had excess Se ( $>3.00 \text{ mg kg}^{-1}$ ), showing a moderate Se content in the Ankang region (Table 5). There were differences in the average Se content among Ziyang ( $1.33 \text{ mg kg}^{-1}$ ), Hanyin ( $1.06 \text{ mg kg}^{-1}$ ), and Pingli ( $0.65 \text{ mg kg}^{-1}$ ), although no significant differences were observed by one-way ANOVA. The percentages of soil Se content in different regions reaching the Se-enriched level are as follows: Ziyang (63.6%) > Pingli (44.1%) > Hanyin (12.5%) (Table 5). Based on Spearman's nonparametric correlation analysis, the Se content of tea leaves was found to be significantly correlated with the soil Se content in the 88 tea plantations (Spearman's  $\rho = 0.449$ ,  $p < 0.01$ ); moreover, there were significant correlations

**Table 3:** Evaluation standard of potential ecological risk indices

Potential ecological risk index of a single element, $E_r^i$	Degree of ecological risk	Comprehensive potential ecological risk index of various elements, $I_R$	Degree of ecological risk
<40	Slight	<150	Minor
[40, 80)	Medium	[150, 300)	Medium
[80, 160)	Strong	[300, 600)	Higher
[160, 320)	Very strong	$\geq 600$	High
$\geq 320$	Extremely strong		

Table 4: Characteristics of Se content in tea leaf samples from different regions

Region	N	Minimum (mg kg <sup>-1</sup> )	Maximum (mg kg <sup>-1</sup> )	Mean (mg kg <sup>-1</sup> )	Standard deviation (mg kg <sup>-1</sup> )	Coefficient of variation (%)	Se enrichment standard (mg kg <sup>-1</sup> )	Se enrichment ratio (%)
Pingli county	34	0.02	1.64	0.27	0.41	150	≥0.15	35.3
Hanyin county	32	0.04	0.31	0.10	0.06	61	≥0.15	15.6
Ziyang county	22	0.04	0.32	0.11	0.07	60	≥0.15	22.7
Ankang city	88	0.02	1.64	0.17	0.27	157	≥0.15	25.0

Table 5: Characteristics of Se content in soil samples from tea plantations in different regions

Region	N	Minimum (mg kg <sup>-1</sup> )	Maximum (mg kg <sup>-1</sup> )	Mean (mg kg <sup>-1</sup> )	Standard deviation (mg kg <sup>-1</sup> )	Coefficient of variation (%)	Se content standard of Se enrichment (mg kg <sup>-1</sup> )	Se content standard of Se excess (mg kg <sup>-1</sup> )	Se enrichment rate (%)	Se excess ratio (%)
Pingli county	34	0.13	2.40	0.65	0.56	86.6	0.4–3.00	>3.00	44.1	0.00
Hanyin county	32	0.05	8.04	1.06	2.06	193	0.4–3.00	>3.00	12.5	9.38
Ziyang county	22	0.31	7.53	1.33	1.79	134	0.4–3.00	>3.00	63.6	13.6
Ankang city	88	0.05	8.04	0.97	1.57	162	0.4–3.00	>3.00	37.5	6.82



**Table 6:** Summary statistics of As, Cd, Cr, Hg, and Pb concentrations in soils from tea plantations

Elements	Maximum (mg kg <sup>-1</sup> )	Minimum (mg kg <sup>-1</sup> )	Mean (mg kg <sup>-1</sup> )	Coefficient of variation (%)	Standard deviation (mg kg <sup>-1</sup> )	Soil background levels of elements in Shaanxi Province, China* (mg kg <sup>-1</sup> )	pH range of tea plantation soil	Screening values for different soil pH segmented ranges**			
								≤5.5	>5.5–6.5	>6.5–7.5	>7.5
As	77.8	2.10	13.4	75.4	10.1	6.42	4.28–7.49	40	40	30	25
Cd	5.90	0.10	0.59	127	0.75	0.09	4.28–7.49	0.30	0.30	0.30	0.60
Cr	181	8.64	83.8	34.6	29.0	61.1	4.28–7.49	150	150	200	250
Hg	0.42	0.01	0.08	72.7	0.06	0.18	4.28–7.49	1.30	1.80	2.40	3.40
Pb	89.5	7.35	26.1	35.9	9.36	20.9	4.28–7.49	70	90	120	170

\* represents the soil background levels of As, Cd, Cr, Hg, and Pb in Shaanxi Province, China; \*\* represents the risk screening values of the Chinese soil environmental quality risk control standard for soil contamination of agricultural land (GB 15618-2018) [23].

between the Se content in tea leaves and soils in tea plantations in Pingli (Spearman's  $\rho = 0.615$ ,  $p < 0.01$ ) and Hanyin (Spearman's  $\rho = 0.507$ ,  $p < 0.01$ ) except Ziyang (Spearman's  $\rho = 0.001$ ,  $p = 0.998$ ). Therefore, results showed that the changes in the Se content in tea plantation soil affected the change in the Se content in tea leaves to a certain extent.

### 3.2 Assessment and analysis of the content status of PTEs in soils and tea leaves in Ankang tea plantations

According to GB15618-2018 [24], 2.27% of the tested soil samples had As and Cr contents higher than the risk screening values but far lower than the risk intervention value; the Cd content of 56.8% of the soil samples was higher than the risk screening values, and 5 of the 88 samples exceeded the risk intervention values; the contents of Pb and Hg did not exceed the risk screening values; moreover, the average contents of As, Cr, Hg, and Pb were all lower, but Cd was higher, than the risk screening values (Table 6). The average contents of As, Cd, Cr, and Pb were 2.09, 6.56, 1.37, and 1.25 times that of the soil background values of Shaanxi Province, China, and the proportion of Cd, As, Pb, Cr, and Hg contents exceeding the background value were 100, 89.8, 83.0, 81.8, and 4.54%, respectively, indicating that in the tea plantation soil of the study area, external factors have led to a high accumulation of Cd, As, Pb, Cr, and Hg, and the accumulated effect of As, Cd, Cr, and Pb was greater (Table 6). In addition, the spatial distribution of As, Cd, and Hg in different tea plantation soils in the study area was quite different, and the spatial distribution of Pb and Cr was relatively uniform [27].

According to NY5244-2004 [25] and NY659-2003 [26], the content of five PTEs of 87 tea leaf samples met the agricultural industry standards NY5244-2004 and NY659-2003; the Cr content in one sample was higher than the standard limit (NY659-2003), exceeding the standard limit by 11.2%. Like other studies have shown [28–31], our results indicated that there were no health hazards to consumers after consuming the tea infusions in this study. Moreover, results indicated that the content of related PTEs in tea leaves in the study area might be affected by the content of PTEs in soil or by other external factors (Table 7). The coefficient of variation values showed that the contents of Cd, Cr, and Hg in tea leaves changed greatly, and the variation range of Pb and As was small.

The soil Cd content significantly correlated with soil As, Cr, Hg, and Pb contents, and there were significant correlations between soil As and Cd or Hg, Cr, and Hg or

**Table 7:** Summary statistics of As, Cd, Cr, Hg, and Pb concentrations in tea leaves from tea plantations

Elements	Maximum (mg kg <sup>-1</sup> )	Minimum (mg kg <sup>-1</sup> )	Mean (mg kg <sup>-1</sup> )	Coefficient of variation (%)	Standard deviation (mg kg <sup>-1</sup> )	Standard values* (mg kg <sup>-1</sup> )
As	0.25	0.04	0.11	35.7	0.04	2.0
Cd	0.31	0.02	0.05	73.9	0.03	1.0
Cr	5.56	0.50	1.36	55.4	0.75	5.0
Hg	0.04	0.00	0.01	54.7	0.01	0.3
Pb	1.02	0.18	0.53	39.2	0.21	5.0

\*represents the Chinese standards for pollution-free tea, including “Pollution-Free Food and Tea” (NY5244-2004) [24] and “Residue limits for chromium, cadmium, mercury, arsenic and fluoride in tea” (NY659-2003) [25].

**Table 8:** Correlation analysis of As, Cd, Cr, Hg, and Pb contents between tea leaves and soils in tea plantations

Elements in soils	Elements in soils					Elements in tea leaves				
	As	Cd	Cr	Hg	Pb	As	Cd	Cr	Hg	Pb
As	1.000					-0.015	0.14	-0.02	0.048	0.007
Cd	0.484**	1.000				0.024	0.345**	-0.116	-0.064	-0.044
Cr	0.159	0.481**	1.000			-0.146	0.017	0.018	-0.316**	-0.216*
Hg	0.631**	0.700**	0.467**	1.000		-0.001	0.128	-0.006	-0.116	-0.004
Pb	0.181	0.231*	0.453**	0.271*	1.000	-0.065	0.029	0.126	-0.174	-0.126

\*\* represents the correlation was significant at the 0.01 level ( $p < 0.01$ ); \* represents the correlation was significant at the 0.05 level ( $p < 0.05$ ).

Pb, and Hg and Pb ( $p < 0.05$ ) (Table 8), showing that Cd, Pb, Cr, and As in soil might have similar sources, and presenting a complex pollution phenomenon accompanied by each other. It could be seen from the correlation analysis that the Cd content in tea leaves significantly correlated with the soil Cd content ( $p < 0.01$ ), but there were no significant correlations between As, Cr, Hg, and Pb in tea leaves and their respective contents in the soil. For soil pH and redox potential can affect the absorption of related components in the soil by tea plants, thus it could not simply determine that these PTEs in tea leaves were not affected by PTEs in soil. The soil pH of the tested tea plantations ranged from 4.28 to 7.49, with an average value of 5.50. If the pH was reduced, the amount of insoluble state to easily soluble state would increase, which would increase the PTE content in tea plants. Moreover, in this study, it might be affected by the pH value, and the content of soluble Cd in soil increased, which increased the content of Cd in tea leaves [18].

### 3.3 Comprehensive assessment of the ecological risks of PTEs in Ankang tea plantations

The average potential ecological risk indexes of As, Cr, Hg, and Pb were all less than 40, while the average potential

ecological risk index of Cd and its highest value were significantly greater than 40, indicating that the ecological risk degrees of Cd were higher, and As, Cr, Hg, and Pb showed low risk (Table 9). In addition, the highest value of potential ecological risk index for As and Hg was greater than 40, while that for Cr and Pb was less than 40, indicating that As and Hg also had certain contribution to the total potential ecological risk of the Ankang tea plantation area. The highest value of the comprehensive potential ecological risk index for As, Cd, Cr, Hg, and Pb in the soil of the Ankang tea plantation area was  $2.16 \times 10^3$ , the lowest value of that was 40.6, and the average value of that was 244, indicating that the Ankang tea plantation area was generally at a moderate potential ecological risk level (Table 9).

In recent years, significant antagonism was found between Se and trace elements such as As, Hg, Cd, and Sb in the soil–rice system [32,33], and this phenomenon was also observed in vegetables [34] and fruits [35]. However, there is no relevant research report on whether Se can reduce the accumulation of toxic elements in tea plants, thereby reducing its health risk. In this study, the soil sampling points in Ziyang, Hanyin, and Pingli were distributed in the high Se background area, and Se in the soil mainly came from the carbonaceous shale in the black rock series [14,15,36]. Moreover, consistent with the



Table 9: Statistical analysis of the ecological risk index of soil As, Cd, Cr, Hg, and Pb

Elements	Highest value of potential ecological risk index of single element, $E_{r,Max}^i$	Lowest value of potential ecological risk index of single element, $E_{r,Min}^i$	Average value of potential ecological risk index of single element, $E_{r,Mean}^i$	Highest value of comprehensive ecological risk index of various elements, $I_{R,Max}$	Lowest value of comprehensive potential ecological risk index of various elements, $I_{R,Min}$	Average value of comprehensive potential ecological risk index of various elements, $I_{R,Mean}$
As	121	3.27	20.9	$2.16 \times 10^3$	40.6	244
Cd	$1.97 \times 10^3$	32.7	197			
Cr	5.91	0.28	2.74			
Hg	92.9	2.60	17.6			
Pb	21.4	1.76	6.24			

characteristics of black rock series widely distributed in other regions of China, the bioavailability of Cd in the soil of the Ankang tea plantation area should be high and therefore the risk of Cd enrichment in crops should be very large [37,38]. However, in this study, although the Cd content in tea leaves significantly correlated with the soil Cd content and the average soil Cd content significantly exceeded the Chinese risk screening value for soil contamination of agricultural land (GB 15618-2018), the Cd content in the tea leaves still met the Chinese standard of pollution-free tea. Our conclusions suggested that tea plants grown in the Se-enriched tea plantations seemed to reduce the accumulation of Cd content. Furthermore, investigation found that the Se-rich soil in the black rock series inherited the characteristics of high Se and Cd content and led to Se enrichment and excessive Cd content in agricultural products; however, there was no mass disease in local residents for a long time and showed the characteristics of strong physique, high Se content in hair, low Cd content in hair, and more long-lived elderly people [39]. These research results provide new ideas and new opportunities for the in-depth development of Se-rich soils in the black rock series.

### 4 Conclusions

This study first presented the content characteristics of Se and five PTEs (As, Cd, Cr, Hg, and Pb) in soils and tea leaves in 88 tea plantations in the Ankang tea planting area, a typical black shale area, where black shales contained toxic elements. We found that although Cd pollution in tea plantation soil posed high ecological risk, the quality of tea across the Ankang tea planting area was generally good. The Se enrichment rate of tea leaves was 25%, and except one tea leaf sample, all samples met the limitation of the Chinese standards for pollution-free tea. The average contents of five PTEs, apart from Cd, in tea plantation soils were lower than their risk screening values in China. Meanwhile, Hakanson potential ecological risk assessment indicated that the ecological risk degree of Cd was very strong and that of As, Cr, Hg, and Pb was slight, and the Ankang tea plantation area was at a moderate potential ecological risk level. Results suggest that tea plants grown in the Se-enriched tea plantations reduced the accumulation of Cd content. These research results are very helpful for a deeper understanding of the ecological risk status of the local tea plantation area and provide new ideas for the in-depth development of Se-rich soils in the black rock series.

**Funding information:** This study was funded by the Natural Science Basic Research Program of Shaanxi (Program No. 2022JQ-245) and was supported by the Shaanxi Public Welfare Special Project of geological prospecting (Program No. 201908).

**Author contributions:** Pingxuan Lin designed the protocol and outlines of this study. Jiping Chen performed the sampling and mapping work. Huawei Ji performed the statistical analysis, drew the figures, and wrote this article. Hui Wang reviewed this manuscript. Rui Ren and Aorui Li performed the sampling work. All authors discussed and approved the included results.

**Conflict of interest:** Authors state no conflict of interest.

**Ethical approval:** The conducted research is not related to either human or animal use.

**Data availability statement:** All data generated or analyzed during this study are included in this published article.

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