Ecological Risk Evaluation and Source Identification of Purple Soil in an Intensive Agricultural Area in Southwest China based on Pb Stable Isotopes

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Abstract. Purple soil is a crucial resource for agricultural development in Southwest China. Using the national background values for purple soil, coupled with the potential ecological risk index and IsoSource software, the potential ecological risks and Pb stable isotope characteristics of eight heavy metals (Hg, Cd, As, Pb, Cu, Ni, Cr, and Zn) were analyzed in purple soil samples, parent material, organic fertilizer, and fish pond sediment from an intensive agricultural area in eastern part of Sichuan Province, China. The results showed that the average concentrations of Hg, Cd, As, Pb, Cu, Ni, Cr, and Zn in the soil were 0.062 mg/kg, 0.26 mg/kg, 10.02 mg/kg, 25.85 mg/kg, 30.17 mg/kg, 36.88 mg/kg, 75.84 mg/kg, and 91.69 mg/kg, respectively, all exceeding the national background values for purple soil in China. The potential ecological risks associated with Cd and Hg was classified as slight to moderate. Pb isotope indicated that the contribution of heavy metals from parent material and rock ranged from 33.3% to 48.8%, while agricultural activities accounted for 51.2% to 66.7%. These findings provide a solid foundation for developing strategies to control heavy metal pollution in the intensive agricultural production of purple soil.

Keywords: Intensive planting, Purple soil, Lead stable isotope, Source identification.

1 Introduction

Intensive agricultural production, which concentrates a large number of production inputs on relatively small land areas to achieve high yields and substantial income, has significantly improved economic returns. However, this approach can also lead to various soil quality issues, such as soil pollution, salinization, and soil compaction [1]. These soil quality problems, including particularly acidification, salinization, and nutrient imbalances, are frequently observed in regions of intensive agriculture due to

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the repeated cycles of production. Furthermore, long-term soil amendment practices, including the continuous application of feed and fertilizers, have resulted in a substantial accumulation of heavy metals in the soil [2]. The high toxicity, non-degradability, and bioaccumulation of heavy metals in soil have attracted significant attention. Consequently, assessing the extent of heavy metal pollution in soil and identifying the sources of these pollutants has become a primary focus of research efforts [3].

The study area with abundant purple soil resources located on the eastern edge of the Sichuan Basin. The region experiences a subtropical humid monsoon climate, characterized by warm temperatures, ample sunshine, and substantial rainfall, with an annual precipitation ranging between 1,100 and 1,200 mm. As a fertile soil resource, purple soil plays a significant role in various industries, including grain, oilseeds, vegetables, and fruits. In Southwest China, the use of purple soil for traditional farming and intensive agricultural practices has been steadily increasing [4]. However, the shallow development layer of purple soil, its limited resistance to erosion, and its vulnerability to nutrient depletion increase the risks of soil degradation and pollution under intensive agricultural practices [5].

The study area selected is an intensive agricultural production region in eastern part of Sichuan Province, China, where purple soil is prevalent. To the west of the region, key production areas include open-field vegetable farming, greenhouse cultivation, and fruit orchards, spanning approximately 1.52 km^2. On the eastern side, there is a fishpond and rice-fish breeding area covering about 0.42 km^2. Additionally, several small-scale livestock farms primarily raise pigs, chickens, and ducks (Figure 1). Through the collection and analysis of soil samples and environmental samples such as soil parent material, fertilizers and fish pond sediment, this study attempted to explore the ecological risks of soil heavy metals such as As, Cd, Cu, Cr, Hg, Ni, Pb, and Zn in the study area, and to explore the indicative significance of Pb stable isotope source analysis in the sources of heavy metals in soils in this area. This study is helpful to understand the heavy metal pollution status of soil in the intensive agricultural production in purple soil areas, and provide basic data for the protection of purple soil resources.

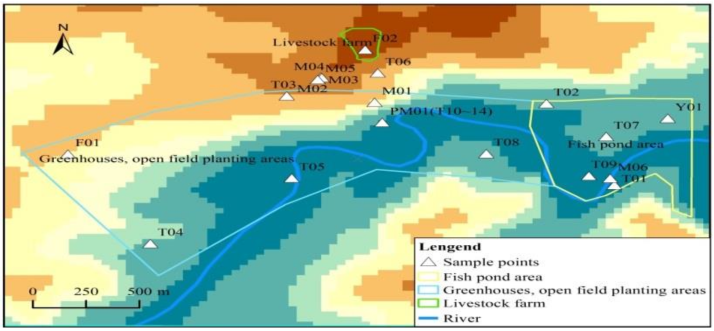

Fig. 1. Location of soil and environmental media sampling sites in the study area ("T" - the soil, "M"- parent material sample, "F"- the fertilizer, "Y" - the fish pond mud sample, and "PM" - the profile)

2 Materials and Methods

2.1 Sample Collection and Experimental Analysis

This intensive agricultural production area was relatively far from the main road, and there were few industrial and mining activities nearby. The purplish-red terrigenous clastic rock weathering in the Jurassic Shaximiao Formation, river alluvial deposits, the bottom of the fish pond returns to the field, and agricultural cultivation were important sources of soil heavy metals. A total of 24 samples of various types were collected, including 14 surface soil and soil profiles samples, 6 rocks and river sediments (parent material), 2 fertilizer samples, and one fish pond sediment (Figure 1). The sampling process complied with the requirements of the Specification of Land Quality Geochemical Assessment (DZ/T0295-2016).

Soil and sediment samples were digested using a tetra-acid solution of HNO_3, $HClO_4$, HCl, and HF. The concentrations of Hg and As in the soil samples were determined by atomic fluorescence spectrophotometer (AFS-3100, China). The contents of Ni, Cd, Cu, Cr, Zn and Pb were determined by inductively coupled plasma mass spectrometer (ICP-MS, XSeries, USA). Soil pH was determined by glass electrode method. National standard substances (GSS17, GSS18, GSS28) were used for quality control of the data and tests. The measurement errors were less than 10%, which meet the quality requirements specified in the Analysis Method for Regional Geochemical Sample (DZ/T0279-2016). The Pb isotope was determined by multi-receiver inductively coupled plasma mass spectrometer (Neptune Plus, Germany). The standard material NBS981 was used to monitor the operational state of the mass spectrometer. The standard material was tested 27 times, and the average error of $^{207}Pb/^{206}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, and $^{206}Pb/^{204}Pb$ were all within twice the standard deviation, indicating that the experimental results were accurate and reliable.

2.2 Potential Ecological Risk Index

The Potential Ecological Risk Index (PERI) is an indicator used to assess the potential impact of a hazardous substance or element on an environmental ecosystem. It typically considers factors such as toxicity, background values, and bioavailability of evaluation indicators to determine their potential harm to the environment [6]. The formula for its calculation formula is as follows:

$$E_r^i = T_r^i \times (C_d^i / C_l^i) \tag{1}$$

$$PERI = \sum_{i=1}^{n} E_r^i \tag{2}$$

where, E_r^i is the single-factor pollution degree of element i. C_d^i represents the test value of element i (mg/kg). C_l^i is the background value of the heavy metal element i, and T_r^i is the toxicity coefficient of the heavy metal. The toxicity coefficients of different heavy metals are follow: Hg (40) > Cd (30) >As (10) >Pb (5) = Cu (5) = Ni (5) > Cr (2) > Zn (1). The Potential Ecological Risk Index (PERI) represents the total hazard coefficients of all heavy metal elements at a specific location.

2.3 Pb Stable Isotope Source Analysis

Compared to lighter isotopes commonly found in nature, Pb isotopes have larger atomic mass numbers and exhibit less pronounced fractionation. As a result, various sources typically maintain distinct isotopic compositions, even under secondary environmental conditions. This unique isotopic fingerprint forms the theoretical basis for tracing pollution sources in the environment [7]. In this paper, the quantitative analysis of Pb stable isotope pollution sources is conducted using IsoSource software. While IsoSource is traditionally employed to quantify dietary sources and proportions in animals based onδ13C and δ15N values, it has recently been applied to estimate the contribution rates of pollution sources in soils [8]. The calculation is shown in the following formulas:

$$\delta_{\text{soil}} = f_1 \times \delta_1 + f_2 \times \delta_2 + \cdots + f_n \times \delta_n \tag{3}$$

$$1 = f_1 + f_2 + \cdots + f_n \tag{4}$$

where, δ_{soil} and δ_{n} represent the Pb isotope ratios of soil samples and potential sources. f_n is the contribution rate of the n potential pollution source.

2.4 Statistical Analysis

Statistical summary and correlation analyze were conducted using Microsoft Excel 2016 and IBM SPSS 26. ArcGIS 10.4 and CorelDRAW 2018 were used to modify the terrain features and sample maps of the study area.

3 Results and Discussion

The soil pH varied from 4.7 to 8.4, with a mean value of 7.3. Samples with a pH greater than 6.5 accounted for 86% of the total samples, indicating the soil in the study area was slightly alkaline to neutral (Table 1). The average concentrations and standard deviations of Hg, Cd, As, Pb, Cu, Ni, Cr, and Zn in the soil were measured at 0.062 ± 0.032 mg/kg, 0.26 ± 0.11 mg/kg, 10.02 ± 4.93 mg/kg, 25.85 ± 2.81 mg/kg and 30.17 ± 3.25 mg/kg, 36.88 ± 5.59 mg/kg, 75.84 ± 5.23 mg/kg, and 91.69 ± 10.88 mg/kg.

Table 1. Background values and parameters of heavy metals and soil pH in the study area

	pH	Hg	Cd	As	Pb	Cu	Ni	Cr	Zn
Max	8.4	0.140	0.51	15.70	32.40	35.70	43.50	87.00	107.00
Min	4.7	0.030	0.08	3.55	22.40	22.00	28.10	68.20	72.20
Mean	7.3	0.062	0.26	10.02	25.85	30.17	36.88	75.84	91.69
SD	1.06	0.032	0.11	4.93	2.81	3.25	5.59	5.23	10.88
Chinese purple soil background value [9]	-	0.0326	0.0752	8.4	25.8	24.6	28.1	60.6	77.5

Note: The unit of heavy metal content was mg/kg; pH has no dimension.

The average concentrations of Cd and Hg in the soil were 3.46 times and 1.90 times higher than the background values for Chinese purple soil, respectively. Additionally, the average concentrations of As, Pb, Cu, Ni, Cr, and Zn were marginally elevated compared to their respective background values in purple soil. According to the Soil Environmental Quality Standard for Soil Pollution Risk Management and Control of Agricultural Land (GB 15618-2018), heavy metal concentrations in most soils were within acceptable risk screening levels; only two samples of Cd exceeded these prescribed limits. The contents of heavy metal in the soil profile of the study area showed a consistent trend in the variation (Figure 2). Notably, there was a significant accumulation in the topsoil, which might indicate similar evolutionary patterns of elements or anthropogenic influences within the soil strata.

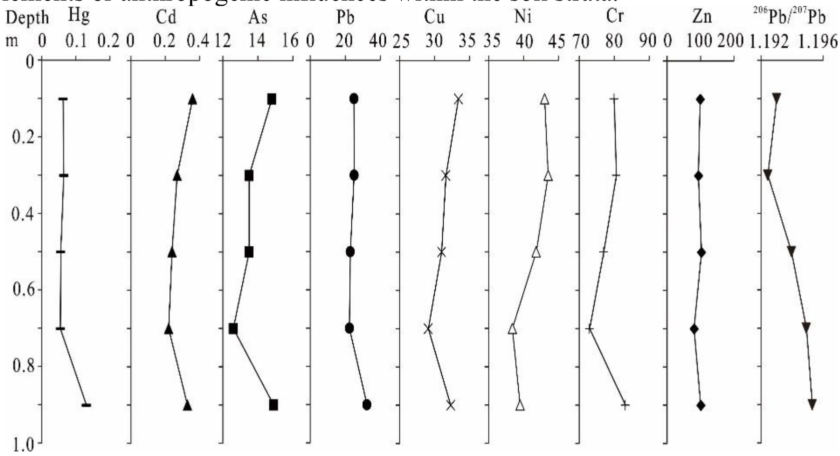

Fig. 2. Metal concentrations and Pb isotope signatures of the soil profile

Correlation analysis is a method used to identify the sources of heavy metals in soil and to examine the relationships between various pollutants. The results of the correlation between heavy metals in soil samples from the study area (Table 2) indicated a significant positive correlation among the concentrations of As, Cu, Ni, Cr, and Zn. Conversely, the Pb content had a weak correlation with the concentrations of As, Cu, Ni, Cr, and Zn and had a significant positive correlation with the concentrations of Cd and Hg. The high correlations might suggest that the distribution and sources of the heavy metals were similar and related. Furthermore, some studies have indicated that under long-term agricultural conditions, the concentrations of heavy metals such as Cd, Hg, Pb, and As in purple soil have increased significantly.

Table 2. Correlation between heavy metal contents of the soil samples (n=14)

	Hg	Cd	As	Pb	Cu	Ni	Cr	Zn
Zn	1							
Cd	0.765**	1						
As	0.660*	0.644*	1					
Pb	0.808**	0.593**	0.240	1				

Cu	0.318	0.390	0.649*	0.149	1			
Ni	0.326	0.434	0.860**	-0.028	0.675**	1		
Cr	0.393	0.406	0.731**	0.329	0.537*	0.792**	1	
Zn	0.630*	0.741**	0.727**	0.403	0.745**	0.714**	0.566*	1

Note: ** P < 0.01; * P < 0.05

The Potential Ecological Risk Index (PERI) was employed to evaluate the potential ecological risks associated with heavy metals in the soil within the study area (Table 3). The average values of the single-factor pollution degree (E_r^i) for Pb, As, Cr, Cu, Ni, and Zn in the soil were 5.01, 11.93, 2.50, 6.13, 6.56, and 1.18, respectively, indicating a low potential ecological risk (< 40). Conversely, the average values of the single-factor pollution degree for Cd and Hg were 104.86 and 75.63, respectively. The proportions of soil samples with low (< 40), medium (80 ~ 160) and strong potential ecological risk (160 ~ 320) for Cd were 21.43%, 71.43%, and 7.14%, respectively. The number of soil samples with low, medium, strong, and very strong potential ecological risk (> 320) for Hg accounted for 14.29%, 64.29%, 14.29%, and 7.14% of the total samples, respectively. The calculation of the Potential Ecological Risk Index (PERI) revealed that 21.43% of the samples had no potential ecological risk (< 150), 64.29% presented a low potential ecological risk (150 ~ 300) and 14.28% had a moderate potential ecological risk (300 ~ 600), indicating that the heavy metals in the soils of the region had a low to moderate potential ecological risk. Consistent with the results of previous studies, the accumulation of heavy metals such as Cd and Hg is a significant pollution factor in cultivated soils, which is related to the application of agricultural and chemical fertilizers in agricultural activities [10].

Table 3. Evaluation of potential ecological risk index of the soil heavy metals

Sample ID	E_r^i								*PERI*
	Pb	As	Cd	Cr	Cu	Hg	Ni	Zn	
T01	5.95	17.98	203.46	2.41	6.18	171.78	6.48	1.38	415.61
T02	4.50	16.19	111.70	2.56	6.59	63.80	7.72	1.25	214.31
T03	5.12	4.33	95.74	2.25	6.59	52.76	5.04	1.12	172.94
T04	5.27	5.50	111.70	2.51	4.47	60.12	5.45	0.98	195.99
T05	5.43	18.69	151.60	2.87	7.26	85.89	7.74	1.37	280.84
T06	4.88	4.26	119.68	2.29	5.67	51.53	5.77	1.21	195.30
T07	4.81	6.85	39.096	2.32	5.43	49.08	5.00	0.93	113.51
T08	4.52	6.46	36.702	2.40	5.75	39.26	5.71	1.05	101.86
T09	4.90	4.23	31.915	2.43	5.94	36.81	6.28	1.12	93.62
T10	4.85	17.62	143.62	2.64	6.79	76.07	7.65	1.28	260.52
T11	4.86	16.07	107.71	2.66	6.42	78.53	7.74	1.21	225.21
T12	4.44	16.07	95.74	2.54	6.30	67.49	7.44	1.33	201.35
T13	4.34	15.00	87.77	2.41	5.92	66.26	6.83	1.04	189.56
T14	6.28	17.74	131.65	2.75	6.57	159.5	7.03	1.30	332.82

Lead-206 (206Pb), which has a relatively light mass, is more abundant in natural sources. Consequently, natural and anthropogenic samples will display distinct end-member characteristics in the Pb isotope diagram (Figure 3) [11]. The results showed that the ratios of 206Pb/207Pb and 208Pb/206Pb in the rock or soil parent material within the study area ranged from 1.164 to 1.187 and from 2.096 to 2.126, respectively (Table 4). These sample points were situated at the lower right end of the Pb isotope diagram. The point from the fishpond sediment was located at the upper left corner of the Pb isotope diagram, with the ratios of 206Pb/207Pb and 208Pb/206Pb of 1.196 and 2.079, respectively. The fertilizer samples had the ratios of 206Pb/207Pb and 208Pb/206Pb ranging from 1.174 to 1.175 and from 2.091 to 2.110, respectively, indicating a tendency towards the natural end-member.

The ratios of 206Pb/207Pb and 208Pb/206Pb in the intensive agricultural soils of the study area ranged from 1.172 to 1.195 and from 2.081 to 2.115, with averages of 1.185 and 2.095, respectively (Table 4). All soil samples in the study area were situated between the end-member mixing lines of anthropogenic sources and natural background levels. The isotopic characteristics of Pb in the agricultural soil profile (Figure 2) showed that the 206Pb/207Pb ratio gradually decreased with shallower soil layers, indicating that surface soil heavy metals were more susceptible to human activities, such as agricultural cultivation.

Table 4. Pb isotopic contents in the soil samples and environmental media of the study area

Sample		$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$	$^{206}Pb/^{207}Pb$
Soil samples (*n*=14)	Min	18.338	15.634	38.726	2.081	1.173
	Max	18.742	15.680	39.019	2.115	1.195
	Mean	18.578	15.663	38.893	2.094	1.186
Soil parent material (*n*=6)	Min	18.151	15.592	38.586	2.096	1.164
	Max	18.586	15.656	38.955	2.126	1.187
	Mean	18.446	15.637	38.785	2.103	1.180
Fertilizer samples	F01	18.383	15.639	38.783	2.110	1.175
	F02	18.370	15.653	38.414	2.091	1.174
Fishpond sediment	Y01	18.758	15.681	39.001	2.079	1.196
	[11]	18.619~19.65	15.638~15.79	38.779~39.86	2.022~12.08	1.191~1.24

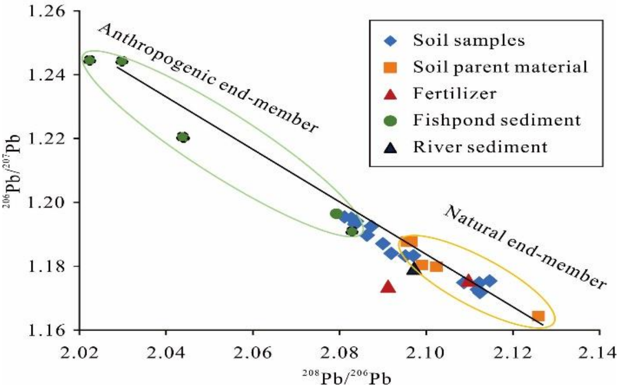

Fig. 3. Comparison of Pb isotopic contents between s the soil samples and environmental media in the study area (The dashed data are from the literature [11])

The contributions of soil Pb calculated using IsoSource software, indicated that natural sources, such as parent material or rock, contributed between 33.3% and 48.8% (Figure 4). Agricultural fertilization accounted for between 34.9% and 45.0%, while fishing ponds contributed between 6.1% and 31.8%. Notably, the contribution ratios from anthropogenic sources accounted for 51.2% to 66.7% of the total soil Pb. Purple soil, a primordial type formed from terrestrial clastic rocks over a relatively short period, exhibits significant inheritance from its soil-forming parent material or parent rock [4]. However, Pb isotopes revealed a substantial proportion of anthropogenic contributions to Pb sources in the soil of the study area, which is characterized by intensive agricultural production. This finding underscores the considerable impact of intensive agricultural practices on the accumulation of heavy metals in the soil.

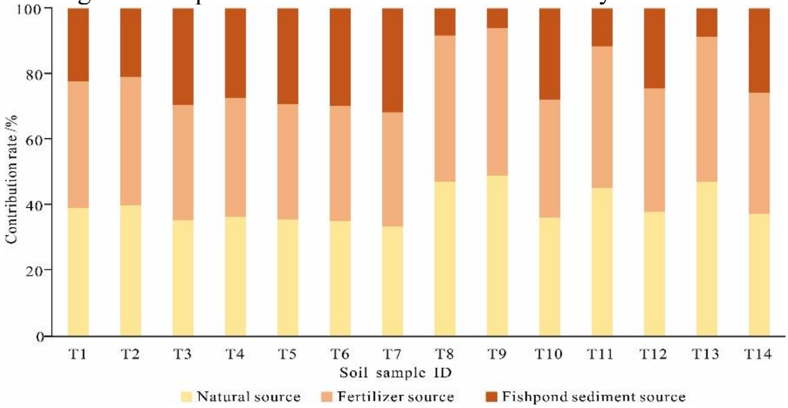

Fig. 4. Contribution rate of main pollution sources to each soil sample based on Pb isotope in the study area

4 Conclusion

The average concentrations of Hg and Cd in the soil samples were higher than the background levels of Chinese purple soil. The Potential Ecological Risk Index indicated that both Cd and Hg posed slight to moderate potential ecological risks, with proportions of 7.14% and 21.43%, respectively. Pb isotope analysis revealed that the sources of heavy metals in these intensively farmed soils were closely associated with natural weathering processes and agricultural practices. The contribution rates from soil parent material and rock ranged from 33.3% to 48.8%, while agricultural activities accounted for an accumulation rate of heavy metals ranging from 51.2% to 66.7%.

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