

ENVIRONMENTAL BACKGROUND VALUES DETERMINATION AND KEY ENVIRONMENTAL CONTROLS OF PB AND ZN IN SOILS OF MOUNTAINOUS PLATEAU WATERSHED: THE BIJIANG BASIN (SW CHINA)

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Abstract. The fragmented and complex topography of mountainous plateau basins resulted in significant regional differences at the watershed scale in soil physicochemical properties, soil texture and soil types, etc. Due to the large watershed range, high altitude, and high sampling difficulty, there was relatively little research on the background values of soil environment in mountainous plateau areas. The purpose of this study was to determine the environmental background values of soil and explore the main environmental controls for the Bijiang Basin in Southwest China. The environmental background value of soil Pb and Zn in the Bijiang River Basin was 30.73 mg·kg⁻¹ and 64.85 mg·kg⁻¹, respectively. The value was mainly affected by altitude, soil type, pH and organic matter. The research results had certain reference value for the selection of background values for regional pollution assessment on soil or sediment in mountainous areas.

Keywords: *environmental background values, mountainous plateau watershed, Lead-zinc mine, redundancy analysis, Bijiang River Basin*

Introduction

The soil environmental background value refers to the chemical composition content and structural characteristics of soil that has not been significantly impacted by human activities or has been minimally disturbed (Meng et al., 1983; Wang et al., 2007; Sheng et al., 2009; Coppola et al., 2010). The determination and research of soil background values serve as fundamental data for soil environmental protection. They provide an important basis for studying the migration and transformation of pollutants in soil, evaluating and predicting soil quality (Zhang et al., 2012; Sanjeevani et al., 2015), and offering valuable information for the control and management of regional soil resources.

The issue of heavy metal pollution caused by metal mining activities and its environmental hazards has gained significant attention in the past few years. Soil serves as an important medium for the accumulation and enrichment of heavy metals (Ye et al., 2019). As a result, numerous studies have focused on evaluating heavy metal pollution in soil under the influence of lead-zinc mining. The index method, including the potential ecological hazard index method, land accumulation index method, pollution load index, among others, has been widely used in these studies (Zhang et al., 2017; Gu et al., 2018; Kumar et al., 2019; Ye et al., 2019). These methods are based on environmental background values. However, the lack of a unified standard for selecting background values led to variations in the evaluation of results.

The potential ecological risk index method generally adopts the average values of deep soil or sediments at the watershed or provincial regional scale as background values

(Zhang et al., 2019; Wu et al., 2021). On the other hand, the geo-accumulation index typically employs the shale standard value, which was proposed as background value (Turwkian et al., 1961). However, many scholars have used national soil environmental standard values or the soil background values specific to their respective provinces and regions (Teixeira et al., 2019; Zhao et al., 2020; Liu et al., 2022). Due to the complex terrain and high altitude of mountainous regions, it is difficult to obtain soil samples. Therefore, there is relatively little research on the background values of heavy metal environment in soil of mountainous watershed. For mountainous regions, soil background value at the provincial level was used for assessing soil heavy metal pollution (Zhang et al., 2019; Shen et al., 2023). However, the range of soil background values at the provincial and municipal levels is relatively large, which lacks representativeness at the watershed or regional scale, and which could lead to the problem of whether the research method of background values at the large scale is suitable for the medium and small scale (Wang et al., 2010). Therefore, many researchers have done relevant research on the soil environmental background values at the watershed scale (Huang et al., 1985; Xiong et al., 2006). For example, the background values of different soil types were significantly different, and the background values were greatly disturbed by human activities in the Henan section of the Yellow River Basin, China (Sheng et al., 2009). Different areas have different environmental backgrounds (Wang et al., 2018). Therefore, it is of great significance for local environmental management to carry out the study of soil environmental background values at the watershed scale, especially for high-altitude mountainous areas.

The main factors affecting the background value of soil environment include soil type, soil parent material, topography, land use, vegetation type, soil texture and soil physical and chemical properties (organic matter, pH, etc.) (Xia, 1986; Salminen et al., 1997). The background value of soil has a great relationship with the parent material of soil formation. Even if the soil type is the same, the difference of parent material has a great impact on the background value of elements. Soils with the same element developed on different parent materials have different levels of background content (Beygi et al., 2018). In addition, climate, precipitation, topography and temperature have a certain influence on the content of soils (Jiang et al., 2018). Among them, climate mainly affects hydrothermal status of the soil and the transformation and migration of various elements in the soil through temperature and precipitation (Ding et al., 2017). Topography affects soil moisture status by controlling the surface runoff, and then affects the redistribution of soil material and energy through topographic slope and aspect (Xu et al., 2017; Yang et al., 2018). Meanwhile, the background values of different metals are significantly different, which may depend on their mobility (Liao et al., 2022).

The Bijiang River is a mountain river and merges into the main stream of the Lancang River in southwest China. The Lanping Pb/Zn mine is the largest lead-zinc mine in Asia, and the Bijiang River is the mainly receiving water body in the basin, so its ecological environment changes directly relate to the water quality safety of cascade reservoirs in the middle reaches and lower reaches of the Lancang River. Long-term mining activities caused the presence of heavy metal pollution along the river. Specifically, the soil, water and sediment in the basin were seriously polluted by Pb and Zn (Zhao et al., 2012; Wen et al., 2015). In recent years, the index method is frequently used in the evaluation of soil heavy metal pollution at a watershed scale, and the selected background values are mostly the national secondary standard limit values

(Huang, 2018), and the arithmetic mean of soil background values or the content of heavy metals in the soil not affected by industrial activities and mining activities in upstream areas in Yunnan Province as the reference values (Zhao et al., 2012). Therefore, research on soil environmental background values at the scale of the Bijiang River Basin is relatively scarce.

Taking into consideration the absence of environmental background values and the significance of lead and zinc in environmental research, especially in assessing soil pollution influenced by lead-zinc mining, we focused on the Bijiang Basin affected by lead-zinc mines in Southwest China. The purpose of our study was to (1) calculate the environmental background values of soil at the watershed scale; (2) explores main environmental controls on the environmental background values.

Materials and methods

Study area

This study was performed on the Bijiang River (99°13'~99°36'E, 25°28'~26°41'N), a middle tributary of the Lancang River. The landform of Bijiang River Basin belongs to the middle part of Hengduan Mountains in western Yunnan, China, which is a plateau canyon landform. The landform and terrain of the watershed are fragmented and complex, presenting characteristics such as undulating mountains, steep slopes, deep rivers, and significant differences in elevation. The landform of the basin mainly includes denuded gentle slope landform of middle and low mountains, eroded steep slope landform of middle mountains and erosional accumulation landform. The upper reaches of the river basin are located in Lanping County (*Fig. 1*). In *Figure 1*, the map review number of China is GS (2024) 0650. The distribution of yearly precipitation is uneven, which was mainly from June to October of the year. The distribution of surface runoff is similar to that of precipitation, mainly in flood season, accounting for 70% ~ 80% (Chen et al., 2013).

Samplings

The principle of sampling soil environmental background value is mainly to avoid obvious anthropogenic pollution sources such as roads, residential areas, pollution sources and industrial areas. In addition, regional differences lead to certain regional and differential sampling of soil environmental background values (Cappuyns et al., 2014; Wang et al., 2018). The Bijiang River Basin covers a large area, and the selection of sampling points for soil environmental background values basically takes into account three factors, as for the main types of soil forming parent materials representing the local area, the main soil type representing the local area, and the distance from known pollution sources.

In April 2016, soil samples were collected on a 7 km × 7 km grid, mainly collecting subsurface soils (0-20 cm) on the left and right banks of the Bijiang River Basin that are far away from the mining area or have not been significantly affected by human interference. Symmetrical sampling was conducted on the left and right banks, with a total of 78 soil samples collected (*Fig. 1*). Each sample point will remove surface animal and plant debris, gravel, and dead branches and leaves, while removing surface soil near the shovel to prevent pollution caused by the shovel itself. Collect 3-5 samples around it and mix them into a bag, weighing approximately 1 kg. After sample collection, employ

GPS to record the longitude and latitude information of the sample points, assign numerical identifiers, and duly document them. Subsequently, seal and label the gathered soil samples before transporting them to the laboratory for further processing.

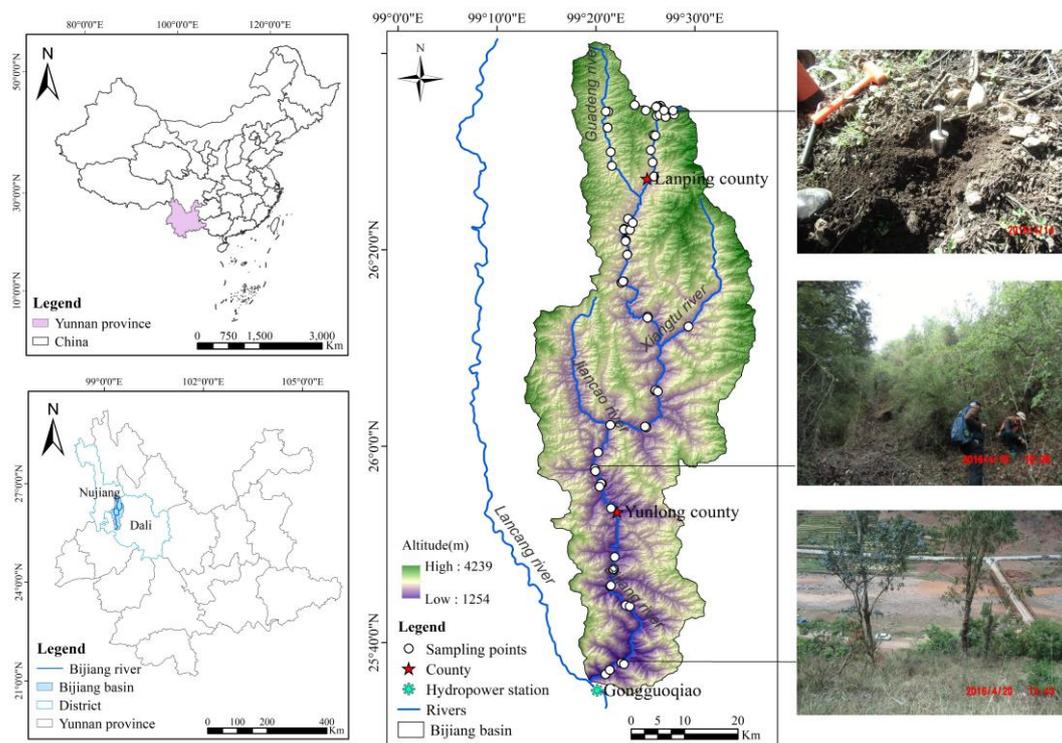


Figure 1. Schematic diagram of the location of sampling sites and the Bijiang River Basin

Laboratory analysis

For the determination of soil pH, the soil samples were passed through a 100-mesh sieve and set aside for further use. Approximately 10 g of the sieved soil was placed in a 25 mL beaker, to which 10 mL of CaCl_2 solution was added. The mixture was stirred and allowed to stand for 30 min. The pH of the resulting suspension was measured using a calibrated pH meter.

Soil organic matter content was measured using the dichromate oxidation method. Before testing, soil samples were passed through a 100-mesh sieve. Approximately 10 g of the sieved soil was weighed for analysis. The soil organic matter was oxidized using an excess of standardized potassium dichromate in sulfuric acid solution at a temperature range of 170°C to 180°C. The remaining potassium dichromate was then titrated with ferrous sulfate solution. The organic matter content was calculated based on the amount of dichromate consumed (Bao, 2000).

The measurements for pH and organic matter were conducted by the Nanjing Institute of Soil Science, Jiangsu Province, China. All results were corrected using blank and parallel samples to ensure a relative standard deviation (RSD) within 5%.

Environmental parameters

This paper utilizes the soil type map (1:750,000) compiled by the Nanjing Institute of Soil Research, Chinese Academy of Sciences. The topographic data utilized in this study

encompass fundamental terrain attributes, including slope, plane curvature, and section curvature, which were directly extracted from the Digital Elevation Model (DEM) of the Bijiang River Basin using ArcGIS 10.2. The DEM accuracy used in this article is 20 meters for vertical accuracy and 30 meters for horizontal accuracy. Additionally, derived terrain attributes such as slope aspect, relative elevation, roughness, relief amplitude, terrain humidity index, sediment power index, topographic wetness index and sediment transport index were calculated. This process involved depression filling of the DEM data, followed by the extraction of slope gradient and slope aspect, and the calculation of river direction and flow accumulation. The topographic wetness index has been used to study the impact of spatial scale on hydrological processes, which in turn affects the accumulation of soil elements (Rong et al., 2017), which was derived from the index of Beven and Michael (1979) by *Equation 1*.

$$TWI = \ln \left(\frac{A_s}{\tan \beta} \right) \quad (\text{Eq.1})$$

where TWI is the topographic wetness index. A_s is the unit catchment area, $\text{m}^2 \cdot \text{m}^{-1}$. β is the slope gradient (degrees), assign a minimum value of 0.0001 to grids with slope of 0.

The sediment power index (SPI) describes the spatial distribution of runoff's ability to transport sediment (Gokceoglu et al., 2005). Theoretically, a higher SPI indicates a greater potential for water flow to erode the surface, which in turn affects soil element accumulation. The calculation formula is shown as *Equation 2*.

$$SPI = A_s \tan \beta \quad (\text{Eq.2})$$

The sediment transport index (STI) describes erosion and deposition processes (Moore et al., 1993). Theoretically, a higher STI indicates greater capacity for sediment transport by water flow, which can lead to increased soil erosion and sediment deposition, thereby influencing the distribution and accumulation patterns of various elements in the soil (Lian et al., 2009). The sediment transport index was determined by *Equation 3*.

$$\tau = \left(\frac{A_s}{22.13} \right)^m \left(\frac{\sin \beta}{0.0896} \right)^n \quad (\text{Eq.3})$$

where $m = 0.6$, $n = 1.3$.

Determination method of soil environmental background value

The concept of soil environmental background values is inherently relative, shaped by the interplay of natural background factors and external pollutants (Dai et al., 2011). The lack of comparability among soil background values primarily stems from the absence of standardized analytical methods for measuring these values across different regions. Factors contributing to this disparity include the randomness in field sample collection, variations in sample pretreatment, and differences in instrument equipment. The absence of a unified method for studying background values is evident in the literature (Beygi et al., 2018). In general practice, samples undergo an outlier elimination test, and the corresponding method is applied until the data adhere to a normal distribution or log-normal distribution. For normally distributed data, the

element's environmental background value is determined using the arithmetic mean and arithmetic standard deviation. In cases of log-normal distribution, the geometric mean and geometric standard deviation are employed (Wang et al., 2018). Many studies adopt the mean standard deviation method, wherein outliers for normally distributed data are those falling outside $\pm 3 S$ (where S is the standard deviation); for elements with log-normal distribution, outliers are excluded beyond the range of M/D^3 to MD^3 (where M is the geometric mean, and D is the geometric standard deviation) (Dai et al., 2011; Xu et al., 2017). Some researchers use the mean value ± 2 times the standard deviation ($\pm 2 S$) to filter data beyond or below this range (Sheng et al., 2009; Zhao et al., 2014). Other outlier elimination methods include the quartile method, box whisker plot, and Grubbs test methods (Zhang et al., 2012; Nogueira et al., 2018; Wang et al., 2018). In this study, the univariate Kolmogorov-Smirnov asymptotic distribution test module were employed to assess the normal distribution and outliers of all heavy metal elements. The mean value and standard deviation of all samples were calculated, and samples exceeding or falling below "mean value ± 3 standard deviation value" were eliminated. This process was repeated until no further samples could be eliminated. When the rejected samples adhered to normal distribution, $\pm 2 S$ was used to represent the background value range. For samples conforming to log-normal distribution, the range of the background value was determined using $M/D^2 \sim MD^2$.

Statistical analyses

One-Sample Kolmogorov-Smirnov (K-S) test was performed to test whether the soil heavy metals variable data follow normal distribution. Coefficient of variation (CV) was identified as a basic parameter for spatial variability in soil heavy metal concentration. The correlations between the heavy metal concentrations and the soil physical and chemical characteristics were measured using Pearson's parametric correlation analysis at significance (P) levels of 0.05 and 0.01, respectively. All above analysis were conducted using SPSS 22.0 for Windows (IBM Co., Armonk, NY). The differences in heavy metal element concentrations among various soil types were tested using One-way analysis of variance (ANOVA), which were performed using Origin 8.0 (OriginLab Co., Northampton, MA, USA).

Redundancy analysis (RDA) was a method employed to analyze the sources of variation in the original variable by examining its correlation with the canonical variable (Rong et al., 2017). It is commonly categorized into linear and unimodal models, each suitable for fitting different environmental gradients. Prior to sorting, detrended correspondence analysis (DCA) was applied to the response data to identify the maximum gradient length on the ranking axis. If the maximum value exceeded 4, the unimodal model was preferred. For values below 3, the linear model was deemed more appropriate. Values falling between 3 and 4 allowed for the consideration of both models for fitting purposes (Šmilauer et al., 2014). Canoco 5 (Microcomputer Power, Ithaca, NY, USA) was utilized to conduct the redundancy analysis.

The inverse distance weighted (IDW) interpolation was used to estimate the spatial distribution of soil heavy metal concentrations in the catchment. The IDW interpolation method determined values based on information from surrounding points. In this method, the influence of each point decreases with increasing distance from the point being estimated. This approach leverages the spatial characteristic that data values were inversely correlated with distance (Xie et al., 2011). The inverse distance weighted (IDW) interpolation was implemented using ArcGIS 10.8 (ESRI, Redland, CA, USA).

Results and discussion

Environmental background values of surface soil Pb and Zn

Figure 2 showed the spatial distribution of heavy metal Pb and Zn content in the surface soil of the Bijiang River Basin. The spatial variation trended for Pb and Zn are consistent, with higher concentrations observed upstream, including some forest and shrub areas, and a smaller concentration found in the forests near Yunlong County downstream. The content of Pb and Zn is uniformly distributed and decreases gradually with increasing distance from the Jinding mining area.

Compared to the screening values for heavy metal pollution risk in agricultural soil for Pb ($120 \text{ mg}\cdot\text{kg}^{-1}$) and Zn ($250 \text{ mg}\cdot\text{kg}^{-1}$) as specified in the “Soil Environmental Quality Agricultural Land Soil Pollution Risk Control Standard (Trial) (GB15618-2018),” neither Pb nor Zn levels exceed the standards. For the coefficient of variation, the coefficients of variation for heavy metals Pb and Zn were 60.03% and 50.24%, respectively. Both elements exhibit strong spatial variability, reflecting the significant impact of local human activities on soil elements. A high coefficient of variation indicates that the spatial distribution of elements within the watershed is uneven.

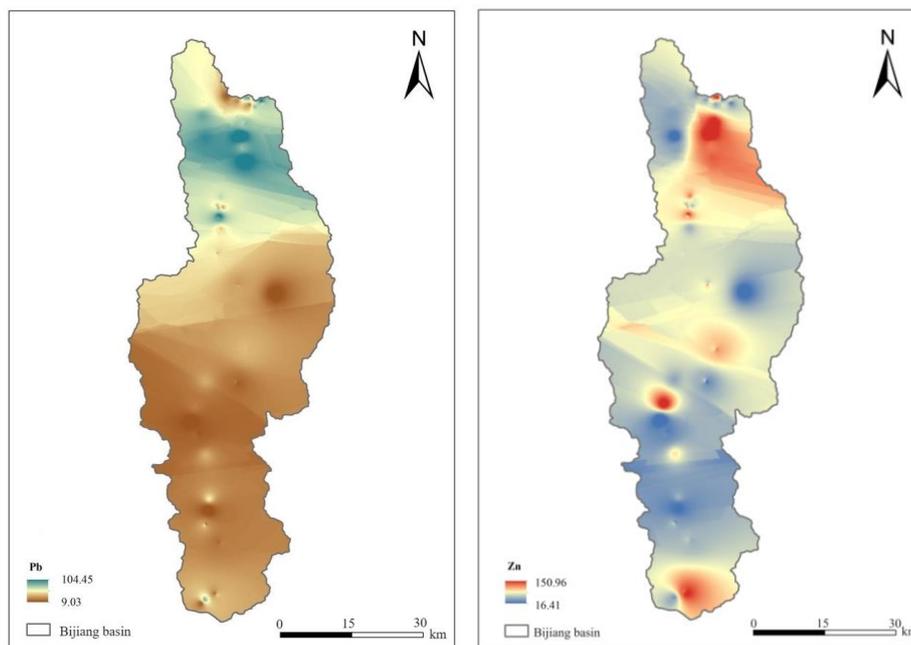


Figure 2. The spatial distribution of lead and zinc heavy metals of the Bijiang River Basin

The Kolmogorov-Smirnov showed that the content of Pb and Zn follows a log-normal distribution (Table 1). Subsequently, the $M/D^2 \sim MD^2$ values for Pb and Zn were calculated to represent the range of background values with a 95% confidence interval in the Bijiang River Basin (Table 2).

Table 1. Normal distribution test of heavy metal elements in the surface soil

Element	Skewness	Kurtosis	K-S test	Conversion mode	Distribution type
Pb	0.784	-0.079	0.228	Logarithmic conversion	Lognormal
Zn	0.941	0.562	0.165	Logarithmic conversion	Lognormal

By calculating the environmental background values of heavy metals, the geometric average of Pb was $30.73 \text{ mg}\cdot\text{kg}^{-1}$, with a variation range of 10.63 to $88.81 \text{ mg}\cdot\text{kg}^{-1}$ and a coefficient of variation of 0.65. For Zn, the geometric mean was $64.85 \text{ mg}\cdot\text{kg}^{-1}$, with a range of 45.79 to 91.83 and a coefficient of variation of 0.47 on the entire watershed (Table 2). Notably, the environmental background value in the Bijiang River Basin was found to be lower than that in the Jinding area of Lanping, China (Yan, 1998). When compared to the national soil environmental quality standard, the concentrations of Pb and Zn in the surface soil of the river basin were below the national first-class standard, classifying the soil as ‘clean’. In comparison with the background values of elements in other regions, the environmental background value of heavy metal Pb in the Bijiang River Basin was significantly higher than the national standard value of shale but lower than the background value of surface soil in Yunnan Province.

Table 2. Comparison of heavy metal contents of the soil background value of the Bijiang River Basin with other areas

Item	Sample number/each	Layer (cm)	Pb ($\text{mg}\cdot\text{kg}^{-1}$)	Zn ($\text{mg}\cdot\text{kg}^{-1}$)
Median	77	0~20	31.20	62.00
Arithmetic mean			36.47	71.64
Arithmetic standard deviation			21.34	34.12
Geometric mean			30.73	64.85
Geometric standard deviation			1.70	1.19
95% range value			10.63~88.81	45.79~91.83
Jinding, Lanping County, Nujiang Lisu Autonomous Prefecture, China		0~20	54.98	66.98*
Yunnan province, China ^a		0~20	40.6 (36.0*)	89.7 (80.5*)
Nationwide (Wang et al., 1995)		0~20	26.0	74.2 (67.7*)
Standard value of shale (Turekian and Wedepohl, 1961)		0~20	20	95
National Soil Environmental Quality Standard for natural soil, China ^b		0~20	35	100

^aRefers to the background values of elements in China

^bIs quoted from grade 1 standard of National Soil Environmental Quality Standard (GB15618-1995), China

*Refers to geometric mean

Influencing factors on soil environmental background values

Soil type

In the Bijiang River Basin, there were primarily 10 soil types as illustrated in Figure 3. The predominant soil types included purple soil, brown soil, and yellow-brown soil, collectively constituting approximately 82.53% of the entire basin.

The content of elements in surface soil and parent material layers of different soil type is compared, and the ratio is shown in Table 3. If the ratio is less than 1, it indicates migration; if the ratio is greater than 1, indicating accumulation. For Pb, the ratio is less

than 1 in dry red soil and purple soil, and the ratio is greater than 1 in other soil types. For Zn, except in lime (rock) soil, the ratio of other soil types is less than 1. So, heavy metal Zn is easier to migrate compared to Pb.

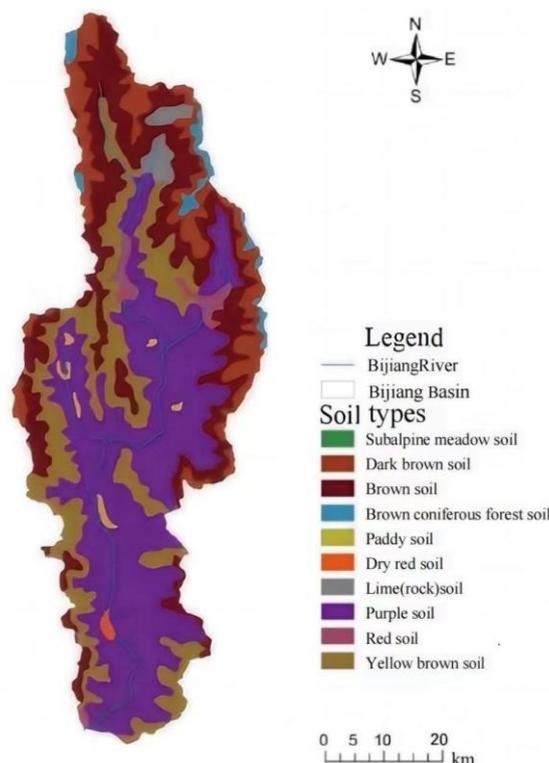


Figure 3. Soil types in the Bijiang River Basin

Table 3. Ration of topsoil and parent layer in each soil type

	Element	Dark brown	Red	Yellow brown	Dry red	Purple	Brown	Limestone (rock)
Number		5	10	4	2	39	12	6
Ratio A/C	Pb	1.24	1.25	1.88	0.78	0.71	1.29	1.69
	Zn	0.77	0.86	0.51	0.63	0.77	0.92	1.27

A: topsoil of the Bijiang River Basin. C: parent material soil of Yunnan Province, China

The result of ANOVA was shown in *Figure 4*. Specifically, for Pb, significant differences ($p < 0.05$) were observed between purple soil and brown soil, dark brown soil, red soil, yellow brown soil, limestone soil, and dry red soil. Additionally, significant differences ($p < 0.05$) were noted between dry red soil and yellow brown soil, as well as between dry red soil and lime soil. Regarding Zn, significant differences ($p < 0.05$) were found between purple soil and limestone soil, yellow brown soil and limestone soil, and dry red soil and limestone soil.

In summary, the environmental background values of heavy metal elements in the Bijiang River basin exhibit distinct migration or accumulation characteristics associated with soil types. This underscores that the background element values in the Bijiang River Basin demonstrate significant migration characteristics in surface soils.

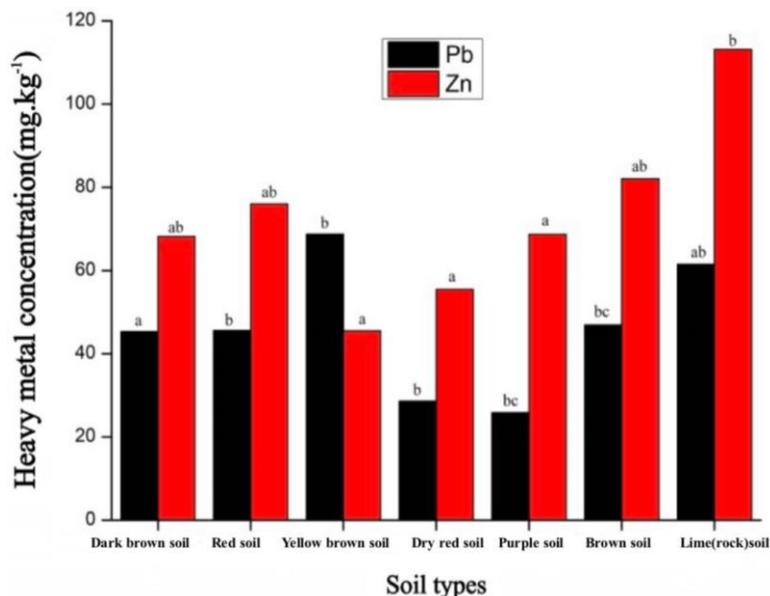


Figure 4. Heavy metal concentrations and differences under different soil types

Topographic factors

The content of heavy metals Pb and Zn was analyzed using the detrending by segments method. The maximum gradient length of the sorting axis (i.e., the first axis is 0.27, which is less than 3), making it suitable for linear models. The RDA analysis results indicate that the topographical factors account for 30.93% the total variation of heavy metal content in the topsoil (Table 4). The first canonical axis explained 27.29% of the response variable, and the cumulative explanation of the first two axes for the response variable reached 58.22%. The cumulative explanation for the relationship between the response variable and the explanatory variable is as high as 88.25% explained by the first axis, indicating that the main control factor is mainly explained by the first axis.

Table 4. The results of redundant analysis of soil heavy metal contents and topographic factors

Canonical axis	Eigenvalue	EV	EFV
First axis	0.27	27.29	88.25
Second axis	0.04	30.93	100.00
Third axis	0.55	-	
Fourth axis	0.14	-	

EV, explained variation, %; EFV, explained fitted variation, %

The correlation coefficients between different terrain factors and the primary canonical axis reveal that altitude exhibits the most significant contribution to the first axis, boasting a correlation coefficient of 0.42 (Table 5). Furthermore, this association has been validated through the Monte Carlo test.

The solid gray arrow in the diagram signifies the response variable, representing the content of Pb and Zn in the soil, while the hollow black arrow denotes the explanatory

variable, encompassing 10 terrain factors (Fig. 5). The length of each environmental factor arrow reflects its impact on the heavy metal content, with a longer arrow indicating a greater explanatory influence on the response variable. The angle formed between the environmental factor arrow and the dependent variable arrow signifies the correlation of the environmental factor with that variable. An angle less than 90° indicates a positive correlation, an angle greater than 90° indicates a negative correlation, and an angle close to 90° suggests a weak correlation. Altitude emerges as the most influential environmental factor, positively correlated with both Pb and Zn, with a notably stronger correlation observed with Zn. Furthermore, terrain undulation exhibits a negative correlation with both Pb and Zn.

Table 5. Correlation between explanatory variable of factor and each axis

Factors	First axis	Second axis
Altitude	-0.42	0.16
Slope gradient	0.13	0.19
Slope aspect	0.03	0.13
Plan curvature	0.15	0.12
Slope curvature	0.12	0.16
Relief amplitude	0.20	0.18
Roughness	0.14	-0.00
STI	0.09	0.02
SPI	-0.08	-0.06
ω	0.25	0.09

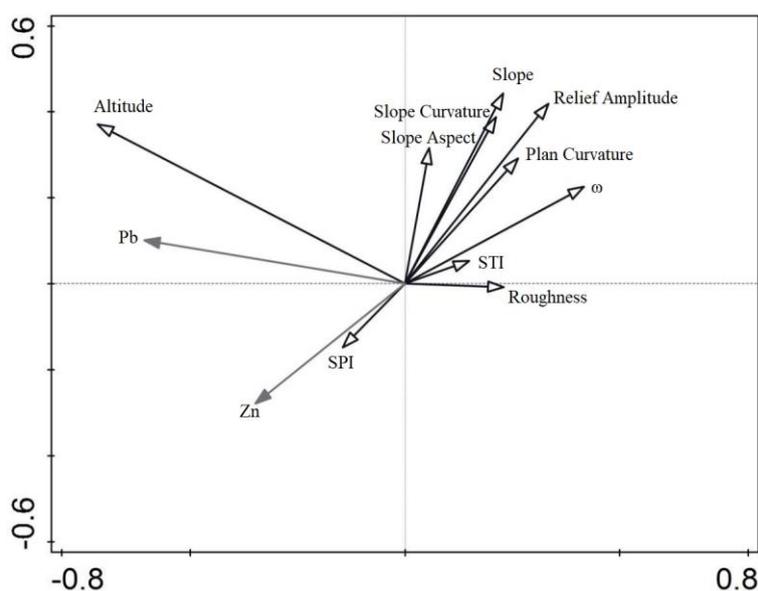


Figure 5. Redundant analysis of soil heavy metals and topographic factors

Soil physical and chemical properties

The concentration of the heavy metal Pb exhibits a declining trend as the pH value increases. The maximum Pb content is reached at a pH of 5.90. In contrast, the content

of Zn initially decreases with rising pH, but within the IV (alkaline) range, there is an upturn in Zn concentration. The maximum Zn content is recorded at a pH of 7.95 (Fig. 6a). Additionally, the concentrations of heavy metals Pb and Zn show an upward trend with increasing organic matter content. The change is relatively gradual, with a noticeable increase observed at the third inflection point (Fig. 6b).

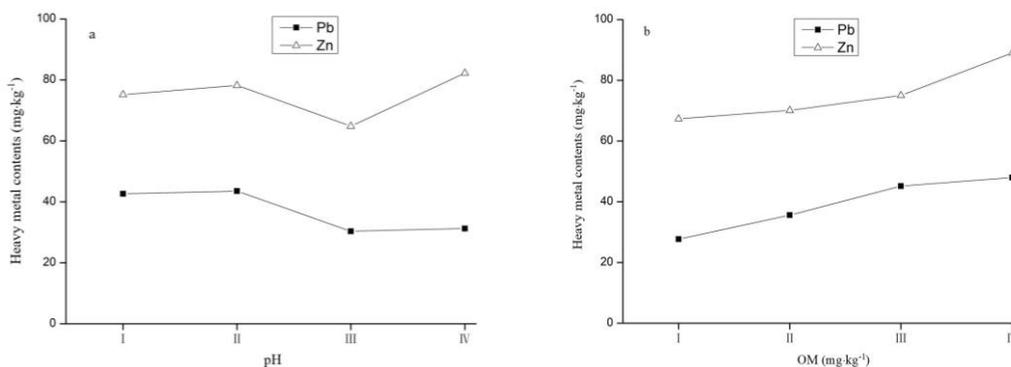


Figure 6. Distribution of heavy metal elements in different pH intervals

A notable and statistically significant negative correlation exists between the concentration of heavy metal Pb and pH, with a correlation coefficient of -0.324 ($p < 0.01$). Furthermore, a significant positive correlation is observed between Pb and organic matter (OM), evidenced by a correlation coefficient of 0.289 ($p < 0.01$) (Table 6).

Table 6. Correlation between heavy metals and each factor

Factors	Pb	Zn	pH	OM
Pb	1	0.527**	-0.324**	0.289*
Zn		1	-0.140	0.219
pH			1	-0.001
OM				1

** $p < 0.01$, the correlation is significant (two-sided); * $p < 0.05$, the correlation is significant (two-sided)

Discussion

The non-uniformity of soil environmental background value sampling

In the preceding analysis, notable disparities were observed in the environmental background values of elements in the soil across different regions, rendering the evaluation results non-comparable. To address this issue, regional soil background values were adopted as the evaluation standards, offering a practical, feasible, and scientifically sound approach. Considering the pragmatic application and ease of sampling, investigating the background values of heavy metals in surface soil emerges as a reasonable and viable strategy. In comparison with the national soil environmental quality standard, the concentrations of Pb and Zn in the surface soil of the Bijiang River Basin were found to be below the national first-level standard, classifying it as “clean” soil. This finding underscores that the measured content effectively represents the regional soil background values in the Bijiang River Basin.

Given the pervasive impact of human activities, identifying uncontaminated soil in areas inhabited by humans has become a challenging task. The Bijiang River Basin poses unique challenges for comprehensive sampling due to its vast scale, high altitude, and diverse soil formation environments. The Bijiang River watershed covers a large area, with the upper reaches containing a high background anomaly zone of metal elements in soil and water system sediments (Chen, 1987). In contrast, the lower reaches are characterized by a typical dry and hot valley zone. Therefore, there are notable differences in soil characteristics and parent material sources throughout the entire watershed. The uneven distribution of sampling points throughout the basin is compounded by the complexities of mountainous terrain, presenting inconveniences in sample collection. Consequently, from a watershed perspective, the number of samples is relatively limited, highlighting the need for further enhancement in future studies.

Environmental control factors of soil environmental background values

The soil environment's background values in the Bijiang River Basin exhibit variations across different soil types, demonstrating characteristics of migration and accumulation. Yan (1998) studied the soil background value in Jinding area of the Bijiang River Basin by means of enrichment coefficient method and topsoil comparative law method. Notably, the background values for heavy metals Pb and Zn were found to be $54.98 \text{ mg} \cdot \text{kg}^{-1}$ and $66.98 \text{ mg} \cdot \text{kg}^{-1}$, respectively. In comparison with the soil background values presented in this study, there is a significant disparity in the content of heavy metal Pb. This discrepancy is primarily attributed to the Jinding area's location on the Jinding super large lead-zinc ore belt (Zhu et al., 2018), resulting in elevated heavy metal concentrations in the soil. Moreover, this investigation reveals that yellow brown soil exhibits high levels of heavy metal Pb, indicating noticeable accumulation, while purple soil showcases elevated levels of heavy metal Zn, reflecting migration tendencies. This suggests a significant influence of soil type on heavy metal distribution. Purple soil, predominantly found in the river valleys of the Bijiang River Basin, may experience leaching and runoff of Zn from surface soil at higher altitudes due to rainfall, leading to migration towards lower altitudes. This results in sedimentation and accumulation of Zn in lower altitude areas, contributing to higher content. On the other hand, yellow brown soil, prevalent in slightly elevated areas, accumulates heavy metal Pb, which is a less mobile element and tends to accumulate in the soil (Mukwaturi et al., 2015).

Terrain factors play a pivotal role in influencing the migration of soil and materials. (Chen et al., 2018) underscored the significant impact of altitude on the distribution of heavy metal content in soil. Consistent with these findings, the present study reveals that altitude serves as a primary controlling factor affecting the soil environment's background values in the Bijiang River Basin. Altitude, in particular, influences the migration of heavy metal elements by altering the potential energy of soil migration. Additionally, alterations in topographic factors are shown to influence the distribution of soil organic matter content (Li et al., 2014). The presence of organic matter in the soil forms complexes or chelates with heavy metals, augmenting the soil's ability to bind and immobilize these metals. Furthermore, an increase in organic matter promotes the absorption and migration of heavy metals in the soil by plant roots, as observed in studies (Zeng et al., 2011; Beygi et al., 2018). Roca et al. (2012) demonstrated that the intricate interaction between organic matter and heavy metal Pb leads to the deposition of less mobile Pb elements on the soil surface.

In the Bijiang River Basin, noteworthy variations in organic matter are observed across different altitude levels. Organic matter content at lower altitudes tends to be relatively low, influenced by rapid nutrient loss due to human interference. The fitting curve depicting the relationship between altitude and organic matter reveals a linear correlation, exhibiting a high coefficient of determination ($R^2 = 0.9536$; Fig. 7). Both excessively steep and extremely gentle slopes are unfavorable for organic matter accumulation. Areas with extremely low slopes, typically found in low-lying terrain at the base of slopes, exhibit poor drainage, adversely affecting organic matter accumulation. Liu et al. (2008) noted higher levels of heavy metal pollution on downhill slopes, highlighting the impact of terrain factors on the diffusion and migration of heavy metal pollution. The observed soil loss in steep slope areas leads to a gradient of soil mineral nutrient levels, resulting in a transition from thin to rich soil mineral nutrients from top to bottom and contributing to the favorable condition of organic matter in this area.

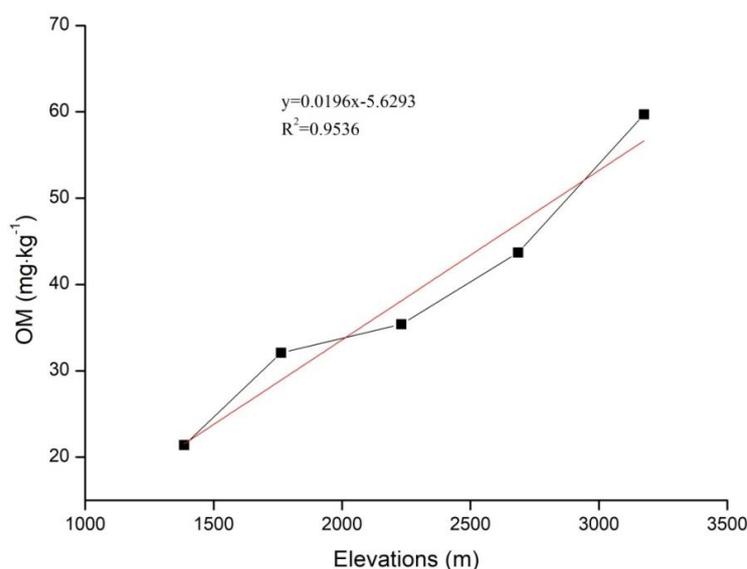


Figure 7. Variations in organic matter content at different elevations

The pH level in soil has a significant impact on the solubility and speciation of heavy metal elements within the soil matrix. A decrease in pH is associated with heightened solubility and desorption of heavy metals such as Pb and Zn in the soil. At the same time, the decrease in pH will also lead to increased mobility and biological activity of heavy metals, further promoting the absorption of heavy metal elements by plants in the soil, thereby endangering human health through the food chain (He et al., 2017). The heavy metal Pb content in this article reaches its maximum under weakly acidic conditions, and the sample site is located upstream, with a relatively high organic matter content of $71.89 \text{ mg} \cdot \text{kg}^{-1}$. The main reason for this sampling point is that the organic layer in the upstream forest is relatively thick, and the collected soil may be greatly affected by organic matter, resulting in a high content of heavy metal Pb. At the same time, the particle characteristics of soil can also affect the distribution of heavy metal content in the soil, generally manifested as an increase in heavy metal content with the increase of clay content in the soil, and vice versa (Nogueira et al., 2018; Yan et al., 2017). However, this factor is not considered in this paper, and the influence of soil particle composition on the heavy metal contents can be further studied in the future.

This study exclusively gathered natural topsoil unaffected by human activities, potentially resulting in variations in measured heavy metal content compared to soil parent material. Previous research has indicated that heavy metal concentrations in surface soil tend to be higher than those in the subsoil. While this phenomenon can be attributed in part to pollution, it may also be a natural outcome of extended soil formation processes, not necessarily linked solely to contamination.

Conclusion

The results showed that the geometric mean value of the soil environmental background values of the Bijiang River Basin for Pb and Zn was $30.73 \text{ mg}\cdot\text{kg}^{-1}$ and $64.85 \text{ mg}\cdot\text{kg}^{-1}$, respectively, which was both lower than those observed in the surface soil across Yunnan Province. Soil type, altitude, pH and organic matter emerged as the principal factors influencing the environmental background values of Pb and Zn in the soil. Specifically, heavy metal Pb tended to accumulate in most soil types, while Zn exhibited migratory behavior. Altitude stood out as the primary topographic factor controlling the content of Pb and Zn in surface soil, with terrain undulation following closely behind. The concentrations of Pb and Zn decreased with an increase in pH value and rose with an increase in organic matter content. The environmental background values calculated in this study could serve as a valuable reference for regional pollution assessment. Further, studies should explore variations in heavy metal content among different soil layers at the watershed scale.

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REFERENCES

- [1] Bao, S. D. (2000): Soil Agrochemical Analysis. – China Agriculture Press, Beijing.
- [2] Beven, K. J., Michael, J. K. (1979): A physically based, variable contributing area model of basin hydrology. – *Hydrological Sciences Journal* 24(1): 43-69.
- [3] Beygi, M., Jalali, M. (2018): Background levels of some trace elements in calcareous soils of the Hamedan Province, Iran. – *Catena* 162: 303-316.
- [4] Cappuyns, V., Mallaerts, T. (2014): Background values of cobalt in Flemish and European soils. – *Geologica Belgica* 17(2): 107-114.
- [5] Chen, C. (2013): A discussion about comprehensive environmental treatment and protection in Bijiang River catchment. – *Environmental Science Survey* 23(2): 52-57.
- [6] Chen, R. Q. (1987): A preliminary probe on effects of Pb, Cd (Heavy metal) element migration to the water body of Bijiang River in upper course of Bijiang. – *Yunnan Geology* 6(4): 332-338.
- [7] Chen, Y. L., Shi, L., Wang, Z. R. (2018): Pollution assessment and spatial distribution of soil heavy metals in mining area based on GIS. – *Science of Surveying and Mapping* 43(4): 80-86.
- [8] Coppola, E., Capra, G. F., Odierna, P., Vacca, S., Buondonno, A. (2010): Lead distribution as related to pedological features of soils in the Volturno River low Basin (Campania, Italy). – *Geoderma* 159(3-4): 342-349.
- [9] Dai, J. R., Pang, X. G., Yu, C., Wang, C. L., Wang, Z. H., Hu, X. P. (2011): Geochemical baselines and background values and element enrichment characteristics in soils in eastern Shandong Province. – *Geochimica* 40(6): 577-587.

- [10] Ding, Z. Y., Ma, L., Jilili, A., Liu, W. (2017): Spatial variations and influence factor analysis of heavy metals in topsoil of Bortala River Basin, Northwest China. – *Ecology and Environmental Sciences* 26(6): 939-948.
- [11] Gokceoglu, C., Sonmez, H., Nefeslioglu, H. A., Duman, T. Y., Can, T. (2005): The 17 March 2005 Kuzulu landslide (Sivas, Turkey) and landslide-susceptibility map of its near vicinity. – *Engineering Geology* 81(1): 65-83.
- [12] Gu, T., Zhao, X. W., Hu, X. Y., Yu, W., Zeng, M., Wang, J. T. (2018): Distribution characteristics and risk assessment of heavy metals in soil from an agricultural park of Xinmadun village, Zhuhai city. – *Rock and Mineral Analysis* 37(4): 419-430.
- [13] He, L. P., Liu, D., Lin, J. J., Yu, Z. G., Yang, X. X., Fu, C., Liu, Z. X., Zhao, Q. H. (2017): Total nitrogen and pH-controlled chemical speciation, bioavailability and ecological risk from Cd, Cr, Cu, Pb and Zn in the water level-fluctuating zone sediments of the Three Gorges Reservoir. – *Chemical Speciation & Bioavailability* 29(1): 89-96.
- [14] Huang, B., Guo, Z. H., Tu, W. J., Peng, C., Xiao, X. Y., Zeng, P., Liu, Y. N., Wang, M. W., Xiong, J. (2018): Geochemistry and ecological risk of metal(loid)s in overbank sediments near an abandoned lead/zinc mine in Central South China. – *Environmental Earth Sciences* 77(3): 68.
- [15] Huang, R. H., You, W. B., Guo, F., Jiang, L. J. (1985): Study on background values of some metal elements in soils of the Luohe river basin. – *Scientia Geographica Sinica* 5(3): 250-254.
- [16] Jiang, Y., Gao, W. W., Zhao, J. L., Chen, Q., Liang, D., Xu, C., Huang, L. S., Ruan, L. M. (2018): Analysis of influencing factors on soil Zn content using generalized additive model. – *Scientific Reports* 8(1): 15567.
- [17] Kumar, V., Shaema, A., Kaur, P., Sidhu, G. P. S., Bali, A. S., Bhardwaj, R., Thukral, A. K., Cerda, A. (2019): Pollution assessment of heavy metals in soils of India and ecological risk assessment: a state-of-the-art. – *Chemosphere* 216: 449-462.
- [18] Li, T., Yi, W., Fu, Q., Li, H. X. (2014): Load estimation of non-point heavy metal pollution in Beijiang River during extreme storm runoff event. – *Research of Environmental Science* 27(9): 990-997.
- [19] Lian, G., Guo, X. D., Fu, B. J., Hu, C. X. (2009): Prediction of the spatial distribution of soil properties based on environmental correlation and geostatistics. – *Transactions of the Chinese Society of Agricultural Engineering* 25(7): 237-242.
- [20] Liao, J. B., Cui, X. Y., Feng, H., Yan, S. K. (2022): Environmental background values and ecological risk assessment of heavy metals in watershed sediments: a comparison of assessment methods. – *Water* 14(1): 51.
- [21] Liu, S. L., Cui, B. S., Wen, M. X., Dong, S. (2008): Influence factors of spatial variability of soil heavy metal contents along roadside. – *Acta Scientiae Circumstantiae* 2: 253-260.
- [22] Liu, X., Dadzie, A. A., Yuan, L. B., Xing, S. Y., Zhou, X. H., Xiao, S. S. (2022): Analysis and potential ecological risk assessment of heavy metals in surface sediments of the freshwater ecosystem in Zhenjiang City, China. – *SN Applied Sciences* 4(10): 258.
- [23] Meng, X. X., She, Z. S. (1983): Background values of certain elements in the soils of second Songhua river basin. – *Acta Scientiae Circumstantiae* 3(1): 25-35.
- [24] Moore, I. D., Gessler, P. E., Nielsen, G. A. E., Peterson, G. A. (1993): Soil attribute prediction using terrain analysis. – *Soil Science Society of America Journal* 57(2): 443-452.
- [25] Mukwaturi, M., Lin, C. X. (2015): Mobilization of heavy metals from urban contaminated soils under water inundation conditions. – *Journal of Hazardous Materials* 285: 445-452.
- [26] Nogueira, T. A. R., Abreu-Junior, C. H., Alleoni, L. R. F., He, Z. L., Soares, M. R., dos Santos Vieira, C., Lessa, L. G. F., Capra, G. F. (2018): Background concentrations and quality reference values for some potentially toxic elements in soils of São Paulo State, Brazil. – *Journal of Environmental Management* 221: 10-19.

- [27] Roca, N., Pazos, M. S., Bech, J. (2012): Background levels of potentially toxic elements in soils: A case study in Catamarca (a semiarid region in Argentina). – *Catena* 92: 55-66.
- [28] Rong, L., Duan, X. W., Feng, D. T., Zhang, G. L. (2017): Soil moisture variation in a farmed dry-hot valley catchment evaluated by a redundancy analysis approach. – *Water* 9(2): 92.
- [29] Salminen, R., Tarvarinen, T. (1997): The problem of defining geochemical baselines. A case study of selected elements and geological materials in Finland. – *Journal Geochemical Exploration* 60(1): 91-98.
- [30] Sanjeevani, U. K. P. S., Indraratne, S. P., Weerasooriya, R., Vitharana, U. W. A., Rosemary, F. (2015): Baseline concentrations of some trace elements in Alfisols of Sri Lanka. – *Geoderma Regional* 4: 73-78.
- [31] Shen, G. H., Ru, X., Gu, Y. T., Liu, W., Wang, K. Z., Li, B. Y., Guo, Y. Z., Han, J. (2023): Pollution characteristics, spatial distribution, and evaluation of heavy metal (loid)s in farmland soils in a typical mountainous hilly area in China. – *Foods* 12(3): 681.
- [32] Sheng, Q., Wang, H. X., Hu, Y. H., Cai, C. N. (2009): Study on soil background value and reference value in Henan section of Yellow River. – *Journal of Anhui Agricultural Sciences* 37(18): 8647-8650.
- [33] Šmilauer, P., Lep, Š. J. (2014): *Multivariate Analysis of Ecological Data Using Canoco 5*. – Cambridge University Press, Cambridge.
- [34] Teixeira, R. A., de Souza, E. S., de Lima, M. W., Dias, Y. N., da Silveira Pereira, W. V., Fernandes, A. R. (2019): Index of geoaccumulation and spatial distribution of potentially toxic elements in the Serra Pelada gold mine. – *Journal of Soils and Sediments* 19: 2934-2945.
- [35] Turwkian, K. K., Wedepohl, K. H. (1961): Distribution of the elements in some major units of the Earth's crust. – *Geological Society of America Bulletin* 72(2): 175-192.
- [36] Wang, F. P., Song, B., Huang, Y. F., Zhang, J., Yu, Y. Y., Lei, M., Li, S. X. (2018): Further study on spatial distribution and background value of chromium in soil in Xijiang river basin, Guangxi, China. – *Acta Pedologica Sinica* 55(4): 889-899.
- [37] Wang, P., Cao, J. J., Wu, F. (2010): Environmental background values and its impact factors of topsoil within the Lake Qinghai catchment, Northeast Tibetan Plateau, China. – *Journal of Earth Environment* 1(3): 189-200.
- [38] Wang, Q. H., Dong, Y. X., Zheng, W., Zhou, G. (2007): Soil geochemical baseline values and environmental background values in Zhejiang, China. – *Geological Bulletin of China* 26(5): 590-597.
- [39] Wen, H. J., Zhang, Y. X., Cloquet, C., Zhu, C. W., Fan, H. F., Luo, C. G. (2015): Tracing sources of pollution in soils from the Jinding Pb-Zn mining district in China using cadmium and lead isotopes. – *Applied Geochemistry* 52: 147-154.
- [40] Wu, Q. M., Hu, W. Y., Wang, H. F., Liu, P., Wang, X. K., Huang, B. (2021): Spatial distribution, ecological risk and sources of heavy metals in soils from a typical economic development area, Southeastern China. – *Science of the Total Environment* 780: 146557.
- [41] Xia, Z. L. (1986): Discussion on the representation method of soil element background values. – *Journal of Agro-Environment Science* 5(02): 19-23.
- [42] Xie, Y. F., Chen, T. B., Lei, M., Yang, J., Guo, Q. J., Song, B., Zhou, X. Y. (2011): Spatial distribution of soil heavy metal pollution estimated by different interpolation methods: accuracy and uncertainty analysis. – *Chemosphere* 82(3): 468-476.
- [43] Xiong, Y. S., He, Y. Q., Liang, L. C. (2006): Assessment of environmental quality and background concentrations of red soil heavy metals on small scale. – *Journal of Huazhong Agricultural University* 25(5): 524-529.
- [44] Xu, F. J., Liu, Z. Q., Yuan, S. Q., Zhang, X. L., Sun, Z. L., Xu, F., Jiang, Z. Z., Li, A. C., Yin, X. B. (2017): Environmental background values of trace elements in sediments from the Jiaozhou Bay catchment, Qingdao, China. – *Marine Pollution Bulletin* 121(1-2): 367-371.

- [45] Yan, X. L., Hu, Y. M., Chang, Y. (2017): Effects of land reclamation on distribution of soil properties and heavy metal concentrations, and the associated environmental pollution assessment. – *Polish Journal of Environmental Studies* 26(4): 1809-1823.
- [46] Yan, Y. L. (1998): Background value research of the soil environment of Jingding district in Lanping County. – *Environmental Science Survey* 17(2): 15-17.
- [47] Yang, Q. P., Wu, W., Liu, H. B. (2018): Prediction of spatial distribution of soil available iron in atypical hilly farmland using terrain attributes and random forest model. – *Chinese Journal of Eco-Agriculture* 26(3): 422-431.
- [48] Ye, C., Butler, O. M., Du, M., Liu, W. Z., Zhang, Q. F. (2019): Spatio-temporal dynamics, drivers and potential sources of heavy metal pollution in riparian soils along a 600 kilometre stream gradient in Central China. – *Science of the Total Environment* 651: 1935-1945.
- [49] Zeng, F. R., Ali, S., Zhang, H. T., Ouyang, Y., Qiu, B. Y., Wu, F. B., Zhang, G. P. (2011): The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants. – *Environmental Pollution* 159(1): 84-91.
- [50] Zhang, J. H., Xu, Y. N., Wu, Y. G., Hu, S. H., Zhang, Y. J. (2019): Dynamic characteristics of heavy metal accumulation in the farmland soil over Xiaoqinling gold-mining region, Shaanxi, China. – *Environmental Earth Sciences* 78: 1-11.
- [51] Zhang, S. L., Yang, G. Y., Luo, W., Guo, S. H. (2012): Changes of background values of inorganic elements in soils of Guangdong province. – *Soils* 44(6): 1009-1014.
- [52] Zhang, W. J., Wang, L. J., Wang, L., Shi, X. M., Lu, X. W. (2017): Assessment of pollution level and health risks of heavy metals in surface dust in Xi'an city. – *Chinese Journal of Soil Science* 48(2): 481-487.
- [53] Zhao, K. L., Zhang, L. Y., Dong, J. Q., Wu, J. S., Ye, Z. Q., Zhao, W. M., Ding, L. Z., Fu, W. J. (2020): Risk assessment, spatial patterns and source apportionment of soil heavy metals in a typical Chinese hickory plantation region of southeastern China. – *Geoderma* 360: 114011.
- [54] Zhao, X. J., Lu, S. J., Xu, R. J., Li, B. L., Wu, G. P., Wei, F. S. (2014): Soil heavy metal Cadmium standard limit and range of background value research. – *Environmental Science* 35(4): 1491-1497.
- [55] Zhao, X. Q., Yang, H. H., Yi, Q. (2012): Characteristics and reasons of heavy metal pollution in farmland soils in Bijiang watershed. – *Journal of Anhui Agricultural Sciences* 40(12): 7569-7573.
- [56] Zhu, Z. J., Zhang, Z. B., Guo, F. S. (2018): Characteristics of ore bearing rock in the Jingding superlarge Lead-Zinc Mine, Lanping Basin, Western Yunan. – *Acta Sedimentologica Sinica* 37(2): 292-300.