Spatial Analysis on Content Distribution of Soil Heavy Metals Copper (Cu) and Cadmium (Cd) in Duanzhou District of Zhaoqing City

Jianqiao QIN^{1*}, Bihai CAI¹, Yuanyuan XU², Dexin XIONG¹

1. School of Environmental and Chemical Engineering, Zhaoqing University, Zhaoqing 526061, China; 2. Shenzhen Degree of Freedom Sci-Tech Co., Ltd., Shenzhen 518100, China

Abstract This paper used atomic absorption spectrophotometry to determine the content distribution of Cu and Cd in the soil of Duanzhou District, Zhaoqing City. The single factor index method, Nemerow comprehensive index method, pollution load index method, geoaccumulation index method, and potential ecological hazard index method were used to analyze the content and pollution status of Cu and Cd in the soil of Duanzhou District, providing a basis for understanding the pollution status of Cu and Cd in the soil of Zhaoqing City.

Key words Atomic spectrophotometry; Single factor index method; Nemerow composite index method; Pollution load index method **DOI** 10. 19547/j. issn2152 - 3940, 2024, 05, 015

Heavy metals refer to metals with a relative density of 5 or higher, such as copper, cadmium, lead, mercury, etc. When pollutants containing these heavy metals enter the soil, they can cause serious pollution, affecting human physical and mental health and daily life, as well as inhibiting or having other adverse effects on crop production. With the circulation of the food chain, they can also have negative impacts on humans. With the development of economy and the progress in industry in recent years, the urbanization process in Zhaoqing City continues to accelerate. Modern high-rise buildings stand tall, and the vegetation area has significantly decreased. The rapid increase in residential areas and factories has led to pollution of the soil environment in the region from industrial wastewater, residential sewage, solid waste, pesticides, fertilizers, and atmospheric dust, resulting in further deterioration of soil environmental quality.

1 Current status and achievements of soil heavy metals research at home and abroad

The industrial revolution that occurred from the 1860s to the mid-19th century not only improved labor productivity, brought more technologies for transforming the environment to humanity, and created a large amount of wealth, but also brought severe environmental problems to people. It is not difficult to remember the

Minamata incident that occurred in Kyushu, Japan from 1953 to 1956, where local residents suffered from mental disorders, hearing loss, and blindness due to Hg pollution of water bodies; the Itai-itai incident that occurred in Fuji Prefecture, Japan from 1931 to 1972, caused by the discharge of cadmium (Cd) containing wastewater from a zinc refinery into water bodies. It was the sudden outbreak of these public hazards that people began to pay attention to heavy metals pollution. The emergence of such sudden pollution incidents has led to an increasing number of domestic and foreign scholars conducting research and further exploration on soil heavy metals pollution.

1.1 Current research status at abroad The earliest reports on soil heavy metals pollution in foreign countries can be traced back to the Zuwei copper-rich mountain pollution incident that occurred in Japan in the 19th century. Afterwards, many foreign scholars conducted extensive exploration and research on heavy metals pollution in urban soil. Bilos et al. thought that there are many sources of pollution in cities, which can release large amounts of heavy metals into the atmosphere and soil^[1]. Numerous studies have shown that the severity of heavy metals pollution is related to the intensity of human activities. The more intense the human activities, the more severe the heavy metals pollution in the region. In addition, soil heavy metals pollution is often more severe in industrialized areas, indicating that soil heavy metals pollution is also closely related to the degree of industrialization. Albasel et al. found that the content of Cu, Pb, and Zn in soil rapidly decreases with increasing distance from the highway. On the one hand, this is because heavy metals released from car exhaust can enter the surrounding environment. On the other hand, tire wear can also lead to the accumulation of heavy metals in the soil^[2]. The research by Blakel et al. showed that atmospheric deposition can lead to an increase in heavy metals in soil and crops, including the accumulation of heavy metals caused by at-

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* Corresponding author.

mospheric precipitation and gas-liquid suspended solids entering the $\mathfrak{soil}^{[3]}$

1.2 Current research status in China Relatively speaking, there is still a certain gap between the research on heavy metals pollution in soil at home and abroad as a whole. In terms of time, due to the influence of its own development ability, the research in this field started relatively late in China, but it developed rapidly after the 1990s. From a spatial perspective, the research in China mainly focuses on the Pearl River Delta and the Yangtze River Delta with early industrial development and developed economy, such as Shanghai, Nanjing, and the old industrial areas in Northeast China. The main region outside of mainland China is Hong Kong.

According to research on the characteristics of heavy metals content in agricultural soil in the suburbs of major cities in the Pearl River Delta region, the highest pollution index in the region is Hg, followed by Cd and Zn. Except for As, the average values of Cu, Pb, Zn, Cr, Ni, Cd and other elements in the surface soil exceed the background values of soil in Guangdong and the whole country, respectively. Except for As and Hg, heavy metal elements in the soil profile are generally higher in the surface layer than in the bottom layer^[4-5]. The pollution status of soil heavy metals in Hong Kong, which is also located in the Pearl River Delta region, shows significant differences compared to neighboring areas. Soil heavy metals pollution is mainly dominated by Pb, As, Zn, and Cu, indicating that there are variations at different spatial scales in the status and types of soil heavy metals pollution^[6-7].

1.3 Research findings In the past decade, the following achievements have been made in the research of heavy metals at home and abroad.

Background values and relevant standards for major soil heavy metal contents in global regions have been established, such as emission standards for heavy metals containing waste, food hygiene and safety standards, and environmental quality standards. The analysis and determination methods, and standard specifications for major heavy metals have been determined and improved. 2 The treatment methods for heavy metals pollution in soil have become increasingly comprehensive with the rapid development of technology, such as plant remediation technology and microbial remediation technology. (3) Plants that are tolerant or sensitive to heavy metals pollution are used to monitor the degree of soil heavy metals pollution, and can also have a certain effect on soil remediation.

Starting from the spatial analysis of heavy metals content in soil in Zhaoqing City, this experiment focused on evaluating and analyzing the content of copper (Cu) and cadmium (Cd) in soil, which contributed to the development and implementation of soil prevention and control research in Zhaoqing City.

2 Materials and methods

2.1 Regional overview Zhaoqing, a prefecture-level city under the jurisdiction of Guangdong Province, is located in the central and western part of Guangdong Province and the western end of the the Pearl River Delta. It is an important transportation hub from the developed coastal areas to the southwest provinces. Zhaoqing connects Wuzhou and Hezhou in Guangxi in the west, Foshan in the east, Yunfu, Yangjiang and Jiangmen in the south, and Qingyuan in the back. The Xijiang River, the main stream of the Pearl River, flows through Zhaoqing, and the Tropic of Cancer also runs through it^[8]. Facing the Xijiang River, controlling Cangwu from above, restricting the South China Sea from below, and backed by the Beiling Mountain, it is the throat of the Pearl River Delta leading to western Guangdong and is known as the "Inkstone Capital of China" [9].

Duanzhou District is located at 112°23′ – 34′ E and 23°2′ – 11′ N, in the central western part of Guangdong Province, on the north bank of the middle and lower reaches of the Xijiang River. It is adjacent to the Xijiang River in the south, the Beiling Mountain in the north, the Dinghu Mountain in the east, and Xiaoxiang Town in Gaoyao City in the west. It belongs to the the Pearl River Delta Economic Zone and is the political, economic and cultural center of Zhaoqing City^[10]. With the development of urban planning, more and more land in Duanzhou District of Zhaoqing City is developed and utilized. High buildings stand tall, and the industries such as non-ferrous metal smelting and rolling processing, chemical raw materials and products manufacturing, ceramic manufacturing, and metal products rise and prosper, which have increased the level of soil heavy metals pollution in Duanzhou District of Zhaoqing City.

2.2 Monitoring points

- **2.2.1** Tools. Small shovel, sample bag, sample label paper, disposable plastic gloves, iron shovel (large).
- **2.2.2** Stationing principle. The block random distribution method was adopted in this paper. A total of 6 monitoring points were set up, with 2-3 sampling points taken from each monitoring point. Sampling locations were shown in Table 1 and Fig. 1.

Sampling method: the sampling points were selected in areas with obvious soil type characteristics, complete soil profile development, clear level, and no invasive objects. Representative sampling points were selected, located 100 m away from highways and railways $^{\mbox{\tiny [11]}}$. At least 2 plots were selected within each land use attribute area, and soil was collected, approximately 1 kg per bag. After removing surface debris and backfill soil that may affect monitoring results, surface soil was collected vertically and uniformly at a depth of 0–20 cm.

Table 1 Location of soil monitoring points in Zhaoqing

No.	Location of sampling point	Site	Land use attribute
1#	112.509 170° E, 23.110 232° N	Beiling Mountain	Construction land
2#	112.522 956° E, 23.069 412° N	Beach land of the Xijiang River	Woodland
3#	112.451 025° E, 23.053 034° N	Concentrated residential area	Residential land
4#	112.473 394° E, 23.060 411° N	Commercial concentration zone	Commercial land
5#	112.463 349° E, 23.077 845° N	Xinghu Scenic Spot	Scenic spot
6#	112.511 968° E, 23.088 733° N	Industrial land	Industrial land

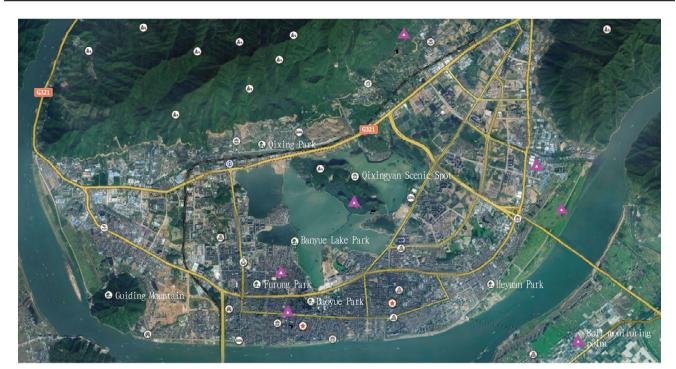


Fig. 1 Satellite image of soil monitoring points

2.3 Analysis standards and methods The sampling and analysis of this project were conducted in accordance with the *Technical Specifications for Soil Environmental Monitoring* (HJ/T 166 –

2004). Cu was detected by flame atomic absorption spectrophotometry, and Cd was determined by graphite furnace atomic absorption spectrophotometry (Table 2) $^{[12]}$.

Table 2 Test items, test methods, and detection limits

Test item	Test method	Standard (the latest version)	Analysis instrument	Detection limit//mg/kg
Cu	Flame atomic absorption spectrophotometry	GB/T 17138 - 1997	Varian 640 type of atomic absorption spectrophotometer	1.00
Cd	Graphite furnace atomic absorption spectrophotometry	GB/T 17141 - 1997	AA6300 graphite furnace atomic absorption spectrophotometer	0.01

3 Data processing

3.1 Preprocessing of raw data After sampling, the specific locations of sampling points such as the Beiling Mountain, the Xijiang River beach, and concentrated residential areas in Du-

anzhou District were determined, and the soil color and type of each point were determined through excavation sampling. The specific situation was shown in Table 3.

Table 3 Soil characteristics at each point

No.	Location of sampling point	Site	Land use attribute	Vegetation and cul- conditions of soil		${\rm Section} \atop {\rm depth}/\!\!/{\rm cm}$	Sampling method	Soil color	Soil type
1#	112°30′33″ E, 23°6′36″ N	Beiling Mountain	Construction land	Eucalyptus spp., Cunninghamia lanc		0 – 20	Excavation and soil collection	Pale brown	Loam
2#	112°3′22″ E, 23°6′36″ N	Beach land of the Xi- jiang River	Woodland	Cynodon dactylon		0 – 20	Excavation and soil collection	Brown	Clay
3#	112°27′3″ E, 23°3′10″ N	Concentrated residential area	Residential land	Bamboo, grassland		0 – 20	Excavation and soil collection	Brown	Sand soil
4#	112°28′24″ E, 23°3′37″ N	Commercial concentration zone	Commercial land	Mixed grassland		0 – 20	Excavation and soil collection	Brown	Sandy soil
5#	112°27′48″ E, 23°4′40″ N	Xinghu Scenic Spot	Scenic spot	Acacia confusa		0 - 20	Excavation and soil collection	Brown	Loam
6#	112°30′43″ E, 23°5′19″ N	Industrial land	Industrial land	Ficus concinna, clematidea, etc.	Praxelis	0 – 20	Excavation and soil collection	Brown yellow	Loam

mg/kg

The environmental quality standard for soils was shown in Table 4.

Table 4	Environmental	quality	standard for	· soils ((GB	15618 – 1995)	
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ън		Level one		Level two		Level three
Pollutant		Natural background	< 6.5	6.5 - 7.5	>7.5	>6.5
Cd≤		0.20	0.30	0.30	0.60	1.00
Hg≤		0.15	0.30	0.50	1.00	1.50
As≤	Paddy field≤	15.00	30.00	25.00	20.00	30.00
	Dry land≤	15.00	40.00	30.00	25.00	40.00
Cu≤	Farmland ≤	35.00	50.00	100.00	100.00	400.00
	Orchard≤	_	150.00	200.00	200.00	400.00
Cr≤	Paddy field≤	90.00	250.00	300.00	350.00	400.00
	Dry land≤	90.00	150.00	200.00	250.00	300.00
Pb≤		35.00	250.00	300.00	350.00	500.00
Zn≤		100.00	200.00	250.00	300.00	500.00
Ni≤		40.00	40.00	50.00	60.00	200.00
$C_6H_6Cl_6 \leq$		0.05	_	0.50	_	1.00
DDT≤		0.05	_	0.50	_	1.00

The soil quality in Zhaoqing City belongs to Class II, and the corresponding level two environmental quality standard for soils should be implemented. The critical value of Class II standard in the *Environmental Quality Standard for Soils* (GB 15618 – 1995) of China was referred to^[13].

3.2 Data processing The soil standard critical values corresponding to the pH measured at each point can be obtained through Table 4-5, and the corresponding values were shown in Table 6.

Table 5 Soil testing items and results

Manitaniananaiat	Test item				
Monitoring point	рН	Cu//mg/kg	Cd//mg/kg		
1# Beiling Mountain	7.17	6.21	0.01		
2# Beach land of the Xijiang River	7.99	36.4	0.49		
3# Concentrated residential area	8.11	50.5	0.55		
4# Commercial concentration zone	8.47	43.2	0.15		
5# Xinghu Scenic Spot	8.16	40.2	0.33		
6# Industrial land	7.81	76.2	0.63		
Mean	7.59	42.1	0.36		

Note: 1. The test results are only responsible for the samples received; 2. pH is non-dimensional.

4 Results and analysis

This paper used single factor index method, Nemerow com-

prehensive pollution index method, pollution load index method, geoaccumulation index method, and potential ecological hazard index method to conduct spatial analysis on the content distribution and pollution level of heavy metals in soil of Zhaoqing City.

4.1 Single factor index method As a commonly used method for evaluating soil in China, the single factor index method uses the soil element background as the evaluation criterion to assess the cumulative pollution level of heavy metal elements when evaluating soil heavy metals. The formula is as follows^[14]:

$$P_i = C_i/S_i$$
 (1)
where P_i is the environmental quality index of pollutant i in soil;
 C_i is the measured concentration of pollutant i , mg/kg; S_i is the
critical value of Class II standard in the *Environmental Quality*
Standard for Soils (GB 15618 – 1995) for heavy metal i when pH
is between 6.5 and 7.5, mg/kg.

When the accumulation pollution index of soil heavy metal $P_i \leq 1.0$, it indicates that the soil heavy metals content is less than the soil background value content, and the soil environment has not been artificially polluted. When the accumulation pollution index of soil heavy metals P_i is greater than 1.0, it indicates that the soil heavy metals content is greater than the soil background value, and the soil is contaminated by human activities. Pollution degree of Cu and Cd in soil at each point was shown in Table 7.

Table 6 National standard critical values of soil for each point

mg/kg

Detection point	Actual Cu content	Actual Cd content	Level two		Soil background value in Guangdong Province	
			Cu	Cd	Cu	Cd
1# Beiling Mountain	6.21	0.01	100	0.30	11.4	0.04
2# Beach land of the Xijiang River	36.40	0.49	100	0.60		
3# Concentrated residential area	50.50	0.55	100	0.60		
4# Commercial concentration zone	43.20	0.15	100	0.60		
5# Xinghu Scenic Spot	40.20	0.33	100	0.60		
6# Industrial land	76.20	0.63	100	0.60		

Table 7 Pollution degree of Cu and Cd in soil at each point

Monitoring point	P_{Cu}	Degree of soil contamination by Cu	$P_{ m Cd}$	Degree of soil contamination by Cd
1# Beiling Mountain	0.062 1	No artificial pollution	0.033 3	No artificial pollution
2# Beach land of the Xijiang River	0.364 0	No artificial pollution	0.8167	No artificial pollution
3# Concentrated residential area	0.505 0	No artificial pollution	0.9167	No artificial pollution
4# Commercial concentration zone	0.432 0	No artificial pollution	0.2500	No artificial pollution
5# Xinghu Scenic Spot	0.402 0	No artificial pollution	0.5500	No artificial pollution
6# Industrial land	0.762 0	No artificial pollution	1.050 0	Artificial pollution

It can be seen that the soil environmental quality index of Cu at each monitoring point in Duanzhou District was less than 1.0 and the critical value of Cu in Class II standard, indicating that the soil in Duanzhou District has not been polluted by Cu in general. Among the monitoring points, only the soil environmental quality index of Cd in industrial land was greater than 1.0 and the critical value of Cd in Class II standard, which may be due to the long-term pollution of Cd containing pollutants in the soil of industrial land, leading to accumulation.

4. 2 Nemerow composite index method Nemerow index method is a weighted multi factor environmental quality index based on single factor index evaluation, taking into account extreme values or highlighting maximum values. It is currently one of the most commonly used methods for calculating comprehensive pollution index at home and abroad [15]. The calculation formula is as below:

 $P_i = C_i/C_{0i}$ ($i = 1, 2, 3, \dots, k, k$ kinds of parameters; $P = 1, 2, \dots, m, m$ monitoring points)

where P_i is single pollution index of pollutant i in soil at monitoring point m; C_i is the measured concentration of pollutant i in the soil at monitoring point m, mg/kg; C_{0i} is soil environmental quality standard value for heavy metal i, mg/kg.

$$P_{\text{comprehensive}} = \sqrt{\frac{\left[\left(\overline{P_i}\right)^2 + \left[\max(P_i)\right]^2}{2}}$$
(3)

where $P_{\text{comprehensive}}$ is soil comprehensive pollution index; $\overline{P_i}$ is the

average index of various pollutants in the soil; $\max(P_i)$ is the maximum pollution index of a single pollutant in soil.

The pollution level is defined according to its pollution index, as shown in Table 8.

Table 8 Soil pollution level by Nemerow index

Grade	Nemerow comprehensive index	Pollution level
I	$P_{\text{comprehensive}} \leq 0.7$	Clean (safe)
II	$0.7 < P_{\text{comprehensive}} \leq 1.0$	Clean yet (warning line)
III	$1.0 < P_{\text{comprehensive}} \leq 2.0$	Mild pollution
IV	$2.0 < P_{\text{comprehensive}} \leq 3.0$	Moderate pollution
V	$P_{\text{comprehensive}} > 3.0$	Heavy pollution

The results were shown in Table 9. From Table 9, it can be concluded that the average indices of Cu and Cd in Duanzhou District of Zhaoqing City were both less than 0.7, and their maximum pollution indices were greater than 0.7. Therefore, the Nemerow comprehensive index of Cu in the soil of Duanzhou District, Zhaoqing City was 0.615 5, which was still less than 0.7. According to Table 8, the soil in this area remained clean and belonged to level I. The Nemerow comprehensive index of Cd was 0.923 4, which was greater than 0.7 and less than 1.0. Although the soil was classified as level II and still clean, early measures needed to be taken to prevent the accumulation of Cd in the soil, which could lead to mild pollution.

Table 9 Degree of soil pollution by Cu and Cd in Zhaoqing City

Element	$\overline{P_i}$	$\max(P_i)$	$[\max(P_i)]^2$	$P_{ m comprehensive}$	Pollution level
Cu	0.177 2	0.762 0	0.580 6	0.615 5	Level I (clean)
Cd	0.6028	1.0500	1.102 5	0.923 4	Level II (clean yet)

4.3 Pollution load index method Firstly, based on the measured heavy metal content at a certain point, the following formula is used to calculate:

$$CF_i = \frac{C_i}{C_{0i}} \tag{4}$$

where CF_i is the highest pollution coefficient of element i; C_i is the measured value of element i, mg/kg; C_{0i} is elevation standard of element i, namely background value, mg/kg.

(1) The pollution load index PLI at a certain point is:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n}$$
 (5)

where PLI is pollution load index of one point; n is number of evaluation elements.

(2) The pollution load index (PLI_{zone}) of a certain region is:

$$PLI_{\text{zone}} = \sqrt[m]{PLI_1 \times PLI_2 \times PLI_3 \times \dots \times PLI_m}$$
 (6)

where m is number of evaluation points (number of sampling points); PLI_{max} is pollution load index of elevation region.

Classification of pollution load index level is shown in Table 10.

Table 10 Level of pollution load index

PLI value	Pollution level	Pollution degree
< 1	0	Non pollution
1 -2	I	Moderate pollution
2 - 3	II	Strong pollution
≥3	III	Extremely strong pollution

The results were shown in Table 11. From Table 11, it was known that the pollution load indexes of the six monitoring points in Duanzhou District, Zhaoqing City were lower than 1, and their corresponding pollution levels were all 0, indicating non pollution.

The pollution load index in Duanzhou District of Zhaoqing City was 0.3642, which was less than 1, indicating that the soil in

Duanzhou District has not been polluted due to the combined effects of Cu and Cd.

Table 11 Degree of pollution caused by Cu and Cd in each point and the entire area

Monitoring point	CF_{Cu}	CF_{Cd}	PLI_i	Pollution level at each point	PLI_{zone}	Regional pollution level
1# Beiling Mountain	0.062 1	0.033 3	0.045 5	Level 0 non pollution	0.364 2	Non pollution
2# Beach land of the Xijiang River	0.364 0	0.8167	0.545 2	Level 0 non pollution		
3# Concentrated residential area	0.505 0	0.9167	0.6804	Level 0 non pollution		
4# Commercial concentration zone	0.432 0	0.2500	0.328 6	Level 0 non pollution		
5# Xinghu Scenic Spot	0.402 0	0.5500	0.470 2	Level 0 non pollution		
6# Industrial land	0.762 0	1.0500	0.8945	Level 0 non pollution		

4.4 Geoaccumulation index method $^{[16]}$ The expression formula for the geoaccumulation index method is:

$$I_{geo} = \log_2\left(\frac{C_n}{k \times B_n}\right) \tag{7}$$

where I_{geo} is geoaccumulation index; C_n is the measured value of element n in the sample, mg/kg; B_n is geochemical background value of element n in the sediment, sometimes the element content

in local unpolluted area is used as the background value, mg/kg; k is revised index, the coefficient taken by considering the possible changes in background values caused by differences in rocks in different regions (the general value of 1.5), to show sedimentary characteristics, rock geology, and other influences.

The commonly used geochemical background values are shown in Table 12.

Table 12 Common geochemical background values for heavy metals pollution assessment

mg/kg

Element	Shale	Sandstone	Clay	Chinese continental crust	Entire continental crust
Cu	45.0	N	250.00	38.000	75.000
Cd	0.3	N	0.42	0.055	0.098

The classification of pollution levels was shown in Table 13.

Table 13 Classification of geoaccumulation index levels of heavy metals in sediments

I_{geo}	Grade	Pollution degree
$I_{geo} < 0$	0	Non pollution
$0 \leq I_{geo} < 1$	1	Non pollution – moderate pollution
$1 \leq I_{geo} < 2$	2	Moderate pollution
$2 \leq I_{geo} < 3$	3	Moderate pollution – heavy pollution
	4	Heavy pollution
$\begin{aligned} &3 \! \leq \! I_{geo} < \! 4 \\ &4 \! \leq \! I_{geo} < \! 5 \end{aligned}$	5	Heavy pollution - extremely heavy pollution
$I_{geo} \geqslant 5$	6	Extremely heavy pollution

The results were shown in Table 14. From Table 14, it can be concluded that the geoaccumulation index of Cu in all monitoring points of Duanzhou District was all less than 0, except for the industrial zone, corresponding to level 0. Overall, the soil has not been polluted by Cu. Among the monitoring points, the geoaccumulation index of Cd in the soil of 2# beach land of the Xijiang River, 3# concentrated residential area, and 6# industrial land

was greater than 0, indicating a pollution level of non pollution to moderate pollution. The pollution level of Cd in the soil of other monitoring points was non pollution, and the soil in Duanzhou District was generally not contaminated with Cd. However, for areas with a geoaccumulation index exceeding 0, people need to constantly prevent and control soil pollution from Cu and Cd, which tends to become more severe.

Table 14 Geoaccumulation and pollution levels of Cu and Cd in soil at various points

Maritania	I_{geo}		Grade		Pollution degree		
Monitoring point	Cu	Cd	Cu	Cd	Cu	Cd	
1# Beiling Mountain	-3.442 2	-5.491 8	Level 0	Level 0	Non pollution	Non pollution	
2# Beach land of the Xijiang River	-0.8909	0.122 8	Level 0	Level 1	Non pollution	Non pollution – moderate pollution	
3# Concentrated residential area	-0.4186	0.289 5	Level 0	Level 1	Non pollution	Non pollution – moderate pollution	
4# Commercial concentration zone	-0.6438	-1.585 0	Level 0	Level 0	Non pollution	Non pollution	
5# Xinghu Scenic Spot	-0.7477	-0.4474	Level 0	Level 0	Non pollution	Non pollution	
6# Industrial land	0.174 9	0.485 4	Level 1	Level 1	Non pollution – moderate pollution	Non pollution - moderate pollution	
Mean	-0.681 1	-0.321 9	Level 0	Level 0	Non pollution	Non pollution	

- **4.5** Potential ecological hazard index method^[17] The specific methods and steps of the potential ecological hazard index method are as follows:
- (1) Calculation of single heavy metal pollution coefficient, namely C_r^i , the formula is as below:

$$C_f^i = \frac{C_s^i}{C_n^i} \tag{8}$$

where C_f^i is enrichment coefficient of heavy metals; C_s^i is the measured content of heavy metal i in soil or sediment; $\operatorname{mg/kg}$; C_n^i is the required reference value by calculation, $\operatorname{mg/kg}$. Hakanson proposed using the highest background value of corresponding heavy metal element content in sediments before modern industrialization as a reference value. Generally, the national soil environmental standard value is taken as the reference value in the evaluation.

- (2) Pollution degree of heavy metals in soil or sediment, namely C_d , sum of pollution coefficients for various heavy metals: $C_d = \sum C_f^i$ (9)
- (3) Toxicity response coefficients of various heavy metals, namely T_r . In Hakanson standard, toxicity response coefficients of Cu and Cd are 5 and 30, respectively.
- (4) Potential ecological hazard coefficient of a certain heavy metal, namely E_r^i . Its calculation formulation is as below:

$$E_r^i = T_r^i \times C_f^i \tag{10}$$

(5) Potential ecological hazard index of multiple heavy metals in soil or sediment, namely RI. The formula is as below:

$$RI = \sum_{i=1}^{n} E_r^i \tag{11}$$

Classification relationships of C_f^i , E_r^i , and RI were shown in Table 15.

Table 15 Classification relationships of C_f^i , E_r^i , and RI

Range and pollution degree of \mathcal{C}_f^i		E_r^i range ϵ	and ecological risk degree of	RI range and overall potential ecological risk degree			
		si	ngle factor pollutant				
$C_f^i < 1$	Minor pollution	$E_r^i < 40$	Mild ecological hazard	RI < 150	Mild ecological hazard		
$1 \leq C_f^i < 3$	Moderate pollution	$40 \leq E_r^i < 80$	Moderate ecological hazard	$150 \le RI < 300$	Moderate ecological hazard		
$3 \leq C_f^i < 6$	Heavy pollution	$80 \le E_r^i < 160$	Strong ecological hazard	$300 \leq RI < 600$	Strong ecological hazard		
$C_f^i \geqslant 6$	Very heavy pollution	$160 \le E_r^i < 320$	Very strong ecological hazard	$600 \le RI < 1\ 200$	Very strong ecological hazard		
		$E_r^i \ge 320$	Very strong ecological hazard	<i>RI</i> ≥1 200	Very strong ecological hazard		

The results were shown in Table 16. From Table 16, it can be seen that the enrichment coefficient of Cu at each monitoring point was less than 1, indicating a slight pollution level. The potential ecological risk parameters at each point were relatively small and far less than 40, indicating a slight ecological hazard level. In industrial land, the enrichment coefficient of Cd was greater than 1, which was considered moderate pollution, while

the enrichment coefficients of other monitoring points were all less than 1, which was considered mild pollution. The potential ecological risk level of each point was also considered mild ecological hazard. After the superposition and average of the potential ecological hazard indices of Cu and Cd at each point, it can be concluded that the corresponding overall potential ecological risk level was mild ecological hazard.

Table 16 Pollution of Cu and Cd at various points

Monitoring point	C_f^{Cu} C_f^{Cd}		E_r^{Cu}	E_r^{Cd}	RI	Pollution degree		Ecological risk degree of single factor pollutant		Overall potential ecological risk degree
						Cu	Cd	Cu	Cd	ecological risk degree
1# Beiling Mountain	0.062 1	0.033 3	0.310 5	0.999 0	1.309 5	Mild pollution	Mild pollution	Mild ecologic	al hazard	Mild ecological hazard
2# Beach land of the Xijiang River	0.3640	0.8167	1.8200	24.321 0	26. 141 0	Mild pollution	Mild pollution	Mild ecologic	al hazard	Mild ecological hazard
3# Concentrated residential area	0.505 0	0.9167	2.525 0	29.0100	31.535 0	Mild pollution	Mild pollution	Mild ecologic	al hazard	Mild ecological hazard
4# Commercial concentration zone	0.432 0	0.2500	2.160 0	7.500 0	9.6600	Mild pollution	Mild pollution	Mild ecologic	al hazard	Mild ecological hazard
5# Xinghu Scenic Spot	0.402 0	0.5500	2.0100	16.5000	18.5100	Mild pollution	Mild pollution	Mild ecologic	al hazard	Mild ecological hazard
6# Industrial land	0.762 0	1.0500	3.8100	31.500 0	35.3100	Mild pollution	Moderate pollution	Mild ecologic	al hazard	Mild ecological hazard
Mean	0.421 0	0.3600	2.105 0	10.8000	12.905 0	Mild pollution	Mild pollution	Mild ecologic	al hazard	Mild ecological hazard

5 Conclusions

- (1) By comparing the content distribution of Cu and Cd in soil at various monitoring points in Duanzhou District of Zhaoqing City, it can be concluded that for Cu, industrial land (6#) > concentrated residential area (3#) > commercial concentration zone (4#) > Xinghu Scenic Spot (5#) > beach land of the Xijiang River (2#) > Beiling Mountain (1#). For Cd, industrial land (6#) > concentrated residential area (3#) > beach land of the Xijiang River (2#) > Xinghu Scenic Spot (5#) > commercial concentration zone (4#) > Beiling Mountain (1#).
- (2) The survey results on the distribution of heavy metals content in soil of Duanzhou District, Zhaoqing City showed that except for 1# Beiling Mountain area, the content of Cu and Cd in the soil of the other five monitoring points was higher than the background value of soil in Guangdong Province, indicating a significant accumulation phenomenon^[18].
- (3) The spatial distribution characteristics indicated that the areas with relatively severe Cu and Cd pollution were concentrated in 6# industrial land and 3# residential area, while the undevel
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oped and unpolluted areas such as 1# Beiling Mountain, which are far away from industrial land and residential area, had relatively lower Cu and Cd content.

- (4) The evaluation results showed that the relatively high content of Cu and Cd in the soil of industrial land and residential area was the main reason for the increase in Cu and Cd content in the soil of Zhaoqing City, resulting in a decline in soil quality in the entire Duanzhou District of Zhaoqing City.
- (5) In Duanzhou District, the accumulation effect of Cd was greater than that of Cu. Therefore, people should pay sufficient attention to the pollution of Cd in soil, especially in industrial land and residential area, to avoid further pollution caused by human factors.

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