Morphological distribution and risk assessment of soil heavy metals in the Belly of the Three Gorges Reservoir area in Chongqing-A Case Study of Fengdu

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Abstract. The study of the morphological distribution and pollution risk of heavy metals in the hinterland of the Three Gorges Reservoir area in Chongqing can be used to provide data support for soil pollution prevention and control, ecological environment safety risk control and agricultural healthy development in the region. In this paper, Fengdu County, the hinterland of the Three Gorges Reservoir Area in Chongqing, was taken as the study area. The total amount and morphology of 8 heavy metal elements in the surface soil of agricultural land were analyzed and determined. The geocumulative index method was used to evaluate the pollution degree. The risk assessment coding method is used to evaluate the potential risk level. The results showed that the average contents of heavy metal elements As, Hg, Cu and Cr in the soil in the study area were relatively low. The average contents of Cd, Zn, Pb and Ni were higher than those in the Three Gorges Reservoir area. The mean value of Cd content was 1.71 times that of the background value. Cd in the soil heavy metal form is dominated by ion exchange state. The proportion of carbonate-bound state and iron-manganese bound state is relatively high. The proportion of bioavailable state was 46.36%, and the biological activity was strong. The other elements are mainly in the stable residue state. The results of the geoaccumulation index method showed that Cd was mainly mild pollution level. The other elements are mainly clean and pollution-free levels. The evaluation results of the risk assessment coding method showed that the risk of Cd contamination was the highest, and the risk of contamination of other elements was relatively low. On the whole, there is a certain degree of potential pollution risk in the soil Cd in the study area. Attention needs to be paid to the prevention and control of Cd.

Keywords: Soil; Heavy metals; Morphological distribution; Risk assessment; the Three Gorges Reservoir area.

1. Introduction

According to the National Soil Pollution Survey Bulletin (2014), the overall soil environment in China is not optimistic. The total exceedance rate of soil was 16.1%, of which the number of heavy metals exceeded 82.8%. Soil heavy metal pollution is a serious problem. Compared with other pollution, soil heavy metal pollution has the characteristics of wide source, universality, concealment, surface aggregation, irreversibility, long-term, migration and biomagnification[1-5]. The extensive development of mineral resources, the disorderly discharge of industrial wastes, the irrational irrigation of sewage, and the excessive input of agricultural production materials such as chemical fertilizers, pesticides, and agricultural films are the main causes of soil heavy metal pollution[6-10]. The physicochemical properties of the soil are affected by these heavy metals entering the soil, resulting in the inhibition of microbial activity in the soil. At the same time, soil quality and productivity are reduced. What's more, these heavy metals can directly or indirectly enter the human body through the "soil-crop-human" food chain. The soil ecological environment has been destroyed. Food security, human health and ecosystems are threatened[3-11]. The Three Gorges Reservoir area is linked by water, connecting Chongqing to Wuhan. It is an important ecological barrier and ecological economic zone in the Yangtze River Basin. As the hinterland of the Three Gorges Reservoir area, the Chongqing section is an ecologically fragile area, a sensitive area and an important production base for agricultural products in the upper reaches of the Yangtze River. The soil heavy metal pollution in the Three Gorges Reservoir area is directly related to the ecological security of the entire Yangtze River Basin. At present, the research on soil heavy metals in the Chongqing section of the Three Gorges Reservoir area at home and abroad mainly focuses on the subsidence zone and inundation area. The content distribution, influencing factors, pollution status and ecological impact of heavy metals in soil have received attention[12, 13]. However, there are few studies on heavy metals in regional agricultural soils, and they are only limited to the total distribution and pollution characteristics of heavy metals[14, 15]. The research on the morphological distribution characteristics and risk assessment of heavy metals is relatively weak. However, the biohazard and environmental impact of heavy metals are not only related to their total amount, but also depend to a greater extent on the morphological distribution characteristics of heavy metals. The mobility, bioavailability and environmental impact of different morphological distributions vary greatly[16-19]. Therefore, it is necessary to analyze the morphological characteristics of heavy metals while studying their total amounts.

In this paper, Fengdu County in the heart of the Three Gorges Reservoir Area of Chongqing was taken as the study area. Take soil heavy metals as the starting point. To study the morphological distribution characteristics and ecological risks of heavy metals in soil in the reservoir area. In order to provide data support for the prevention and control of soil pollution, ecological environment safety risk management and control, and the healthy development of agriculture in the reservoir area.

2. Materials and Methods

2.1 Overview of the study area

The Three Gorges Reservoir area refers to the administrative area that was inundated due to the impoundment of 175 meters of water by the Three Gorges Project. From the main urban area of Chongqing to Yichang, Wuhan. The study area is located in the hinterland of the reservoir area in the upper reaches of the Yangtze River. It is a national key ecological function area and belongs to the subtropical monsoon climate zone. Its landform type is mainly hilly, supplemented by mountains. Sedimentary rocks are widely developed, and Mesozoic Jurassic strata are exposed in large areas. The soil types are mainly paddy soil, purple soil, lime soil and yellow soil. The main types of land use are paddy fields, dry land, orchards, and forested land. The main crops are rice, corn, etc.

2.2 Sample collection and analysis

This work is based on the results of a 1:50,000 soil survey conducted in the previous study area. The principles are based on the research purpose, topographic and geomorphological characteristics, representativeness and uniformity. The topsoil corresponding to the high value, low value and average value of heavy metal content in agricultural land soil was selected as the sampling site. Samples are collected to a depth of between 0-20 cm. A total of 95 samples were collected. The sampling points are shown in Figure 1.

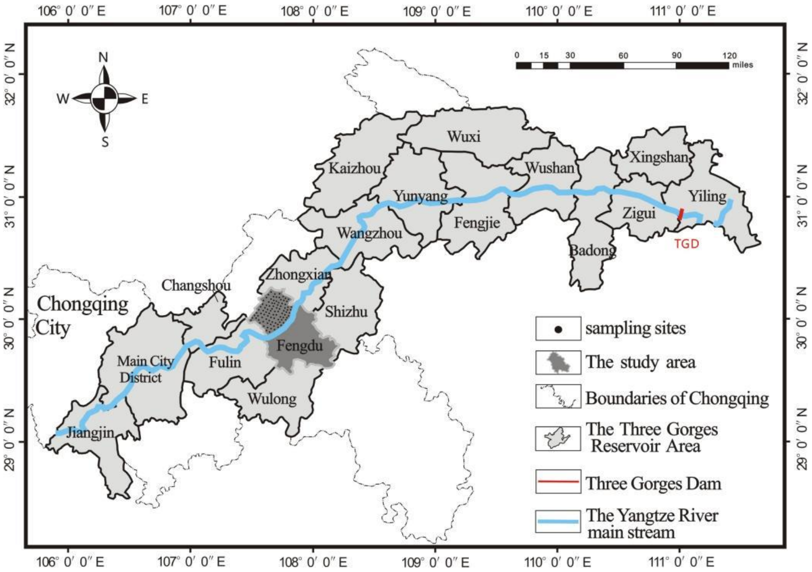

Figure.1 Schematic diagram of the location of the study area and sampling points

Plant debris, grit and gravel were removed from the collected soil samples. It is naturally dried and ground in pieces. Samples were screened through 10-, 100-, and 200-mesh nylon sieves. Samples passed through a 10-mesh nylon sieve are used for pH determination. Samples passed through a 100-mesh nylon sieve are used for heavy metal speciation. Samples passed through a 200 mesh nylon sieve were used for the determination of the total amount of heavy metals. The pH of the soil was determined using the ion electrode method (ISE). The As and Hg of soil were determined by atomic fluorescence spectroscopy (AFS). Ni, Cd, Cu and Pb of soil were determined by inductively coupled plasma mass spectrometry (ICP-MS). The Zn and Cr of the soil were determined by X-ray fluorescence spectroscopy (XRF). The seven-step sequential extraction method was used for the speciation analysis of heavy metals in soil. Water, magnesium chloride, sodium acetate, sodium pyrophosphate, hydroxylamine hydrochloride and hydrogen peroxide were used as extraction agents. The soil was acid-treated and determined using inductively coupled plasma mass spectrometry (ICP-MS) and atomic fluorescence (AFS). The testing process is strictly in accordance with the relevant provisions of the "DZ/T0295-2016 Code for Geochemical Evaluation of Land Quality". Methods of external laboratory quality control and internal quality control are employed to control the quality of sample analysis.

2.3 Pollution degree and risk assessment

The Geoaccumulation Index (I_{geo})[20] takes into account the effects of anthropogenic activities and natural geology that may cause changes in the background values of heavy metals. The formula for this is $I_{geo} = \log_2 C_i/(KB_i)$. C_i is the measured content of heavy metal element (i) in soil. K is the background value fluctuation parameter caused by diagenesis, the value is 1.5. and B_i is the regional background value of heavy metal (i). The background values of heavy metal elements in the soil of Chongqing were adopted[14]. The background values of As, Hg, Ni, Cd, Cu, Pb, Zn and Cr were 5.835 mg·kg^{-1}, 0.046 mg·kg^{-1}, 29.47 mg·kg^{-1}, 0.134 mg·kg^{-1}, 25.00 mg·kg^{-1}, 23.88 mg·kg^{-1}, 69.88 mg·kg^{-1} and 78.03 mg·kg^{-1}, respectively. The classification standard of pollution degree is shown in table 1[21].

Table 1 Grading criteria for the geoaccumulation index method

I_{geo}	Degree of contamination	I_{geo}	Degree of contamination
$I_{geo} \leq 0$	Clean	$3 < I_{geo} \leq 4$	Heavy pollution
$0 < I_{geo} \leq 1$	Mild pollution	$4 < I_{geo} \leq 5$	Heavily polluted

1< I_{geo} ≤2	Moderate pollution	I_{geo} >5	Extremely heavily polluted
2< I_{geo} ≤3	Severe pollution		

The Risk Assessment Coding Method (RAC) is widely used to evaluate the chemical activity, bioavailability and risk degree of soil heavy metals[22][23]. The formula for this is $RAC = (F_1 / HM) \times 100\%$. Among them, F_1 is the content of weak acid extraction state (including water-soluble, ion-exchange and carbonate-bound state). HM is the total amount of heavy metals. The pollution risk classification criteria are shown in Table 2[21][24].

Table 2 Grading criteria for risk assessment coding method

RAC	Degree of risk	RAC	Degree of risk
RAC≤1	Risk-free	30<RAC≤50	High risk
1<RAC≤10	Low risk	RAC>50	Extremely high risk
10<RAC≤30	Moderate risk		

3. Results and Discussion

3.1 Characteristics of total distribution of heavy metals in soil

The total amount of heavy metals and pH in the soil of the study area are shown in table 3. The contents of As, Hg, Ni, Cd, Cu, Pb, Zn and Cr were 1.05-12.80mg·kg^{-1}, 0.01-0.13mg·kg^{-1}, 10.90-43.30mg·kg^{-1}, 0.08-0.44mg·kg^{-1}, 6.97-36.40mg·kg^{-1}, 17.90-35.00mg·kg^{-1}, 32.50-110.00mg·kg^{-1}, 23.30-85.70mg·kg^{-1}, respectively. The average contents were 5.33mg·kg^{-1}, 0.03mg·kg^{-1}, 30.71mg·kg^{-1}, 0.23mg·kg^{-1}, 22.44mg·kg^{-1}, 25.56mg·kg^{-1}, 81.06mg·kg^{-1} and 60.47mg·kg^{-1}, respectively.

Table 3 Statistics of soil heavy metal content in the study area

Area	Item	Heavy metal elements（mg.kg-1）							
		As	Hg	Ni	Cd	Cu	Pb	Zn	Cr
Aegion of interest(n=95）	Minimum value	1.05	0.01	10.90	0.08	6.97	17.90	32.50	23.30
	Maximum value	12.80	0.13	43.30	0.44	36.40	35.00	110.00	85.70
	Mean value	5.33	0.03	30.71	0.23	22.44	25.56	81.06	60.47
	Standard deviation	2.22	0.02	7.73	0.07	5.65	3.52	16.13	12.36
Background value of Three Gorges Reservoir Area		5.84	0.05	29.47	0.13	25.00	23.88	69.88	78.03

3.2 Morphological distribution characteristics of heavy metals in soil

The geochemical behavior of heavy metals in soil is not only related to the total amount of heavy metals in soil. It is largely determined by its morphological distribution. The water soluble state, ion exchange state and carbonate bound state are easy to migrate, transform and absorb, which is called biologically effective state, and has great biological hazards and environmental impacts. Humic acid bound state, iron-manganese bound state and strong organic bound state are relatively stable, which can release and transform in appropriate environment to cause harm. The residual state is the most stable and difficult to release under normal conditions in nature, and is less harmful to biology and the environment[25]. The forms of heavy metals in the soil of the study area are shown in Fig.2. The distribution ratio of heavy metal elements in soil is quite different. As, Hg, Ni, Cu, Pb, Zn and Cr accounted for 78.77 %, 50 %, 75.19 %, 81.34 %, 61.39 %, 73.76 % and 89.75 %, respectively, and mainly existed in the soil in a stable form.Cd is mainly in ion exchange state. Carbonate-bound and iron-manganese-bound states account for a relatively high proportion. The mean values of the three were 27.02 %, 18.73 %, and 20.34 %, respectively, and the proportion of bioavailable state was 46.36 %. This indicates that it has strong biological activity and is easy to migrate and transform. We should pay attention to its toxicity and prevention and control. Except for the residual state, the humic acid bound state and strong organic bound state of Hg were significantly higher than other elements, with an average proportion of 12.5 %. The proportion of iron-manganese bound state of Pb was 27.14 %, which was significantly higher than that of other heavy metal elements. Previous studies have suggested that this is due to the strong adsorption capacity of iron and manganese hydroxides in soil for lead[26].

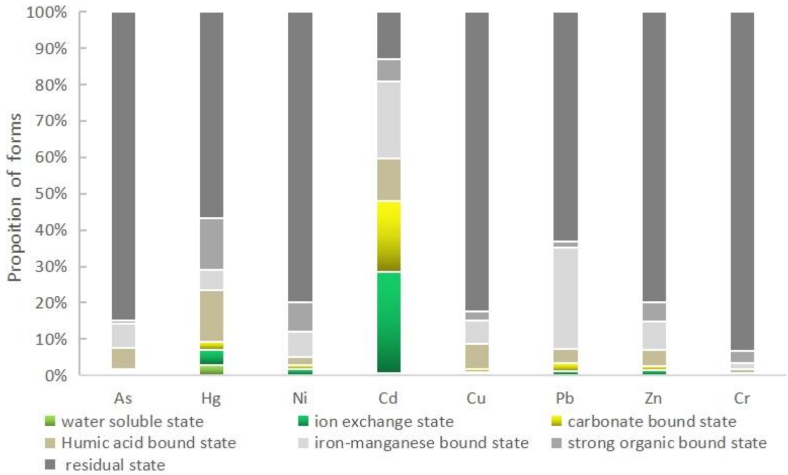

Figure.2 The distribution map of heavy metals in the soil of the study area

3.3 Degree and risk assessment of soil heavy metal pollution

3.3.1 Evaluation of the land accumulation index

The evaluation results of soil heavy metal accumulation index are shown in Fig.3. The *Igeo* of Cu, Pb, Cr and Ni in the soil of the study area is less than 0, which is at a clean and pollution-free level. The average value of *Igeo* of Zn, As and Hg is less than 0, and the accumulation degree is low, which is mainly at the clean level. Only some points were at mild pollution level. The *Igeo* of Cd ranged from-1.29 to 1.12, with an average value of 0.12, which was between clean and moderate pollution. Most of them are at the level of mild pollution, and only a few points are at the level of moderate pollution. On the whole, the soil environment in the study area is good, and only the slight pollution of Cd is more prominent, which indicates that there is a certain potential risk in the soil.

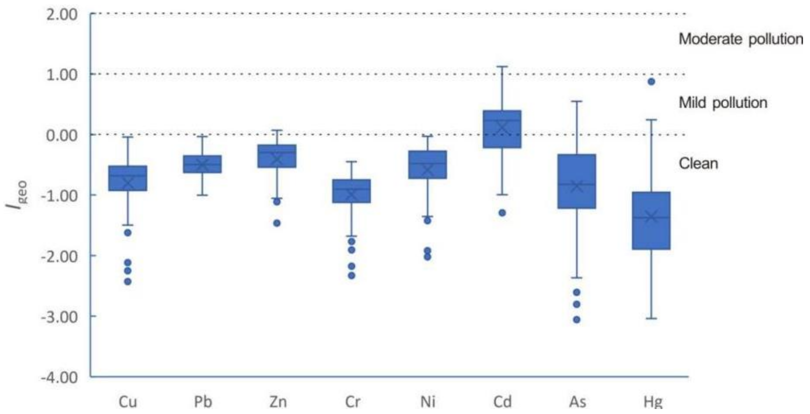

Figure.3 Distribution of geoaccumulation index (Igeo) of soil heavy metals in the study area

3.3.2 Risk assessment code evaluation

The evaluation results of soil heavy metal risk assessment coding method are shown in figure 4. The *RAC* range of soil Cr, As and Cu in the study area was 0.39 % -1.75 %, 0.43 % -5.43 % and 0.62 % -6.53 %, respectively. The mean values were 0.77 %, 1.85 % and 1.95 %, respectively, which belonged to the risk-free to low-risk level. Most of the Cr samples are at risk-free level. Most of the samples of As and Cu are at low risk level. The *RAC* ranges of Zn, Ni, Pb and Hg were 0.92 % -10.34 %, 0.72 % -10.55 %, 1.72 % -10.76 % and 1.58 % -20.24 %, respectively, and the mean values were 2.61 %, 2.78 %, 3.31 % and 8.77 %, respectively. It belongs to risk-free to medium risk level or low risk to medium risk level, and most of the samples are low risk level. The *RAC* of Cd ranged from 10.89 % to 69.72 %, with an average of 8.77 %, which was at a medium to very high risk level, and most of the samples were at a high risk level. On the whole, the pollution risk level of most heavy metal elements in the soil of the study area is relatively low. The risk level of Cd pollution is high, and the potential ecological risk to soil environment cannot be ignored. This result is similar to the conclusion of other research results in the Three Gorges Reservoir area[21].

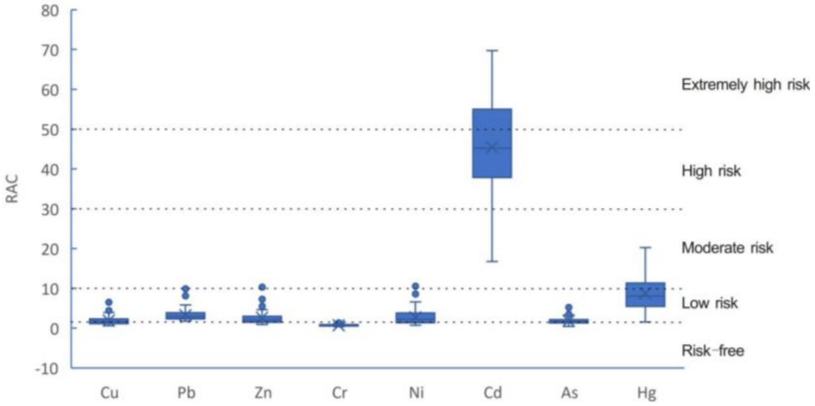

Figure.4 The distribution of soil heavy metal risk assessment code index (RAC) in the study area

3.3.3 Analysis of evaluation results

The results of the cumulative index method showed that Cd in the soil was mainly at a light pollution level. Zn, As and Hg were mainly at clean level. Cu, Pb, Cr and Ni are all clean levels. The results of risk assessment coding method showed that Cd in soil was mainly high risk. Zn, As, Hg, Cu, Pb and Ni are mainly low risk. Cr is risk-free. The results of the two evaluation methods are quite different. The reason is that the ecological risk evaluated by the cumulative index method is caused by the total amount of heavy metals. The ecological risk evaluated by the risk assessment coding method is caused by the effective state of heavy metals. However, both indicate that Cd in the soil of the study area has a certain degree of ecological risk, and the biological toxicity and prevention and control of the study area need to be taken seriously.

4. Conclusion

(1) The average contents of Cd, Zn, Pb and Ni in the soil of the study area were higher than the background values of the soil in the Three Gorges Reservoir area. The Cd content was 1.71 times of the soil background value. Except that the proportion of Cd super-screening value was 2.11 %, the contents of other elements were lower than the screening value.

(2) The forms of heavy metal elements in soil are mainly stable residual state except Cd. Cd is mainly in the ion exchange state, and its bioavailable state accounts for a relatively high proportion and has strong biological activity.

(3) The evaluation results of geo-accumulation index method showed that Cd in the soil of the study area was mainly mildly polluted. Other elements are clean and pollution-free as a whole. The results of risk assessment coding method showed that the soil Cd in the study area was dominated by high risk. Other elements generally belong to low ecological risk, and attention should be paid to Cd prevention and control.

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