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Characteristics and sources of heavy metal pollution in surface sediments of Futuan River Estuary

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Abstract: *This study systematically collected surface sediment samples from the Futuan River Estuary, carried out heavy metal analysis and testing, analyzed the pollution characteristics of heavy metals in surface sediments, and studied the source of heavy metals based on correlation analysis and principal component analysis. The average contents of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn were 4.92, 0.09, 9.34, 46.03, 17.74, 0.015, 733.07, 20.16, 23.78, 48.94 mg/kg. As, Cd , Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn elements have strong correlation and high homology. Ten heavy metals such as As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn, and Fe2O3 have larger loadings on the first principal component, indicating that these elements are affected by the natural background. As, Cu, Mn and Pb have larger loads on the second principal component, which may represent the source of human activities.*

Keywords *: heavy metals, sediment, source, pollution*

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I. Introduction

Estuary sediments are natural "sinks" of heavy metals, and heavy metals immobilized in sediments will not enter the overlying waters under normal conditions[1]. However, under the action of water bioturbation and waves and currents, the sediment deposited on the river bottom will be suspended and transported again, and heavy metals will enter the overlying water body and become the secondary pollution "source" of heavy metals[2-3]. Therefore, estuarine sediment is not only an important place for the occurrence of pollutants such as heavy metals, but also an endogenous source of estuarine pollution. Heavy metals have toxic effects on estuarine ecosystems, thereby changing the service functions of estuarine ecosystems, is recognized as one of the main pollutants in the water environment[4-5].

In this study, the surface sediment samples of Futuan were collected systematically, and the contents of 11 heavy metal elements such as As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn and Li were measured, and the enrichment degree of heavy metals in the surface sediments of the estuary was analyzed.

II. Descriptive statistics of heavy metal content in sediments

The average value of As in the sediments is 4.92 $mg \cdot kg^{-1}$, which is significantly lower than the background value of sediments in the shallow seas of China, indicating that As can maintain the natural background, and there is basically no external input. The average contents of Co, Cr, Hg, Ni and Zn were 9.34, 46.03, 0.015, 20.16 and 48.94 $mg \cdot kg^{-1}$, respectively, which were all lower than the background values of shallow sea sediments in China. The average content of Cd is 0.09 $mg \cdot kg^{-1}$, which is 1.41 times of the background value of shallow sea sediments in China, and the content range is 0.02-0.19 $mg \cdot kg^{-1}$. The average Cu content was 17.74 $mg \cdot kg^{-1}$, which was slightly higher than the background value of the shallow sea sediments in China, ranging from 2.00-45.72 $mg \cdot kg^{-1}$. The average value of Mn is 733.07 $mg \cdot kg^{-1}$, which is 1.38 times of the background value of shallow sea sediments in China, and the highest value of Mn is 3.29 times of the average value. The average value of Pb was 23.78 times, which was 1.19 times the background value. Therefore, Cd, Cu, Mn and Pb may be subject to certain exogenous input. The coefficients of variation of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn are all highly variable, indicating that the ten heavy metals are not uniformly distributed. From the perspective of skewness, the skewness of these ten heavy metals are 1.22, 0.12, 0.26, -0.07, 0.85, 0.37, 1.51, 0.56, 0.54 and 0.39, respectively, and their order of magnitude is Mn>As>Cu>Ni>Pb> Zn>Hg>Co>Cd>Cr, no prominent skewness.

III. Correlation analysis

The correlation coefficients between heavy metal elements and Fe_2O_3 in surface sediments are shown in Table 1. The correlation coefficients between 10 heavy metals such as As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn are between 0.599 (Cd-Pb) and 0.982 (Ni and Zn), and all pass Significance test at 0.01 level. The above results show that As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn elements have strong correlation and high homology. Studies

have shown that Fe_2O_3 is closely related to the weathering of the parent rock. The elements with high correlation with Fe_2O_3 usually belong to natural sources, while the elements with low correlation with Fe_2O_3 belong to the sources of human activities. The correlation coefficients of Cd, Co, Cr, Ni, Zn and Fe_2O_3 were 0.865, 0.954, 0.971, 0.922 and 0.930, respectively, and all passed the significance test at the 0.01 level, indicating that these seven elements may be affected by the parent material. The correlation coefficients of As, Cu, Pb and Fe_2O_3 are relatively small, 0.758, 0.638 and 0.637, respectively, indicating that these three elements may be affected by soil-forming parent materials, and at the same time may be affected by exogenous input caused by human activities.

Table 1 Correlation analysis of heavy metals in surface sediments

	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	Fe_2O_3
As	1										
Cd	0.756**	1									
Co	0.872**	0.902**	1								
Cr	0.801**	0.868**	0.957**	1							
Cu	0.853**	0.684**	0.741**	0.694**	1						
Hg	0.872**	0.903**	0.894**	0.814**	0.767**	1					
Mn	0.907**	0.651**	0.846**	0.827**	0.778**	0.738**	1				
Ni	0.927**	0.877**	0.976**	0.956**	0.817**	0.895**	0.900**	1			
Pb	0.804**	0.599**	0.684**	0.724**	0.810**	0.644**	0.784**	0.791**	1		
Zn	0.888**	0.911**	0.960**	0.959**	0.806**	0.887**	0.856**	0.982**	0.801**	1	
Fe_2O_3	0.758**	0.865**	0.954**	0.971**	0.638**	0.780**	0.802**	0.922**	0.637**	0.930**	1

IV. Principal Component Analysis

There are two main sources of heavy metals in surface sediments, namely natural sources and human activities. The principal component analysis method is an effective method to identify the source of heavy metal pollution. Table 2 shows the results of the principal component analysis of heavy metals in the surface sediments of the Futuan River Estuary. The variance contribution rates of the first two principal components are 84.78% and 6.74%, respectively, and the cumulative variance contribution rate reaches 91.52%; the eigenvalues are 9.326 and 0.741, respectively, indicating that the data in Table 9-17 can represent the information contained in the data. Ten heavy metals such as As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn, and Fe_2O_3 have larger loads on the first principal component (PC1), which are 0.932, 0.894, 0.970, 0.949, and 0.845, respectively. , 0.910, 0.898, 0.994, 0.813, 0.987 and 0.919 indicate that these 10 heavy metals are controlled by the first principal component and may belong to natural sources. The loadings of As, Cu, Mn and Pb on the second principal component are 0.226, 0.390, 0.224 and 0.456, respectively, so these four elements are affected by the second principal component and may come from human activities; therefore, As, Cu, Mn and Pb are the common source of the first principal component and the second principal component, that is, the natural source and the source of human activities.

Table 2 Analysis of main components of heavy metals in surface sediments

	PC1	PC2
As	0.932	0.226
Cd	0.894	-0.318
Co	0.970	-0.191
Cr	0.949	-0.199
Cu	0.845	0.390
Hg	0.910	-0.106
Mn	0.898	0.224
Ni	0.994	-0.024
Pb	0.813	0.456
Zn	0.987	-0.064

Ten elements including As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn have large loads on the first principal component. The correlation analysis shows that the correlation between these 10 heavy metal elements is relatively high (Table 2), and the correlation with Fe_2O_3 is higher than 0.637, indicating that these 10 elements are affected by the parent material of soil formation and may belong to natural source. The average contents of As, Co,

Cr, Cu, Hg, Ni, Pb and Zn are 4.92, 9.34, 46.03, 17.72, 0.02, 20.16, 23.78 and 48.94 mg/kg, respectively, which are close to the background values of heavy metals in shallow seas in China, indicating that these 8 Elements belong to lithologic sources. Normally, Cr and Ni in soil and sediments are controlled by soil parent material, and are much larger than chemical fertilizers and organic fertilizers on the content of these two elements. Cr and Ni are the least polluting heavy metals in soil. Normally, when other elements are classified into the same component as Cr and Ni when using multivariate analysis for heavy metal source analysis, this component is considered to be controlled by natural sources. Therefore the first principal component represents the natural source, ie the lithological source.

As, Cu, Mn and Pb have larger loads on the second principal component, which may represent the source of human activities. The Futuan River is located in Rizhao City, Shandong Province, and the entire river basin has extensive agricultural development. In the process of agricultural production, excessive chemical fertilizers and organic fertilizers are often used to increase crop yields, but chemical fertilizers are not fully utilized by crops after entering the soil. According to statistics, the utilization rate is only 15% to 35%. In addition, inorganic arsenic compounds are important components of pesticides or herbicides, and the use of pesticides and herbicides inevitably increases the As content in soil. According to statistics, 8% to 25% of As in agricultural and agricultural soils in my country comes from livestock manure, and As in organic fertilizers mainly comes from arsenic-containing feeds. Crops lacking Mn are susceptible to yellowing disease, so manganese sulfate is usually added to fertilizers to increase soil fertility and maintain normal crop growth; spraying Mn-containing pesticides can prevent pests and diseases and increase crop yield. The average content of Pb in the organic fertilizer was 87.4 mg/kg, which was 4.37 times the background value of China's shallow sea sediments. The utilization rate of chemical fertilizers and pesticides is very low, only about 30% is absorbed and utilized by crops, and 70% enters the soil, air and surface runoff. In summary, the second principal component represents the sources of agricultural activities, such as the use of pesticides, chemical fertilizers, and organic fertilizers.

V. Conclusion

The average contents of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn are 4.92, 0.09, 9.34, 46.03, 17.74, 0.015, 733.07, 20.16, 23.78, 48.94 mg/kg. Cd, Co , Cr, Ni, Zn and Fe_2O_3 have large correlation coefficients, indicating that these seven elements may be affected by soil-forming parent materials. However, the correlation coefficients of As, Cu, Pb and Fe2O3 are relatively small, indicating that these three elements may be affected by soil-forming parent materials, and at the same time, they may be affected by exogenous input caused by human activities. Principal component analysis showed that As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn were affected by natural background; meanwhile, As, Cu, Mn and Pb were affected by human activities.

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