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Research Article

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Heavy metals in sediments of Yangzonghai Lake, China

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ABSTRACT

The content of the heavy metals lead, copper, chromium, manganese, zinc and arsenic in Yangzonghai surface sediment was determined, the pollution level of heavy metal was evaluated by adopting geo-accumulation index method, and the source of the heavy metal in sediment was studied through principal component analysis. The results indicate that the mean values of lead, copper, chromium, manganese, zinc and arsenic in the surface sediment of Yangzonghai were 40.3, 97.6, 145.8, 617.9, 149.2, 31.4mg kg^{-1} respectively. The accumulation of copper was the most serious, with the I_{geo} value reaching 2.42. The accumulation of lead was least serious, which was in mild pollution level. Heavy metals in the descending order of their pollution levels were copper, arsenic, chromium, zinc, manganese and lead. The principal component analysis indicates that the contribution rates of the first three principal components were 44.858%, 30.887% and 13.141% respectively, and the pollutants under high load were (lead, zinc, arsenic), (copper, manganese) and (chromium) in sequence. Industrial pollution and geochemical processes were the two main sources of heavy metals in sediment.

Keywords: sediment, heavy metal, principal component analysis, Yangzonghai Lake.

INTRODUCTION

Heavy metal is one class of conservative pollutants with potential hazards [1]. As heavy metal is characterized by recalcitrance, general biotoxicity, bioaccumulation and biomagnifications, heavy metal pollution in the environment has drawn great attention [2]. In recent years, heavy metal contamination of surface water occurs frequently, which threatens the water safety of local residents and also causes huge economic losses. Once heavy metal enters into surface water environment, the vast majority of heavy metals quickly transfer into suspended matter and sediment. And the suspended matter gradually changes into sediment during the water removal process. The distribution characteristic of the heavy metals in sediment can present evident pollution plume law while its distribution in water has no rule [3]. Therefore, the study on the content and distribution of the heavy metals in sediment is significantly important for identifying the current situation of water pollution, analyzing the history of water pollution, determining the source of pollution and evaluating the environmental effect of the human activities in the watershed area on water body [4].

Yangzonghai (E102°59'-103°02', N24°51'-24°58') is one of the nine plateau lakes in Yunnan Province and the freshwater lake which the local residents live by. The lake is spindle-like, it is 2.5km from east to west and 12.7km from north to south, and its lake shoreline is 32.3km long. The lake area is 31.9km^2 and the watershed area is 192km^2. The maximum depth of water is 29.7m, the average depth of water is 20m, the water storage capacity is 604 million m^3 and the period of exchanging water is 13 years [5-6]. In the recent 20 years, with the rapid development of industry, agriculture, fishery and tourism on the both sides, a large amount of pollutants is discharged into the lake. The heavy metals in the lake increase continuously, accumulate in the bottom sediment and become the "second source of pollution" in the overlying water body. In this paper, the distribution characteristics of the heavy metals was found out through the determination of the content of the heavy metals lead (Pb), copper (Cu), chromium (Cr), manganese (Mn), zinc (Zn) and arsenic (As) in Yangzonghai sediment, the pollution level of heavy metal was evaluated by adopting geo-accumulation index method and the source of the pollutants was studied by using principal component analysis in the hope of providing a theoretical basis and decision support for heavy metal pollution control in Yangzonghai.

EXPERIMENTAL SECTION

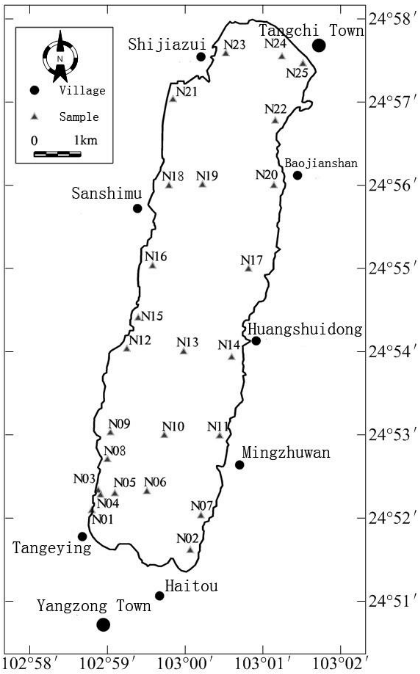

Fig. 1 The sampling stations

From April 2 to April 4, 2009, a total of 25 groups of 0-5cm surface sediment samples were collected from the Yangzonghai with a grab sampler (Figure 1). After well mixed, these samples were placed in polythene plastic bags to naturally dry in the shade in the laboratory. Then, by eliminating plant and animal residues and stones, the samples were grinded. Through 200-mesh screening, they were placed in a 105℃ oven to be dried for 8 hours, taken out, and put into dry basins. 4.00g of soil samples were weighted and squashed, and elements were determined with a PW4400 X-ray fluorescence spectrometer in accordance with JY/T016-1996 General Method of Wavelength-Dispersive X-ray Fluorescence Spectrometry published by the State Education Commission of China.

RESULTS AND DISCUSSION

Content and Distribution of Heavy Metals: The average content of the six kinds of heavy metals in Yangzonghai sediments exceeds the soil environmental background value of Yunnan Province in 1990 (Table 1). The minimum value of the content of Pb is 21.2 mg kg^{-1}, the maximum value is 69.1mg kg^{-1}, and the average value is 40.3 mg kg^{-1}, which is slightly higher than the background value. The content is in the range of 30mg kg^{-1} to 40mg kg^{-1}. In horizontal distribution, the content of Pb in the sediments around the Tangeying on south bank is relatively high, and the content of Pb in the sediments around Huangshuidong on east bank is relatively low. The content of Cu is in the range of 48.3mg kg^{-1} to 270.3mg kg^{-1}, it is 97.6mg kg^{-1} in average, which is about three times the background value. The content around Huangshuidong on east bank is relatively high, and the content in the rest areas is basically in the range of 50 mg kg^{-1} to 150mg kg^{-1}. The content of Cr is usually in the range of 100mg kg^{-1} to 150mg kg^{-1}, the average value is 145.8mg kg^{-1}, which is nearly three times the background value. The point with high value locates around Tangeying on south bank and Shijiazui on north bank. The majority of the content of Mn is below 800mg kg^{-1}, the average value is 617.9mg kg^{-1}, which is slightly higher than the background value. The content around Huangshuidong is the highest, which is 1077.4mg kg^{-1}; the average content of Zn is 149.2 mg kg^{-1}, which is nearly twice the background value, except for the content around the Tangeying on south bank is relatively high, the majority of the content in the rest areas is in the range of 100mg kg^{-1} to 200mg kg^{-1}; the content of As is basically below 40mg kg^{-1}, the average value is 31.4 mg kg^{-1}, which is three times the background value. The maximum value is around Tangeying on south bank, and the content is 113.2mg kg^{-1}. Figure 2 is the chart of the content of each metal in Yangzonghai sediment.

Table 1 Background values of heavy metals of Yunnan (mg ·kg^{-1})

Elements	Pb	Cu	Cr	Mn	Zn	As
Background values	36	33.6	57.6	461	80.5	10.8

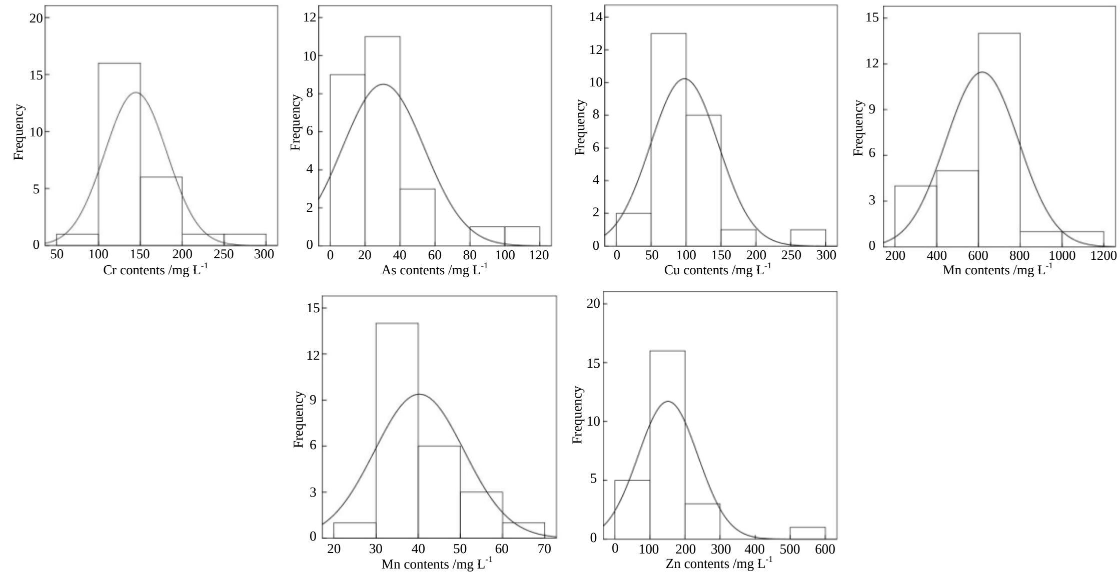

Fig. 2 Statistical histogram of heavy metals in sediments from Yangzonghai

Figure 3 is the contour map of the content of each heavy metal. According to the degree of similarity of the pollution halo shape, the horizontal distribution characteristics of heavy metals divide it into two types. The distribution of Pb, Cr, Zn and As is similar, the north and south sides are relatively high, the highest values all locate around the Tangeying on south bank, the rest locates around the Shijiazui on north bank, and the content of heavy metal in the middle of the lake is relatively low. The distribution characteristics of Cu and Mn are similar, the high-value points locate around the Huangshuidong on the east bank of lake, and the content around the Baojianshan in east bank and in the northern area of the Tangeying on south bank is relatively low.

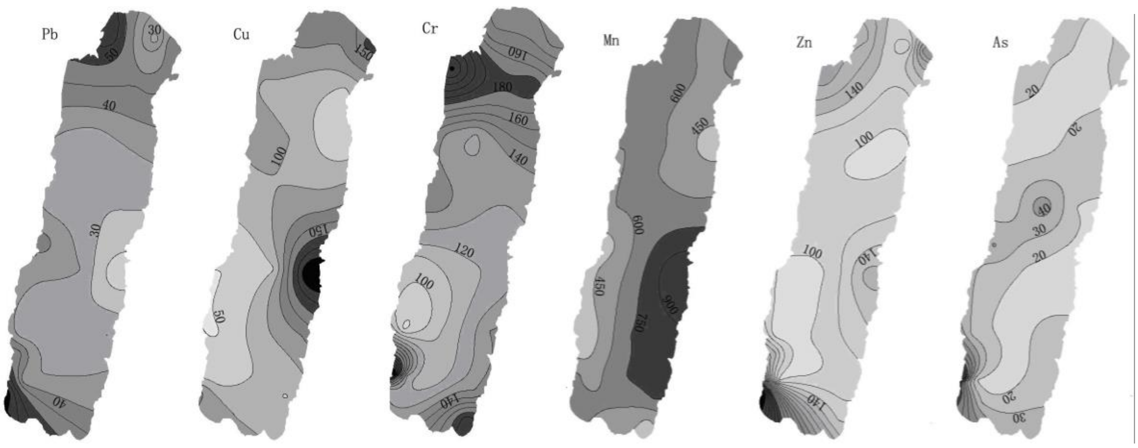

Fig. 3 Isograms of heavy metals in sediments from Yangzonghai (mg ·kg^{-1})

Assessment of Contamination degree: Geo-accumulation index (I_{geo}) was proposed by Müller, University of Heidelberg (Germany), in 1979, it is the quantitative indicator which is used to study the heavy metal pollution in the sediments of water environment [7]. The equation is shown as follows:

$$I_{geo}=\log_2^{Cn\div(1.5\times Bn)}$$

where c_n is the content of element *n* in the sediment (measured value); B_n is the geochemical background value in the sedimentary rock; 1.5 is a constant, which takes the changes of background value that may be caused by diagenesis into account. The geo-accumulation index is divided into 7 levels, which indicate that the level of pollution ranges from none to extremely strong, see Table 2. The element mass fraction of the highest level may be hundreds of times the background value [8]. As the different geochemical background may cause the differences in the heavy metal pollution information obtained in various regions, the heavy metal background values of the soil in Yunnan Province are used as computing standard in this paper.

Table 2. Müller's classification for the geo-accumulation index

I_{geo} value	Class	Quality of sediment
<0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
>5	6	Extremely polluted

The geo-accumulation index and classification of the heavy metals in sediment are shown in Table 3, it can be seen that the classification of most of the heavy metals' I_{geo} are 1, which means the pollution is in mild to moderate pollution. Except for the I_{geo} value of N01 sampling point around Tangeying is greater than 0, the rest sampling points are less than 0, and the content is close to background value, which almost has no pollution problems. Most of the I_{geo} value of Mn is less than 0, which accounts for three fifth of the total number of sampling points, and the classification of the rest I_{geo} is 1, which means the pollution is in mild to moderate level. Most of the I_{geo} values of Cu, Cr, Zn and As are greater than 0, which means the pollution is relatively serious. But the I_{geo} value of Cu of N14 sampling point around the Huangshuidong on east bank, the I_{geo} value of Zn and As of N01 sampling point around the Tangeying on south bank and the I_{geo} value of As of N03 sampling point are all greater than 2, which means the pollution is in moderate to strong level. On the whole, the order of the accumulation degree of the six heavy metals is Cu> As> Cr> Zn> Mn> Pb.

Source of Pollutants: Principal Component Analysis (PCA) is a multivariate statistical method that adopts the correlation between the original variables, and it is to realize dimensionality reduction by using a few linear combinations of original variables to explain the original variables. The nature of the analysis is to conduct the best integration and simplification of high-dimensional variable system. From the perspective of environmental quality assessment, it is to replace the original relatively more indexes with a certain correlation with less composite indexes, and to reflect the original multiple-factor information to the maximum[9]. As an important statistical method, Principal Component Analysis has been widely applied in the areas like the determination of the sources of pollution, the contribution of natural and anthropogenic factors on heavy metals and so on [10].

The heavy metals in the sediments of Yangzonghai have a strong correlation, and Bartlett sphericity test accompanying probability is 0.000, which is less than the significance level 0.01, so it is suitable for factor analysis. It can be seen from Table 4 that all the information of the six kinds of heavy metals (6 variables) in the sediment can be 88.886% represented by three principal components through the calculation of Principal Component Analysis, that is, the analysis on the first three principal components can reflect most information of all the data.

The contribution rate of the first principal component is 44.858%, and it is characterized by that the factor variables have relatively higher positive loading in the content of Pb, Zn and As. The source of Pb is closely related to atmospheric deposition, and the combustion of lead bearing coal, the industrial use of lead bearing ore, crude oil and the combustion of lead bearing gasoline are the main source of Pb [11]. The industrial and mining enterprises on the banks of Yangzonghai and the vehicle exhaust from the highway on both banks are the important source of Pb in the lake. Zn is mainly from the effluent discharge of various industries like the manufacture of galvanized steel, alloys, machine, etc., and the industrial use of the zinc bearing ore like zinc sulfide concentrates and so on is also the important source of Zn. As mainly comes from the use of arsenic ore. The lignite, pyrite and zinc sulfide concentrate in Yangzonghai region contain a relatively large amount of arsenic. The industrial utilization of these ores is the main source of As. In addition, there are many high-arsenic hot springs on the north bank of Yangzonghai, and the unreasonable discharge of hot spring water is also one of the arsenic sources in Yangzonghai. Table 4 reflects the Pearson correlativity between the various pollutants, among which Pb, Zn and As have a highly significant correlation. The high-value areas of pollutants basically locate on the banks where the development time is longer and industrial and mining enterprises and tourism are distributed. Therefore, the first principal component mainly reflects the impact of the sewage from the human activities like industry, mining and tourism on the sediment. The contribution rate of second principal component is 30.887%, and it is characterized by the relatively higher positive loading on Cu and Mn. The high-value area of Cu and Mn locates around the Huangshuidong on the east bank of Yangzonghai, which has not been affected by human development activities yet. Mn mainly comes from the geochemical processes, and Pearson correlation coefficient between Mn and Cu is 0.696, which means they have a very significant correlation. Therefore, it can be considered that the second principal component dominates the sources of Mn in the sediment while it dominates the source of Cu at the same time, which mainly reflects the impact of geochemical processes like rock weathering on the heavy metal contamination of sediment. The contribution rate of the third principal component is 13.141%, and only Cr has relatively great loading. The pollution source of Cr is mainly from discharged wastewater of chromium bearing ore processing, metal finishing, leather tanning, printing, dyeing and so on. And the high-value area locates on the south and north banks where there are high dense human activities. Therefore, the third principal component also reflects the impact of human activities on sediment. Figure 3 is the 2D and 3D loading situation of each pollutant, and it directly reflects the two major sources of the heavy metals in the surface sediment of Yangzonghai, which are the impact of human activities and the natural weathering and erosion process of rock. The two sources are the main reasons for the two different characteristics generated by the horizontal distribution of heavy metals in sediment.

Table 3. The indexes of geoaccumulation (I_{geo}) and series of I_{geo} for metals in sediments from Yangzonghai lake

Sample	Pb	Cu	Cr	Mn	Zn	As
N01	0.36 (1)*	1.34 (2)	0.57 (1)	0.05 (1)	2.08 (3)	2.51 (3)
N02	-0.30 (0)	0.93 (1)	1.19 (2)	-0.76 (0)	0.25 (1)	1.17 (2)
N03	0.00 (1)	0.41 (1)	1.55 (2)	-0.09 (0)	0.91 (1)	2.80 (3)
N04	-0.03 (0)	0.64 (1)	1.00 (1)	-0.14 (0)	0.90 (1)	1.69 (2)
N05	-0.61 (0)	0.29 (1)	0.58 (1)	-0.47 (0)	-0.31 (0)	0.31 (1)
N06	-0.61 (0)	0.55 (1)	0.35 (1)	0.08 (1)	-0.22 (0)	0.11 (1)
N07	-0.54 (0)	0.55 (1)	0.71 (1)	0.19 (1)	-0.04 (0)	0.74 (1)
N08	-0.21 (0)	0.14 (1)	0.83 (1)	-0.80 (0)	0.51 (1)	1.69 (2)
N09	-0.78 (0)	-0.06 (0)	0.02 (1)	-1.00 (0)	-0.53 (0)	0.69 (1)
N10	-0.80 (0)	0.84 (1)	0.38 (1)	0.09 (1)	-0.16 (0)	0.16 (1)
N11	-0.62 (0)	1.32 (2)	0.70 (1)	0.30 (1)	0.16 (1)	0.71 (1)
N12	-0.56 (0)	0.01 (1)	0.26 (1)	-0.62 (0)	-0.46 (0)	0.73 (1)
N13	-0.60 (0)	0.50 (1)	0.45 (1)	0.08 (1)	-0.21 (0)	0.11 (1)
N14	-1.35 (0)	2.42 (3)	0.49 (1)	0.64 (1)	0.51 (1)	-0.46 (0)
N15	-0.36 (0)	0.29 (1)	0.53 (1)	-0.83 (0)	-0.15 (0)	1.34 (2)
N16	-0.75 (0)	0.85 (1)	0.78 (1)	-0.18 (0)	-0.17 (0)	0.30 (1)
N17	-0.82 (0)	1.16 (2)	0.60 (1)	-0.13 (0)	-0.12 (0)	0.23 (1)
N18	-0.69 (0)	1.12 (2)	0.65 (1)	-0.20 (0)	-0.17 (0)	-0.05 (0)
N19	-0.74 (0)	1.01 (2)	0.57 (1)	-0.11 (0)	-0.22 (0)	0.00 (1)
N20	-0.51 (0)	-0.02 (0)	0.86 (1)	-0.91 (0)	-0.37 (0)	0.77 (1)
N21	-0.19 (0)	1.00 (1)	1.43 (2)	0.09 (1)	0.66 (1)	0.60 (1)
N22	-0.24 (0)	0.52 (1)	1.12 (2)	-0.31 (0)	-0.11 (0)	0.09 (1)
N23	0.11 (1)	1.45 (2)	0.80 (1)	0.07 (1)	0.58 (1)	0.64 (1)
N24	-0.75 (0)	1.35 (2)	0.75 (1)	-0.52 (0)	-0.29 (0)	-0.43 (0)
N25	-0.12 (0)	1.86 (2)	0.63 (1)	0.00 (1)	0.91 (1)	0.84 (1)

** values in brackets were series of I_{geo}.*

Table 4. Total variance explained and component matrices for the heavy metals

	Comp 1	Comp 2	Comp 3
Eigenvalue	2.691	1.853	0.788
Of variance (%)	44.858	30.887	13.141
Cumulative (%)	44.858	75.745	88.886
Pb	0.907	-0.128	-0.139
Cu	0.035	0.924	0.054
Cr	0.577	-0.165	0.794
Mn	0.064	0.898	0.171
Zn	0.864	0.336	-0.316
As	0.885	-0.191	-0.081

Table 5. Pearson correlation coefficients of the pollutants

	Pb	Cu	Cr	Mn	Zn
Cu	-0.091				
Cr	0.439*	-0.067			
Mn	-0.084	0.696**	-0.006		
Zn	0.766**	0.326	0.207	0.280	
As	0.709**	-0.164	0.454*	-0.089	0.698**

**P<0.05, **P<0.01*

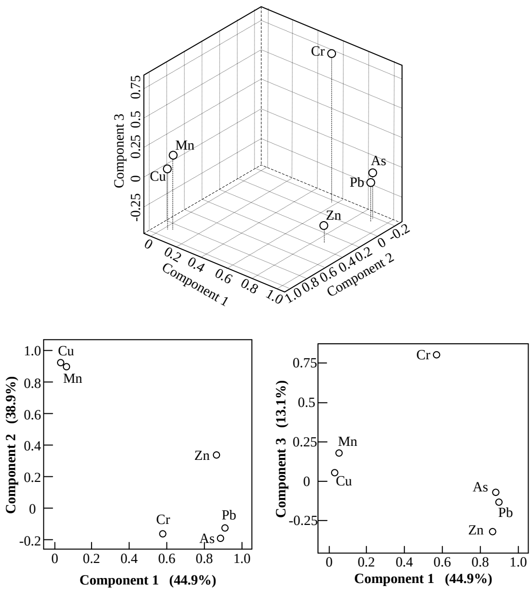

Fig. 4 Loading plots of the pollutants in the space defined by three components and two components

CONCLUSION

The average values of the heavy metals Pb, Cu, Cr, Mn, Zn and As in surface sediment of Yangzonghai are 40.3mg/kg, 97.6mg/kg, 145.8 mg / kg, 617.9mg/kg, 149.2mg/kg and 31.4mg / kg respectively. The evaluation results on the enrichment of heavy metals and the degree of pollution by using geo-accumulation index method show that the accumulation of Cu in the sediment is the most serious and As, Zn and Cr also have obvious accumulation. The accumulation degree of Mn is relatively lesser, which is in mild to moderate pollution level. The content of Pb is close to the background value, which means there is almost no pollution. The order of the pollution degree of heavy metals is Cu> As> Cr> Zn> Mn> Pb.

It can be found out from the Principal Component Analysis that all the information of the six kinds of pollutants in the sediment can be reflected by three principal components, and their contribution rates are 44.858%, 30.887% and 13.141% respectively. The pollutants with high load are (Pb, Zn, As), (Cu, Mn) and (Cr) respectively.

There are two main sources of the heavy metals in sediment, one is sewage from the human activities such as industry, mining, tourism and so on, the contribution rate is relatively high, and the main pollutants are Pb, Zn, As and Cr. The horizontal distribution characteristics of these pollutants also show obvious pollution plume and the diffusion and extension of the coastal drain outlet to the center of lake. The second source is the geochemical processes such as rock weathering and so on, the major pollutants are Mn and Cu, the contribution rate accounts for about one third, which indicates that natural process is also the important factor that affects the heavy metal pollution of Yangzonghai. The two sources are the main reasons for the two different characteristics generated by the horizontal distribution of the heavy metals in sediment.

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