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Heavy Metal Ecological Risk in Bottom Sludges of Yangzong Lake, China

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The concentrations of 10 heavy metals in bottom sludges of Yangzong lake in Yunnan, China were analyzed. Ecological risk index presented by Håkanson to assess the potential ecological risk of Yangzong lake was utilized. The results showed that the mean concentrations of titanium, manganese, zinc, vanadium, chromium, copper, nickel, cobalt, lead and arsenic in surface bottom sludges were up to 9413.1, 617.9, 149.2, 189.6, 145.8, 97.6, 55.1, 27.4, 40.3 and 31.4 mg/kg, respectively, which are higher than their natural background values. Pearson's correlation analysis indicated that zinc, chromium, lead and arsenic were highly correlated and they were originate from activities. Titanium, manganese, vanadium, copper, nickel and cobalt were also well correlated and mainly from natural factors. The evaluation of pollution index revealed a clear accumulation of the 10 heavy metals, all reaching the level of moderate pollution. Enrichment of arsenic, copper and chromium was more prominent than other heavy metals. Heavy metals in Yangzong lake in the descending order of their ecological risks were arsenic, copper, cobalt, nickel, lead, chromium, vanadium, zinc, manganese and titanium. Among them, arsenic was the most prominent factor of ecological risk in bottom sludges of Yangzong lake.

Keywords: Heavy metal, Ecological risk, Bottom sludge, Yangzong lake.

INTRODUCTION

Heavy metal is one class of conservative pollutants with potential hazards. Due to the poor degradability, general biological toxicity, bioaccumulation and biomagnification, heavy metal pollution in the environment have attracted continuous attention^{1,2}. In recent years, heavy metal pollution of surface water has occurred frequently, threatening the water security of local residents and also incurring enormous economic losses. Bottom sludge is the storage of heavy metals in water³. When entering water, most heavy metals are absorbed by particles in water and then precipitated to the bottom sludge. Studies in different countries have shown that in the heavy metal-polluted water, the content of heavy metal in bottom sludge can be up to several hundred or tens of thousands times more than that in water⁴. Additionally, under the changes of water environment or the effects of aquatic organisms, heavy metals in the bottom sludge may be released again, resulting in the secondary pollution and potential biological toxicity risk⁵⁻⁷. Therefore, the contents of heavy metals in the bottom sludge are often used as an important reference index to determine the quality of water environment^{8,9}.

As one of nine plateau lakes in Yunnan Province, China, Yangzong lake (E102°592-103°022, N24°512- 24°582) is a

fresh water lake indispensable for local residents. 2.5 km wide from east to west and 12.7 km long from north to south, the spindle-shaped lake has a shoreline of 32.3 km, a surface area of 31.9 km² (at the water level of 1,770 m) and a drainage area of 192 km². With an average depth of 20 m, the deepest part being 29.7 m, it has a storage capacity of 604 million m³ and a water exchange period of 13 years^{10,11}. The water supplied to the lake is mainly from natural precipitation, the catchment between Great Yangzong river and Qixing river, the artificial water supply from Baiyi river and groundwater. Tangchi river is the only outlet and the river flows into the Nanpanjiang river finally. Over the past 20 years, many companies, mines and holiday villages have been constructed along the lake. The major enterprises include the thermal power plant, the coal mine, the phosphate fertilizer plant and hot springs on the north bank, the aluminum plant in the south of Sanshimu, the golf course in the south of Baojianshan and the refractory factory and the phosphate fertilizer plant near Tangying on the south bank. With the rapid development of industry, mining and tourism, more and more heavy metals are poured into the lake to accumulate in the bottom sludge. The systematic sampling and the analysis of bottom sludge in Yangzong lake in this study identified the contents and distributions of heavy metals (Ti, Mn, Zn, V, Cr, Cu, Ni, Co, Pb, As) and evaluated potential

ecological risk in the hope of providing a theoretical basis and decision support for heavy metal pollution control in Yangzong lake.

EXPERIMENTAL

Sampling and analysis: From April 2 to April 4, 2009, a total of 25 groups of 0-5 cm surface bottom sludge samples were collected from the Yangzong lake with a grab sampler (Fig. 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 °C oven to be dried for 8 h, taken out and put into dry basins. 4 g 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.

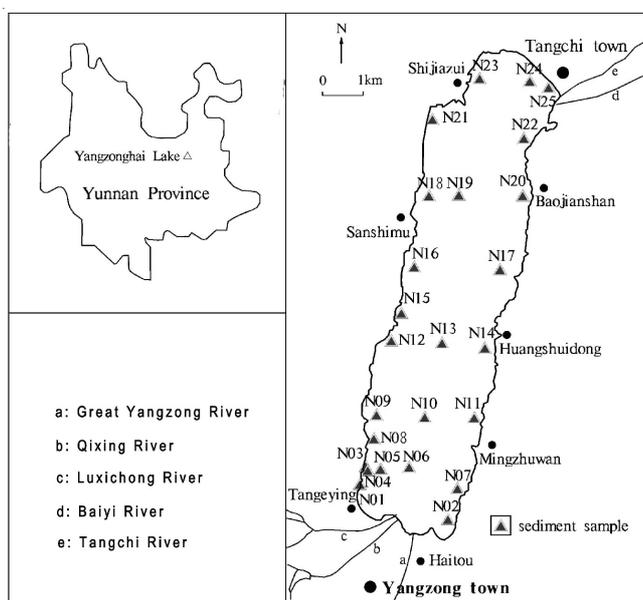


Fig. 1. Sampling stations in Yangzong lake

Evaluation methods: To determine the environmental pollution and the level of ecological damage of heavy metals in the bottom sludge, many evaluation methods have been studied in Britain, Japan, Germany, Sweden, *etc.* Among them, methods such as the index of geoaccumulation, the pollution load index, the excessive regression analysis and the potential ecological risk index are globally advanced for studies on heavy metals in bottom sludge¹²⁻¹⁶. The potential ecological risk index, proposed by Swedish scientist Håkanson from the sedimentological perspective based on properties and environmental behavioural characteristics of heavy metals, is a method for evaluating heavy metal pollution in the soil or bottom sludge. Considering the content of heavy metals in soil and linking their ecological, environmental and toxicological effects, it quantitatively determines the level of potential ecological damage, so it is advantageous in studies on ecological effects of bottom sludge^{17,18}. Since this study is focused

on the potential ecological damage of heavy metals in bottom sludge, the method of potential ecological risk index is adopted for evaluation. The equation of potential ecological risk index is shown as follows:

$$RI = \sum E_i$$

$$E_i = T_i f_i$$

$$f_i = \frac{C_i}{B_i}$$

RI is the potential ecological risk index, which is calculated as the sum of all risk factors for heavy metals in bottom sludges; E_i is the monomial potential ecological risk factor; f_i is the metal pollution index; C_i is the concentration of metals in bottom sludge; and B_i is a reference value for metals, with the statistical background values of heavy metals in Yunnan Province in 1990 as the reference (Table-1) in this study; T_i is the metal toxic factor, reflecting the responsive relationship between the aqueous phase, sedimentary solid phase and biological phase of heavy metals and according to Xu *et al.*¹⁹, $T_i = Mn = Zn = 1 < V = Cr = 2 < Cu = Ni = Co = Pb = 5 < As = 10$ is set. The categories of potential ecological risk are shown in Table-2.

TABLE-1
BACKGROUND VALUES OF HEAVY METALS
OF YUNNAN PROVINCE (mg/kg)

Element	Ti	Mn	Zn	V	Cr
Background value	7100	461	80.5	126.7	57.6
Element	Cu	Ni	Co	Pb	As
Background value	33.6	33.4	13.9	36	10.8

TABLE-2
POTENTIAL ECOLOGICAL RISK FACTOR (E_i)
AND INDEX (RI) FOR POLLUTION LEVEL

E_i	Ecological risk level	RI	Ecological risk level
< 40	Low	< 150	Low
40-80	Moderate	150-300	Moderate
80-160	Considerable	300-600	Considerable
160-320	High	≥ 600	High
≥ 320	Very high	-	-

RESULTS AND DISCUSSION

Spatial distribution of heavy metals: The content of heavy metals in the bottom sludge of Yangzong lake is shown in Fig. 2. The average contents of ten heavy metals all exceeded the background values of soil in Yunnan Province.

The contents of Ti ranged from 5000 to 10000 mg/kg, averaging 9,413.1 mg/kg. The highest content, 30,798.6 mg/kg, was found at Point N14 near Huangshuidong, while the lowest, 4,460.3 mg/kg, was measured at Point N01 near Tangzeying. The content of Mn ranged between 600 and 800 mg/kg with the average of 617.9 mg/kg. The highest value was 1,077.4 mg/kg at Point N14 and the lowest 344.8 mg/kg at Point N09. The average Zn contents was 149.2 mg/kg, mostly in the range of 100-200 mg/kg. According to National Soil Environmental Quality Standard of China (GB-15618-1995), the Zn content in five samples reached Class 1 of soil environmental quality standards and 19 samples reached Class 2. The highest Zn content was 511.9 mg/kg, at Point N01, exceeding Class 3 of soil environmental quality standards. The lowest was 83.8 mg/kg at Point N09.

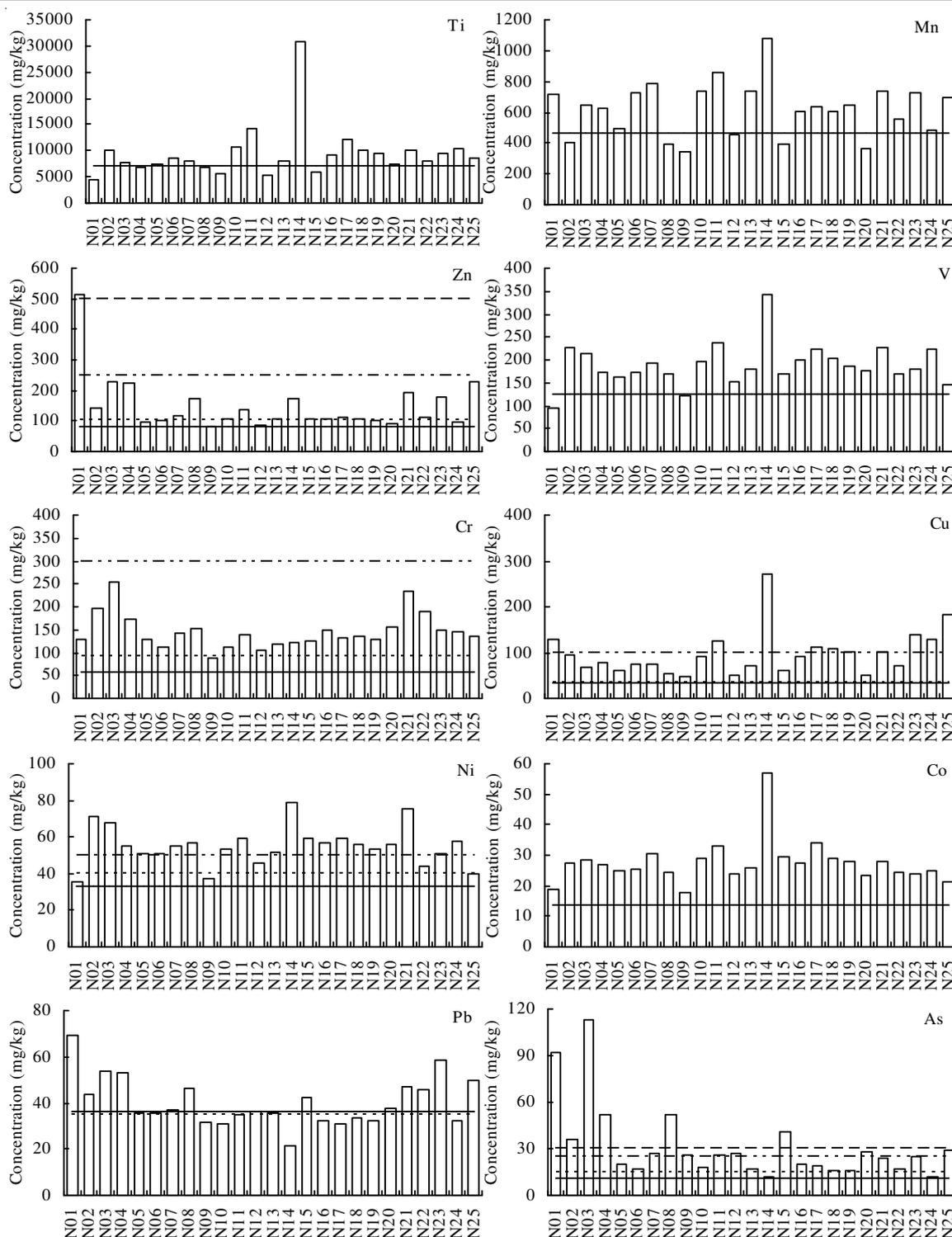


Fig. 2. Concentrations of heavy metals in surface bottom sludges from Yangzong lake

The content of V was mostly in the range of 150-250 mg/kg, averaging 189.6 mg/kg. The highest value was 341.5 mg/kg at Point N14, while the lowest value was 95.1 mg/kg at Point N01.

The content of Cr ranged between 100-150 mg/kg with the average of 145.8 mg/kg. The content of Cr at Point N09 point was the lowest, 87.7 mg/kg, reaching Class 1 of soil environmental quality standards and other samples reached Class 2. The highest value was 253.1mg/kg at Point N03 near Tangying.

The content of Cu averaged 97.6 mg/kg and 15 samples reached Class 2 of soil environmental quality standards and

10 reached Class 3. The highest value was 270.3 mg/kg, at Point N14, while the lowest value was 48.3 mg/kg at Point N09. The content of other samples mostly ranged between 50 and 150 mg/kg.

The Ni content was mainly concentrated between 50 and 60 mg/kg, averaging 55.1 mg/kg. Three samples reached Class 1 of soil environment quality standards, two reached Class 2 and other 20 reached Class 3. The highest value was found at Point N14, 78.4 mg/kg, while the lowest point was at Point N01, 35.9 mg/kg.

TABLE-3
PEARSON CORRELATION COEFFICIENTS BETWEEN DIFFERENT HEAVY METALS (n = 25)

	Ti	Mn	Zn	V	Cr	Cu	Ni	Co	Pb
Mn	0.662 ^b	–	–	–	–	–	–	–	–
Zn	-0.096	0.277	–	–	–	–	–	–	–
V	0.881 ^b	0.522 ^b	-0.269	–	–	–	–	–	–
Cr	-0.049	-0.004	0.228	0.253	–	–	–	–	–
Cu	0.806 ^b	0.693 ^b	0.306	0.576 ^b	-0.078	–	–	–	–
Ni	0.607 ^b	0.283	-0.165	0.863 ^b	0.533 ^b	0.293	–	–	–
Co	0.927 ^b	0.627 ^b	-0.140	0.894 ^b	0.002	0.646 ^b	0.708 ^b	–	–
Pb	-0.502 ^a	-0.079	0.774 ^b	-0.510 ^b	0.457 ^a	-0.107	-0.260	-0.505 ^a	–
As	-0.343	-0.085	0.708 ^b	-0.286	0.468 ^a	-0.176	-0.024	-0.234	0.720 ^b

Levels of significance: a. $p < 0.05$; b. $p < 0.01$.

The content of Co was between 20 and 30 mg/kg with the average of 27.4 mg/kg. The highest value was 57.2 mg/kg at Point N14, while the lowest value was 18.0 mg/kg at Point N09.

The Pb content was mostly between 30 and 40 mg/kg with the average of 40.3 mg/kg. Among them, eight samples reached Class 1 of soil environment quality standards and 17 reached Class 2. The content at Point N01 was the highest, 69.1 mg/kg, while Point N14 was the lowest, 21.2 mg/kg.

The content of As was mainly between 15 and 30 mg/kg with the average of 31.4 mg/kg, exceeding the limits of Class 3. Among them, two samples reached Class 1, 10 reached Class 2, seven reached Class 3 and six exceeded Class 3. Compared with other nine heavy metals, As pollution was relatively serious. The highest value was 113.2 mg/kg, at Point N03, while the lowest was 11.8 mg/kg, at Point N14.

Fig. 3 reveals that the spatial distributions of heavy metals in surface bottom sludge of Yangzong lake are of two types. Zn, Cr, Pb and As had similar distributions, with relatively higher contents on the north and south banks. All highest values were found near Tangyeying on the south bank, followed by Shijiazui on the north bank, while the contents were relatively low in the middle of the lake. The results of Pearson's correlation analysis show that (Table-3) Zn, Cr, Pb and As were highly correlated and in particular, Zn, Pb and As were extremely significantly correlated, indicating that they might have similar pollution sources. The distribution pattern extending from the north and south bank with intensive human activities to the center of the lake indicates that the four heavy metals might be primarily influenced by anthropogenic factors. The distributions of Ti, Mn, V, Cu, Ni and Co were similar, with their

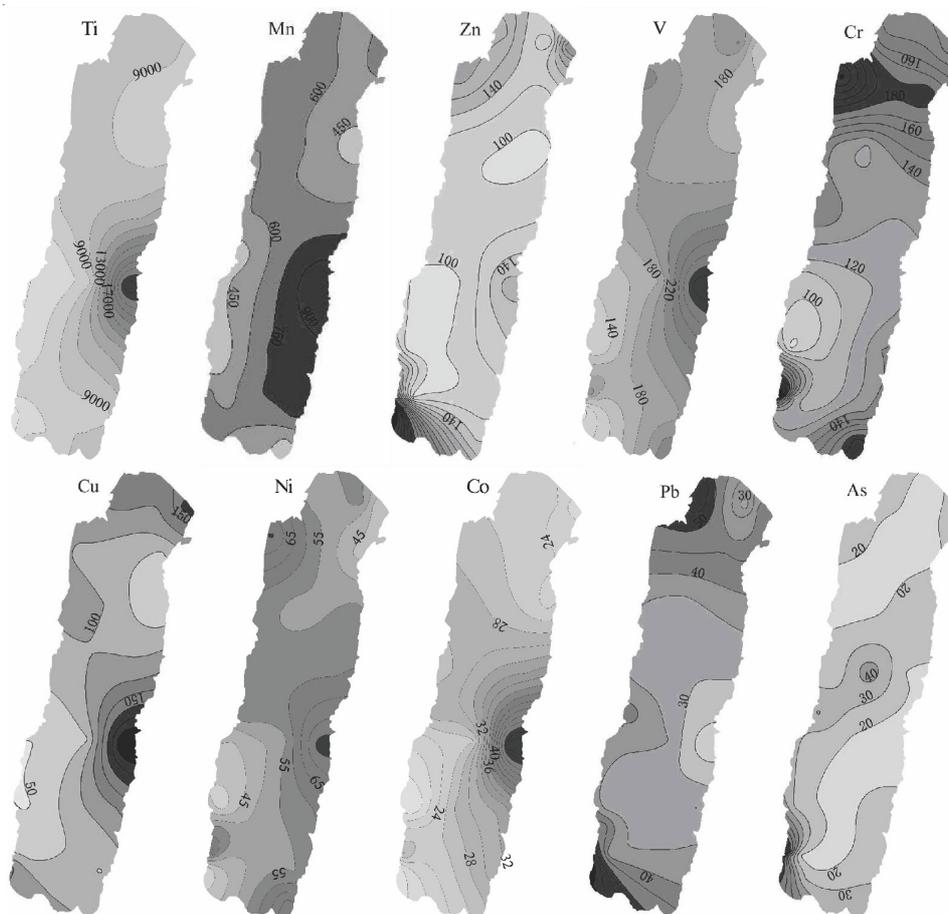


Fig. 3. Isograms of heavy metals in surface bottom sludges from Yangzong lake (mg/kg)

TABLE-5
POTENTIAL ECOLOGICAL RISK FACTORS (E_i) AND RISK INDICES (RI) OF HEAVY METALS

	E_i										RI	Pollution degree
	Ti	Mn	Zn	V	Cr	Cu	Ni	Co	Pb	As		
N01	0.63	1.56	6.36	1.50	4.47	19.05	5.37	6.73	9.60	85.19	140.45	Low
N02	1.41	0.88	1.79	3.56	6.86	14.33	10.67	9.86	6.08	33.80	89.24	Low
N03	1.07	1.41	2.82	3.39	8.79	9.94	10.16	10.18	7.49	104.8	160.06	Moderate
N04	0.96	1.36	2.80	2.75	6.01	11.73	8.28	9.60	7.35	48.24	99.07	Low
N05	1.05	1.08	1.21	2.57	4.48	9.17	7.62	8.88	4.92	18.61	59.59	Low
N06	1.21	1.58	1.29	2.74	3.83	10.98	7.56	9.17	4.93	16.20	59.5	Low
N07	1.15	1.72	1.45	3.05	4.92	10.95	8.23	10.90	5.15	25.00	72.53	Low
N08	0.98	0.86	2.14	2.70	5.33	8.24	8.49	8.71	6.49	48.43	92.35	Low
N09	0.78	0.75	1.04	1.92	3.05	7.19	5.60	6.47	4.38	24.17	55.33	Low
N10	1.49	1.59	1.34	3.12	3.91	13.44	7.96	10.36	4.31	16.76	64.27	Low
N11	1.99	1.85	1.67	3.75	4.86	18.68	8.89	11.80	4.88	24.54	82.91	Low
N12	0.75	0.98	1.09	2.39	3.60	7.56	6.81	8.53	5.08	24.91	61.70	Low
N13	1.13	1.59	1.30	2.84	4.10	10.58	7.78	9.28	4.94	16.20	59.75	Low
N14	4.34	2.34	2.13	5.39	4.23	40.22	11.74	20.58	2.94	10.93	104.83	Low
N15	0.83	0.84	1.35	2.67	4.32	9.18	8.88	10.65	5.86	37.96	82.55	Low
N16	1.28	1.32	1.33	3.14	5.14	13.53	8.44	9.93	4.44	18.52	67.08	Low
N17	1.73	1.37	1.38	3.53	4.54	16.79	8.88	12.23	4.25	17.59	72.28	Low
N18	1.42	1.30	1.33	3.21	4.71	16.35	8.41	10.40	4.65	14.44	66.23	Low
N19	1.32	1.39	1.29	2.95	4.47	15.12	8.02	10.00	4.50	15.00	64.06	Low
N20	1.05	0.80	1.16	2.78	5.44	7.41	8.34	8.45	5.25	25.65	66.33	Low
N21	1.44	1.60	2.37	3.56	8.10	15.01	11.35	10.07	6.56	22.69	82.74	Low
N22	1.14	1.21	1.39	2.66	6.54	10.73	6.59	8.71	6.35	16.02	61.33	Low
N23	1.32	1.58	2.24	2.86	5.22	20.52	7.66	8.67	8.08	23.33	81.48	Low
N24	1.47	1.04	1.23	3.52	5.06	19.18	8.58	8.92	4.46	11.11	64.57	Low
N25	1.20	1.50	2.82	2.28	4.65	27.25	5.99	7.70	6.90	26.85	87.15	Low
Mean	1.33	1.34	1.85	2.99	5.07	14.53	8.25	9.87	5.59	29.08	79.90	Low

highest contents all found near Huangshuidong on the east bank that is not influenced by human activities. However, the contents were relatively low in the Baojianshan on the east bank of intensive human activities and northern Tangeying on the south bank. Since Mn is mainly from the geochemical processes² and six heavy metals are well correlated, the six heavy metals can be considered to be mainly from natural sources.

Analysis of contamination degree: The pollution index (f_i) was used for evaluating the pollution degree of heavy metal and four categories of metal pollution were low contamination ($f_i \leq 1.0$), moderated contamination ($1.0 < f_i \leq 3.0$), considerable contamination ($3.0 < f_i \leq 6.0$) and high contamination ($f_i > 6.0$). The results are shown in Table-4. The mean pollution indexes of all heavy metals in Yangzong lake were between 1 and 3, reaching the level of moderate pollution and revealing a clear accumulation. 76, 76, 100, 92, 100, 100, 100, 100, 52 and 100 % of the soil samples were moderately or heavily contaminated by Ti, Mn, Zn, V, Cr, Cu, Ni, Co, Pb and As, respectively. In the descending order of their average pollution index, the heavy metals were As, Cu, Cr, Co, Zn, Ni, V, Mn, Ti and Pb. Among them, As, Cu and Cr had $f_i > 6.0$ in 4, 9 and 5 samples, respectively, indicating a higher pollution level. Co, Ni, Zn and V had a lower pollution level, with the mean pollution index between 1 and 3. Mn, Ti and Pb had the lowest pollution level, each had $f_i < 1.0$ in 12, 6 and 6 samples, respectively. Therefore, As, Cu and Cr were the most important environmental contaminants in Yangzong lake. In particular, the pollution index of As at Points N01 and N03 and the index of Cu at Point N14 were greater than 6, reaching high pollution degree.

TABLE-4
POLLUTION INDEX OF HEAVY METALS
IN BOTTOM SLUDGE OF YANGZONG LAKE

	Pollution index (f_i)			Number of samples			
	Min	Max	Mean	$f_i \leq 1$	$1 < f_i \leq 3$	$3 < f_i \leq 6$	$f_i > 6$
Ti	0.63	4.34	1.33	6	18	1	0
Mn	0.75	2.34	1.34	6	19	0	0
Zn	1.04	6.36	1.85	0	24	0	1
V	0.75	2.70	1.50	2	23	0	0
Cr	1.52	4.39	2.53	0	20	5	0
Cu	1.44	8.04	2.91	0	15	9	1
Ni	1.07	2.35	1.65	0	25	0	0
Co	1.29	4.12	1.97	0	24	1	0
Pb	0.59	1.92	1.12	12	13	0	0
As	1.09	10.48	2.91	0	19	4	2

Assessment of potential ecological risk: The calculation results of potential ecological risk factor (E_i) and potential ecological risk index (RI) of heavy metals in surface bottom sludge of Yangzong lake are shown in Table-5 and Fig. 4, indicating that As was more prominent than other heavy metals in terms of potential ecological risks. The E_{As} was over 80 at Points N01 and N03, reaching the considerable ecological risk level; the E_{As} at Points N04 and N08 was more than 40, reaching the moderate level. The E_{Cu} at Point N14 was also over 40, reaching the moderate level. The E_i of other heavy metals at different sampling points were less than 40, with the average between 1.33 and 29.08, indicating the level of low ecological risks. In particular, the factors of the four metals, Ti, Mn, Zn and V, were basically less than 5. In the descending order of their potential ecological risks, the heavy metals were As, Cu, Co, Ni, Pb, Cr, V, Zn, Mn, Ti.

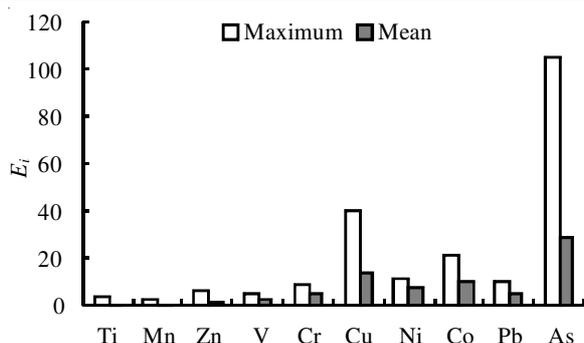


Fig. 4. Comparison of potential ecological risk factors of heavy metals

Fig. 5 represents the distribution of the potential ecological risk index of heavy metals in Yangzong lake. Overall, the integrated potential ecological risk index of heavy metals was generally within 150. Although RI was relatively high in some regions near Shijiazui on the north bank and Huangshuidong on the east bank, they as a whole just reached the level of low ecological risks. Only the RI at Point N03 near Tangying was relatively high, 160.06, reaching the moderate level. Combined with the contents and distribution characteristics of all heavy metals, it was mainly the result of the relatively high potential ecological risk of As. At Point N03, the contribution of E_{As} to RI reached 65 %, while at Point N01 which had a relatively high RI, the contribution of E_{As} also reached 61 %. Therefore, As was the most important factor of potential ecological risk of surface bottom sludge in Yangzong lake. Although both Cu and Cr were important environmental contaminants, due to relatively low biological toxicity, they were not major factors of potential ecological risk.

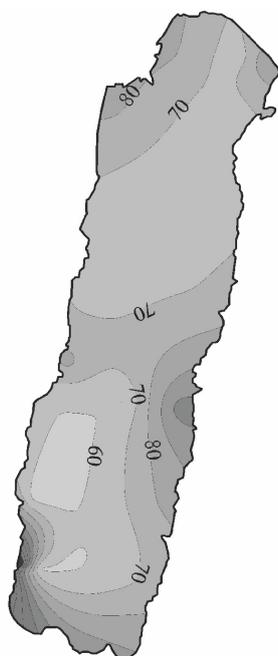


Fig. 5. Isograms of RI of heavy metals in bottom sludges

Conclusion

The concentrations of Ti, Mn, Zn, V, Cr, Cu, Ni, Co, Pb and As in surface bottom sludge of Yangzong lake varied between

4460.3, 30798.6, 344.8, 1077.4, 83.8, 511.9, 95.1, 341.5, 87.7, 253.1, 48.3, 270.3, 35.9, 78.4, 18.0, 57.2, 21.2, 69.1, 11.8 and 113.2 mg/kg, respectively, with an average of 9,413.1, 617.9, 149.2, 189.6, 145.8, 97.6, 55.1, 27.4 and 40.3 mg/kg, respectively, each exceeding the background value of soil in Yunnan Province. Pearson's correlation analysis indicated that Zn, Cr, Pb and As were highly correlated and the distributions indicated that they might originate from activities. Ti, Mn, V, Cu, Ni and Co were also well correlated and the distributions indicated that they were mainly from natural factors.

76, 76, 100, 92, 100, 100, 100, 100, 52 and 100 % of the soil samples were moderately or heavily contaminated by Ti, Mn, Zn, V, Cr, Cu, Ni, Co, Pb and As, respectively. Heavy metals in the descending order of the average pollution index were As, Cu, Cr, Co, Zn, Ni, V, Mn, Ti and Pb. Among them, As, Cu and Cr were the most important environmental contaminants in Yangzong lake.

The comprehensive potential ecological risk index of heavy metals in Yangzong lake was generally within 150, reaching the level of low ecological risk. Only the region near Tangying on the south bank, influenced by the potential ecological risk of As, reached the moderate ecological risk level. The descending order of the ecological risk of heavy metals was As, Cu, Co, Ni, Pb, Cr, V, Zn, Mn and Ti. Among them, As was more prominent than other heavy metals in terms of the ecological risk and thus the most important potential ecological risk factor in surface bottom sludge of Yangzong lake.

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