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Original Research

Speciation and Ecological Risks of Cobalt and Antimony in Black-Necked Crane (*Grus nigricollis*) Habitat Sediments in China's Caohai Lake

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Abstract

The potential ecological risks of cobalt (Co) and (Sb) in the sediments of the black-necked crane habitats in Caohai Lake, Guizhou Province were assessed based on total concentration and speciation via Tessier sequential extraction procedure. The results showed that the concentration of Co in the study region is in the range of 4.29-23.79 $mg\cdot kg^{-1}$, with an average of 15.41±3.4 $mg\cdot kg^{-1}$, which is lower than the soil background concentration in Guizhou Province. The concentration of Sb is in the range of 1.4-1.69 $mg\cdot kg^{-1}$, with an average of 1.51±0.3 $mg\cdot kg^{-1}$, which is 13.7 times higher than the soil background value of Sb in Guizhou Province. The concentrations of Sb in the west and southeast regions were greater than those in the other parts of the habitats. Co mainly existed in residual and Fe-Mn oxides forms, which account for 68.73-89.14% of total Co. However, Sb mainly existed in residual forms, which account for 79.84-93.11% of the total Sb. The carbonate and organic forms of the two elements and the Fe-Mn oxides of Sb decreased along with decreased water depth. The exchangeable fractions of the two elements were lower than 1% and do not exhibit obvious changes with water depth. The potential ecological risk index of Co (E_{Co}) shows that Co in the five habitats (Liujiaxiang, Zhujiawan, Wangjiayuanzi, Huyelin, and Yangguanshan) was at a moderate risk level. The potential ecological risk index of Sb (E_{Sb}) shows that Sb in the five habitats was at a considerable risk level. All of the *RI* indexes were at mild and moderate risk levels, which Sb makes a large contributor. According to an assessment of the ratio of the secondary phase to the primary phase, Co and Sb present little pollution and potential ecological risk in the study regions. It can be seen that the evaluation of the ecological impact by the total

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amount of heavy metals does not necessarily reflect its hazards objectively, and should be monitored and evaluated in combination with heavy metal forms.

Keywords: black-necked crane habitat, sediment, heavy metal speciation, ecological risk

Introduction

Among all ecosystems, wetlands have the most abundant biodiversity and are home to various plants and animals [1]. However, irrational human activities have resulted in severe damage and irreversible consequences to the environments and ecosystems of wetlands [2]. Heavy metal pollution in wetlands is one of the most complex and severe problems in recent years [3, 4]. For centuries, heavy metal pollution of water bodies has attracted significant attention because of its toxicity, slow removal efficiency, abundance and bio-accumulation [5, 6]. The distribution of heavy metals in water is usually low and random, and it varies based on different emissions and hydraulic conditions. The concentration of heavy metals in sediments is usually higher than that in cover water. The environmental behavior, bioavailability and toxicity of heavy metals in sediments are related not only to their total concentrations, but also to their chemical speciation. A large amount of research has been carried out on heavy metal pollution in sediments around the world. These studies have mainly focused on distribution characteristics, pollution sources and ecological risk assessments [7, 8]. The speciation distribution of heavy metals is greatly influenced by environmental factors (e.g., pH, salinity and redox property) and the characteristics of the sediments, such as particle size [9-12]. Different species produce different ecological risks and biological toxicities in the biogeochemical cycle.

With the development of industrial technology in the 19th century, the application of antimony (Sb) and its compounds in industrial production and life has been unprecedentedly expanded. At present, it is not only used in printing, lead-acid batteries, pigments and ceramic glazes, but also as the main component of lanthanide flame retardants and automotive brake pads [13]. Sb has strong sulfophilicity and certain oxophilicity, mainly in the form of trivalent sulphide or oxide in the mineral deposit. In different strontium minerals, the content of strontium varies greatly, with oxides and sulfides. The content of strontium in the ore is the highest, and the strontium in the sediment is mainly in the form of Sb (Ill), Sb (V) and organic strontium [14]. A large amount of strontium and its compounds enter various environmental media, and the harm to the environment and human health is gradually emerging, and more and more people pay attention to it [15]. The source of cobalt (Co) is the emission of automobile exhaust, the settlement of coal-fired fly ash (such as from thermal power plants), and the agricultural use of sludge. Co is a trace element necessary for nitrogen fixation in legumes and non-legumes. It is involved in plant respiration and synthesis of proteins and enzymes [16]. It can be seen that the absorption, migration and transformation of Co in the process of plant growth, and that the Co content of wetland soil can reflect the supply of trace elements in the soil and its available level [17]. Both Co and Sb can accumulate in the ecosystem through the food chain [18] – directly or indirectly affecting the survival and reproduction of wetland organisms, but these two metal elements are rarely involved in previous studies.

The black-necked crane (*Grus nigricollis*) is the flagship species in the plateau wetland and is also a Class I-protected bird in China. Caohai is the largest wintering location of the crane, an engendered species, and also the largest natural freshwater wetland in Guizhou Province in southwest China. Caohai Lake plays important roles in maintaining ecological equilibrium, regulating floods and protecting regional biodiversity. Previous studies have found that heavy metals (such as Pb, As, Hg, Cd, Cr, Cu and Zn) in the sediments of Caohai Lake have caused significant environmental hazards [19, 20]. However, studies on Co and Sb (which are also environmentally toxic) in the sediments of Caohai Lake have rarely been reported. Pollution sources of Co and Sb include the exploitation of mineral resources, emissions of industrial and domestic sewage, combustion of coal and the wear of automotive parts. Research has shown that once Co reaches a certain concentration in water it will pose a hazard to aquatic organisms, such as fish and water fleas, even to their death in extreme cases [21]. Sb and Sb compounds exhibit certain toxicities to organisms [22-24], and they can migrate long distances. In the present study, the black-necked crane habitats in Caohai Lake, including Liujiaxiang, Zhujiawan, Wangjiayuanzi, Huyelin and Yangguanshan regions, were selected as the study objects. The main aims were to study the pollution levels, speciation and ecological risk of Co and Sb in surface sediments and soils of selected regions in Caohai wetland.

Materials and Methods

Overview of the Study Area

The Caohai Plateau wetland is situated 360 km west of Guiyang in Guizhou Province within Weining County (26°49′-26°53′N, 104°12′-104°18′E), and it is a national natural reserve. Caohai Lake is a freshwater lake that formed due to a karst dam. Its complete, typical plateau wetland ecosystem provides an important wintering place and migration transfer station for many rare bird species, including the black-necked crane. The wet season of the reserve lasts from May to October, and followed by the dry season of November to April. The reserve has an annual mean temperature of 10.6ºC, an annual mean precipitation of approximately 1000 mm and a relative humidity of 80%. Its average depth is 2 m, and its greatest depth is approximately 5.13 m.

Sample Collection and Analysis

During the period of July to August in 2017, the black-necked crane habitats in Caohai Lake were selected and divided into four categories based on the water depth (deep-water areas, shallow-water areas, transition areas and agricultural areas). A total of 20 sampling regions (Fig. 1) were designated: A1-A4 representing Liujiaxiang (LJX), B1-B4 representing Zhujiawan (ZJW), C1-C4 representing Wangjiayuanzi (WJY), D1-D4 representing Huyelin (HYL), and E1-E4 representing Yangguanshan (YGS). Column mud samplers were used to collect surface sediment samples (0-10 cm), which were sealed in plastic Ziploc bags, stored at low temperature and transported to the laboratory. After removing impurities such as stones and the remains of plants and animals from the samples in the lab, the samples were air dried. After thorough mixing, the samples were sieved through 100-mesh filters. The heavy metal contents and relevant physiochemical indexes were determined.

The main physicochemical properties of the surface soil samples were characterised by the following methods: soil pH was measured using a pH meter (Mettler Toledo FE20, Switzerland) (soil:water = 1:2.5), TC concentrations were measured by TOC analyzer (determined by titration with $FeSO_4$ after digestion with $K_2Cr_2O_7$–H_2SO_4 solution [25]), total nitrogen (TN) content was measured with the semi-micro Kjeldahl method [26], and total phosphorus (TP) content was analyzed with the Mo-Sb colorimetric method [27]. Total contents of heavy metals were detected using national standards [28, 29]. Studied metals fractions using a sequential extraction scheme and procedure proposed by Tessier et al. was used to partition the toxic metals, which was widely applied in various studies of heavy metal [30-32]. In brief, Tessier's five sequential extractions were carried out: exchangeable fraction (F1, 1 M $MgCl_2$, pH 7.0); carbonate-bound fraction (F2, 1 M NaOAc, pH 5.0); Fe-Mn oxides-bound fraction (F3, 0.04 M $NH_2OH{\cdot}HCl$ in 25% HOAc, pH 2.0); organic matter-bound fraction (F4, 0.02 M HNO_3 in 30% H_2O_2; 3.2 M NH_4OAc in 20% HNO_3, pH 2.0); and residual fraction (F5, digested with HF HNO_3 $HClO_4$) [33]. Metal concentrations were determined using a PerkinElmer NexION300X inductively coupled plasma mass spectrometer (ICP-MS) and reported on a dry weight basis (mg·kg^{-1}). To ensure the data accuracy, a parallel sample and national references (GSS8 and GSS25) were inserted every four samples for quality control; the recovery rates (measured value/standard reference value×100%) were between 88% and 110%, with a deviation of less than 10%.

ArcGIS10.2 was used to draw the map of the sampling sites, SPSS19.0 was used for data correlation analysis, and Origin 9.0 was used to draw all the remaining figures.

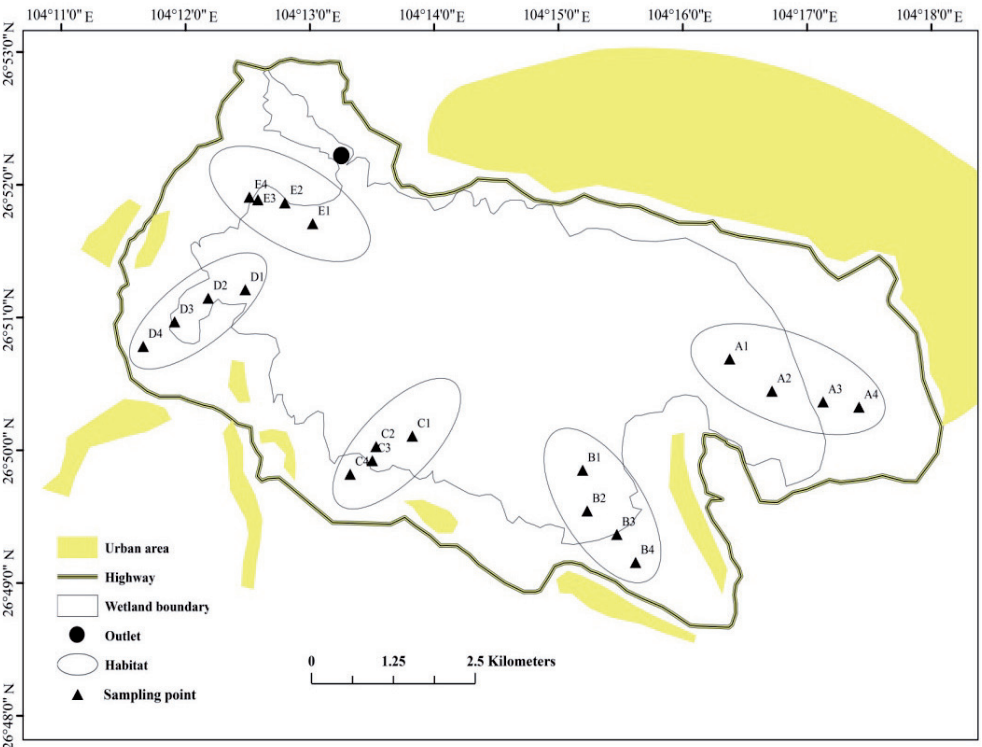

Fig. 1. Sampling sites of habitat.

Data Analysis

Bioavailability and Migration Ability

Bioavailability represents the ability of different heavy metals in sediments to be adsorbed by organisms and consequently cause potential hazards to the eco-environment. It can be described by the mobility factor (*MF*) [34, 35]. The smaller the *MF*, the higher the stability of heavy metals in the sediments; thus, they cannot be easily used and pose little hazard. In contrast, the greater the *MF*, the higher the hazard and the lower the stability of the heavy metals.

Tessier:

$$MF = \frac{F1 + F2}{F1 + F2 + F3 + F4 + F5} \tag{1}$$

…where *F1*: exchangeable fraction; *F2*: bound to carbonate; *F3*: bound to Fe-Mnoxides; *F4*: bound to organic matter; and *F5*: residual fraction.

The migration ability of different heavy metals in sediments is evaluated by the ratio of exchangeable state to total amount, which is called *M* [36].

$$M_j = \sum_{i=1}^{n} \frac{F_i / T_i}{n} \tag{2}$$

…where M_j represents the mobility coefficient of heavy metal *j*; *i*: sampling point; *n:* number of sampling points; and T_i: the total amount of element *j* in sediment *i*.

Hakanson Potential Ecological Risk Asessment

The Hakanson [37] potential ecological risk assessment considers the concentrations of heavy metals in the soil and takes into account the ecological effects, environmental benefits and toxicological effects of heavy metals. Therefore, it is a commonly used risk assessment method in studies of heavy metal pollution in soil/sediment [38-41]. The calculation equation is as follows:

$$C_f^i = C^i / C_n^i \tag{3}$$

$$E_r^i = C_f^i \cdot T_r^i \tag{4}$$

$$RI = \sum_{i=1}^{2} E_r^i \tag{5}$$

…where C_f^i is the pollution index of heavy metal *i*; C^i is the measured concentration of heavy metal *i* (mg·kg^{-1}); C_n^i is the background concentration of the heavy metal in the soil in Guizhou Province; E_r^i is the individual potential ecological risk index; T_r^i is the toxicity response parameter of the individual pollutant (T_r^i for Co and Sb is 5 and 10 [42,43], respectively based on the standard heavy metal toxicity response index established by Hakanson); and *RI* is the potential ecological risk index. The grading criteria are shown in Table 1.

Ratio of the Secondary Phase to the Primary Phase (RSP)

In sedimentary geology, the residual metal that exists in the primary mineral lattices and generally does not migrate is called the primary geochemical phase. The exchangeable carbonate Fe-Mn oxide-bounded and organic-bounded fractions are called secondary geochemical phases, and these species can transform to each other when the external environment changes [30]. The extent of the potential ecological hazards attributable to heavy metals can be reflected by the ratio of the secondary phase to the primary phase of the heavy metals (*RSP*); the higher the ratio of the secondary phase, the greater the potential ecological hazard the heavy metals pose [45]. The calculation equation is as follows:

$$RSP = \frac{M_{\mathrm{sec}}}{M_{prim}} \tag{6}$$

…where M_{sec} is the concentration of the secondary phases of heavy metals in the sediment, and M_{prim} is the

Table 1. Dividing standards of heavy metal pollution and ecological risk levels [44].

Contamination factor		Ecological risk index			
Contamination index		Potential ecological index		Ecological risk index	
Range	Category	Range	Category	Range	Category
C_f^i<1	Low	E_i<40	Low	*RI* < 150	Low
1≤ C_f^i< 3	Moderately	40≤E_i<80	Moderately	150 ≤ *RI* < 300	Moderately
3≤C_f^i<6	High	80≤E_i<160	High	300 ≤ *RI* < 600	High
C_f^i≥6	Very high	160≤E_i<320	Very high	*RI* ≥ 600	Very high
		E_i≥320	Extremely strong		

concentration of the primary phases of heavy metals in the sediment. *RSP*<1 denotes no ecological hazard, 1<*RSP*<2 denotes mild ecological hazard, 2<*RSP*<3 denotes moderate ecological hazard, and *RSP*>3 denotes heavy ecological hazard.

Results and Discussion

Physiochemical Characteristics of the Sediment and the Concentrations and Distributions of Co and Sb

The physiochemical characteristics of the surface sediments in the habitat and the concentrations of Co and Sb are shown in Table 2. The pH of the sediment ranges from 5.60 to 7.72, which represents an acidic to weakly alkaline soil environment, the water content ranges from 25.17% to 60.57%, and the TC ranges from 20.54 to 391.6 g·kg^{-1}.

The concentration of Co in the surface sediment was in the range of 4.29-23.79 mg·kg^{-1}, with an average of 15.41±3.4 mg·kg^{-1}, which was lower than the soil background concentration in Guizhou Province (19.2 mg·kg^{-1}) [40]. The overall coefficient of variation was 17.23%, and except for the coefficient of variation of WJY, which was less than 15%, the coefficients of variation were between 15% and 35%, corresponding to moderate variations. The concentration of Sb ranges from 1.4 to 1.69 mg·kg^{-1}, with an average of 1.51±0.3 mg·kg^{-1}, which was 13.7 times greater than the background value (0.11 mg·kg^{-1}) [46]. The overall coefficient of variation was 17.43%; HYL and YGS exhibit small variations in the soil properties, whereas the others exhibit moderate variations. The maximum Co concentration was located near effluent site E4 (23.79 mg·kg^{-1}) at YGS, whereas the maximum Sb concentration was located near influent site A3 (2.05 mg·kg^{-1}).

Contents of Co and Sb varied with the water depth gradient in each habitat (Fig. 2). The variations of the total Sb concentrations were the same at the five habitats; i.e., they all decreased with increasing water depth. The reason may be that the wetland farmland is close to the road and human gathering place, and is

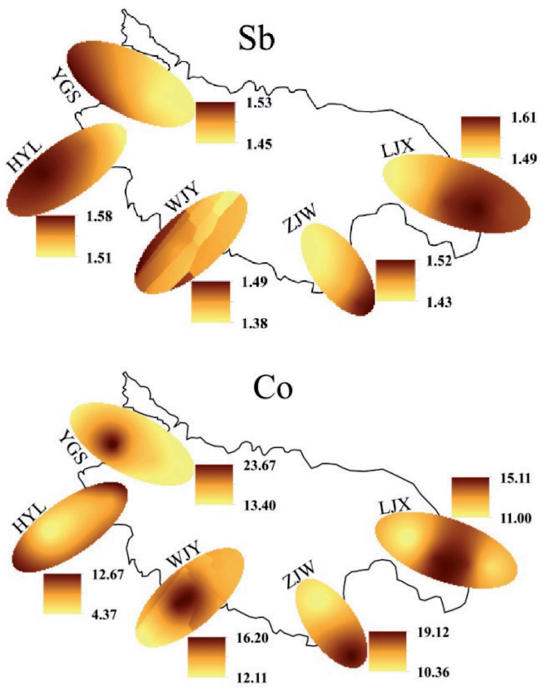

Fig. 2. Content of Co, Sb in the surface sediments of habitat.

close to the pollution source, while the transitional area vegetation intercepts the rainwater runoff, so that the surface sediment adsorption Sb content from the water body is reduced. The total Co concentrations were high in the middle and low on the two ends in the LJX, WJY and YGS habitats, whereas the variation in the HYL habitats exhibited the opposite trend. The main reason may be that the land-water transition zone of the wetland is the main activity location of black-necked cranes and many birds, whose droppings are mostly concentrated here. Studies have shown that the entry of bird droppings will cause Co to rise significantly [47]. Secondly, the vegetation is rich in species and quantity in the transition zone. Co can be absorbed by plants and enriched in plants during plant growth. When the plants die, the two are released into the surface soil again during the decomposition process. The accumulation of Co increases continuously over a long period of time. The metabolism of a large number

Table 2. Value of sediment physical and chemical characteristics and total heavy metals.

HB	DW (cm)	MC (%)	pH	TC (g·kg^{-1})	Co		Sb	
					Content (mg·kg^{-1})	CV (%)	Content (mg·kg^{-1})	CV (%)
LJX	0-130	39.38±10.7	6.78±0.8	173.59±151.7	13.09±2.0	15.24	1.64±0.5	28.60
ZJW	0-120	42.05±12.1	6.56±0.8	145.37±77.5	15.19±3.8	25.04	1.42±0.3	23.79
WJY	0-180	39.24±15.1	6.99±0.4	38.35±12.5	15.52±1.1	6.79	1.43±0.2	18.10
HYL	0-273	35.03±6.1	7.16±0.7	45.01±33.3	13.76±2.8	20.68	1.69±0.1	4.18
YGS	0-227	38.06±11.5	7.23±0.7	67.34±24.2	19.48±3.6	18.42	1.40±0.2	12.46

Value is mean±standard deviation; DW: water depth; HB: habitat; MC: moisture content; CV: coefficient of variation of elements in the process of plant growth is inevitably accompanied by the participation of trace elements. Due to the differences in the ability of different plant communities to absorb, enrich, store and return Sb and Co, the content of the two may be different in the horizontal direction. Overall, the average Co concentrations followed the trend YGS > WJY > ZJW > LJX > HYL, while those of Sb followed the trend HYL > LJX > ZJW > WJY > YGS. The results show that the total Co concentrations were low and that the concentrations in the habitats close to the western lake region were significantly higher than those in other regions. The Sb concentrations were high in the habitats in the west and southeast. These results were similar to the survey results by Song [48].

Distribution and Characteristics of Co and Sb Speciation in the Sediment

The speciation of Co and Sb in the sediment in the LJX, ZJW and HYL habitats were further analyzed; the results were shown in Fig. 3. The speciation of Co in the sediment of the three habitats were dominated by residual and Fe-Mn oxides fractions, whereas the speciation of Sb was dominated by residual fraction. The exchangeable fraction of Co and Sb accounted for 0.13-0.24% and 0.40-2.18% of the total concentrations, respectively. Of these, the exchangeable fraction of Sb was the highest at site B1 in ZJW, which represented approximately 2.18% of the total concentration. The average percentage of Co carbonate fraction was 3.92%, whereas that of Sb was 2.1%. The percentages of both carbonate fraction Co and Sb decreased with decreasing water depth, but increased slightly in shallow water. The Fe-Mn oxide fraction of Co accounts for 20.09-33.78% of the total Co content and was much higher than that of Sb; in general, the percentage of the Fe-Mn oxide fraction of Co increased with decreasing water depth and was the highest at site B4 in ZJW. The percentage of the Fe-Mn oxide fraction of Sb was very low and comparable to the mass fraction bound to carbonate, and it decreased with decreasing water depth but increased slightly at site D4 in HYL. The percentages of the organic species of Co and Sb were 7.58-26.33%; the highest values for both Co and Sb occurred in deep water (A1 and B1), and the lowest values occurred at D3 and D4. The percentage of the Sb residual species was much higher than that of the other species and played a dominant role in the total Sb concentration; it was 29.31% higher than the percentage of the Co residual species. Both the Co and Sb residual species exhibited high concentrations in shallow water and transition areas and low concentrations in deep water and farmland.

The bioactivity and potential migration ability of Co and Sb are shown in Fig. 4. The *MF* of Co in the three habitats followed the order: HYL < ZJW < LJX, whereas the potential migration coefficients (*M*) followed the order: ZJW < HYL < LJX. The *MF* and *M* of Sb in the three habitats had the same order (i.e.,

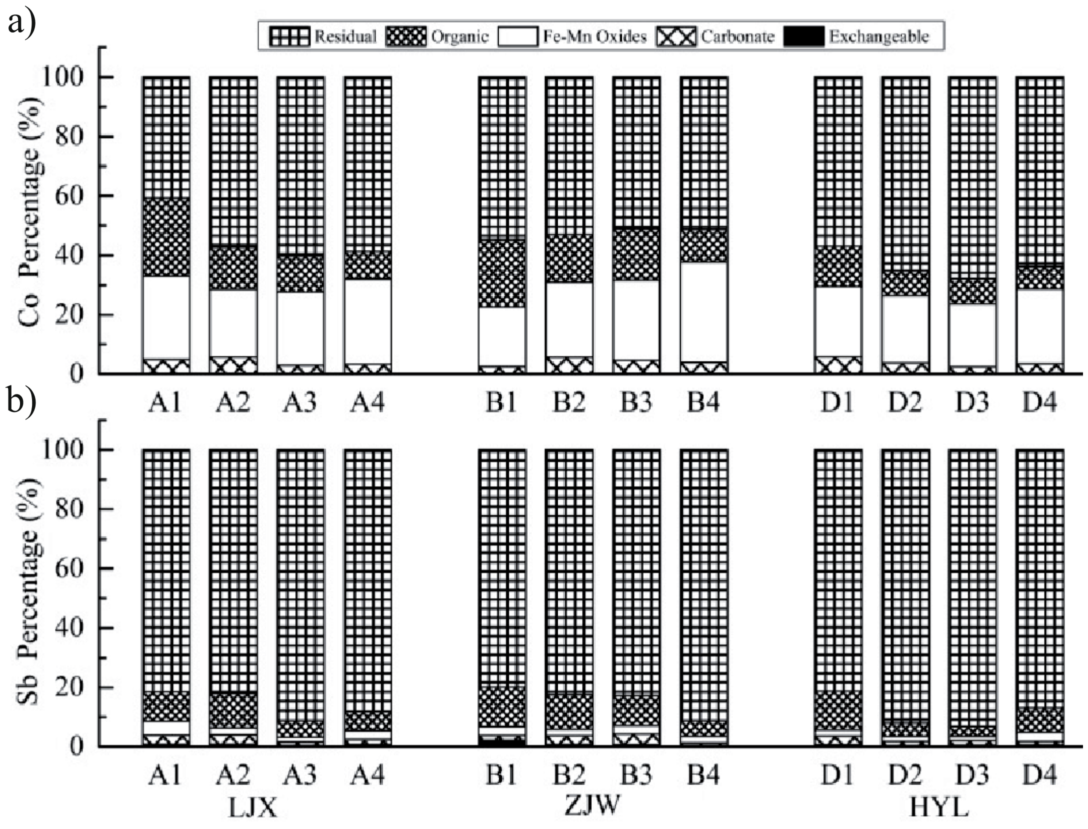

Fig. 3. Chemical speciation of heavy metals in sediment.

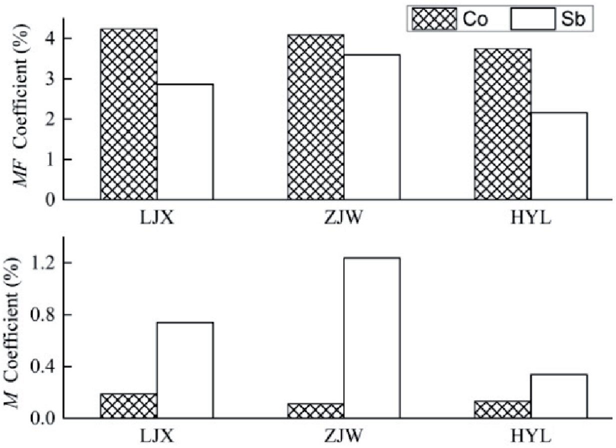

Fig. 4. Distribution characteristics of heavy metals *MF* and *M* in sediments of different habitats.

HYL < LJX < ZJW). The *MF* and *M* values indicated that Co and Sb had the lowest stability in LJX and ZJW, respectively. When the external environment undergoes change, Co and Sb could be used by organisms and thus easily migrate to lake water bodies, causing potential hazards to the eco-environments in the habitats. Because LJX and ZJW were close to cities and towns, exogenous inputs, such as domestic sewage, gas combustion, wearing of automotive parts and mining [22, 49], resulted in the redistribution of the different speciation of heavy metals in the soil solid phase [50]. In addition, the acidity of the soil in these habitats increased the leaching solubility of heavy metals in the soil.

From Fig. 5 we can know that the *M* of Co did not vary significantly with the water depth, whereas its *MF* decreased with decreasing water depth except at ZJW. Both the *M* and *MF* of Sb were higher in deep water than in farmland, and they exhibited small fluctuations in the transition area, which was likely due to the easy change of acidity and alkalinity in the transition area. Sb and its compounds possessed amphoteric characteristics. As a result, Sb in rocks and minerals could migrate to the surface environment through leaching, dissolution and groundwater effects [51], and its concentration generally decreased from deep water to farmland. The comparison of the total amounts and bioactivities of different heavy metals in the sediments in the habitats showed that the Sb concentrations in the surface sediment were significantly higher than the background value. However, the amount of bioavailable Sb was low; this was related to the migration, conversion and bioavailability of Sb in the soil, the speciation and adsorption state of Sb and the soil properties [52]. Sb existed in soil mainly as low-solubility sulfides. It also tended to bind to immobile Fe and Al oxides and organic matter in the soil, which resulted in a decreased migration ability of Sb [53]. Co easily down-migrates in the organic layer under acidic soil conditions because in acidic soil solutions, the hydrophilic group-containing small molecules of humus did not coagulate easily and form soluble chelate with Co. Thus, Co could easily leach and migrate to mineral soil [54, 55].

Correlation Analysis of Different Speciations of Co and Sb

The impacts of the total amounts of heavy metals and the physiochemical properties of soil on the distribution of heavy metal speciation occurred through a series

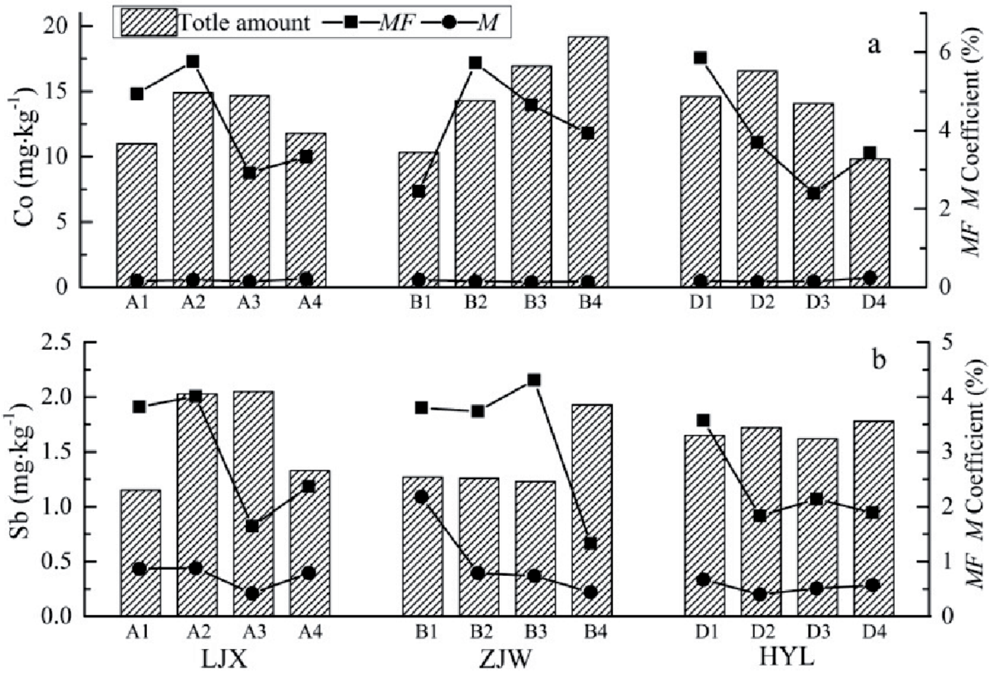

Fig. 5. Total content, *MF* and *M* distribution characteristics of heavy metals in the sediments of habitat.

Table 3. Pearson's correlations between various forms of heavy metals and sediment physical and chemical characteristics.

Element	Physical and chemical parameters	Form				
		F1	F2	F3	F4	F5
Co	pH	0.304	0.562	0.277	0.036	0.742**
	TC	-0.455	0.010	-0.255	0.707*	-0.745**
	TN	-0.562	-0.126	-0.408	0.656*	-0.712**
	TP	0.369	-0.259	-0.041	-0.329	-0.416
	DW	-0.519	0.042	-0.44	0.663*	-0.573
	Total	0.391	0.661*	.871**	0.237	0.845**
Sb	pH	-0.415	0.584*	-0.453	0.129	0.437
	TC	0.475	0.197	0.516	0.29	-0.598*
	TN	0.623*	0.126	0.365	0.292	-0.617*
	TP	0.062	-0.189	0.651*	0.16	0.212
	DW	0.667*	0.295	0.165	0.513	-0.55
	Total	-0.159	0.065	0.008	0.170	0.976**

*Correlation is significant at the 0.05 level; **Correlation is significant at the 0.01 level.

of physical and chemical reactions of heavy metals in soil (e.g., adsorption-desorption, migration-conversion, complexation and chelation) [56-58]. Caohai Lake is located on the Weining anticline, which was composed mainly of middle and lower Carboniferous limestone. A lake corrosion terrace was present on the lake shore, and lacustrine sediment up to 85 m thick has accumulated in the middle of the lake and in the surrounding areas. Due to the complicated development history and evolution process (including multiple cycles of water accumulation-shrinkage-drying-reaccumulation), the lake environment is unique. Therefore, based on the characteristics of Caohai Lake, SPSS19.0 was used to perform a correlation analysis to reflect the relationships among the chemical speciation of heavy metals, the total amount of heavy metals and the physiochemical properties of the sediment (Table 3).

Table 3 shows that TC and TN exhibit a significant negative correlation ($p<0.01$) and a significant positive correlation ($p<0.05$) with the residual form of Co and the Fe-Mn oxides, respectively, and exhibited a significant negative correlation ($p<0.05$) with the residual form of Sb. The results show that different pollution load levels have significantly different levels of impact on the different heavy metals and their speciations. The increases or decreases of some species of one metal must correspond to conversion from or to other species [20]. Therefore, when inputs from external carbon and nitrogen sources occurred, the primary phase was easily converted to a secondary phase. Of these, the impact on the migration of Co was the greatest. In addition, analysis of the bioavailability of Co showed that Co had the poorest stability. Therefore, the change of Co species must be given special attention. DW exhibited a significantly positive correlation with the Fe-Mn oxides of Co and the exchangeable species of Sb ($p<0.05$), which indicated that when the water level increases, their adsorption by animals and plants increased. As a result, their transfer and accumulation in the food chain also increased. These species also likely enter and accumulate in black-necked cranes through the food chain and thus pose a health hazard to them. The pH showed a highly significant positive correlation with the residual form of Co ($p<0.01$) and a significant positive correlation with the carbonate species of Sb ($p<0.05$). The anaerobic decomposition of organic matter under long-term flooding conditions affects the Eh and pH of the soil [59]. Under long-term flooding conditions, the pH value increases, and the stable Co element changes its morphology. It is easy to be adsorbed by organic matter in the soil solution. These results indicated that when the pH of the surface sediment is abrupt, some of the residual state of heavy metal Co may be decomposed and transformed into other forms, so that bioavailability and migration ability are increased; the carbonate-bound state of Sb is easily dissolved, and its re-release increases the risk of entering the water body.

Ecological Risk Assessment of Heavy Metals in Habitat Sediments

The concentrations of most heavy metals in the sediment were an order of magnitude higher than those in the water body. Under certain conditions, the pollutants in the bottom muds were released and can cause secondary pollution in the water body. Therefore, the selection of an appropriate assessment method for heavy metals can correctly reflect the pollution status due to heavy metals.

Table 4. The *Ci, Ei* and *RI* of heavy metals in surface sediment of habitat.

HB	C_i		E_i		*RI*
	Co	Sb	Co	Sb	
LJX	0.68	14.90	3.41	149.03	152.43
ZJW	0.79	12.95	3.95	129.46	133.41
WJY	0.81	12.87	4.04	128.74	132.78
HYL	0.72	15.38	3.58	153.83	157.41
YGS	1.01	12.75	5.08	127.49	132.57
Average value	0.80	13.77	4.01	137.71	141.72

Hakanson Potential Ecological Risk Assessment

The pollution coefficient C_f^i, the potential ecological risk coefficient E_i, and the potential ecological risk index *RI* of heavy metals in the sediments in the habitats of Caohai Lake were investigated and are listed in Table 4.

The assessment of the pollution coefficients C_f^i of the individual heavy metals showed that the average Co pollution levels in the surface sediments of the five habitats were at mild risk levels, whereas the average pollution levels of Sb were at considerable risk levels. The assessment of the potential risk indexes of the individual heavy metals showed that the average potential risks of Co in the five habitats were at mild levels, whereas the average potential risks of Sb in the five habitats were at considerable levels and followed the trend HYL > LJX > ZJW > WJY > YGS. Sites A2(184.18), A3(186.70), B4(175.59) and D4(161.52) exhibit very high potential risks. The potential risk index (*RI*) of multiple heavy metals showed that the surface sediments in the habitats were at mild or moderate levels. At each sampling site, Sb was the main contributor to *RI*. This likely occurred because the exploitation and smelting of minerals around Caohai Lake accelerate the migration of Sb to the surface environment [51], which resulted in the total concentration of Sb in the surface sediments in the study area being higher than the background value. The high toxicity of Sb also led to higher *RI* values.

Ratio of the Secondary Phase to the Primary Phase

The assessment of the total concentrations of heavy metals was helpful for understanding the pollution levels of different heavy metals. To better reflect the activity of heavy metals in the sediments, the ratio of the secondary phase to the primary phase was also used to assess the heavy metal pollution in the sediments (LJX, ZJW and HYL). These were important data for the assessment of heavy metal pollution, and the results are shown in Fig. 6.

In the sediments from ZJW and HYL, there was no pollution of Co and Sb; only site A1 in LJX shows mild Co pollution. The assessment of the water depth showed that the *RSP* of Sb generally decreased with decreasing water depth; although the values rebound at sites A4 and D4, they were still much lower than 1. The *RSP* of Co showed no evident change, but it increased with decreasing water depth and approaches 1; i.e., it reached a mild pollution level. There was a difference between the heavy metal pollution level obtained from the analysis of the concentrations of heavy metal species and that obtained from the total heavy metal concentration. This was because the pollution assessment based on the analysis of speciation takes the bioavailability of heavy metals into account more. Sb is not essential for plants, but when it exists in a soluble form, it can be easily absorbed by plant roots. The wintering food of black-necked cranes is divided into plant foods and animal foods – mainly plant foods and underground plants [60]. Plant underground blocky stem is the main part of its feeding. Plants absorb heavy metals in the soil and continue to accumulate in the body. Entering the black-necked crane through the food chain may cause heavy metals to be enriched in the black-necked crane, which is harmful to the health of the black-necked crane. Therefore, we should treat these two heavy metals as highly valued.

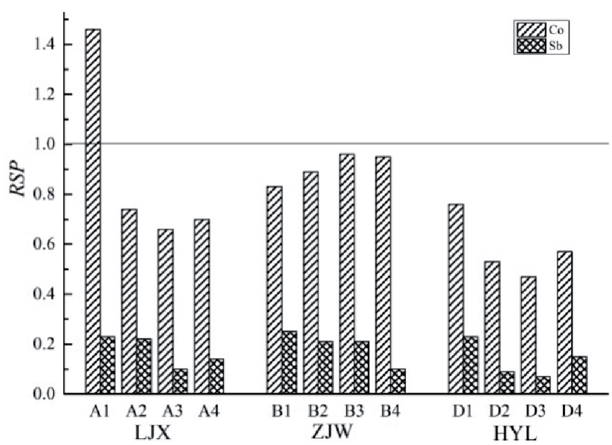

Fig. 6. The *RSP* value of heavy metals in the different sampling sites of habitat.

Conclusions

1) Using the soil background values of Guizhou Province as references, there was no Co pollution in the surface sediments in the five habitats of Caohai Lake, and Sb caused more severe pollution; the two heavy metals have moderate variations in concentration. The concentration of Co in each habitat had no significant correlation with the water depth, whereas that of Sb decreases with increasing water depth.
2) From the biological activity and migration coefficient of heavy metals, Co has a very high secondary release potential in LJY and Sb in ZJW, and the secondary phase content of secondary Co and Sb should be of particular concern in these two habitats.
3) The Hakanson potential ecological risk assessment showed that the potential risk of Co was at a mild level, whereas the likelihoods of high and very high potential risk indexes of Sb were 80% and 20%, respectively. Based on the potential ecological risk index *RI*, 65% of the sampling sites show mild risk levels, and the remaining sites exhibit moderate risk levels. Therefore, attention must be paid to Sb pollution.
4) The assessment based on the morphology showed that both Co and Sb represent mild ecological risks and no pollution. The results for Co were similar to the Hakanson analysis; however, the results for Sb were the opposite. Thus, the use of the total heavy metal concentration to determine the ecological impacts may not objectively reflect the hazards. The heavy metal speciation should be taken into account in monitoring and assessment.

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Conflict of Interest

The authors declare no conflict of interest.

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