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Seasonal and spatial variations of heavy metals in surface sediments collected from the Baoxiang River in the Dianchi Watershed, China

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ABSTRACT

To explore potential ecological hazards due to heavy metals in the Dianchi Lake Watershed, a three-stage European Community Bureau of Reference (BCR) sequential extraction procedure was applied to examine the spatial distributions and relative speciation ratios of Zn, Cu, Ni, Pb, and Cr in Baoxiang River sediments during wet and dry seasons. The metal species have similar spatial variations during different seasons. In the upstream reaches of the Baoxiang River, heavy metals reside primarily in the non-extractable residual fraction (72–90%). In the midstream, the residual fraction (35–89%) remains dominant, but the extractable fraction increases, featuring especially notable increases in the reducible fraction (5–40%). Downstream, the Cu, Ni, Pb, and Cr residual fractions remain high (46–80%) and the extractable fractions increase rapidly; the Zn extractable fraction is quite high (65.5%). Anthropogenic sources drive changes in heavy metal speciation. Changes in the river environment, such as pH and oxidation-reduction potential, also affect speciation. The reducible fraction of heavy metals in Baoxiang River sediments is most sensitive to pH. Potential ecological risk assessments for these five elements indicate that risks from Zn and Pb are mild to moderate in the middle and lower reaches of the river.

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Introduction

Heavy metals are transitional chemical elements that do not readily undergo microbial decomposition, and are therefore bioaccumulated and potentially converted into more toxic metals and organic compounds (Chen *et al.* 1993). In contrast to organic pollutants, which can be transformed into less detrimental species through biological or chemical degradation, metals in the water system are not prone to natural decomposition, and often cause irreversible harm to human health and water ecosystems through physical, chemical, and biological processes (Xu *et al.* 2017). Heavy metals in sediments exist not simply as ions or groups, but

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in various combined forms with other sediment components. Different heavy metal species have different chemical activity and bio-availability (Qiu *et al.* 2013). Heavy metals that possess an exchangeable fraction can be released in neutral and weakly acidic conditions; these species are easily absorbed and used by organisms, and are thus relatively toxic (Tang *et al.* 2015). The reducible heavy metal fraction is released into water when the redox potential leads to reduction or the water is oxygen-poor, which causes overlying water pollution (Wang *et al.* 2002). The oxidizable heavy metal fraction can become active under strongly oxidizing conditions (Lin *et al.* 2017). Thus, heavy metal migration, transformation, toxicity, and potential environmental harm in water body sediments greatly depend on speciation (Li *et al.* 2016). The total amount of heavy metals in water body sediments reflects the amount of sediment pollution to a certain degree, but does not effectively distinguish the specific modes of environmental harm (Davidson *et al.* 1994; Moćko *et al.* 2004; Singh *et al.* 2005; Wu *et al.* 2007). Research on heavy metal speciation in river sedimentary facies can reveal information on heavy metal sedimentation, release, conversion between species, and other environmental processes (Lu *et al.* 2010). Such research can also provide theoretical support for the exploration of heavy metal environmental behavior and pollution formation mechanisms.

Dianchi Lake is located in southwest Kunming City and is the largest freshwater lake in the Yunnan–Guizhou Plateau. As the standby water reserve for the city, Dianchi Lake plays an important role in social economic development and industry, agriculture, aquaculture, shipping, tourism, and climate regulation (Li *et al.* 2013). In recent years, due to the lake's unique geological location and rapid regional population, industrial, and agricultural growth, 35 branches of the watershed have, directly or indirectly, fed large amounts of toxic and harmful pollutants and nutritive salts into Dianchi Lake (Liu *et al.* 2014). Thus, Dianchi Lake, together with Taihu Lake and Chaohu Lake, are listed among the "three rivers and three lakes" targeted for remediation by the Chinese Government. Thus far, most research has focused on eutrophication in Dianchi Lake, and work on sediment heavy metals has focused primarily on the total amount of heavy metals and associated pollution evaluations (Chen *et al.* 2008; Jiao *et al.* 2010a; Li *et al.* 2010; Wang *et al.* 2014; Zhang *et al.* 2014). However, there have been few reports on heavy metal speciation (Jiao *et al.* 2010b; Li *et al.* 2007; Lu *et al.* 2010), and no research has been performed, to our knowledge, on the transport of sedimentary heavy metals into the lake via major rivers.

Focusing on the Baoxiang River, a sub-stream of Dianchi Lake, this study presents an examination of the spatial distributions of various phases of Zn, Cu, Ni, Pb, and Cr in surface sediments via sequential extraction of 13 soil and sediment microelements. Then, enrichment coefficients and heavy metal form evaluation methods are used to analyze the sources and potential ecological risks. We also discuss correlations between heavy metal phases and the physical and chemical characteristics of the water body. The purpose of this study is to provide a reference for the construction of an ecological assessment system and pollution abatement strategy in the Dianchi Lake Watershed.

Methods

The Baoxiang River is located in the northeast Dianchi Watershed and is the second-largest river flowing into Dianchi Lake. The Baoxiang River originates from Laoyeling in the southwestern Guandu District, converges into the Baoxianghe reservoir across the Sancha River, and then passes through Dabanqiao, Ala, Xiaobanqiao, Guandu, and other counties before finally flowing into Dianchi Lake in Baofeng Village (Yang *et al.* 2011). The river is 41.4 km long, 36.2 km of which comprises the main stream, with a drainage area of 302 km^2, accounting for 10.3% of the Dianchi basin (Xia *et al.* 2010). Regarding land utilization, the Baoxiang River Basin is a typical mixed rural and urban area, dominated by forests upstream, agricultural land midstream, and urban land downstream (Li *et al.* 2013). The area features a typical northern subtropical humid monsoon climate, with a multi-year average rainfall of 937.1 mm (data from 1999–2010). The rainfall distribution is seasonally heterogeneous; more than 85% of the rainfall occurs between May and October (Ren *et al.* 2015).

Surface sediment samples were obtained in two representative wet and dry season months, i.e., August 2016 and April 2017, respectively. The sampling points spanned 10 monitoring points located between the Baoxiang River source and the lake inlet (Figure 1), including four in the upstream region (S1, S2, S3, and S4), three in the midstream region (S5, S6, and S7), and three in the downstream region (S8, S9, and S10). Using a bottom grab sampler, 20 samples in total were collected from the 0–1 cm surface layer of the river bottom. Samples were sealed in polyethylene for transport to the laboratory. After natural drying, sand and plant roots were removed and the samples were ground with an agate mortar and screened through a 200-mesh nylon sieve. Screened samples were dried at 60 °C until they reached a constant weight then stored in the dryer before analysis.

Speciated heavy metals were extracted from the sediment using a sequential extraction procedure (GB/T25282-2010), developed based on the method of the European Community Bureau of Reference (BCR) by adding the extraction procedure of residual fraction. Heavy

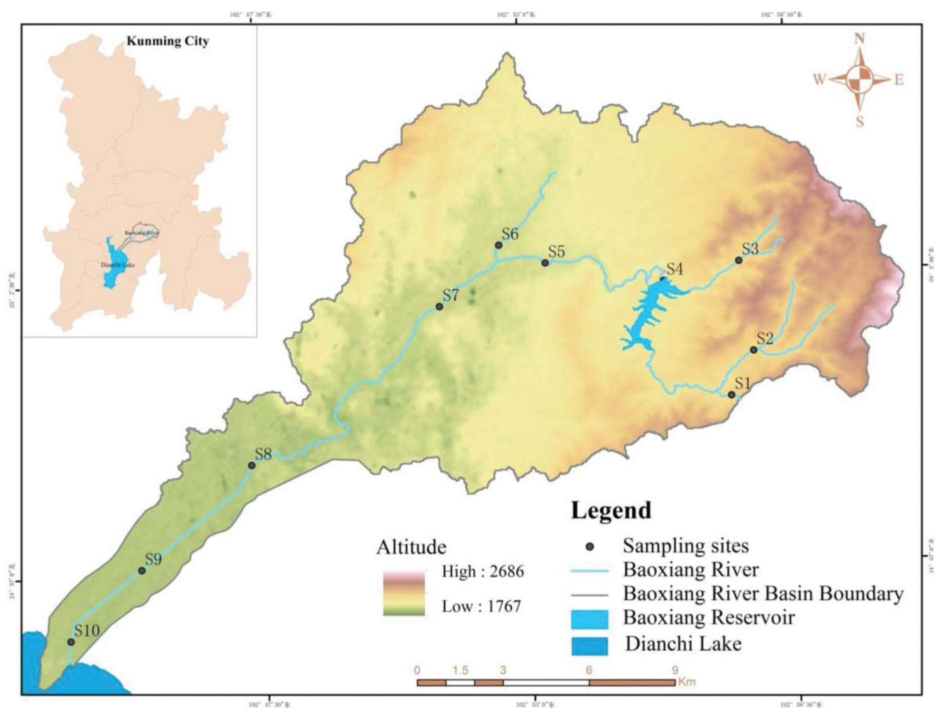

Figure 1. Sediment sampling in the Baoxiang River.

metal forms extracted from the mineral crystal lattice include primarily the exchangeable fraction and carbonate bonded form (weak-acid-extractable fraction B1), the Fe/Me oxide combined form (reducible fraction B2), the organism and sulfide combined form (oxidizable fraction B3), and the residual fraction (B4). The total amount is the sum of acid-extractable fraction, reducible fraction, oxidizable fraction and the residual fraction. The extractable content is the sum of the acid-extractable fraction, reducible fraction, and oxidizable fraction.

The heavy metal content in the extracted solution was analyzed using a microwave plasma atomic emission spectrometer MP-AES (Agilent, model 4200). Guaranteed reagents were used in the experiment. During this process, two samples from each batch were randomly selected for triplicate parallel testing; the triplicate test errors were < 5%. Meanwhile, stream sediment (GBW07305 GSD-5) was used throughout the experiments as a blank quality control sample. Table 1 shows the recovery of standard heavy metal elements; 96.96–105.43% of five heavy metals were recovered, which meets the 80–120% standard recovery range required by the USEPA.

The distributions of river surface sediment heavy metal phases are closely related to phase sources. Heavy metals from anthropogenic sources, such as mining, exhaust emissions, domestic wastewater, industrial water discharge, and the use of products containing heavy metals, tend to be enriched in the extractable fractions. The influence of human factors on target elements in sediments can be explored using the enrichment factor (EF) (Guo *et al.* 2011), which is calculated as follows:

$$\mathrm{EF} = \left(\frac{C_x}{C_{\mathrm{Al}}}\right)_s \Big/ \left(\frac{C_x}{C_{\mathrm{Al}}}\right)_n \tag{1}$$

where C_x and C_{AI} are the contents of target metals x and Al (aluminum) in the sediment sample (s) and regional background (n). Al is chosen as the background factor as it is the most accurately measured major element, and is frequently used for normalization in geochemistry literature (Sutherland 2000).

The major elements (Al, K, Na, Ca, Mg, Si, etc.) in sediment samples (s) were determined using an X-ray fluorescence spectrometer (XRF; Axios advanced (PW4400), PANalytical). Analytical uncertainties, as checked by parallel analysis of the standard sample (GBW07408 GSS-8), were less than 5% for the detected elements. The research area background value for each heavy metal was calculated according to the geometrical mean of the heavy metal concentration in soil layer A in Yunnan Province (Wei 1990). An EF ≤ 1 indicates that the metal is below the background concentration; an EF of 1–2 indicates less than the minimum enrich-

Table 1. Standard samples recovery test results (GSD-5).

Elements	Measured value (mg/Kg)	Tolerance scope (%)	Standard value (mg/Kg)	Recovery rate(%)
Zn	237.83	1.82	243 ± 15	97.87
Cu	132.83	4.18	137 ± 7	96.96
Ni	33.83	2.64	34 ± 3	99.51
Pb	118.08	0.93	112 ± 9	105.43
Cr	68.67	3.63	70 ± 6	98.10

ment; an EF of 2–5 indicates moderate enrichment; an EF of 5–20 indicates significant enrichment; and an EF of 20–40 indicates extremely high enrichment (Singovszka *et al.* 2016).

Chen *et al.* (1987) classified sedimentary original minerals as progenetic geochemical facies (or progenetic phases) according to the origins of the different sediment chemical phases, and the chemical activity and bio-availability of the various heavy metal phases. They regarded original mineral weathering products (such as carbonates and iron- and manganese oxides) and alien secondary compounds as secondary geochemical facies (or secondary phases), and proposed that the ratio of the secondary phase to the progenetic phase (RSP) could be used to evaluate heavy metal pollution via the following formula:

$$\mathrm{RSP} = M_{\mathrm{sec}} \ / \ M_{\mathrm{prim}} \tag{2}$$

where RSP indicates the degree of pollution and M_{sec} and M_{prim} refer to the heavy metal content in the sediment secondary and primary phases, respectively. The secondary phase content was calculated based on the extractable content (i.e., B1 + B2 + B3), while the progenetic phase heavy metal content was calculated based on the residual content (i.e., B4). The magnitude of RSP indicates the degree of pollution, where RSP < 1 indicates no pollution, $1 \leq$ RSP < 2 indicates mild pollution, $2 \leq$ RSP < 3 indicates moderate pollution, and RSP ≥ 3 indicates heavy pollution (Han *et al.* 2017).

Results

Surface sediment heavy metal content and speciation in the Baoxiang River

Table 2 shows the surface sediment heavy metal content and speciation in the Baoxiang River during the sampling period. Heavy metal contents throughout the river during the wet season are: Zn = 57.25–245.75 mg/Kg, average = 164.8 mg/Kg; Cu = 53.25–262.5 mg/Kg, average = 129.9 mg/Kg; Ni = 38.25–75.25 mg/Kg, average = 56.75 mg/Kg; Pb = 8.5–77.25 mg/Kg, average = 51.88 mg/Kg; and Cr = 74.5–148 mg/Kg, average = 108.25 mg/Kg. Zn and Pb are clearly higher in the dry season than in the wet season at 159.25–697.5 mg/Kg and 22.5–171.5 mg/Kg, respectively. Concentrations of Cu, Ni, and Cr do not differ between the wet and dry seasons.

The various heavy metal contents show clear spatial trends. Zn increases from the upstream region to the middle and downstream regions, with concentrations of 129.63 mg/Kg, 165.67 mg/Kg, and 210.83 mg/Kg, respectively. Cu content is highest in the upstream region (180.06 mg/Kg) and substantially reduced in the midstream region (99.17 mg/Kg), but there is no clear difference between downstream and midstream concentrations. Cr content increases notably between upstream and midstream regions, but decreases between midstream and downstream areas. The midstream average Cr content is 119.08 mg/Kg, which is 20% and 80% higher than the upstream and downstream concentrations, respectively. The variations in Ni and Pb are opposite to those of Cr, with the lowest concentrations in the midstream region and the highest in the downstream area. There are no significance differences in heavy metal spatial distributions between wet and dry seasons.

There are obvious spatial and temporal changes in heavy metal speciation. Upstream, in both the wet and dry seasons, heavy metals are predominantly in the residual fraction (72–90%), with some reducible fraction (4–6%) and oxidizable fraction (4–12%) content; the exchangeable fraction accounts for the smallest proportion (0–2%). Midstream, the

Table 2. Characteristics of heavy metals in Baoxiang River surface sediments in different seasons.

		Wet season					Dry season				
		Maximum	Minimum	Average value	Standard deviation	Coefficient of variation	Maximum	Minimum	Average value	Standard deviation	Coefficient of variation
Zn	B1	68.32	0	14.72	22.84	1.55	185.36	0.56	43.77	63.62	1.45
	B2	108.32	2.72	47.1	37.05	0.79	242.6	12.84	71.32	75.28	1.06
	B3	24.93	2.48	13.77	7.24	0.53	78.38	6.68	21.67	21.19	0.98
	B4	128.31	51.56	88.7	28.22	0.32	327.67	70	140.95	76.58	0.54
	Extractable fraction	169.51	5.2	75.6	58.94	0.78	506.7	23.84	130.66	148.37	1.14
	Total content	245.75	57.25	164.8	55	0.33	697.5	159.25	272.08	162.69	0.6
Cu	B1	13.72	0.44	2.76	3.93	1.42	6.64	0.48	2.13	2.23	1.05
	B2	60.36	4.84	22.82	15.39	0.67	49	2.88	20.89	14.8	0.71
	B3	38.35	1.9	15.1	11.36	0.75	52.1	8.55	21.63	13.8	0.64
	B4	158.78	33.69	87.55	46.52	0.53	187.79	41.33	101.16	56.68	0.56
	Extractable fraction	112.58	11.57	40.99	28.47	0.69	77.58	21.02	45.37	20.34	0.45
	Total content	262.5	53.25	129.9	68.24	0.53	259.75	63.75	147.93	69.89	0.47
Ni	B1	10.52	0.4	2.07	3.1	1.49	9.48	0.32	2.76	3.21	1.16
	B2	12.12	1.04	4.64	3.22	0.69	11.08	1.56	4.87	2.97	0.61
	B3	5.33	2.33	3.45	0.95	0.27	6.58	2.43	3.78	1.21	0.32
	B4	64.6	33.16	45.76	11.17	0.24	53.64	28.07	40.87	7.86	0.19
	Extractable fraction	28.19	4.29	10.21	6.9	0.68	27.76	4.89	11.08	6.28	0.57
	Total content	75.25	38.25	56.75	13.23	0.23	69	37.75	52.68	9.91	0.19
Pb	B1	/	/	/	/	/	/	/	/	/	/
	B2	37.58	/	16.1	15.47	0.96	91.78	/	21.47	29.4	1.37
	B3	5.95	1.15	3.15	1.53	0.49	30.5	0.9	7	9.03	1.29
	B4	61.68	2.55	30.15	15.32	0.51	46.65	11.8	34.03	12.08	0.36
	Extractable fraction	41.51	1.48	19.31	16.14	0.84	122.28	0.96	28.51	37.17	1.3
	Total content	77.25	8.5	51.88	20.51	0.4	171.5	22.5	65.25	40.43	0.62
Cr	B1	1.04	0	0.16	0.31	1.92	1.92	0	0.63	0.78	1.23
	B2	12.08	1.48	6.12	3.11	0.51	17.16	2.16	6.24	4.63	0.74
	B3	16.2	5.75	10.13	3.12	0.31	25.3	5.85	12.99	6.67	0.51
	B4	137.14	56.29	90.11	22.49	0.25	97.5	48.91	72.82	17.02	0.23
	Extractable fraction	28.38	8.28	16.43	6.12	0.37	40.29	8.11	19.5	10.17	0.52
	Total content	148	74.5	108.28	22.46	0.21	123	58.75	94.05	23.18	0.25

"/" means that there are no corresponding data; the symbol indicates the same below.

residual fractions of Zn and Pb are clearly reduced in comparison to the upper reaches at 48% and 25%, respectively; however, the reducible fractions are 23% and 34% higher, respectively, than the upstream concentrations. The Zn oxidizable fraction shows no obvious changes, but the midstream Pb oxidizable fraction is 25% larger than that in the upper reaches. The Zn exchangeable fraction is 12% higher than that in the upper reaches, while the Pb exchangeable fraction does not vary significantly. The Cr residual fraction is slightly reduced, while the Cr reducible and oxidizable fractions increase slightly; there is no change in the Cr exchangeable fraction. Cu and Ni show no clear changes in speciation between the upper and middle reaches. Downstream, the Zn residual fraction decreases, accounting for 34% of the total Zn content. The Zn reducible and exchangeable fractions increase gradually, accounting for 38% and 21% of the total Zn content, respectively; however, there is no obvious change in the Zn oxidizable fraction. The Pb oxidizable fraction accounts for only 6% downstream, and the residual fraction increases to 53%. The Pb reducible and exchangeable fractions do not vary significantly between downstream and midstream. Likewise, the speciation proportions of Cu, Ni, and Cr do not differ significantly between downstream and midstream.

During the wet season, the upstream Zn is primarily residual (81%) (Figure 2), with some reducible and oxidizable Zn (10% and 8%, respectively) and a smaller amount of exchangeable Zn (1%). The midstream residual fraction (56%) is substantially reduced compared to the upstream region, but the reducible fraction increases notably to 33%. The midstream oxidizable and exchangeable fractions do not vary significantly from those upstream. The Zn exchangeable fraction downstream reaches 38%; however, the oxidizable fraction is not significantly difference from that measured upstream and midstream. The changes in Zn fractionation in different river sections in the dry season is essentially consistent with those in the wet season, although the midstream exchangeable fraction is clearly higher, and the residual fraction is slightly lower than those in the wet season.

During the wet season, the upstream Cu distributions mirror those of Zn, with the residual fraction accounting for 72%, the reducible and oxidizable fractions accounting for 16% and

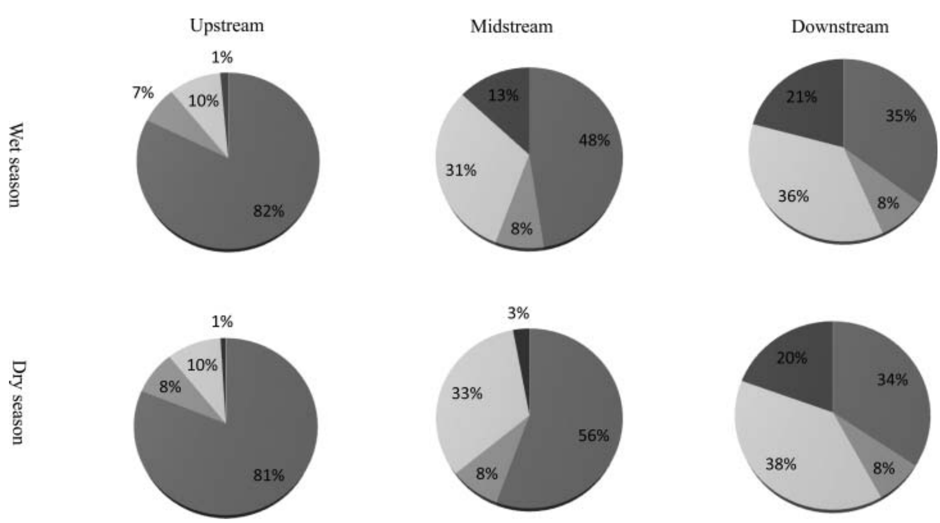

Figure 2. Relative proportions of Zn in surface sediments in different Baoxiang River valleys.

10%, respectively, and the exchangeable fraction accounting for only 2%. There is no significant difference in fractionation between the mid- and upstream regions. Downstream, the reducible fraction is substantially increased (27%), while the residual fraction is substantially reduced (60%). The dry-season Cu fractionation in different river sections is generally consistent with the wet season distribution. However, the dry-season midstream and downstream oxidizable fractions are clearly higher than those in the wet season (at 19% and 20%, respectively), and the upstream reducible fraction is markedly lower than that in the wet season, at 18%.

Exchangeable Pb was not detected in any section of the river. Upstream, Pb resides mainly in the residual fraction in the wet season (90%), with smaller amounts in the oxidizable and reducible fractions (6% and 4%, respectively). The oxidizable and reducible fractions clearly increase in the midstream (to 33% and 29%), and the residual fraction decreases to 38%. Downstream, the reducible fraction increases to 48%, but the oxidizable fraction decreases to 6%. The upstream Pb characteristics in the dry season are consistent with those in the wet season. However, downstream residual Pb increases slightly from the midstream residual Pb (53%). The reducible and oxidizable fractions decrease from 40% and 25% midstream to 32% and 15% downstream, respectively.

During the wet season, the upstream Ni distribution is similar to those of Zn and Cu, with the residual, reducible, oxidizable, and exchangeable fractions accounting for 84%, 8%, 7%, and 1%, respectively. The residual fraction increases slightly in the midstream (89%), the midstream exchangeable fraction is consistent with that upstream, and the reducible and oxidizable fractions are slightly decreased. Downstream, the residual fraction is obviously reduced (73%), the exchangeable fraction is clearly increased (9%), and the reducible fraction (11%) is larger than that upstream and midstream. The Ni fractionation in different river sections in the dry season is generally consistent with that in the wet season; however, the midstream residual fraction, which decreases from 81% upstream to 77%, is opposite to that in the wet season.

The proportions of exchangeable and residual Cr in the wet season (approximately 0% and 80%, respectively) show no obvious changes with stream location. The reducible and oxidizable fractions increase slightly from upstream to downstream. The proportions of different forms of Cr in the dry season are consistent with those in the wet season.

Factors influencing heavy metal phase changes in the Baoxiang River

Figure 3 shows the EF of surface sediment heavy metals in different sections of the Baoxiang River during the wet and dry seasons. During the wet season, Zn enrichment increases from upstream to downstream; while the Zn EF does not reach minimum enrichment upstream, and moderate enrichment is seen mid- and downstream. Cu shows significant enrichment upstream, but moderate enrichment midstream and downstream. Ni does not reach minimum enrichment in any of the river sections. Pb does not reach minimum enrichment upstream and midstream, but shows moderate enrichment downstream. Cr does not reach minimum enrichment upstream and downstream, but shows moderate enrichment midstream. In the dry season, Zn shows moderate enrichment upstream and downstream and significant enrichment midstream. Dry-season Cu and Ni enrichment levels are consistent with those in the wet season, while Pb and Cr do not reach minimum enrichment upstream, but show moderate enrichment mid- and downstream.

Water chemistry also exerts considerable influence on heavy metal phase changes. For example, exchangeable heavy metals (fraction B1) adhere to soil and surface sediment and

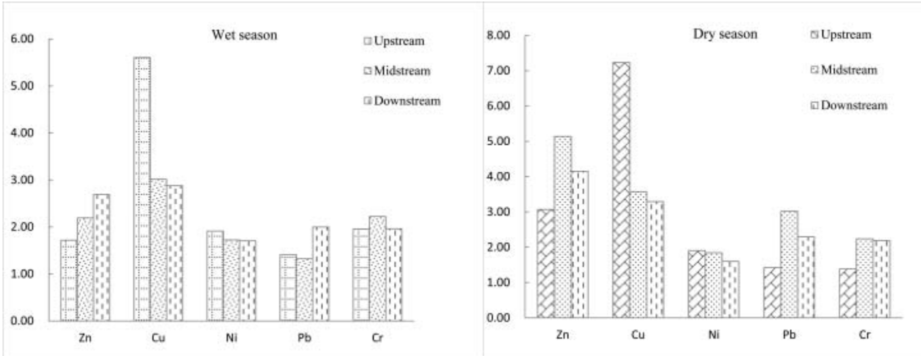

Figure 3. Heavy metal enrichment coefficients for Baoxiang River surface sediments.

may be released upon exchange with ions in weak electrostatic environments (Gleyzes *et al.* 2002). On the one hand, different sections of the Baoxiang River have different hydrodynamic characteristics, which, together with irregularities caused by human disturbance, may result in different spatial distributions of exchangeable (B1) content. On the other hand, research has shown that B1 mass will migrate to the water body when water conditions change (e.g., pH decreases) (Chen and Lin 2001); pH is the major factor influencing heavy metal release in sediments (Wen 1996). On-site water pH measurements in the Baoxiang River show pH tends to first increase, then decrease with the direction of flow; the highest pH value is found at sampling point S8. The results above show that the exchangeable (B1) fractions of the five target heavy metals do not change in response to pH changes in Baoxiang River sediments.

Reducible fraction (B2) contents show continuous increases due to the slightly alkaline river water. The reducible form is not easily released into the water body, as it combines via strong ionic bonds with a carrier and precipitate. However, when the water body experiences decreased redox potential or an oxygen deficit, the heavy metallic bond in the combined form is restored, which causes secondary pollution in the water body (Wang *et al.* 2002). Research has shown that, in many redox systems, a decrease in pH can cause a 60 mv Eh increase (Chen *et al.* 1993). Thus, there is a negative correlation between pH and Eh over a certain range. Moreover, the B2 form is released into sediments as the pH increases (Figure 4). The B2 fractions of our five target heavy metals increase continuously with the direction of flow to varying degrees. The B2 forms of Zn and Pb show the strongest responses to pH; for these metals, B2 content increases greatly from the upstream region to the midstream region due to pH increase, then decreases downstream due to a slight decrease in pH.

The oxidizable (B3) fractions of the various heavy metals show no clear spatial variability. Thus, the B3 fraction shows no obvious response to changes in pH. Of course, other environmental factors besides pH (such as ion strength, redox potential, and the competitive effects of other heavy metals) will influence the release of heavy metal elements in sediments (Wang *et al.* 2012); these factors are not specifically analyzed herein.

Heavy metal ecological risk assessments

The pollution degree of the five heavy metals in the sediments of Baoxiang River was assessed using the secondary phase and progenetic phase (RSP). In the wet season, the RSP

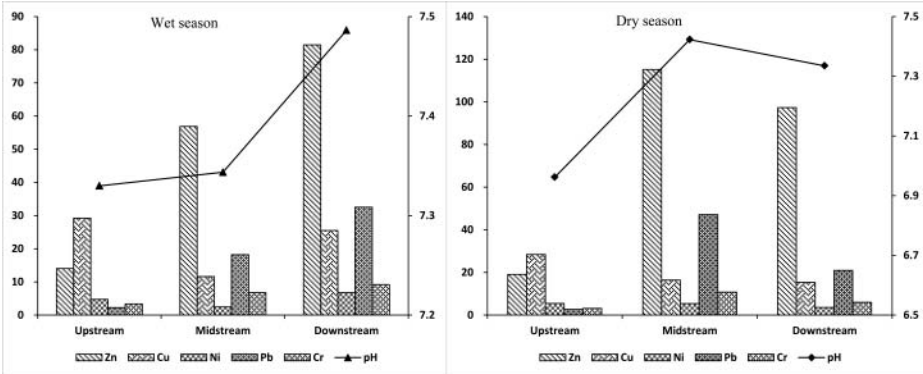

Figure 4. Relationship between pH and B2 in different reaches of Baoxiang River.

values of heavy metals Cu, Ni, and Cr are all less than 1, indicating that there no significant enrichement of them due to anthropogenic activity (Figure 5). The heavy metals Zn and Pb show mild to moderate enrichment, especially in the middle and lower reaches of the river, with the RSP values between 1 and 3. In the dry season, the RSP values of the five heavy metals were almost the same as those of the wet season. However, in S8 samples of the downstream Zn showed obvious enrichment with a high RSP value, which deserved further investigation.

RSP reflects the ratio between the secondary and progenetic phases. Because alien heavy metal pollutants entering river sediments are largely secondary, this influx makes the secondary phase content increase much faster than the progenetic phase content, increasing the RSP value. The results show that the potential ecological hazards due to heavy metals in

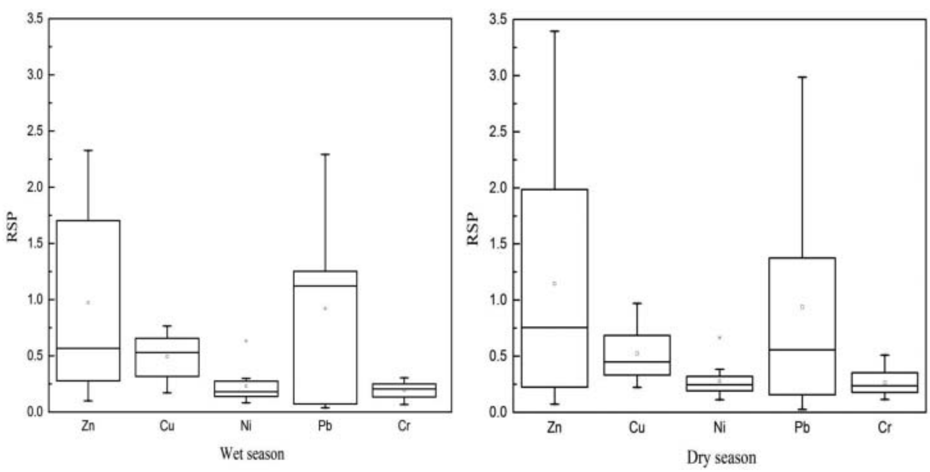

Figure 5. Potential risk indexes for heavy metals in Baoxiang River surface sediments. The horizontal line within the box represents the median sample value. The ends of the box represent the 25th and 75th quantiles. The lines that extend from each end of the box are whiskers, which extend to the outermost data point that falls within the distances. This is computed as follows: 1st, 1.5 (interquartile range), and 3rd quartiles + 1.5 (interquartile range). If the data points do not reach the computed ranges, then the whiskers are determined by the highest and lowest data point values (excluding outliers). Data points that are not within the range of the whiskers are considered to be outliers.

Table 3. Anion concentrations in the Baoxiang River.

	Wet season				Dry season			
	Cl^-	NO_3^-	SO_4^{2-}	F^-	Cl^-	NO_3^-	SO_4^{2-}	F^-
S1	0.48	0.04	/	9.04	0.08	0.69	9.30	0.18
S2	4.74	/	/	/	/	64.56	132.54	0.22
S3	/	/	/	/	/	/	/	/
S4	/	2.36	0.98	16.32	0.20	/	/	/
S5	5.90	7.28	4.08	20.05	0.19	3.28	17.85	0.18
S6	12.69	13.37	17.55	21.93	0.17	17.01	20.78	0.13
S7	19.22	35.98	7.57	31.11	0.22	17.09	26.15	0.22
S8	19.30	30.14	24.99	33.37	0.54	17.71	32.68	0.28
S9	19.30	39.12	25.11	31.85	0.26	10.69	36.91	0.40
S10	27.29	60.75	27.48	34.78	0.31	8.93	42.41	0.47

Baoxiang River surface sediments can be ranked as follows: Zn > Pb > Cu > Ni > Cr. Ecological risk assessments for Baoxiang River sediment heavy metals in different seasons reveal that Zn and Pb pose high ecological risks in the downstream region. The EF results indicate that Zn and Pb are influenced by human activities to varying degrees. Field investigations show that the midstream section of the Baoxiang River consists of a rural–urban fringe zone, in which the development of the Kunming airport economic zone has accelerated urbanization; the downstream section of the river flows through ancient Guandu town, Guandu Government district, and other densely populated areas. Chen (1983) found a positive correlation between the concentration of household detergent additive NTA and the release of Zn and Pb. Thus, a strong human presence can influence the acid–base equilibrium, salt concentration, and amount of synthetic complexing agents in water bodies, which can increase the amount of extractable Zn and Pb in the river. Conversely, research shows that organic acids and salts can promote heavy metal release during reactions with organic acid anions, releasing large amounts of activated Zn and Pb (Song *et al.* 2010). Meanwhile, chloride ion complexation can greatly improve the solubility of highly insoluble heavy metal compounds; when $Cl^- = 1$ mol/L, the solubilities of Zn, Cd, and Pb compounds can increase by factors of 3 to 39 (Chen *et al.* 1993). This effect can be observed in anion measurements in the Baoxiang River; for details, see Table 3. The Cl ion concentration increases between the upstream and downstream sections, which may effectively promote the dissolution of Zn and Pb extractable fractions. This may, in turn, increase the secondary-to-progenetic phase ratio, which increases the potential ecological risks due to heavy metals.

Conclusions

Obvious spatial differences exist between the content and speciation of heavy metals in Baoxiang River surface sediments. Upstream, heavy metals reside primarily in the residual fraction (72–90%), with lower amounts in the reducible (4–16%), oxidizable (4–12%), and exchangeable (0–2%) fractions. Midstream, Zn, Cu, Ni, and Cr remain chiefly in the residual (48–89%) and reducible (5–33%) fractions; the oxidizable fraction (5–19%) increases continuously, as does the exchangeable fraction (0–13%). The midstream Pb residual fraction (35–38%) is no longer dominant, while the reducible (33–44%) and oxidizable (25–29%) fractions increase greatly. Downstream, the Cu, Ni, Pb, and Cr residual fractions remain high (46–80%), while the reducible, oxidizable, and exchangeable fractions do not vary discernably from their midstream values. The Zn residual fraction, which accounts for 34% to 35% of the total Zn, is lower than the midstream region, but reducible (36–38%) and exchangeable (20–21%) Zn are higher. Generally, the five heavy metals show continuous increases in the extractable fraction and decreases in the residual fraction with the direction of flow.

Artificial sources are primarily responsible for the increase in extractable heavy metals in river sediment. Changes in water chemistry also contribute significantly to the spatial differences between different heavy metal phases. We find clear relationships between spatial changes in reduced heavy metal forms and changing pH values. Ecological risk assessments for Baoxiang River surface sediment heavy metals show that the risks posed by the five heavy metals can be ranked as follows: Zn > Pb > Cu > Ni > Cr. Cu, Ni, and Cr do not pose significant pollution risks. Zn and Pb show obvious enrichment midstream and downstream, and pose mild to moderate pollution risks. Zn and Pb pollution is closely related to human activities; it is also exacerbated by large amounts of organic acid anions midstream and downstream, which can increase the release of heavy metal pollution.

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Conflict of interest

There are no conflicts of interest to declare.

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