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TECHNICAL ARTICLE

Spatial Attenuation of Mining/Smelting-Derived Metal Pollution in Sediments From Tributaries of the Upper Han River, China

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Abstract
Spatial variations in contaminant distribution in river sediments are useful for pollutant diagnosis. This study investigated 18 metals/metalloids (Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Sn, Tl, U, V, Zn, and Hg) in sediments of rivers impacted by Sb and Hg mining/smelting activities in headwater catchments of the Han River Basin, China. Source and pollution assessments of the metals were examined based on their spatial variations. The results showed that sediment concentrations of Cu, Cr, Tl, U, Pb and typically, Ag, Mo, Sb, and Hg were generally elevated. However, their concentrations decreased from upstream to downstream along the river gradient. By combining their spatial variations with the results of multivariate analyses, it was deduced that the elevated concentrations were due to mining/smelting activities. At downstream sites, all elevated concentrations decreased to near background levels, except for those of Hg and Sb. The maximum concentrations of Hg and Sb in the river sediments, which were two- to three-orders of magnitude higher than the reference values, are still considered to pose very high potential ecological risks.

Keywords Spatial variations · Metal transport · Source identification

Introduction

The toxicity, abundance, persistence, and subsequent bioaccumulation of metals mean that their presence in aquatic environments has become a very serious environmental pollution problems (Moore and Aghazadeh 2012; Sin et al. 2001). Excess metals in water bodies generally originate from anthropogenic activities and natural weathering of rocks (Singh et al. 2005). Once present in the aquatic environment, metals can be transported in multiple phases (e.g. dissolved or bound to suspended particulates) via the processes of dispersion, sorption, dissolution–precipitation, and chemical reaction (Zhang et al. 2014a). Metals partly associated with fine-grained particulates can accumulate in bottom sediments via settling (Sims et al. 2017; Zhang et al. 2014b). When the flow regimes or other factors of river channels are altered, the contaminants in bottom sediments (e.g. metals) can be resuspended, released, and transported into surrounding drainage systems (Audry et al. 2005; Gibson et al. 2015; Hammarstrom et al. 2005; Moncur et al. 2005; Wei et al. 2017). Thus, river sediments are important repositories of contaminants in aquatic environments, and they constitute an excellent source of data with which to investigate anthropogenic impacts (García-Ordiales et al. 2016). Because of the various physical and biochemical conditions of riverbeds, most contaminants are influenced by transformation and retardation processes that act along flow paths, which can contribute to natural attenuation of pollution loads (Thorslund et al. 2012). Thus, variation in the spatial distribution of contaminants in river sediments

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provides useful information for elucidating pollution source and transport processes.

The Han River is the largest tributary of the Yangtze River in China. The upper Han River supplies clean water for China's South-to-North Water Transfer Project, which diverts water to dry areas of northern China, including Beijing. Thus, the water quality of the upper Han River is important (Li et al. 2008). Previous studies have characterized this water quality, including the nutrients, hydrogeochemistry, and dissolved metals (Li et al. 2008, 2009a, b, c; Li and Zhang 2008, 2010; Liu et al. 2016a). As for the sediments, Yan and He (1996) investigated the geochemistry of Cu, Pb, Zn, Cd, Co, Ni, As, Hg, Cr, Mn, and Fe in 45 sediment samples from the Han River, while Zhao (2014) investigated and evaluated Cu, Pb, Zn, Cd, and Cr in the Hanzhong reach of the upper Han River. The deposits of the upper Han River Basin contain abundant nonferrous metal mineral resources, such as Hg, Sb, Pb, Au, and Zn (Peng 1997). However, there have been few reports on metal pollution resulting from mining/smelting activities in the upper Han River Basin. Therefore, the objectives of this study were to quantify the impact of mining/smelting activities on the metal pollution of river sediments in the headwaters of the Han River, and to identify the possible sources and assess the pollution risks based on the distribution patterns of such metals.

Materials and Methods

Study Area and Sample Collection

The Xunyang mining district, located in southern Shaanxi Province, is the largest Hg/Sb mining area in China. The mining/smelting activities that have been conducted there for centuries have caused a large volume of contaminated waste to be discharged into the Gongguan and Zhutong Rivers, which ultimately flow into the Han River (Fig. 1). To determine the effect of these activities on metal/metalloids pollution in the river sediments, samples were collected on August 30, 2015, from the nine sampling sites shown in Fig. 1. Triplicate samples were collected close to each other from the upper 15 cm of the surface sediments at each site using a stainless steel grab sampler. The collected samples were homogenized using coning and quartering, and approximately 200 g of sediment from each site was obtained for subsequent laboratory analysis.

Chemical Analyses, Quality Assurance, and Quality Control

The sediment samples were freeze-dried, powdered, and sieved through a 2 mm sieve and then stored in plastic containers. A 0.5 g sediment sample was placed in a polytetrafluoroethylene (PTFE) tube, and then digested successively with an $HCl–HNO_3–HF–HClO_4$ mixture (ST-6™). Subsequently, the digestion solution was diluted to 50 mL using pure water (Wu et al. 2014). Inductively coupled plasma–mass spectrometry and atomic fluorescence spectrometry were used to determine the metals/metalloids, except for Hg, which was determined using an automatic solid total mercury analyzer (Hydrate-C, Leeman, USA).

Quality assurance and control were performed using duplicates, with method blanks and standard reference materials for each batch of samples (including one blank and one standard for each group of 10 samples). The relative standard deviation was $\leq 10\%$ for all tests. The quality of the analytical procedures was tested using the recovery measurements of Chinese national geostandards (GBW-07333 and GBW-07314). The results were consistent with the reference values and all differences were within $\pm 10\%$.

Evaluation Indices

To understand the spatial variations of metals/metalloids in the river sediments, a metal concentration attenuation rate along the river gradient (ΔCC). was developed in this study:

$$\Delta CC = \frac{\frac{C^i_{x1} - C^i_{x2}}{C^i_{x1}}}{L^*}, \tag{1}$$

where c^i_{x1} and c^i_{x2} are the concentration of metal/metalloid i at upstream site x1 and downstream site x2, respectively. Sediment deposition has found to be affected by the friction slope of the river (Velleux et al. 2008). This effect should be excluded when comparing attenuation rates. Here, L^* is the adjusted distance based on the elimination of the effect of riverbed slope:

$$L^* = l(E_{x1–}E_{x2}) \tag{2}$$

where l is the stream distance from x1 to x2, and E_x. E_{x2} are the elevations of sites x1 and x2, respectively. Thus, ΔCC represents the concentration difference per stream distance per elevation (ppm/m/m) and was used for evaluating the spatial variation in metals/metalloids. Two pollution indices were employed to assess the sediment pollution. The first was the contamination factor (CF), which is used widely in the field (Håkanson 1980):

$$CF = \frac{C^i}{C^i_b}, \tag{3}$$

where c^i is the concentration of metal/metalloids i in the sediment and c^i_b. is the geochemical background concentration of metal/metalloids i. According to the CF value, a sample could be classified as slightly contaminated ($CF < 1$),

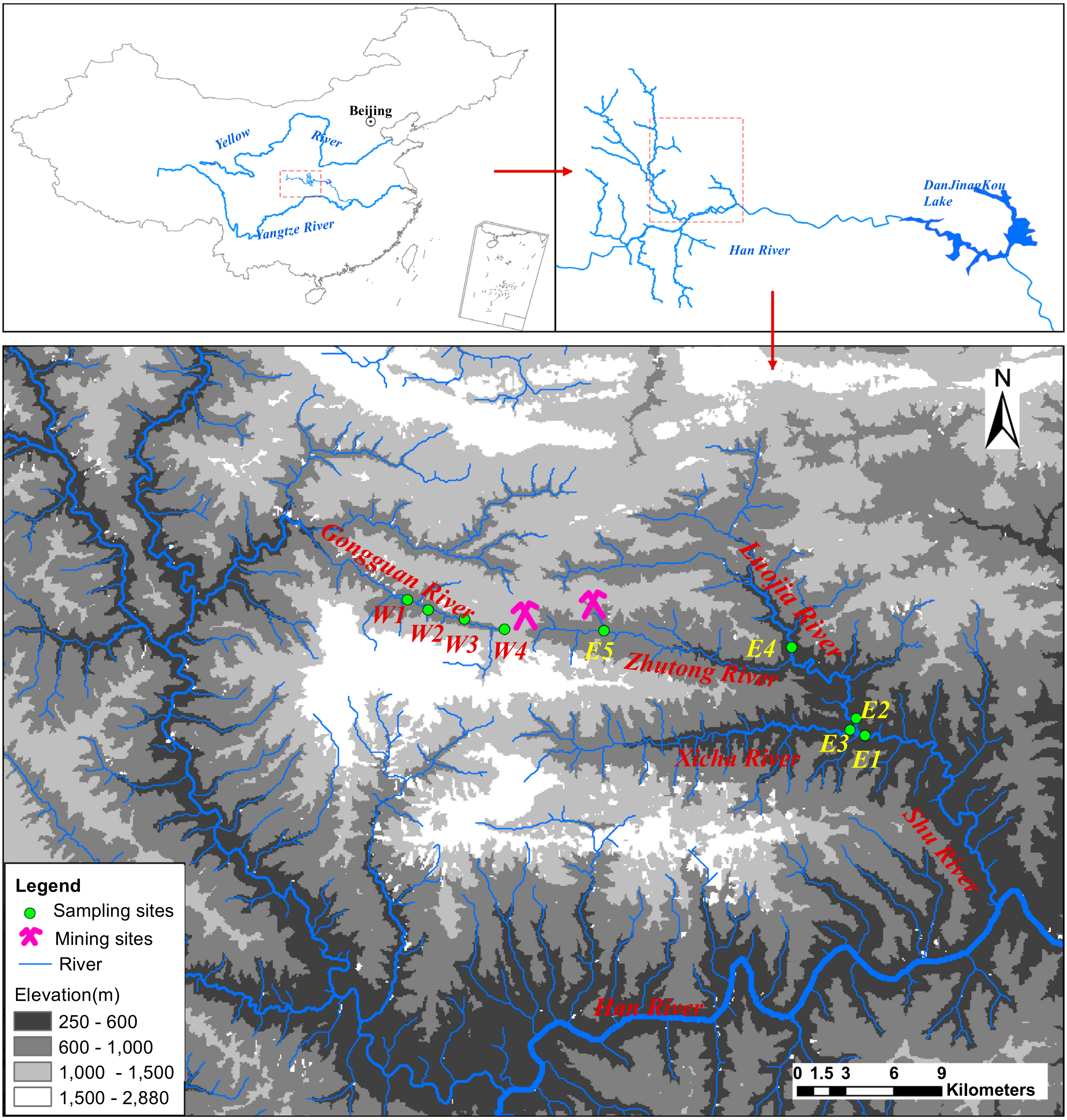

Fig. 1 Locations of the rivers and sampling sites investigated in this study

moderately polluted ($1 \le CF < 3$), considerably polluted ($3 \le CF < 6$), or very highly polluted ($CF \ge 6$) (Liu et al. 2017).

The second index used was the potential ecological risk index for single metal/metalloids (E_r^i) (Håkanson 1980):

$$E_r^i = T_r^i \frac{C^i}{C_b^i}, \quad (4)$$

where T_r^i is the corresponding toxicity coefficient of metal/metalloids i. The metal/metalloids toxicity response factors adopted were as follows: Mn = Zn = 1, V = Ba = Cr = 2, Cd = 30, Co = Pb = Cu = Ni = 5, Hg = Sb = 40, As = 10, and Tl = 60 (Håkanson 1980; Li et al. 2011; Lin 2009; Xu et al. 2008).

Statistical Data Analyses

Various multivariate techniques such as correlation analysis (CA) and principal component analysis (PCA) have been used to identify the sources of metal pollutants in surface sediments (Anju and Banerjee 2012; Bartoli et al. 2012; Chai et al. 2017; Saeedi et al. 2012). If the correlation coefficient between elements is positive, it can be deduced that the elements have mutual dependence and identical behavior or that they are affected by the same factor(s) during transport (Zhang et al. 2017). PCA is used both to reduce the collinearity and dimensionality of a data set and to identify a small number of factors that could explain most of the variance observed in a large number of manifest variables (Wentzell et al. 1997). In this study, CA and PCA were processed using SPSS 18 for Windows (SPSS, Inc., USA).

Results and Discussion

Concentrations of Metals/Metalloids

The concentrations of all the metals/metalloids measured at the sampling nine sites are listed in Table 1. Concentrations with considerable variances were 0.05–0.53 mg/kg for Ag, 6.8–61.8 mg/kg for As, 330–1790 mg/kg for Ba, 0.13–0.84 mg/kg for Cd, 47–131 mg/kg for Cr, 0.79–4.70 mg/kg for Mg, 0.60–26.90 mg/kg for Mo, 15.9–95.6 mg/kg for Pb, 3.02–2410 mg/kg for Sb, 1.7–12 mg/kg for U, and 0.21–5.96 mg/kg for Hg. These results were compared with the findings of previous studies on the 2nd order mainstream (e.g. the Han River), 1st order mainstream (e.g. the Yangtze River), and Chinese average levels (Table 1). The concentrations of As, Pb, and Hg in the tributary sediments were found to be generally higher than those in the upper Han River, where as those of Co, Cd, and Cr were lower. In comparison with those of the Yangtze River, the As, Cd, Cr, Cu, Ni, Pb, Zn, and Hg concentrations in the tributary sediments were higher. The average concentrations of metals/metalloids, except for those of Mn and Sn in the river sediments, exceeded the Chinese average levels. The maximum concentrations of Sb and Hg measured in the sediments were two to three orders of magnitude higher than those of both the mainstream and Chinese average levels.

Spatial Variations in Metals/Metalloids in River Sediments

Figure 2 shows the concentrations of some metals/metalloids at the nine sampling sites. Ag, Cu, Cr, Tl, U, Mo, Pb, Sb, and Hg had similar spatial patterns with maximum concentrations at E5 or W4 and minimum concentrations at W3 or W4 (Fig. 2a). The concentrations gradually decreased from W4 and/or E5 to sites downstream, e.g. the concentrations of Sb and Hg decreased exponentially, fitting the attenuation of diffusion of point-source pollutants (Fig. 3). The concentrations of Ag, Tl, Cr, Cu, U, Mo, and Pb at site W2 or W1 were higher than those at site W3, implying that point-source pollution was not the dominant factor influencing sediment pollution in the river reaches downstream of site W1. Most metals/metalloids at the ends of the studied reaches (E1 and W1) exhibited low levels, except for Hg and

Table 1 Metal/metalloid concentrations in sediment samples from the rivers investigated in this study and other river sediments in China (unit: mg/kg)

	Ag	As	Ba	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Sn	Tl	U	V	Zn	Hg
E1	0.09	14.1	570	0.23	17.8	66	28.8	635	0.92	41.0	27.2	6.1	2.7	0.67	2.7	93	89	1.91
E2	0.12	17.8	450	0.13	11.1	55	25.8	455	1.18	34.0	15.9	25.7	2.0	0.44	2.3	81	82	1.92
E3	0.05	8.7	490	0.16	12.6	55	23.8	490	0.60	32.4	32.7	3.02	2.2	0.47	2.1	77	71	0.21
E4	0.06	6.8	330	0.13	10.4	54	22.9	618	0.64	29.1	19.0	7.23	2.0	0.41	1.7	67	66	1.57
E5	0.53	25.2	1120	0.58	9.8	131	30.5	381	26.90	29.8	60.6	2410	2.0	1.51	12.0	62	108	5.96
W1	0.11	61.8	1790	0.79	9.0	47	22.4	502	1.17	26.3	37.5	346	1.9	0.43	2.3	63	116	1.03
W2	0.19	33.7	1070	0.67	11.2	59	28.9	538	1.22	32.0	68.4	277	2.5	0.54	2.7	76	140	0.33
W3	0.16	16.2	780	0.84	13.2	63	25.8	691	0.84	36.8	27.9	283	2.7	0.60	2.4	80	90	4.11
W4	0.28	20.9	1170	0.52	12.9	58	34.6	859	4.62	30.5	95.6	2100	2.2	0.56	5.6	73	106	5.63
Average	0.18	22.8	863	0.45	12.0	65	27.1	574	4.23	32.4	42.7	606	2.2	0.63	3.7	75	96	2.52
Upper Han River[1]	–[4]	6.55	–	0.59	15.4	85.9	30.3	970	–	33.7	22.1	–	–	–	–	–	96.7	0.03
Yangtze River[2]	–	7.60	–	0.148	12.1	52.3	21.5	589	–	26.4	21.4	–	–	–	–	–	73.6	0.034
China[3]	0.07	9.00	485	0.13	12.0	54.0	20.0	653	0.80	23.0	23.0	0.7	2.8	–	2.4	77	67	0.034

[1–3]Data cited from Yan and He (1996), Zhang et al. (1995), and Shi et al. (2016) respectively

[4]No data in referenced works

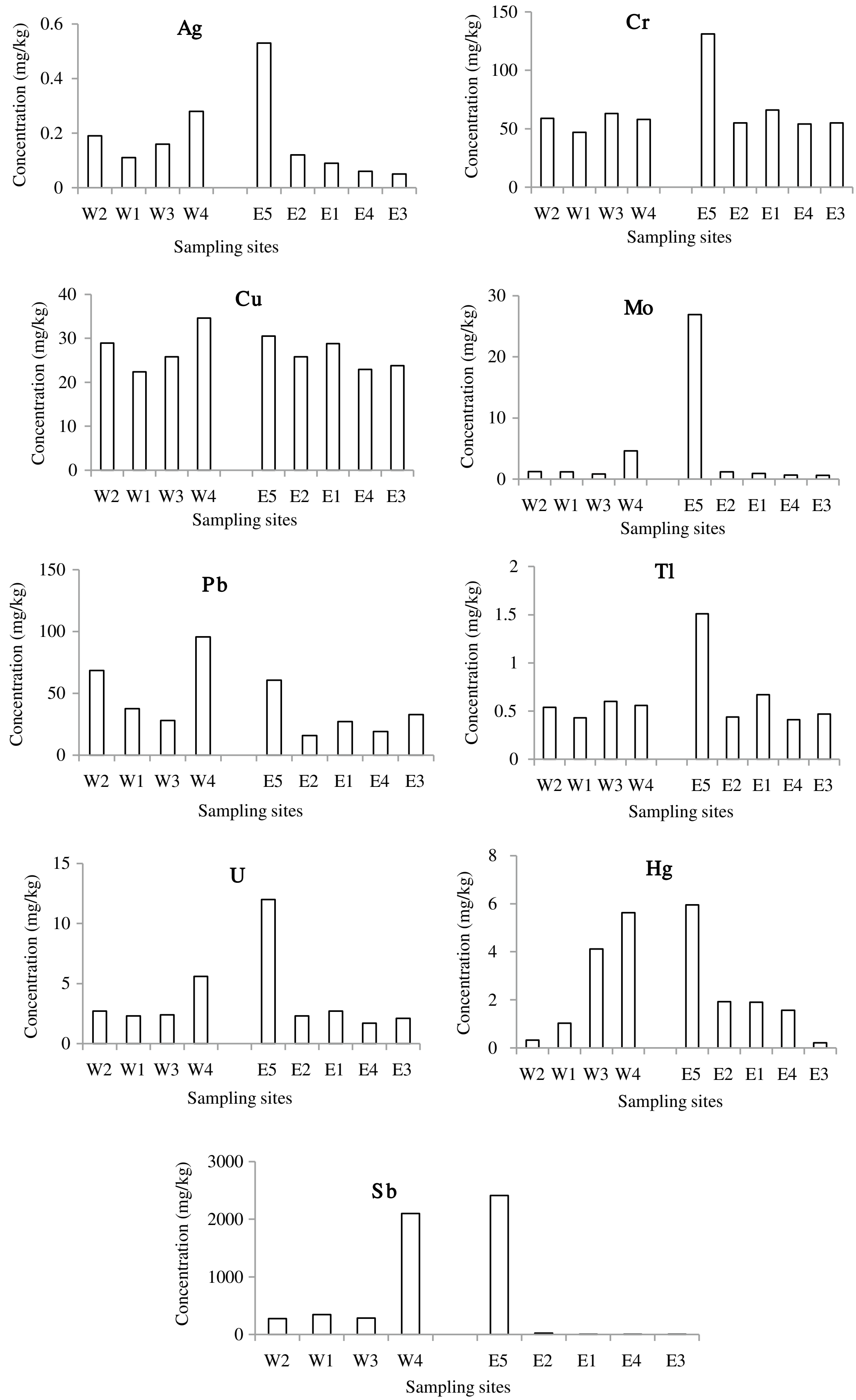

Fig. 2 **a** Comparison of metal concentrations at the nine sampling sites. **b** Comparison of metal/metalloid concentrations at the nine sampling sites

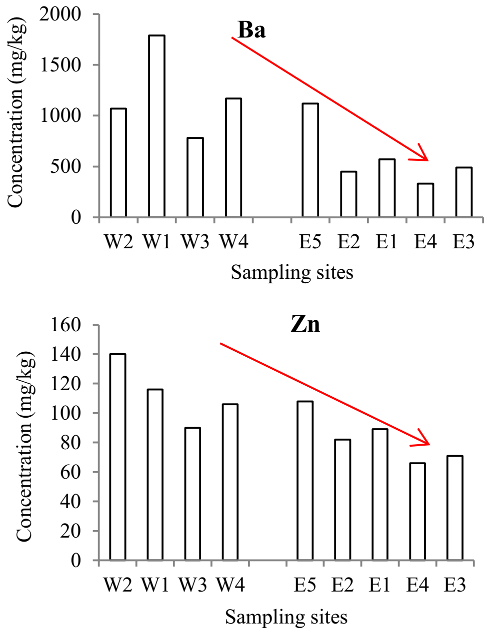

Fig. 2 (continued)

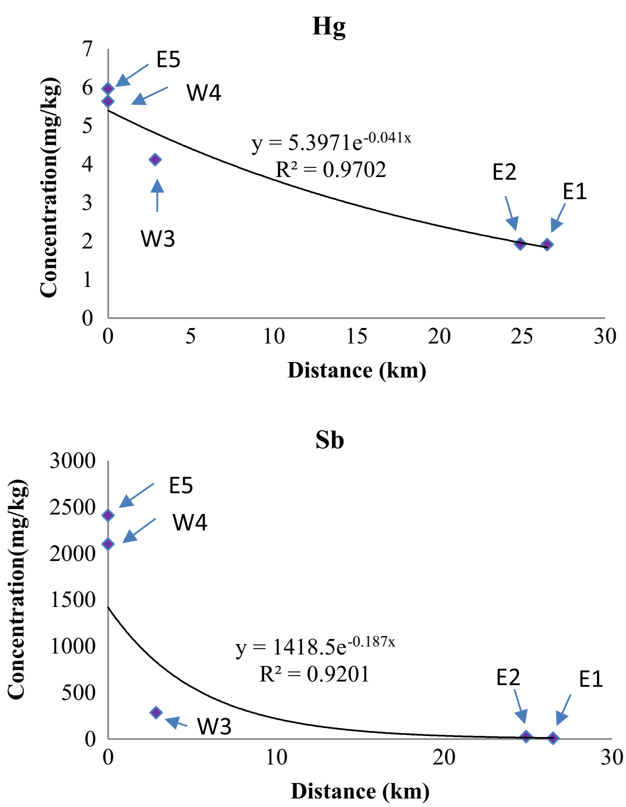

Fig. 3 Relationship between metal concentrations and distance along the river from pollution source

Sb. Noticeably, the concentrations of Cr and Tl decreased only in the Zhutong–Shu River reach, whereas their distributions in the Gongguan River appeared random (Fig. 2a). One possible reason is the different roles of the two mining/smelting sites. Smelting activities are conducted mainly in the Zhutong River watershed. Liu et al. (2016b) found that labile Tl fractures increase dramatically during Pb–Zn smelting processes. This means that Tl retention in the sediments would be lower because it could be transported earlier in the Zhutong River after smelting; consequently, its spatial variation in the river sediment was not significant.

The attenuation rates of metal concentration (ΔCC) illustrated in Fig. 4 show another difference between the spatial variation trends of the metals/metalloids, i.e. the concentrations of Hg, Sb, and Mo decreased faster along the rivers. Moreover, the ΔCCs in the left reach (i.e. the Gongguan River) were faster than those of corresponding metals in the right reach (i.e. the Zhutong–Shu River). This could be attributable to nonlinear decreases of point-source pollution with distance, as shown in Fig. 3. As the distance from W4 to W1 is shorter than that from E5 to E1, the attenuation rate of the W4–W1 reach was larger. Additionally, another observed spatial characteristic was that the metals/metalloids in the river sediments exhibited decreasing trends from western to eastern sites for Zn, As, Ba, and Cd.

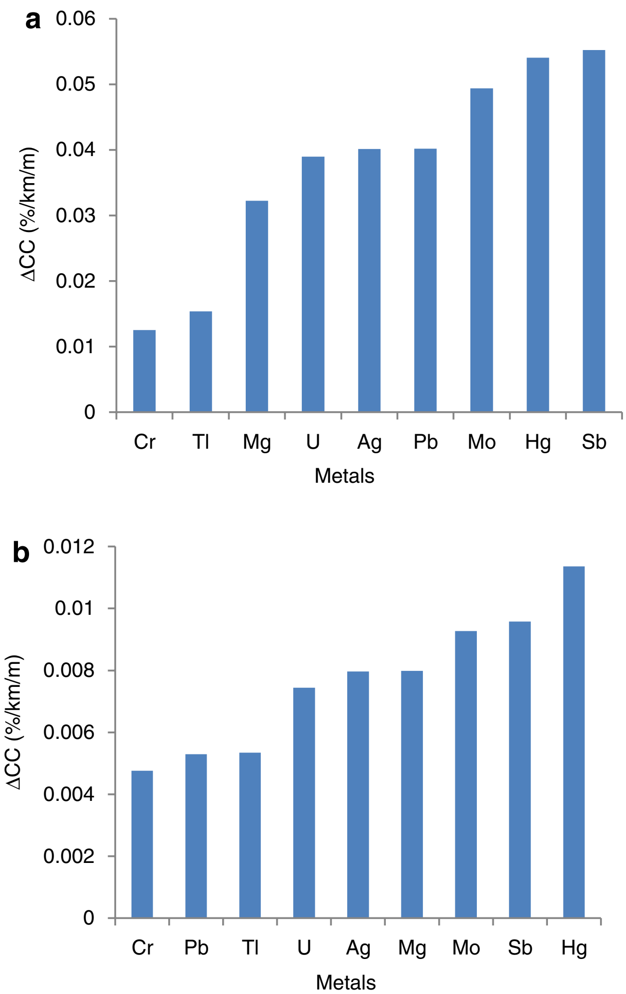

Fig. 4 Attenuation rate of concentration (Δ*CC)* of metals along river gradient (**a**) from W4 to W1 and (**b**) from E5 to E1

Sources of Metals/Metalloids in Sediments

Spatial variations in metals/metalloids in river sediments helped to distinguish their possible sources, as more likely due to mining activities or natural weathering processes. Because metal elements are essential components of the earth's crust, the natural occurrence of such elements in a lacustrine system tends to show weak spatial variation (Roussiez et al. 2005). In contrast, considerable spatial variation implies substantial input from external sources (Li et al. 2013). Although we focused on a river system, spatial variations still provide substantial evidence of the different sources of the metals/metalloids in our case. Based on the spatial variations in Ag, Cu, Cr, Tl, U, Mo, Pb, Sb, and Hg found in this study (Figs. 3, 4), it can be deduced that these metals had a similar, presumably anthropogenic source. The multivariate analyses (CA and PCA) performed in this study further helped to determine the sources of the metals. Undoubtedly, the extremely elevated Sb and Hg concentrations in the river sediments were attributable to mining activities because the rivers receive Sb/Hg mining/smelting discharges. The correlation matrix in Table 2 shows significant positive relationships among the Sb and Ag, Cr, Cu, Mo, Pb, Tl, U, and Hg, as well as among Hg and Ag, Cu, Mo, and U ($p < 0.05$), indicating that they have similar anthropogenic sources. This finding was confirmed by the PCA results, which indicated that three eigenvectors–factors explained 83.8% of the variance in the metals. Moreover, the metals could be categorized into three groups according to the variation diagram in rotated space (Fig. 5). Group one comprised Ag, Cu, Cr, Tl, U, Mo, Pb, Sb, and Hg, which were established as mining/smelting-related pollutants. The other two groups appear to be associated with the earth's crust and geological formations in the area. Hou and Tang (2006) reported that the ranges of As, Zn, and Ba in rocks sampled in the Xunyang mining area were 7.36–100.00, 71.80–424.38, and 297.31–1000.00 mg/kg, respectively, comparable with the concentrations of these metals/metalloids in the river sediments found in this study. Additional tools, such as isotope tracers, are needed to identify the definite sources of the metals/metalloids in the future research.

Pollution Evaluation

From the discussion above, it appears that all the studied sites, except for E3, E4, and W2, were polluted by mining/smelting activities. The metal concentrations in the sediments at sites E4 and W2 were high, although they were probably not directly affected by the two mining/smelting sites. It is possible that these elevated concentrations reflect historical mining activities in upstream watersheds. Generally, the metal concentrations at site E3 were lowest, and these can thus be considered to represent background values. Therefore, taking site E3 as an example of the unpolluted background, the pollution status and potential ecological risk quantified by the *CF* and E_r indices, respectively, are presented in Figs. 6 and 7. The sediments in the rivers were found highly polluted by Ag, Mo, Sb, and Hg. The E_r of the mining/smelting-derived metals showed that Cr, Cu, Mn, and Pb present low ecological risk, whereas Hg and Sb present very high ecological risks. Consistent with their concentrations in the sediments, the potential ecological risks associated with these metals also decreases from upstream

Table 2 Pearson's correlation matrix between metals/metalloids in sediment samples

	Ag	As	Ba	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Sb	Sn	Tl	U	V	Zn	Hg
Ag	1																	
As	0.149	1																
Ba	0.397	0.915**	1															
Cd	0.396	0.667*	0.790*	1														
Co	−0.274	−0.486	−0.415	−0.265	1													
Cr	0.883**	−0.066	0.111	0.158	−0.131	1												
Cu	0.659	−0.104	0.188	0.172	0.314	0.424	1											
Mn	−0.170	−0.230	−0.013	0.129	0.470	−0.408	0.425	1										
Mo	0.930**	0.066	0.257	0.193	−0.307	0.967**	0.432	−0.407	1									
Ni	−0.234	−0.516	−0.534	−0.222	0.893**	−0.029	0.182	0.221	−0.252	1								
Pb	0.614	0.254	0.549	0.431	−0.087	0.260	0.810**	0.372	0.367	−0.309	1							
Sb	**0.914****	0.127	0.451	0.334	−0.220	**0.699***	**0.746***	0.117	**0.805****	−0.34	**0.765***	1						
Sn	−0.169	−0.295	−0.228	0.208	0.784*	−0.096	0.259	0.426	−0.304	0.824**	0.009	−0.256	1					
Tl	0.897**	0.001	0.193	0.224	−0.099	0.994**	0.460	−0.372	0.965**	−0.022	0.309	**0.727***	−0.063	1				
U	0.968**	0.067	0.313	0.233	−0.225	0.932**	0.596	−0.244	0.978**	−0.227	0.524	**0.902****	−0.247	0.942**	1			
V	−0.448	−0.459	−0.532	−0.335	0.887**	−0.312	0.134	0.285	−0.497	0.937**	−0.285	−0.483	0.755*	−0.302	−0.448	1		
Zn	0.451	0.724*	0.770*	0.722*	−0.236	0.174	0.432	−0.044	0.228	−0.243	0.664	0.362	0.118	0.235	0.293	−0.229	1	
Hg	**0.789***	−0.117	0.204	0.315	0.011	0.638	**0.679***	0.311	**0.671***	−0.012	0.486	**0.854****	−0.018	0.656	**0.761***	−0.227	0.087	1

$^{*}p < 0.05$, $^{**}p < 0.001$: significant correlation

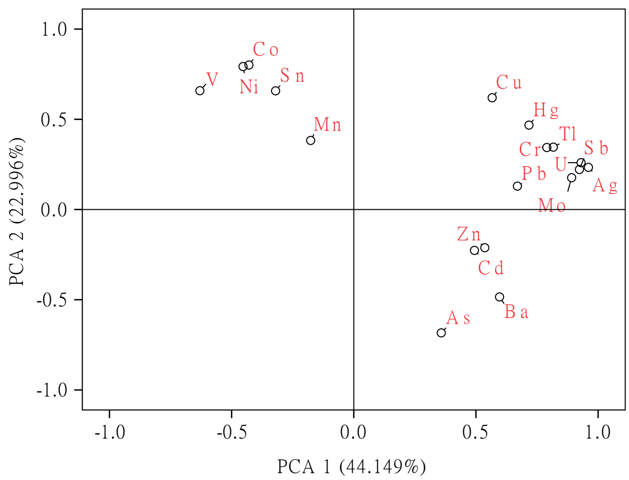

Fig. 5 Loading plot of principle component analysis (PCA) (PC 1 vs. PC 2) for sampled metals/metalloids (numbers on the axes indicate percent of variance)

to downstream. In addition, considering its high mobility and toxicity to humans (Xiao et al. 2007), special attention should be paid to Tl, even though its concentration in the sediments was found to pose only a moderate ecological risk.

Conclusions

We investigated 18 metals/metalloids found in the sediments of two mining-impacted tributaries of the upper Han River in China. The results showed that the sediment concentrations of Cu, Cr, Tl, U, Pb and typically, Ag, Mo, Sb, and Hg were generally elevated. The maximum concentrations of Sb and Hg measured in the sediments were two to three orders of magnitude higher than the levels in the upper Han River, Yangtze River, and Chinese average levels. Significant variations were found in the spatial distributions of the metals/metalloids in the sediments. The concentrations decreased from upstream to downstream sites along the river gradient. By combining the spatial variations and the results of multivariate analyses, it was deduced that the elevated concentrations due to mining/smelting activities. At downstream sites, the concentrations of all the metals/metalloids in the river sediments decreased to near background levels, except for Hg and Sb, which are still considered to pose very high potential ecological risks.

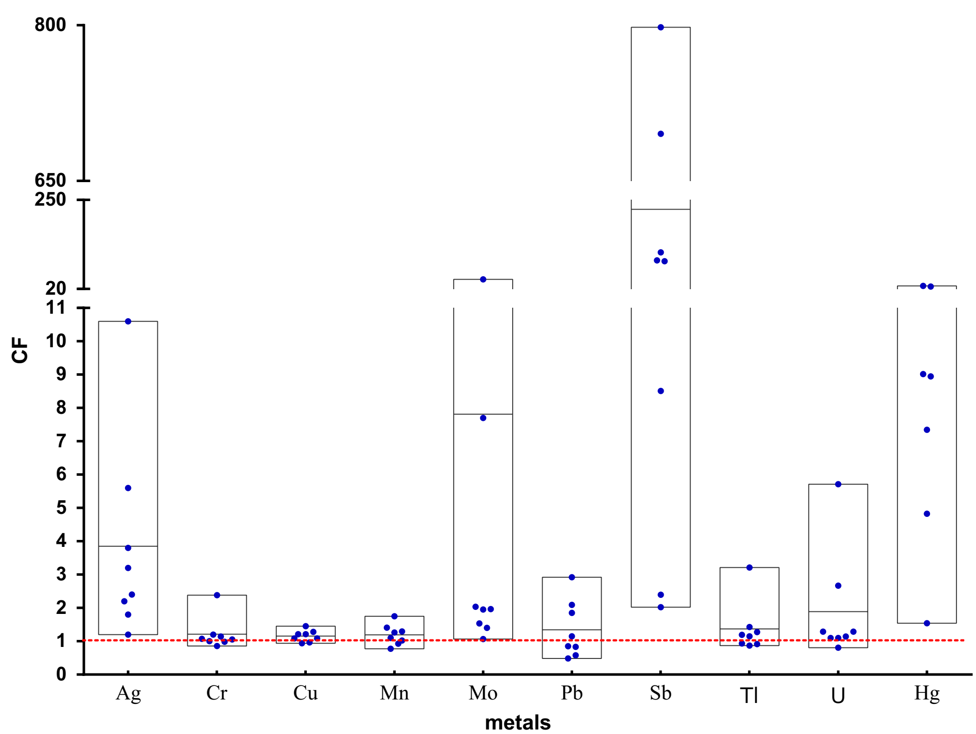

Fig. 6 Contamination factor (*CF*) of metals in the sediment impacted by mining/smelting activities (red line means *CF* = 1, blue dots represent the *CF* values at the nine sites, and the bars indicate the max, min, and mean of the *CF*s)

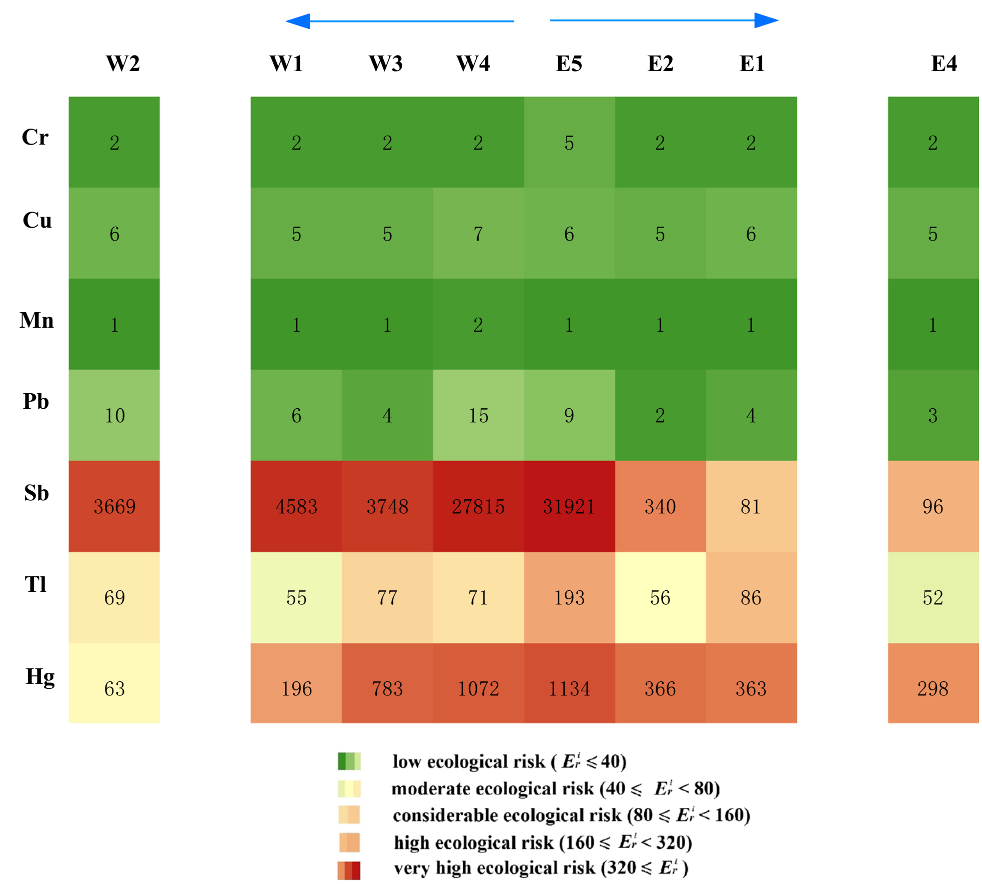

Fig. 7 Ecological risk index (*Er*) of metals at the sampling sites along the river gradient

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