Bull Environ Contam Toxicol (2011) 87:91–95
DOI 10.1007/s00128-011-0303-2

Environmental Geochemistry of Abandoned Flotation Tailing Reservior from the Tonglvshan Fe-Cu Sulfide Mine in Daye, Central China

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Received: 22 December 2010 / Accepted: 3 May 2011 / Published online: 12 May 2011

Abstract This study investigated metals of tailings from Tonglvshan mine in Daye and assessed the effect of metal contamination in water and sediment near the tailing reservoir. The concentration of copper, lead, zinc, cadmium, chromium and nickel was measured in deposit samples taken from a profile in an abandoned flotation tailing reservoir, as well as in water and sediment samples near the reservoir. The results of this study indicate that copper concentration ranges from 780 to 4390 mg/kg, 2–10 times higher than the limit values in soil, while the contents of other metals are below the limit values. Metal levels in water and sediments are high and varied widely in different sampling sites. The mean concentrations of copper, lead, zinc, cadmium, chromium and nickel in waters are 27.76, 2.28, 8.20, 0.12, 5.30 and 3.04 mg/L, while those in sediments are 557.65, 96.95, 285.20, 0.92, 94.30 and 4.75 mg/kg, respectively. All of the results indicate that the environment near the tailing reservoir is polluted to some extent by some kinds of metals, especially by copper, lead, zinc and cadmium, which may be caused not only by some discharge sources of metals, but also by life garbage and sewage.

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Keywords Tailing · Metals · Water · Sediment

Introduction

Metal contamination is a common problem encountered at many hazardous waste sites. Mine tailings are known to have the highest environmental effects (Dudka and Adriano 1997) due to the presence of low pH and high concentration of metals (Wong et al. 1998). Mining activities generate a large amount of waste rocks and tailing, deposited on the earth surface, and lead, chromium, cadmium, copper, nickel, arsenic, vanadium and mercury are among the most frequently observed metal contaminants. These pollutant effects can reach local and, in some cases, regional scales and affect the urban or agricultural zones (Conesa et al. 2007), and consequently, causes a risk of metal uptake by humans.

Tonglvshan Fe-Cu sulphide mine is one of the oldest in the world, with more than 2,000 years of mining history. Extensive mining of metal ore has left a legacy of contaminated mine wastes distributed in the west of Daye city. This fact constitutes a potential health and environmental risk due to its bioaccumulative behavior. Metals such as lead, copper, chromium, cadmium and nickel are serious pollutants of environmental ecosystems and have attracted considerable attention over the past few decades because of their environmental persistence, toxicity and ability to be incorporated with food chains (Feng et al. 2010). Therefore, it is necessary to conduct a comprehensive environmental and geochemical investigation in order to safeguard public health and to protect mining envionments. Previously, the studies of tailings were done in the South Korea (Lee and Lee 2004), Spain (Cabrera et al. 2008; Martin et al. 2007), Italy (Marescotti et al. 2008), Greece

(Triantafyllidis et al. 2007) and some other countries, which have studied the migration and transformation of metals and evaluated the environment impact of metals near tailing reservoir.

The study area is located in Tonglvshan Fe-Cu sulfide mine, Hubei Province, China. The area has a typical subtropical monsoonal climate, with the annual average temperature of 16.9°C and a rainfall of 1,385.8 mm. Tonglvshan Fe-Cu deposit belongs to the Yangtze River metallogenic belt, mainly bounded and controlled by Daye Group carbonates of Lower Triassic. The tailing reservoir is on the northeast of mining pit. The specific location and sampling sites are described in Fig. 1.

The overall objectives of this research were: (1) to determine the concentrations of metals in the tailings; (2) to study the vertical distribution and migration of metals in a tailing profile, and (3) to assess the effect of metal contamination in water and sediment near the tailing reservoir.

Materials and Methods

A sampling scheme was carried out in September 2010. Eight samples(T1–T8) were obtained from a vertical profile of the tailings based on color change, mineralogical and textural variations, as well as physical and chemical properties, and both water and sediment samples were simultaneously collected at ten sites in the wetland near the tailing reservoir. Water samples were filtered through a 0.45 μm Millipore filter and acidified with 1.0% HNO_3 and collected in 250 ml polyethylene bottles. Tailing and sediment samples were air-dried at the room temperature (25°C), and rock, gravel, plant residues and other debris in the samples were picked out by hand, and were ground using a wood roller to pass through a 20-mesh sieve and then were mechanically ground to less than 100 μm for analysis.

Metals including copper, lead, zinc, cadmium, chromium and nickel were analysed by inductively coupled plasma mass spectrometry (PerkinElmer Elan). About 0.5 g of the prepared samples were digested in Teflon beakers with a mixture of nitric acid (HNO_3) and perchloric acid ($HClO_4$) according to the standard analytical procedures. For quality assurance and quality control (QA/QC), we analyzed duplicates, method blanks, and standard reference materials. The analytical results showed that the precision and bias of the analytical method were generally <10%. The recovery rates for metals in the standard reference material were between 85% and 105%.

Results and Discussion

The concentration of metals Cu, Pb, Zn, Cd, Cr and Ni in the tailing samples are present in Table 1. The limit values

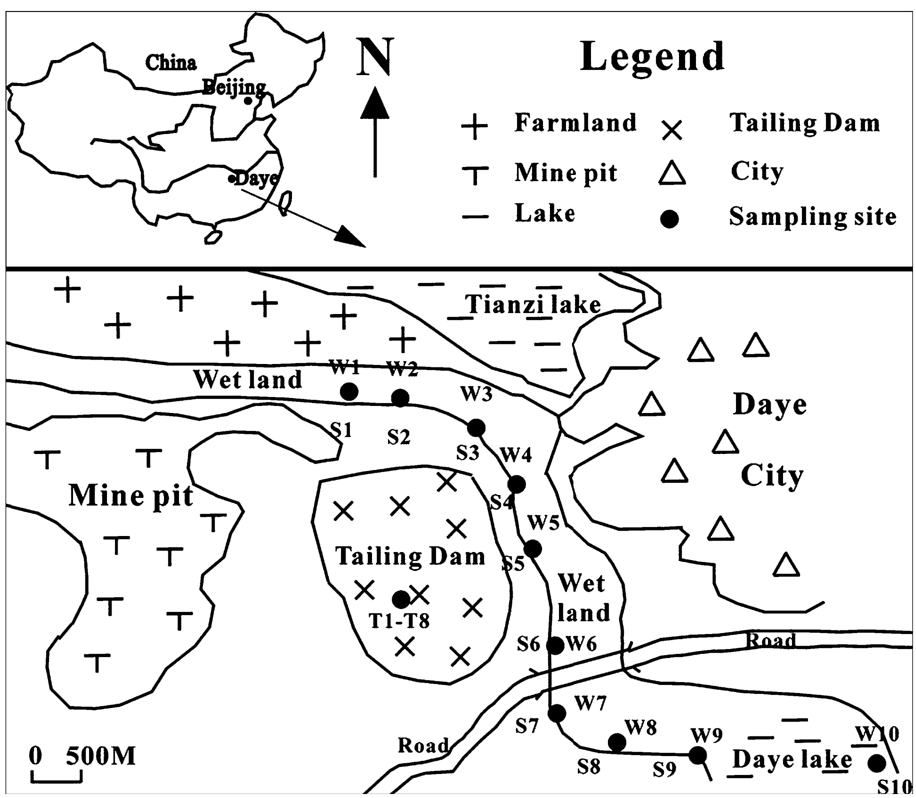

Fig. 1 Study area and sampling locations

Table 1 Basic statistics of metals in tailing (mg/kg)

N = 8	Cu	Pb	Zn	Cd	Cr	Ni
Mean	1851.75	13.89	333.75	0.66	20.63	9.85
Min	780.00	8.60	256.00	0.33	11.00	8.30
Max	4390.00	23.40	385.00	1.23	29.00	11.50
SD	1213.41	5.58	43.65	0.34	5.93	0.98
CV	0.66	0.40	0.13	0.51	0.29	0.10
Limit	400	500	500	1.00	300	200

for metals set by the State Environmental Protection Administration of China (SEPAC 1995) in soils used as guidelines for metals are also shown in Table 1. The analytical results indicate that Cu contents in all tailing samples are 2–10 times higher than the limit values and Cd concentrations in certain samples slightly exceed the limit values, while the other metals in all tailing samples do not exceed the threshold values. Coefficient of variation (CV) reflects the discreteness of the element distribution, the CV of Cu and Cd are more than 50%, indicating that contents of these two elements change greatly and there exists a significant differentiation among different samples.

Correlation analysis was performed on metals in tailings at each layer to assess possible co-contamination from the similar sources among the data set. The Pearson correlation coefficients of metals in tailings are summarized in Tables 2, which shows that there are strong associations between Pb and Cu, Zn and Cu, Ni and Zn,and between Pb and Zn, and weaker associations between Ni and Cr, Cu, Pb. No remarkable correlation between the elements of Cd and others, Cu and Cr was observed.

Vertical profiles of metal concentrations (Fig. 2) are influenced by changes in depth because of different elements geochemistry and environment conditions. Initially, the concentrations of metals, such as Cu, Cd, Pb and Zn, are increased from the bottom to the overlying tailing pile until −120 cm, which reflects the increase of mineral production during this period. The variability of Cr and Ni, associated in the same changes, is controlled by the similar geochemical relationship. It is interesting to note that, the

Table 2 Correlation among different metals in tailing

	Cu	Pb	Zn	Cd	Cr	Ni
Cu	1.000					
Pb	0.821**	1.000				
Zn	0.681**	0.697**	1.000			
Cd	−0.210	−0.203	−0.142	1.000		
Cr	−0.142	0.285	−0.223	−0.258	1.000	
Ni	0.280	0.279	0.473*	−0.546	0.312	1.000

** Correlation is significant at the 0.01 level (2-tailed); * correlation is significant at the 0.05 level (2-tailed)

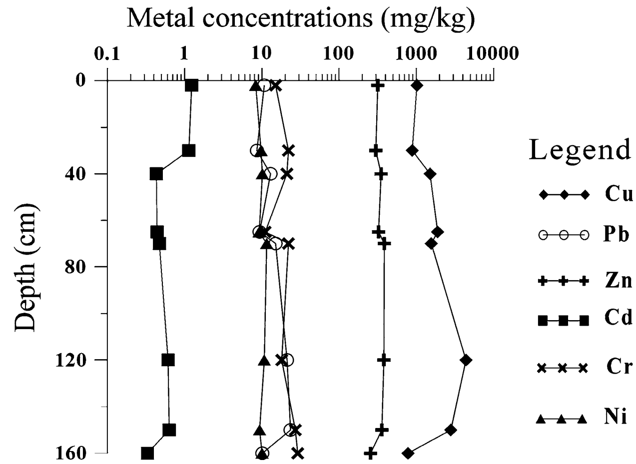

Fig. 2 Vertical profile of metal contents in tailings (mg/kg)

concentrations of most metals such as Cu, Pb, Zn, Cr and Ni are low in the upper layer, which may result from surface weathering and downward leaching. Based on these relationships, it is apparent that these elements have behaved simultaneously and have the same pattern of dispersion behaviors. On the contrary, Cd was at high concentrations in the upper layer, which shows that Cd was relatively mobile and preferred to enrich in upper layer, a conclusion similar to previous study (Bi et al. 2010).

In addition, spatial variability of metal vertical distribution may be ascribed to anthropogenic perturbation by mining tailing type in certain circumstances, but it is obviously not the case in our study area.

Table 3 shows the metal contents in waters from a wetland near the reservoir. Also listed in the table are the

Table 3 Metal concentrations in water samples near tailing reservoir (mg/L)

Water samples	Cu	Pb	Zn	Cd	Cr	Ni
W1	29.92	4.86	12.15	0.38	26.71	8.02
W2	58.41	11.93	27.21	0.48	18.14	7.49
W3	18.61	0.05	11.21	0.03	0.42	1.85
W4	14.44	0.47	3.35	0.02	0.47	1.94
W5	25.43	1.19	3.43	0.04	0.42	1.78
W6	25.65	0.88	5.87	0.05	0.42	1.58
W7	16.30	0.65	3.43	0.02	0.35	1.94
W8	14.58	0.08	3.67	0.05	0.44	1.70
W9	46.53	0.37	3.49	0.03	0.34	1.09
W10	17.75	0.93	4.80	0.06	0.85	1.80
Average	27.76	2.28	8.20	0.12	5.30	3.04
Limit[a]	1.50	0.10	5.00	0.01	0.10	0.10
N[b]	18.51	22.80	1.64	12.00	53.00	30.40

[a] Surface water environmental standards (GB3838-2002) Class V, [b] (average/Limit)

quality standards adopted in China for Class V waters, or the water bodies for agricultural use and landscape requirement.

As shown in Table 3, metals in water samples exceed seriously compared with the surface water environmental standards (GB3838-2002) for Class V waters (SEPAC 2002), Cu, Cd, Cr and Ni exceed the limit values in all samples, with their average values as high as 18.51, 12, 53 and 30.4 times of the corresponding standard, respectively. Except two samples (W3 and W8), Pb concentration in most water samples are higher than the standard value, with the sample in site W2 being the highest, as high as 119 times of the standard value. Zn concentration in water samples is seemingly not so high, exceeding Zn standard only 1.64 times. Of all the samples, the highest concentrations of metals are found in W1 and W2, probably due to a small sewage outfall from a small private dressing plant near the sampling sites. The metal concentrations at W3 and W4 are significantly reduced, attributed mainly to the reeds, other plants and microoganism which reduce the contaminants through the absorption and metabolism. The outlet of tailing reservoir is located between W5 and W6, where no significantly high metal contents are found, only Cu content being slightly higher than those in nearby sites, a phenomena consistent with the measurement of metal concentrations of the tailings mentioned above, which reveals only abnormally high contents of Cu. Metal concentrations decreased in W7 and W8 sites, which is thought of the effect of river widen resulting dilution but also the role of ecological restoration of wetland. The last two samples W9 and W10 are near the entrance of the lake and subject to life garbage and sewage, and therefore the metal contents are quite variated.

Sediment is the source or sink of metals in water environment, and plays as an indicator of metal pollution in water environment (Agrawal et al. 2010; Lai et al. 2010; Zhang et al. 2007). Most of the metals discharged into the water can be quickly transferred from water phase to solid phase by various channels such as bound to suspended solid and sediment (Liu et al. 2009; Yu et al. 2010). Pollution conditions near the mining area can be seen from the analysis of metals in sediment. Due to the regional mineralization, mining, dressing, smelting and in particular the impact of tailings, contents of metals in sediment were usually at high levels.

The concentrations of examined metals Cu, Pb, Zn, Cd, Cr and Ni in the surface sediments of the wetland are presented in Table 4. In the study area, metal concentration of Cr remain almost constant. Higher levels of Cu and Cd occurred in the site W6, while Zn and Ni occurred in the site W5, that was due to the long years of accumulation from tailing outfall in these two sites. The spatial variations of metal levels in the sediments were related to the pollution discharging points along riverside.

Table 4 Metal concentrations in sediment samples near tailing reservoir and compared with those from other rivers in China(mg/kg)

Sediment samples	Cu	Pb	Zn	Cd	Cr	Ni
S1	704.00	95.50	232.00	2.37	85.00	6.50
S2	787.50	70.50	326.50	0.42	96.50	1.50
S3	924.00	92.00	209.00	0.44	99.00	1.00
S4	465.00	96.00	386.50	0.32	95.00	8.00
S5	245.50	121.00	465.00	0.45	92.50	12.00
S6	1370.50	102.00	327.50	2.49	90.50	5.50
S7	317.50	44.00	156.50	1.84	80.00	3.50
S8	318.50	44.50	413.00	0.32	90.50	5.50
S9	272.00	161.00	154.00	0.27	99.00	3.50
S10	172.00	143.00	182.00	0.23	115.00	0.50
Average	557.65	96.95	285.20	0.92	94.30	4.75
Background[a]	30.70	26.70	83.60	0.17	86.00	37.30
Yellow River[b]	17.54	32.24	74.77	0.48	52.44	24.71
Yangtze River[c]	67.72	50.45	146.23	1.91	88.25	36.45
Yangtze River estuary[d]	30.70	27.30	94.30	0.26	78.90	31.90
Pearl River estuary[e]	53.40	28.40	273.00	3.60	73.10	55.80

[a] China Environmental Monitoring Station (1990)

[b] (Feng et al. 2010); [c] (Song et al. 2010); [d] (Zhang et al. 2009); [e] (Song et al. 2010)

The concentrations of metals (except for Ni) in surface sediments determined in this study are considerable high compared with the results obtained from other literature. When compared to the background values, our results show that the concentrations of metals are much higher (especially the Cu content was 18 times higher than the background value). However, Ni content was much lower than the value. Most of the metal concentrations are much higher than those in other river and estuary. The similar metal levels of Zn are present in the Pearl River estuary, while the metal levels of Cr in the sediment of Yangtze River, Yangtze River estuary and the Pearl River estuary are almost the same. All of the results indicate that the wetland near the reservoir is polluted to some extent by some kinds of metals, especially Cu, Pb, Zn and Cd, which may be caused by some discharge sources of metals, such as tailing wastewater containing Cu, Zn and Cd and life waste water including Pb.

Conclusions

The purpose of this study is to investigate the metals of tailings and determine the metal contamination in the surrounding water and sediments. The results demonstrate that Cu content in tailing is significantly higher than other elements. Metal levels in the water and sediments are high and varied widely among different sampling sites. In all, the water and sediments near the tailing reservoir have been contaminated by metals seriously. To minimize the environmental impacts on the wider disposal site immediate protective action should be taken. Strict treatment before the discharge of the tailing water is necessary to reduce the metal concentrations, and the proper handling of the sewage and municipal waste is equally important to control pollution.

Acknowledgments This work was supported by National Natural Science Fund of China (40872195). We are grateful to the anonymous reviewers and editors for their constructive suggestions of the manuscript.

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