Analysis on Heavy Metal Distribution in Overlying Deposit and Pollution Characteristics in Drainage Basin of Xiaojiang River in Dongchuan District, China

Qianrui Huang [1], Xianfeng Cheng [1], Jun Xu[1], Wufu Qi [1], Shuran Yang [1], Tao Dong [2], Xiangqun Zhang [1]

[1] Yunnan Land and Resources Vocational College, 652501 Kunming Yunnan, China
[2] Ministry of Land and Resources Kunming Mineral Resource Supervision Inspecting Center, 650218 Kunming Yunnan, China

148428471@qq.com

Abstract. The distribution characteristics of heavy metal (Cu, Zn, As, Pb and Cd) content in overlying deposit in Xiaojiang River is analyzed in this thesis, and potential ecological risk index is adopted to evaluate the potential ecological risk of heavy metal pollution in the overlying deposit. Results indicate that the heavy metal (Cu, Zn, As, Pb and Cd) content in overlying deposit in Xiaojiang River all has exceeded standard, especially the content near diggings which is much higher than the national first standard value. And this will affect the bottom mud and river system of Jinsha River to some extent. Cu and Cd are the key pollutants and should be taken as the key object of study. It can be seen from comparison between samples in wet season and that in dry season that pollutants in bottom mud will be released due to the effect of pH value, and secondary pollution of the river will be caused.

1. Introduction

As human’s mining activity gets more active, sand content in rivers near diggings gradually increases, and the sand has brought lots of pollutants in the river, and then the pollutants will rapidly sediment in the bottom mud under certain conditions. When the external conditions of the mud such as chemical or dynamic condition change, the pollutants in bottom mud will be released and again enter the water which will cause secondary pollution of the water, [1]. Due to the limitation of geological landforms, rocks of mountains in the drainage basin of Xiaojiang River often break and this results many fractures. And unfavourable geological phenomena develop. In addition, the strength of people’s economic activity has greatly exceeded the bearing capacity and capacity of adjustment of the mountain land. So geological disasters including collapse, landslide and debris flow have happened frequently. These all have increasingly deteriorated the ecological environment.

It has been found in investigating some relatively severe polluted river that heavy metals significantly aggregate in sediments, although the heavy metal content in the relevant water does not present great abnormity or presents no abnormity, and this indicates that the heavy metals input from different resources (including natural resource and human’s activity) can rapidly move from the water to sediment [2]. The metal content in bottom sediment is 1~3 orders of magnitudes higher than that in overlying water [3]. Hence, strengthening research on migration and transformation of heavy metal in suspended solids and sediment in river has significant meaning. The project team has carried out sampling and analysis on water and bottom mud of Xiaojiang River in Feb. (dry season) and Aug. (wet season) 2016. And results indicate that the five heavy metals, Pb, Zn, As, Cd and Cu in all fracture surfaces of Dabai River, Kuai River, Wulong River, Zhongchang River and Jinsha River do not exceed standard and the water all conforms to standard of type I water. In water of Xiaojiang River, only 6 samples exceed standard, As in S01 and S02 as type III, Cd and Pb as type II; As in S04, S09 and S10 as type III, Cd as type II and Cd in C11 as type II, and other water samples all contain no exceeding heavy metal of the five. However, the sediment in bottom seems not good. Hence, strengthening research on migration and transformation of heavy metal in suspended solids and sediment in river has significant meaning. This thesis will further study heavy metal distribution and pollution characteristics in bottom mud of drainage basin of Xiaojiang River, so as to provide basis and reference for prevention and cure of heavy metal pollution in water of drainage basin of Xiaojiang River- Jinsha River.

2. Resource development and geological environment of studied area

2.1. Introduction of resource development in Dongchuan

As the ten cities of resource exhaustion, Dongchuan in Yunnan Province has experienced exploitation and smelting for over two thousand years, and it's one of the six copper production base in China. Dongchuan copper industry still has significant role in Chinese nonferrous metals industry and economic development, and plays its active role. The single industrial structure causes insufficient drive of subsequent economic development, and this affects other industries. Located in mountain area of Sichuan and Yunnan where is one of the six distribution areas of debris flow in China, it has also suffered debris flow disaster, with area of water and soil loss accounts for above 70% of the national territorial area of the whole area. Smelting slag and tailings have intensified the environmental pollution, and some harmful gases will be released around the area and will pollute the air through atmospheric propagation; fine sand will result in severe harm on surroundings, and even sand and dust storm will be caused; in flood season, it will flow to farmland and rivers together with rainwater, and thus harm will be imposed on underground water and lower course of river.

2.2. Background of regional geological environment

Xiaojiang River originates from Yuwei Houshan in Xundian County, and flows through Xundian, Dongchuan and Huize, with total length of 130.4km, drainage area of 3040km^2, the highest altitude of 4344m, and the lowest altitude of 691m. And it flows into Jinsha River from the south to north [4]. Within the drainage basin, mountain area accounts for 97% of the total area. Xiaojiang River is a typical deeply-cut structural river valley, with famous Xiaojiang fault zone passing through, which contains both vertical vibration and typically horizontal twist. The drainage basin of Xiaojiang River totally contains 178 first branches, including 138 branches of debris flow. In Doungchuan, there are 107 catastrophic debris flows, including 27 flows with severe disasters, which are all slope and cheuch-type debris flow having relatively strong destructive effect.

Since A.D. 1500, the existing earthquake data in history indicates that Xiaojiang active fault zone is a significant fault zone of induced seismicity. Totally over 50 destructive earthquakes have happened along the zone, including 3 earthquakes above 7.0 magnitude, and about 10 at 6.0 magnitudes. The greatest earthquake in history is the 8.0 earthquake in Songming on Sep. 6, 1833, which has caused a huge earthquake surface rupture deformation zone.

The climate of drainage basin of Xiaojiang River is monsoon climate of Plateau Mountain in low latitude. Due to the influence of general atmospheric circulation, solar radiation and landform, 3D climate with vertical zonality and distinct rainfall in dry and wet season are also features of this area. In the drainage basin, dry season is from Nov. to Apr. of the next year, with amount of precipitation of 8.8-128mm; wet season is from May to Oct., with amount of precipitation of 600-1025mm, accounting for 88% of yearly rainfall [5]. Intense strong rainfall is the main water source of the frequent debris flow.

3. Sampling and testing

3.1. Sampling of bottom mud

As for the layout principle of bottom mud sample, it's located in the same spot of the water samples. Sample the bottom mud samples while taking water samples of the river. To present the situation of bottom mud in a certain river segment, and reduce the influence of individual pollution spot on samples, the bottom mud samples should be collected at least 3 different points. After collecting samples at three different sampling points with military shovel, mix the collected bottom mud samples as the collected samples for this time, to avoid distortion of sample due to special sediment or pollution in local segment. Then, screen it and put it into polyethylene barrel. Indicate sampling number and date at exterior of the barrel with marking pen. Attach label after collecting samples, and fill "Bottom mud sampling record" as required, recording sampling points and surroundings in detail. While sampling, use digital camera to shoot the surroundings and physical state of the river water. Position the sampling points with GPS. In Feb. 2016 as dry season, totally 15 bottom mud samples are collected, and 9 samples are taken in July (figure 1). Take C01 and FC01 respectively as background value of dry season and wet season, which are bottom mud samples in about 50m depth of Dabai River, Kuai River and Wulong River, both of which do not flow through mineral compact district in Dongchuan and contain less mineral activity. C02-C12 in dry season (FC02, FC05, FC07 and FC09-FC12) are bottom mud samples of Xiaojiang River, C13 is bottom mud from the place about 5km downstream from intersection mouth of Jinsha River and Xiaojiang River, and C17(FC17 in wet season) and C19 are respectively bottom mud from Dabai River and Zhongchang River as branches of Xiaojiang River.

3.2. Test of samples

Submit the bottom mud samples to Kunming Mineral Resources Supervision and Testing Center of Ministry of Land and Resources for test and analysis. The test steps are carried out strictly based on Requirements of Ecological Geochemical Evaluation Sample Analysis Technique (Trial) in Geological Survey Technical Norms of China Geological Survey (DD2005-03). Atomic fluorescence method is taken to measure heavy metal content As in bottom mud. The instrument used here is AFS-3100 full-automatic dual-channel atomic fluorescence spectrophotometer, with precision<1.0% and detection limit of As <0.005μg/ml. Inductive coupling plasma mass spectrometry is used to measure, and ICAP Q mass spectrometer is used here, with Cu≤0.001μg/ml, Pb<0.001μg/ml, Cd<0.0001μg/ml and Zn<0.005μg/ml.

4. Research method

In this research potential ecological risk index is used to evaluate potential ecological harm of heavy metal pollution in overlying deposit of Xiaojiang River, which is a set of method evaluating heavy metal pollution and its ecological harm by using principles of sedimentology established in 1980 by Hakanson, a Swedish scholar. The computational formula of potential ecological risk index is as below [6]:

$$E_{Rt} = \sum E_r^i = \sum T_r^i \times \frac{C^i}{C_n^i} \quad (1)$$

Where C^i is measured concentration of heavy metal i in sediment (mg/kg); C_n^i is the reference value of heavy metal i in sediment (mg/kg); E_r^i refers to the potential ecological risk index of heavy metal i; T_r^i stands for toxicity response coefficient of heavy metal i, which can reflect the toxicity of heavy metal and sensitivity of biology toward heavy metal pollution; E_{Rt} is the overall potential ecological risk index [7].

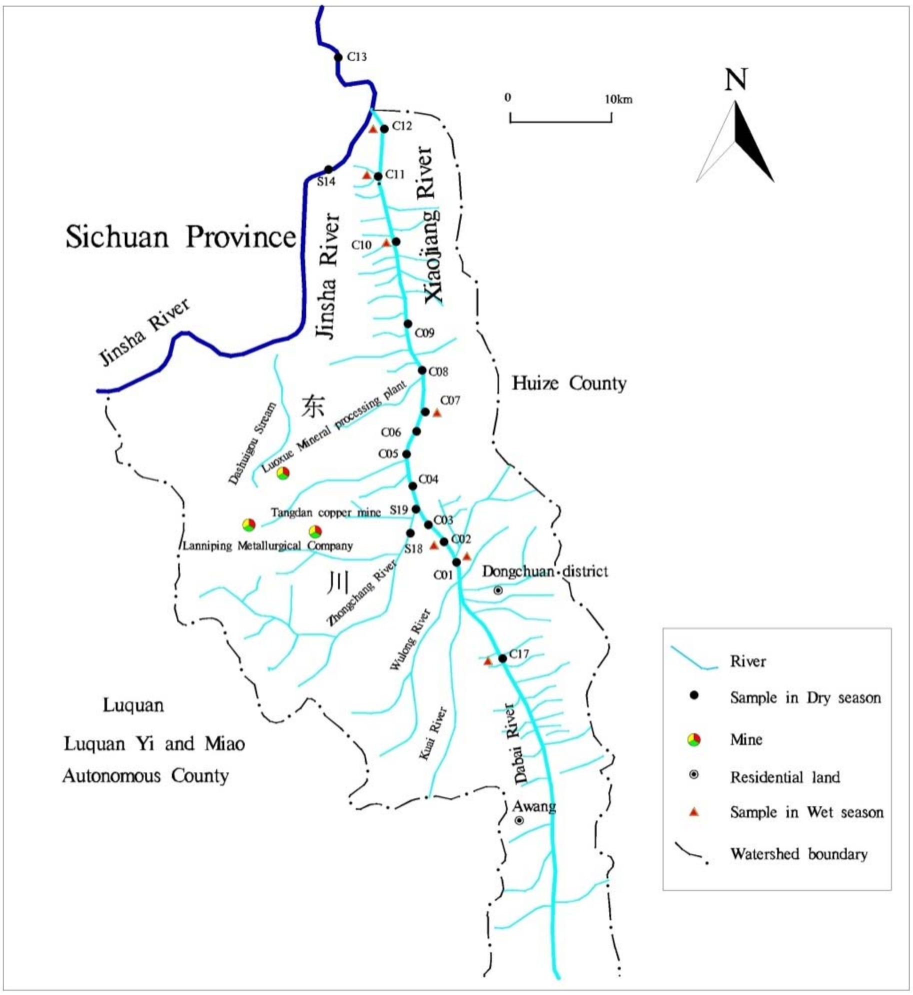

Figure 1. Sampling locations of bottom mud in drainage basin of Xiaojiang River

5. Results and Analysis

5.1. Geochemical distribution of heavy metal in bottom mud

The analysis of test results of Cu, Pb, Zn, As and Cd in sediment is as Table 1. The reference values cited in this thesis are values of bottom mud samples from mineral areas not greatly affected. As is 27.9mg/kg, Cd is 1.15mg/kg, Cu is 71.3mg/kg, Pb is 83.6mg/kg and Zn is 261 mg/kg. The toxicity response coefficients of them are respectively Cu= 5, Zn =1, As =10, Pb=5 and Cd=30.

Since there is no environmental quality standards of sediment, Chen Jingsheng [8] et al has collected quality standard of heavy metal element in water sediment applied now by 15 environmental management department, with reference value of As of 3～70mg/kg, Cd of 0.2～12mg/kg, Pb of 23~30mg/kg and Zn of 100～820mg/kg. Even if it's based on the standard above, the five heavy metals in bottom mud of Xiaojiang River exceed the standard far and away. And according to National Soil Environment Quality Standard(GB15618-2009)(class III) specifying As=30 mg/kg, Cd=0.4 mg/kg, Cu=100 mg/kg, Pb=280 mg/kg and Zn=300, among the average values, As content is 1.32 times of the standard, Cd is 5.86 times, Cu is 1.3 times, Zn is 1.88 times, and Pb does not exceed the standard; among the maximum values, As content is 2.17 times of the standard, Cd is 11.53 times, Cu is 2.86 times, Zn is 4.46 times and Pb does not exceed the standard.

Table 1. Main heavy metal content in bottom mud of Xiaojiang River (mg/kg)

No. of sampling point	Position of sampling point	As	Cd	Cu	Pb	Zn
D16-C01	Bottom mud from the point about 50m at downstream at Dabai River, Kuai River and Wulong River	27.9 (6.55)	1.15 (0.43)	71.3 (65.7)	83.6 (31.5)	261 (142)
D16-C02	Bottom mud from Xiaojiang River	61.6 (29.2)	4.11 (1.85)	158 (105)	221 (84.3)	1338 (746)
D16-C03		51.6	4.61	110	173	951
D16-C04		65.0	4.45	114	165	799
D16-C05		53.1 (19.1)	4.10 (1.10)	122 (194)	144 (69.5)	946 (390)
D16-C06		55.8	4.23	134	145	845
D16-C07		17.0 (23.1)	0.41 (1.24)	81.4 (226)	36.5 (73.4)	151 (383)
D16-C08		30.8	1.69	145	69.5	509
D16-C09		54.4 (18.2)	3.34 (0.87)	127 (155)	112 (64.7)	691 (326)
D16-C10		42.5 (13.6)	1.32 (0.49)	133 (134)	40.3 (34.8)	292 (185)
D16-C11		41.5 (20.8)	0.48 (0.92)	117 (130)	57.6 (66.1)	398 (259)
D16-C12		40.5 (14.7)	2.91 (0.49	122 (143)	92.2 (36.3)	589 (195)
D16-C13	Bottom mud from the point about 50km at downstream at intersection entrance of Jinsha River and Xiaojiang River	11.4	0.58	184	29.9	134
D16-C17	Bottom mud from Dabai River	19.6 (13.0)	1.20 (0.72)	54.1 (55.8)	108 (72.4)	335 (226)
D16-C19	Bottom mud from Zhongchang River	19.6	0.57	286	75.3	235
Minimum value		20.3 (6.55)	0.56 (0.43)	9.01 (55.8)	28.7 (31.5)	252 (142)
Maximum value		65.0 (29.2)	4.6 (1.9)	286.2 (226.2)	220.6 (84.3)	1338.0 (746)
Mean value		39.5 (17.6)	2.3 (0.9)	130.4 (134.2)	103.4 (59.2)	564.9 (317)
Standard value		16.85 (6.19)	1.59 (0.43)	52.22 (51.92)	54.28 (18.48)	342.33 (173)
International standard value		20.0	0.5	35.0	60.0	150.0

Note: Data in bracket indicates analysis results from sampling points in wet season.

Each index is relatively low near the reference value area, and will obviously rise after flowing through mineral area, indicating the content exceeding standard is greatly related to the exploitation in mineral areas, between which there exists close relation. Relative standard deviation (RSD) is the ratio of standard deviation to mean value, which can reflect dispersion degree of heavy metal content. Table 1 indicates RSD of Cd is relatively small, indicating relatively uniform distribution, and RSD of Cu, As, Pb and Zn is relatively large, indicating very non-uniform distribution. According to spatial contrastive analysis, the overall distribution trend of five heavy metals is consistent with each other. Areas with heavy pollution mainly locate in segments of Xiaojiang River flowing through mineral areas, till the intersection of Xiaojiang River and Jinsha River, where the heavy metal content gradually drops, but Cd and Cu content still exceed the standard. Changes of heavy metal content in each sampling point are as indicated in figure 2 and figure 3.

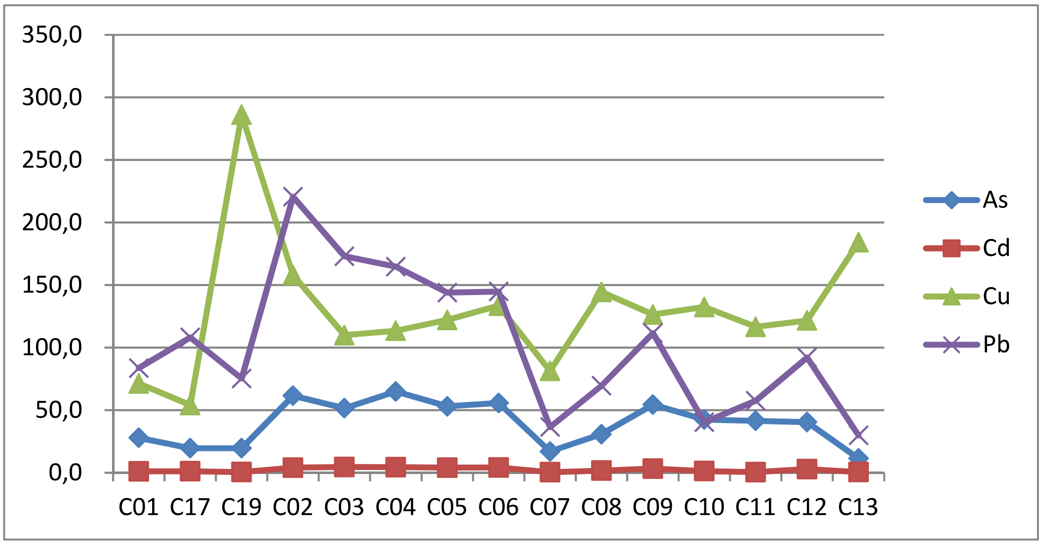

Figure 2. Changes of heavy metals (As, Cd, Cu and Pb) content

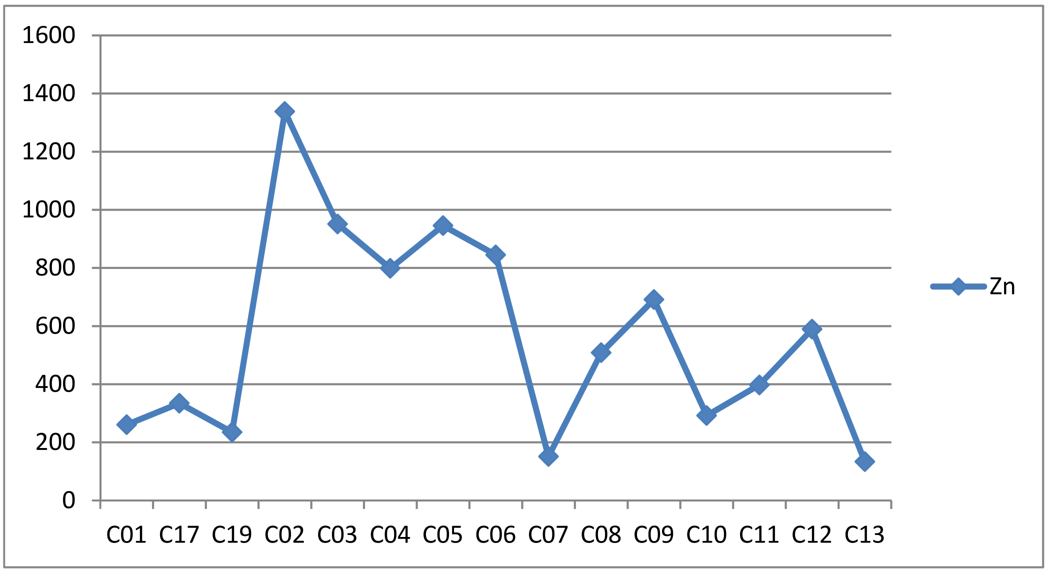

Figure 3. Changes of heavy metal (Zn) content

Compared to national standards, enrichment index of pollutants in bottom mud is much severer than the water pollution. Seen from the cause of formation, sampling is carried out in dry season, and the volume of runoff is relatively small. Particularly, the water velocity of Xiaojiang River is relatively rapid and contains much sand and mud, so the water flow cannot resolve heavy metal elements around, and the heavy metal elements in water can be easily absorbed by the carried silt, so the water is purified to some extent. Thus, as the buffer zone of heavy metal pollution of water, the bottom mud of Xiaojiang River becomes the storage warehouse of heavy metal element. Since debris flow frequently happens in branches of Xiaojiang, and the main type of debris flow is waste slag, that is to say, the main provenance of debris flow is the direct piling up of tailings produced from mineral activities in cleugh. In this way, many gushes forming from heavy rainfall will directly sweep the tailings to the water of Xiaojiang River, which will deposit in the bottom, and is the main component of bottom mud.

5.2. Potential ecological risk index of single heavy metal and overall heavy metal

As seen from table 2 and table 3, from the view of potential ecological risk index of single heavy metal, except for bottom mud from about 50m at downstream at Dabai River, Kuai River and Wulong River as the reference value, the E_r^i value of Pb, Zn and As is all less than 40; that of Cd from four sampling points is less than 40, respectively from the bottom mud from the point about 50km at downstream at intersection entrance of Jinsha River and Xiaojiang River, and those from Zhongchang River and those flowing to Jinsha River. E_r^i Value of Cd from two sampling points is from 40 to 80, and E_r^i value of Cd from three sampling points is from 80 to 160, and that from six sampling is from 160 to 320, indicating severe potential ecological risk. And the maximum value appears at the curve of river about 10km downstream in Tangdan mineral area, indicating strong enrichment of heavy metal Cd. For Cu, only the value of that from three sampling points is less than 40, others from 80 to 160, indicating severe potential ecological risk. Hence, Cu and Cd pollution are taken key objects of risk decision management.

6. Conclusions and suggestions

6.1. Cu and Cd pollution as key object of risk decision management

[9] has analyzed heavy metal pollution in vegetable in Tangdan and Luoxue, Dongchuan, Kunming. Results indicate that Cu and Cd pollution are relatively severe, and it's suggested that local residents selectively plant crops, and avoid vegetables enriching heavy metals such as Cu and Cd. Based on sampling analysis in this project, Cd and Cu risk degree is the highest from the view of potential ecological risk index of individual heavy metal, indicating extremely high potential ecological risk. Hence, Cd and Cu pollution should be taken as the key objects of risk decision management.

6.2. Heavy metal pollutant released from bottom mud to water due to pH value

After investigating samples of water from Xiaojiang River, it's found that pH value of water relatively drops in wet season due to the influence of acid rain. Chemical activity and biotoxicity of heavy metal in water are greatly related to pH value. The lower pH value is, the greater the chemical activity and biotoxicity will be, and vice versa [10]. In water of low pH value, heavy metal mainly takes fine particulate matter as migration carrier, with those at suspended state accounting for the highest proportion. So it can migrate more easily with water flow, and the potential risk will gets much stronger. Based on sampling bottom mud, the comparison of heavy metal content in bottom mud between dry season and wet season tells that content of heavy metal Pb, Zn, As, Cu and Cd in bottom mud in wet season is all lower than that in dry season, while the heavy metal content in water relatively rises. Hence, secondary pollution of bottom mud on water is actually verified in this research.

6.3. Debris flow of waste slag causing severe out of limits of heavy metal in bottom mud

As seen from field investigation by project team, due to limitations of geographic and geomorphic conditions and communication and transportation in drainage basin of Xiaojiang River, most of the tailings in mineral area are piled up in cheuch, providing provenance for debris flow. Dongchuan government has built a great amount of controlling measures of debris flow, but in rainy season, debris flows frequently happen and a great number of waste slag crush into cheuch, which requires manpower and material resources to clean it.

Table 2. Potential ecological risk index of single heavy metal and overall heavy metal

No. of sampling point	Position of sampling points	E_r^i(As)	E_r^i(Cd)	E_r^i(Cu)	E_r^i(Pb)	E_r^i(Zn)	E_{Rt}
D16-C01	Bottom mud from the point about 50m at downstream at Dabai River, Kuai River and Wulong River	7.67	57.60	30.22	11.15	0.89	107.54
D16-C02	Bottom mud from Xiaojiang River	16.91	205.40	66.95	29.41	4.58	323.26
D16-C03		14.18	230.50	46.61	23.07	3.26	317.61
D16-C04		17.84	222.30	48.09	21.96	2.74	312.93
D16-C05		14.58	205.10	51.74	19.20	3.24	293.85
D16-C06		15.32	211.70	56.57	19.31	2.89	305.79
D16-C07		4.67	20.72	34.50	4.87	0.52	65.27
D16-C08		8.47	84.70	61.23	9.26	1.74	165.41
D16-C09		14.95	167.00	53.60	14.88	2.37	252.80
D16-C10		11.69	65.75	56.14	5.37	1.00	139.96
D16-C11		11.40	24.03	49.41	7.67	1.36	93.87
D16-C12		11.11	145.70	51.57	12.29	2.02	222.69
D16-C13	Bottom mud from the point about 50km at downstream at intersection entrance of Jinsha River and Xiaojiang River	3.13	29.07	78.05	3.98	0.46	114.69
D16-C17	Bottom mud from Dabai River	5.39	60.00	22.93	14.41	1.15	103.88
D16-C19	Bottom mud from Zhongchang River	5.40	28.55	121.27	10.05	0.81	166.07

Table 3. Grading for the potential ecological risk of heavy metal pollution

E_r^i	Potential Ecological Risk Grading of Single Metal	E_{Rt}	Potential Ecological Risk Grading of Multiple Metals
<40	Slight ecological hazards	**<105**	Low risks
40-80	Middle ecological hazards	**105-210**	Middle risks
80-160	Strong ecological hazards	**210-420**	High risks
160-320	Relative strong ecological hazards	**>420**	Extremely high risks
>320	Extremely strong ecological hazards		

The cheuch on both sides of Xiaojiang River has increased to 107 from 38 in 1950s, and the frequency of debris flow is rising. Disasters get stronger and scale gets larger and larger. Water and soil loss area has reached 1273.5 sq. Km, which is quite serious, and accounts for 68.5% of the total amount in China

Due to the constant development of collapse [11], landslide and debris flow, a great amount of quicksand and rock are poured into Xiaojiang River. Each year 30-40 million stere sand and rocks accumulate in riverbed. The deposition fan of debris flow is adjacent to one and another to form a large area, and fans will connect to form a skirt or overlay to form accumulation stairs. The height of stairs of debris flow on both sides is 7-10m high. Opposite to each other, they form a interdigitating posture. In rainy season, Xiaojiang River becomes a river of debris flow. Silt poured into Jinsha River every year is more than 610 tons, and it will block the watercourse, so as to harm farmland and villages, which is more harmful to the development of Jinsha River [12].

6.4. Standard management of tailings pond and comprehensive utilization of tailings are key points for heavy metal pollution regulation in drainage basin of Xiaojiang River.

After the foundation of China, due to the practical urgent need of mineral development and the unique deep cheuch and lack of flat ground in Dongchuan, no tailings pond was built by various mill plants and smelting plants upon the approval of Zhou Enlai in 1964, Prime minister of the State Council. And all plants poured the tailings directly into the small rivers such as Jinsha River. Till 2007, national environmental protection administration made mandatory provisions to forbid enterprises directly discharging mill tailings into rivers and require them to build tailings pond. However, some small mill plants have privately constructed without standard design, project approval, land and safety evaluation, causing incomplete procedures of construction and management of tailings pond, and unreasonable site selection, and so forth. As for the built tailings pond, due to steep mountain and poor geographic position and geological conditions, the accumulation and disposition facilities on solid wastes are not perfect, and some tailings pond even contain potential safety hazard, which will easily lead to stacking pollution of tailings. For a long time, some enterprises with waste discharge has insufficient understandings about the importance and urgency of comprehensive utilization of industrial solid wastes and tailings, and do not regard the comprehensive utilization of tailings as a significant source of resource supply, but only take that as wastes, and they would use simple disposition measures. Hence, the understandings about the importance and urgency of comprehensive utilization of industrial solid wastes and tailings should be improved.

Acknowledgments

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