Analysis on Heavy Metal Distribution in Overlying Deposit and Pollution Characteristics in Rivers around Dahongshan Fe&Cu Mine in Yunnan Province, China

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Abstract. Dahongshan Fe&Cu mine in Yunnan Province was endowed with the title of "National Green Mine Pilots" by Chinese Ministry of Land and Resources in April 2013. In order to verify the implementation effects of the green mine and better drive the construction of the green mine by other mine enterprises in Yunnan, the project team investigated overlying deposit in rivers around the Dahongshan mine in the wet season (August) of 2016, investigated mine enterprises, and applied the Potential Ecological Risk Index to evaluate potential ecological hazards of heavy metal pollution in overlying deposit. The results showed that all sampling points were less than 105, indicating the lower ecological hazard degree.

1. Introduction

Wastewater from underground mining, ore processing, smelting in mines often contains lots of heavy metals, thus they become the pollution sources in body of water. Nine heavy metals are listed into the "blacklist" of 68 pollution to be optimized in China, including Pb, Zn, Cd, Cr, Cu and Ni, etc. [1]. Most of heavy metals flowing into rivers through a variety of ways change into solid phase from aqueous phase through physical sediment and chemical adsorption and deposit in sediment. As a result, sediment is the primary deposit bank of heavy metals in rivers and it is the indictor of heavy metal pollution in water environment, affecting effects of river dredging and governance. At the same time, heavy metals have toxicity or even poison (such as Cd, Hg, Pb and As), which can't be degraded by microorganism and they will be accumulated through concentration.

Dahongshan iron-copper mining area is located in Jiasa Town of Xinping County, 101°73′52″E-101°39′51″E and 24°04′58″N-24°6′49″N. the area of it is 15.2km^2. It is considered as large-scale iron deposit formed by Volcano lava and gas-liquid formation and the large-scale copper-iron deposit formed by paroxysmal eruption in 1959[2].

With the large hypsography, high terrain in the northeast and low terrain in the southwest, mountain chains and rivers present the east-west trend and it is controlled by folding fracture in the east-west direction. It belongs to the second level, third level and fourth level. Tributary and main streams are distributed as arborisation. Both of them are intermittent stream. River discharge is controlled by seasonal climate. With the large river gradient, it is Infancy v-shaped valley. There are three rivers in the mine area, including Mangang River, Feiwei River and Laochang River. Feiwei River is located in the

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southeastern mine. Mangang River is located in the northwestern mine. It is intersected with Feiwei River in the western mine, which is called as Erdao River. Laochang River is located in the northwestern mine for 3km. The downstream is intersected with Erdao River to form the Kunlong River, which flows into Jiasa River from 9km of the southwestern mine for 9 km.

Mangang River flows to 511.87m of confluence from the source elevation as 875m. The catchment area is 164km^2. The flow in the flood period reaches 430m^3/s, while the flow in the dry season only reaches 0.1-0.25m^3/s. Laochang River is reduced to 610.8m of the confluence from the source elevation as 722m. The fall is 111.2m and catchment area is 114km^2. The flow in the flood period is 83m^3/s, while the flow in the dry season is only 0.3-1.0m^3/s. Feiwei River flows to 670m of confluence from the source elevation as 680m. The fall is only 10m. The catchment area is 55km^2. The flow in the flood period is 135m^3/s, while the flow in the dry season is 0.05-0.1m^3/s [3].

2. Sample Collection and Testing

Sediment samples were located in the same place of water samples. River water samples and sediment samples were collected at the same time. In order to embody the situation of sediment in a reach and reduce influences of individual pollution points on samples, sediment samples at least should be collected in three different areas. After using a military shovel to collect samples at least in three areas, sediment samples collected were mixed as the samples in this collection, so that special deposition or pollution in local district will result in sampling distortion. After sieving, samples were installed in the polyethylene, marked with a marking pen for sampling number and sampling date. After samples were collected, they were labelled, filling in "Record Chart of sediment Sampling" as required to record sampling point and surrounding situations. As sampling, a digital camera was used to take a picture for surroundings and physical behaviours of rivers. GPS was used to locate the sampling points. The diagram of sampling points is shown in figure 1.

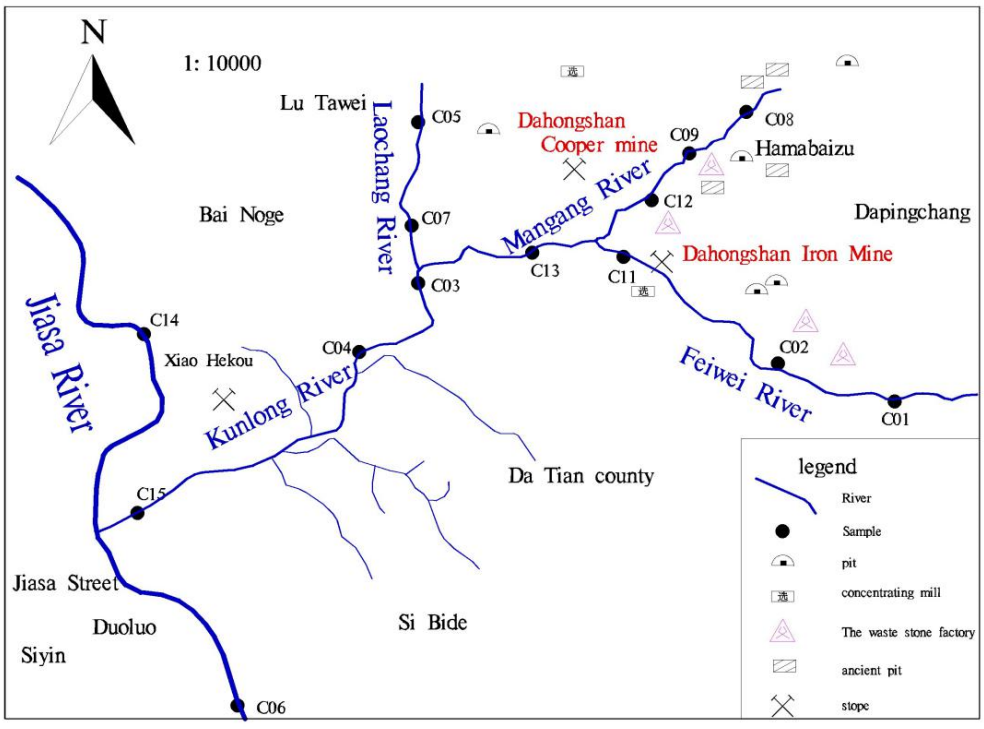


Figure 1. Diagram of Sampling Points in Rivers Around the Dahongshan Mine Sediment samples were sent to Ministry of Land and resources Kunming mineral resource supervision

Ministry of Land and resources Kunming mineral resource supervision inspecting centre, according to "Analysis Technique Requirements (Trial) of Eco-geochemical Assessment in Geological Survey Technique in China Geological Survey (DD2005-03). Atomic fluorescence spectrometry was used to detect heavy metal contents of As in Sediment, using the instrument AFS-3100 full-automatic atomic fluorescence spectrometer, accuracy<1.0%, detection limit: As<0.005μg/ml. Inductively coupled plasma mass spectrometry was used to detect , using ICAP type-Q mass spectrometer ,detection limit:Cu≤0.001μg/ml ,Pb<0.001μg/ml,Cd<0.0001μg/ml,Zn<0.005μg/ml.

3. Evaluation Methodology

In the study, Potential Ecological Risk Index was used to evaluate potential ecological hazards for heavy metal pollution of overlying deposit in rivers around Dahongshan. The method uses principles of sedimentology to evaluate heavy metal pollutions and ecological hazards established by a Swedish scholar Hakanson in 1980. The computational formula of potential ecological risk index is shown as follows [4]:

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

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^irefers to the potential ecological risk index of heavy metal i; T_r^istands 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 [5]. The specific evaluation grading is shown in table 1.

Table 1. Potential Ecological Risk Index and Grading Relationship

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		

Risk index method focuses on ecological effects of heavy metals on the environment and considers different biotoxicity of different heavy metals, so as to result in different ecological hazards for the environment. Under the circumstance of analysing heavy metal element situations, the pollution degree of heavy metals in certain deposit can be studied from features of sedimentology in heavy metals, biological characteristics and toxicology, as well as pathological features, namely it is the potential ecological hazard degree [6].

The background reference value was the sediment samples collected from upper reaches of Jiasa River, which is greatly affected by the mine. As, Cd, Cr, Cu, Pb, Zn and Ni were 5.05mg/kg, 0.14mg/kg, 53.1mg/kg, 96mg/kg, 34.0mg/kg, 85.1mg/kg and 63.1mg/kg, respectively; according to Hakanson's method, in order to standardization and convenience, in actual use, toxic response factor was calibrated as Cu=5, Zn=1, As=10, Pb=5, Cd=30, Ni=5 and Cr=2 [7-8].

4. Results and Analysis

4.1. Gross Evaluation

Five rivers around Dahongshan Copper-iron Mine were selected as five sampling units for studying, including Feiwei River, Kunlong River, Mangang River, Laochang River and Jiasa River. Every sampling unit collected several Sediment samples. Sediment in several rivers and heavy content distribution with aqueous phase were studied. Total heavy metals in deposit and pH measuring results are shown in table 2.

Table 2. Heavy Metal Content and pH Value Record in Sediment of Rivers around Dahongshan Cu&Fe Mine (mg/kg)

No.	Sampling point No.	Description	pH	Cd	Cr	Cu	Ni	Pb	Zn	As
1	**DH-C01**	Sediment without passing through the mine in the upstream Feiwei River	7.75	0.20	53.3	33.5	28.5	53.2	148	10.7
2	**DH-C02**		7.92	0.19	48.2	96.8	28.2	28.2	98.7	20.1
3	**DH-C11**	Sediment in the downstream Feiwei River	8.35	0.14	52.0	119	30.5	29.1	61.0	7.23
4	**DH-C03**	Sediment under Kunlong River	8.39	0.10	66.7	172	45.3	25.4	87.2	7.63
5	**DH-C04**		8.27	0.17	79.9	150	68.0	229	127	6.63
6	**DH-C15**		8.48	0.12	64.5	155	43.1	24.9	92.8	6.93
7	**DH-C05**	Sediment in Laochang River	8.17	0.20	105	149	89.5	27.4	156	5.20
8	**DH-C07**		8.19	0.13	114	131	70.0	45.8	145	4.39
9	**DH-C08**	Sediment in upstream and midstream in Mangang River	7.56	0.15	64.2	70.5	34.6	37.5	97.2	7.93
10	**DH-C09**		7.57	0.16	63.5	64.1	36.6	86.6	115	6.84
11	**DH-C12**		8.33	0.13	59.3	227	46.1	17.3	76.8	6.04
12	**DH-C13**	Sediment from Mangang River to Feiwei River	8.26	0.14	80.5	185	57.2	43.9	100	11
13	**DH-C14**	Sediment from Jiasa River to Kunlong River	8.84	0.14	53.1	96	63.1	34.9	85.1	5.05
14	**DH-C06**	Sediment in 5km of downstream from Jiasa River to Kunlong River	8.59	0.16	54.0	42.7	31.4	46.7	85.6	8.10
		Max	8.59	0.20	114.00	227.00	89.50	229.00	156.00	20.10
		Min	7.75	0.10	48.20	33.50	28.20	17.30	61.00	4.39
		Mean	8.30	0.15	68.44	120.83	48.01	52.14	105.39	8.13
		Median	8.30	0.15	64.20	120.83	45.30	37.50	98.70	7.23
		Standard deviation	2.92	0.05	26.13	62.81	21.99	53.48	38.82	4.33
		First-level standard of national soil	Natural background	0.2	90	35	40	35	100	15
		Second-level standard of national soil	＜6.5	0.3	300	100	50	300	250	20
		Third-level standard of national soil	＞6.5	10	400	400	200	400	500	30

The analysis results showed that heavy metal contents in deposit of five rivers had the large difference. Seven heavy metal contents in Sediment of five rivers almost exceeded the reference sampling points on the upstream copper mine with less man-made interference, showing that iron-copper producing activities have already caused a great influence on heavy metal content distribution in downstream environment. Heavy metal contents in sampling points referred to the first-level standard of Environmental Quality Standard for Soils (GB15618-1995). Mean Cd and Cr were lower than first-level standard of soil quality, while mean Ni, Pb, Zn and As were lower than second-level standard of soil quality. Mean Cu was lower than third-level standard of soil quality. Maximum of Cd was lower than first-level standard of soil quality.

By comparing with unit sampling analysis results studied by Li Xiaoyan in 2008 as shown in Table 3, most of heavy metals in 2016 exceeded total heavy metal sin 2008, showing that digestion of heavy metal pollution was relatively slow and it had some enrichment to some extent. Though water quality has been slightly improved, digestion of heavy metals in sediment may be still a long-term process.

Table 3. Comparison of Sediment Contents between 2016 and 2008

Comparison		Cu (mg/Kg)	Cr (mg/Kg)	Cd (mg/Kg)	Pb (mg/Kg)	Zn (mg/Kg)	Ni (mg/Kg)
Laochang	This study	70.5-149	64.2-114	0.1-0.17	27.4-45.8	97.2-156	34.6-89.5
River	Li Xiaoyan	8.64-246.64	1.29-26.38	0.02-1.75	1.10-18.8	4.79-45.74	15.92 -72.08
Mangang	This study	64.1-227	52-63.5	0.13-0.16	17.3-86.6	61-115	30.5-46.1
River	Li Xiaoyan	0.67-359.49	0.49-52.17	0.07 -0.25	2.59-19.44	6.38-63.03	18.46-74.14
Kunlong	This study	150-172	64.5-79.9	0.1-0.17	24.9-229	87.2-127	45.3-68
River	Li Xiaoyan	36.80-382.11	7.67-41.25	0.12 -0.28	4.27-17.99	19.94 -51.40	21.03-36.40
Feiwei	This study	0.16-0.22	48.2-54	0.16-0.22	28.2-53.2	85.6-148	28.2-31.4
River	Li Xiaoyan	30.94 -45.58	16.14-26.93	0.05-0.23	9.22-24.16	32.56-7 8.98	18.45-30.26

4.2 Potential Ecological Risk index Evaluation Results of Single Heavy Metal and Total Heavy Metals

Sediment in 5km of upstream entrance between Kunlong River and Jiasa River was selected as the background reference value, namely Cd=0.14mg/Kg, Cr=53.1mg/Kg, Cu=96mg/Kg, Ni=63.1 mg/Kg, Zn= mg/Kg and As=5.05 mg/Kg.

It can be observed from table 1 and table 4 that from the perspective of potential ecological risk index of single heavy metal, in addition to the background value, sediment applied by the upstream reaches of Jiasa River, the value of six heavy metals was smaller than 40, including Cu, Zn, As, Pb, Cr and Ni, etc., belong to the low risk. 86% of sampling points in Cd were smaller than 40, while 14% of sampling points were between 40 and 80, belonging to the middle risk. The maximal value presented in the Sediment of Feiwei River, showing that Cd gathered here. As a result, Cd pollution should be regarded as the key object of risk decision-making management. The heavy metals' incidence sequence of causing hazards for ecological risks in rivers was shown as follows: Cd>Cu>Pb>Ni>Cr>Zn.

As a whole, Potential Ecological Risk Index of heavy metals showed that all sampling points were smaller than 105, belonging to the lower ecological hazard degree. In terms of every sampling point, comprehensive pollution status was extremely serious in sediment of Kunlong River.

Table 4. Potential ecological risk index evaluation results

Sampling point No.	Sampling point Description	E_r^i (Cd)	E_r^i (Cr)	E_r^i (Cu)	E_r^i (Ni)	E_r^i (Pb)	E_r^i (Zn)	E_r^i (As)	E_{Rt}
DH-C01	Sediment without passing through the mine in the upstream Feiwei River	42.43	2.01	1.74	2.26	7.62	1.74	21.19	78.99
DH-C02		41.14	1.82	5.04	2.23	4.04	1.16	39.80	95.24
DH-C11	Sediment in the downstream Feiwei River	30.43	1.96	6.20	2.42	4.17	0.72	14.32	60.20
DH-C03	Sediment in Kunlong River under the mine	21.43	2.51	8.96	3.59	3.64	1.02	15.11	56.26
DH-C04		37.29	3.01	7.81	5.39	32.81	1.49	13.13	100.93
DH-C15		25.93	2.43	8.07	3.42	3.57	1.09	13.72	58.23
DH-C05	Sediment in Laochang River	42.43	3.95	7.76	7.09	3.93	1.83	10.30	77.29
DH-C07		28.29	4.29	6.82	5.55	6.56	1.70	8.69	61.91
DH-C08	Sediment in upstream and midstream of Mangang River	32.79	2.42	3.67	2.74	5.37	1.14	15.70	63.83
DH-C09		33.43	2.39	3.34	2.90	12.41	1.35	13.54	69.36
DH-C12		27.86	2.23	11.82	3.65	2.48	0.90	11.96	60.91
DH-C13	Sediment from Mangang River to Feiwei River	30.00	3.03	9.64	4.53	6.29	1.18	21.78	76.45
DH-C06	Sediment in 5km of downstream from Jiasa River to Kunlong River	35.14	2.03	2.22	2.49	6.69	1.01	16.04	65.62

5. Discussion and Suggestion

5.1. Cd was the key object in risk decision-making management

As a toxic element, Cd flows into human body through digestive tract and respiratory tract, causing vascular hypertension, chronic intoxication or even itaiitai disease [10]. In the investigation, 14% of sampling points for Cd were between 40 and 80, belonging to middle risk. It gathered to some extent. Particularly, it must notice risk decision-making management. Cd content was lower than the mean value, while the maximal value was lower than first-level standard of soil quality and the contents were lower. However, toxic response factor of Cd was 30, which was the highest one in all heavy metals, thus after calculating through the formula of potential ecological risk index, Cd had the highest pollution index among heavy metals. Such a method is often used to evaluate heavy metal pollution situations in Sediment in domestic. As long as Cd is detected, it basically can be used as the key object of risk-decision management. As a result, such a result is greatly affected by toxic response factor. It is necessary to do specific analysis by combining with specific contents and local background value of Cd.

5.2. Heavy metal contents in water were obviously reduced, but heavy metal contents in Sediment were still increasing

The investigation conclusion of the project team showed that by comparing with water quality standard in national surface water, Fe in aqueous phase in Laochang River reached IV national water standards. Hg, Cd, Se, Ag, Pb, Cu, Zn and As reached I water standard.

Fe in Mangang River and Kunlong River reached III national water standard. In addition, Se, Ag, Pb, Cu, Zn and As reached I water standard, Fe, Se, Ag, Pb, Cu, Zn and As in Feiwei River and Jiasa River

reached I water standard. By comparing with relevant research data studied by Li Xiaoyan 8 years ago [9], the study in the project team showed that over-limit ratio of heavy metals has been very low. Previous contaminative status was slightly improved, showing that after Dahongshan Mining Company was confirmed as the second national green mine, and circular economy has already acquired obvious achievements. Until 2016, mineral wastewater and tailing wastewater can be fully recycled and surrounding water environment has been greatly improved [11]. The investigation data of Sediment showed that heavy metal contents of Sediment were slightly improved, showing that growth of heavy metal contents was slightly relieved through green mine construction, but digestion of heavy metal pollution was slow and it still gathered in some period. Though water quality was slightly improved, natural digestion of Sediment still needed the long-term process. When necessary, it needs human intervention governance to greatly reduce heavy metal contents in Sediment.

5.3. Reduction of pH resulted in secondary polluted water from heavy metals in sediment

Heavy metal ions will conduct circulation in Sediment and water through chemical and biological functions. Sediment will become the second pollution source of body of water. Under the acidic condition, it is easy to release, especially for metal elements in carbonate combined state that are most sensitive to pH changes [12]. If pH in water and Sediment around Dahongshan is reduced, such as acid rain or discharge of acid mine wastewater, ion exchange state and water soluble speciation of three elements (Pb, Cd and Zn) will be greatly increased, thus heavy metal elements in water also will be greatly increased, causing the great potential hazards for the drainage basin. The investigation showed that pH in body of water in Dahongshan mine was higher, between 7.75 and 8.59. Relative to surrounding water in other large-scale non-metal mines in Yunnan, heavy metal elements in Sediment around Dahongshan mine were not easy to release and water quality was also good. However, it couldn't exclude other factors affecting pH, and heavy metals were released again to pollute body of water, especially for acid wastewater in iron mine. Thus it should be valued. The following situations will accelerate generation of acid wastewater in the mine, so as to affect changes of water quality and heavy metals in Sediment. Direct oxidation of pyrite and chalcopyrite, oxidation of Fe^{3+} and iron pyrite are easy to be oxidized by the oxidized sulphide, the generated vitriol can promote dissolution of other minerals in an individual or a mutual mode. Dahongshan iron-copper deposit presents the layered form or layered-alike form. It includes seven ore belts. The form of Dahongshan iron-copper deposit is obviously controlled by the stratum. The ore body is integrated and contacted with the layered form or layered-alike form. Mineral compositions include copper pyrites and magnetite, as well as a few hematite, copper, chalcocite, cobaltite, iron pyrite, pyrrhotite and galena. Non-metallic minerals include tourmaline and apatite, etc. It has the condition to generate lots of acid wastewater and it should be strictly supervised [13].

5.4. The higher copper contents was related to background values of cupper elements in local parent materials in Yunnan

In all sampling points, Cr, Cd, Pb and Zn contents in five rivers were relatively lower. Ni contents had little difference from most of Sediment, showing that the higher Cu contents in Laochang River, Mangang River and Kunlong River in Dahongshan copper mine were the prominent problems. In addition, Cu contents in Yunnan Erhai Lake, Yunnan Outside Caohai Lake and Yunnan Inside Caohai

Lake also have the higher contents than other areas in China. This may be related to the higher background values of Cu in local parent materials in Yunnan. Perhaps, it also may be attributed to copper exploitation, ore washing and smelting, etc., thus heavy metal elements which may be fixed before can be introduced to environmental media excessively, resulting in accumulation in environmental media.

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