Distribution and Pollution Characteristics Analysis of Heavy Metals in Surface Sediment in Bi River

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Abstract. The author analyzes distribution characteristics of heavy metals’ content in surface sediments of Bi River (Cu, Zn, As and Cd) and evaluates the potential ecological harm of heavy metal pollution in surface sediment by index method of potential ecological harm. Results show that heavy metals, such as Cu, Zn, As, Pb and Cd in surface sediments of Bi River are badly out of limitation. Especially, the heavy metals’ content in Jinding mining area is far higher than the national first class standard. The content of heavy metal is still high in the intersection of Bi River and Lancang River, which have certain influence on the Lancang River sediment and its water system. And, Pb and Cd, as the main pollutants, should be regarded as a key research subject.

1. Introduction

Because of their toxicity, persistency and bio-concentration effect, heavy metals receive much concern. Most heavy metals in the water rapidly transform from aqueous phase to solid phase under the physical precipitation and chemical adsorption, and deposit in river’s sediment, and then will be released if environmental conditions changes, causing higher concentrations of heavy metals in water and secondary pollution. Therefore, it is of great significance to systematically analyse and evaluate pollution status, pollution sources and distribution of heavy metals in sediment [1].

Pollution status of water sediment is an important factor of the comprehensive evaluation of water environment quality conditions. Rivers in mining area provide convenient water for mining activities [2]; meanwhile, their river ways have become the main concentrated places of all kinds of waste and have been continually polluted by ore leaching, sewage and garbage [3]. After mud and tailings which contain heavy metals entering into the water, on the one hand, they will migrate, transfer and accumulate along with the water movement, thus changing the structure of water quality.

Research area belongs to continental cool temperature zone, controlled by Himalayan - Tibet climate zones, June to October is the rainy season and November to May of the following year is the dry season. For many years, the average temperature is 11.3°C, extreme maximum temperature is 31.7°C (on May 21, 1972) and extreme minimum temperature is minus 10.2°C (on December 18, 1961) [4].

LanPing County is a state-level poverty-stricken county in Yunnan Province, but a huge treasure was buried under this piece of barren land. After years of exploration, geological department has proven that...
Lanping County owns the largest Pb-Zn mine in Asia with reserves of over 15 million tons and a potential value of over 200 billion Yuan [15]. The Pb-Zn deposit has proven reserves of Pb and Zn metal of over 15 million tons, with a combined grade of Pb and Zn of 9.44%, and is the super-large ore deposit in China and Asia and the fourth largest Pb-Zn mine in the world. The Pb-Zn deposit is located 18 km northwest of Lanping County and in the Phoenix Mountain vein. Currently, it is mainly strip mined at low cost, with production capacity of about 2000 tons per day. According to the current speed, the mine could be exploited for nearly a century.

Lanping County is located in the longitudinal valley Zone of the Hengduan Mountains, with unique and rich mineral resources and enjoys the reputation of "crown of non-ferrous metal kingdom" in Yunnan province. Nowadays, it has been proven and found that there are over 150 points of ore deposits of Pb, Zn, copper, strontium, mercury, antimony, silver, salt, sulfur, iron, gypsum, mica, pyrophyllite, crystal stone and etc. The large-sized deposit is the Jinding Pb-Zn deposit in Phoenix Mountain with large reserves, high grade, mineralization concentration, and easy for exploitation. With further increase of exploration, more new deposit and mines will be found in the future.

With the exploitation of the Jinding Pb-Zn deposit, a large number of individual or joint ventures participated in mining activities, promoting the development of the local mining economy. Mining activities became the main economic sources of Lanping County and spread over the entire county. Lanping Pb-Zn mine began its large-scale mining in 1984, and had been continuously investigated and monitored from 1986 to 1988. Results showed that because waste water and tailings were directly discharged into Bi River without effluent treatment and smelting waste were piled up on both sides of the river, the average over-standard rate of Pb content was 26%, the average over-standard rate of Cd was 38%, but the upstream surface water, groundwater and main tributaries are not affected by pollution, [4].

2. Samples collection and analysis

2.1 Samples collection

Sampling was conducted in the end of January 2016, which is dry season in Bi River. Due to the water quality of Bi River was greatly influenced by Jinding mining area, the layout of sampling point was based on the principles of the distance from mining area. The closer distance from mining area is, the higher sampling density is, the shorter the interval is. Conversely, the smaller density is, the longer the interval is.

In the process of sample collection, GPS was employed to track and put sampling points. Sampling began from Bi River's upstream to intersection of Bi River and Lancang River, with the total 18 sediment samples. The sampling points of SX20, SX21 and SX22 were located in the upstream mining area, basically not affected by mining activities, and available for truly reflecting water condition of Bi River that was not affected by the mining activities, which could represent the background value of Bi River. The sampling points of C06, C08, SX30, SX31, SX33 and SX35-39 were located in LanPing County, the sampling points of C14-18 were set in Yunlong County (figure 1). Sediment samples were about 1-2 kg dig from deposit where the shore water flows slowly, and then were placed into polyethylene plastic bucket after sieving.

The sediments in upstream Bi River of Jinding mining deposit for a long time, and original sediments dominated. And, the sediments in downstream Bi River of Jinding mining deposit for a short time, whose vast majority consisted of a lot of waste slag caused by recent mining activities.

2.2 The sample analysis

Water and sediment samples were handed up to mineral resources supervision and inspection center of Ministry of Land and resources of Kunming for analysis. The testing steps strictly accord with the technical requirements of ecological geochemical assessment sample analysis (trial) in Geological Survey Technology Standards of China Geological Survey (DD2005-03).
Heavy metal content in the sediment samples was measured by atomic fluorescence and the instrument is AFS – 3100 automatic dual channel atomic fluorescence spectrometer. Its precision is less than 1.0%, detection limit is the content of As, Pb is less than 0.01μg/L, Cd less than 0.001μg/L, Cu less than 0.005μg/ml, Zn less than 1.0μg/L. PH value of water is measured by pH measurement in laboratory. And the instrument is PHS - 3c acidity meter, with its measuring resolution ratio: pH: 0.01pH and its precision: pH±0.01mm.

3. Research methods
At present, there are many methods to evaluate heavy metal pollution of sediments in river in China, widely employing geo-accumulative index method, of potential ecological risk index method, regression excessive analysis, face graph method, comprehensive pollution index method, internal ROM the comprehensive pollution index method, the enrichment coefficient method and pollution load index method, sediment secondary enrichment coefficient method and so on, which all have their own advantages and disadvantages and applicable scope. The geo-accumulative index method and potential ecological risk index method are the most commonly used evaluation methods in China.

This time, heavy metal pollution in surface sediment in Bi River will be evaluated by the method of potential ecological harm index. The method was raised by Swedish scholars Hakanson in 1980 on the basis of the principle of sedimentology to evaluate heavy metal pollution and its ecological harm. The computation formula of potential ecological harm index is as follows [5]:

\[
P = \sum_i C_{i}\log\frac{C_i}{B_i}
\]

where \(P\) is the potential ecological harm index, \(C_i\) is the concentration of the metal in the sediment, \(B_i\) is the background value of the metal in the natural environment, and \(n\) is the number of metals considered.
In the formula, \( C^i \) is the measured concentration (mg/kg) of heavy metal “i” in sediment; \( C^i_b \) is the background reference (mg/kg) for heavy metal “I” in sediment; \( E^i_r \) is the potential ecological harm index for heavy metal “i”; \( T^i_r \) is the response coefficient for toxicity of heavy metal “i”, which can reflect the level of toxicity of heavy metals and biology’s sensitive degree of heavy metal pollution; \( E_{RE} \) is the overall potential ecological harm index for various heavy metal[16].

4. The results and discussion

4.1 The geochemical distribution of heavy metals in sediments

The test results of copper, Pb, Zn, As, Cd in the sediments are shown in table 1.

| Sample number | Sampling locations | As  | Cd  | Cu  | Pb  | Zn  |
|---------------|--------------------|-----|-----|-----|-----|-----|
| L16-C06       |                    | 43.3| 2.87| 30.7| 119 | 514 |
| L16-C08       |                    | 52.9| 7.64| 40.0| 284 | 869 |
| L16-SX33      |                    | 40.3| 30.3| 28.9| 750 | 3758|
| L16-SX35 Bi River mining area in period of Lanping county samples | 57.9| 37.9| 33.9| 3030| 4414|
| L16-SX36      |                    | 37.4| 32.7| 29.0| 589 | 4110|
| L16-SX37      |                    | 34.4| 31.3| 26.4| 613 | 4208|
| L16-SX38      |                    | 20.8| 10.4| 26.3| 168 | 1462|
| L16-SX39      |                    | 25.2| 14.6| 29.9| 382 | 1858|
| L16-SX30      |                    | 39.3| 10.8| 39.9| 245 | 1246|
| L16-SX31      |                    | 64.0| 54.7| 36.9| 867 | 5020|
| L16-SX20      | The control area (Bi River upstream is not polluted by mining section) | 43.5| 0.56| 9.01| 28.7| 310 |
| L16-SX21      |                    | 30.2| 0.57| 14.0| 28.9| 252 |
| L16-SX22      |                    | 35.7| 0.80| 12.3| 54.8| 314 |
| L16-C14       | Bi River downstream in Yunlong county | 35.3| 9.06| 83.1| 154 | 1322|
| L16-C15       |                    | 26.4| 11.4| 41.9| 160 | 1746|
| L16-C16       |                    | 27.2| 13.1| 49.4| 162 | 1879|
| L16-C17       |                    | 28.1| 3.33| 37.8| 45.2| 444 |
| L16-C18       |                    | 20.3| 9.84| 34.6| 133 | 1679|
| The minimum value |                    | 20.3| 0.56| 9.01| 28.7 | 252 |
| The maximum value |                    | 64.0| 54.7| 83.1| 3030.0 | 5020.0 |
| The average value |                    | 36.8| 15.7| 33.6| 434.1 | 1966.9 |
| The standard deviation |                    | 11.88| 14.87| 15.79| 677.23 | 1555.07 |
| Chinese standard value |                    | 20.0| 0.5 | 35.0 | 60.0 | 150.0 |

Because there is no environmental quality criteria of sediment, Chen Jing sheng [13] collected quality benchmark heavy metal elements used by 15 environmental management departments. The benchmark of As is 3~70 mg/kg, the benchmark of Cd is 0.2~12 mg/kg, that of Pb is 23~30 mg/kg and that of Zn is 100~820mg/kg. Even if, in accordance with the ceiling of benchmark, 5 heavy metal elements in the Bi River’s sediment far exceed. And according to the Chinese national soil environment quality standard (GB15618-2009) (Ⅲ), which are As = 30 mg/kg, Cd = 0.4 mg/kg, Cu = 100 mg/kg, Pb = 280 mg/kg, Zn= 300 mg/kg, As is excessive of 1.22 times of standard value, Cd is excessive of 37.2 times excess, Pb is excessive of 1.47 times and Zn is excessive of 6.26 times. All indicators were lower in the vicinity
of the background value, and increased obviously after flowing through the Jinding mine area. So it can be easily seen that over proof content has intimately relationship with mine exploitation.

Compared with the national standards, the index of sediment pollutant concentration is higher than water pollution. In the sense of causes, sampling period belongs to the dry season when the volume of runoff is small. In particular, water velocity of Lanping section of Bi River is fast and carries large amount of sediment. Heavy metals in the surrounding environment are not dissolved by water flow in time, and the heavy metals in the water are easily absorbed by sediment that results in water purification. And Bi River’s sediment, as the storage buffer of water heavy metal pollution, becomes the accumulation library of heavy metal element.

Relative standard deviation is the ratio of standard deviation and average, which can reflect the discrete degree of heavy metal content. In table 1, relative standard deviations of As, Cd, Cu, are small, showing that the distribution is uniform, while relative standard deviations of Pb is big, showing that distribution is uneven. Based on spatial analysis, distribution trend of 5 kinds of heavy metals is consistent. And pollution area mainly concentrated from the Lanping section of Jinding Mine area to intersection of Yunlong and Lancang River of downstream Bi River, where the content of heavy metal does not remarkably reduce.

4.2 Potential ecological harm index of single heavy metal \( \langle E_i^l \rangle \)

The background reference is not affected by the mining area of the three average sediment samples as background values. As is 36.4mg/kg, Cd is 0.6 mg/kg, Cu is 11.8 mg/kg, Pb is 37.5 mg/kg, Zn is 291.9 mg/kg. Toxic response coefficient is Cu=5, Zn =1, As =10, Pb=5, Cd=30[14]. The degrees of potential ecological harm hierarchies of heavy metal pollution are shown in table 2.

| Sample number | Sampling locations | \( E_i^l \) As | \( E_i^l \) Cd | \( E_i^l \) Cu | \( E_i^l \) ( Pb) | \( E_i^l \) ( Zn) | \( E_{BE} \) |
|---------------|--------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| L16-C06       | Bi River mining area in period of Lanping county | 11.89          | 143.35         | 13.02          | 15.87          | 1.76           | 185.89         |
| L16-C08       | Bi River          | 14.53          | 381.95         | 16.96          | 37.84          | 2.98           | 454.26         |
| L16-SX33      | Bi River          | 11.07          | 1515.50        | 12.26          | 100.03         | 12.87          | 1651.73        |
| L16-SX35      | Bi River mining area in period of Lanping county | 15.91          | 1895.00        | 14.36          | 404.00         | 15.12          | 2344.39        |
| L16-SX36      | Bi River          | 10.28          | 1634.50        | 12.31          | 78.47          | 14.08          | 1749.63        |
| L16-SX37      | Bi River          | 9.45           | 1565.50        | 11.19          | 81.68          | 14.42          | 1682.23        |
| L16-SX38      | Bi River          | 5.70           | 520.50         | 11.16          | 22.36          | 5.01           | 564.73         |
| L16-SX39      | Bi River          | 6.92           | 732.00         | 12.65          | 50.99          | 6.37           | 808.92         |
| L16-SX30      | Bi River          | 10.80          | 540.50         | 16.89          | 32.71          | 4.27           | 605.17         |
| L16-SX31      | Bi River          | 17.59          | 2735.00        | 15.64          | 115.65         | 17.20          | 2901.08        |
| L16-C14       | Bi River downstream in Yunlong county | 9.70           | 453.20         | 35.21          | 20.53          | 4.53           | 523.17         |
| L16-C15       | Bi River downstream in Yunlong county | 7.25           | 568.00         | 17.76          | 21.33          | 5.98           | 620.33         |
| L16-C16       | Bi River downstream in Yunlong county | 7.47           | 655.50         | 20.93          | 21.59          | 6.44           | 711.93         |
| L16-C17       | Bi River downstream in Yunlong county | 7.71           | 166.25         | 16.03          | 6.02           | 1.52           | 197.53         |
| L16-C18       | Bi River downstream in Yunlong county | 14.64          | 17.68          | 5.75           | 17.68          | 5.75           | 61.51          |

From table 2 and table 3, we can see that \( E_i^l \) values of Cu, Zn, As are less than 40 from potential ecological harm \( E_i^l \) of a single index of heavy metal, except upper sediment of Bi river as background value; \( E_i^l \) of Pb is less than 40 in 60% of sample points such as in LanPing County city, Jinding mining area that Bi river does not flow through, Yunlong county and sediment of Bi River away from the mining area. \( E_i^l \) value is 40-80 in 13% of the sample points, \( E_i^l \) value is 80-160 in 20% of the sample point and its ceiling value is over 320, which belongs to the serious potential ecological harm degree. The ceiling value appeared in the river bend about 10 km away from downstream Jinding mining area, where
accumulate a lot of visible heavy metal. For Cd, $E_{rt}$ is less than 40 in only one sample point, a $E_{rt}$ is 160-320 in two sample points, and $E_{rt}$ values are over 320 in the remaining 80% sample points, which belongs to the super serious potential ecological harm degree. $E_{rt}$ comes to its maximum of 2735.00 in the intersection of Lancang River and Bi River. Therefore, the Pb and Cd should be regarded as the key subjects of the risk decision-making management.

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

| $E_{rt}$ | Pollution levels | $E_{rt}$ | Pollution levels |
|----------|------------------|----------|------------------|
| <40      | low              | <105     | Low              |
| 40-80    | medium           | 105-210  | medium           |
| 80-160   | heavy            | 210-420  | heavy            |
| 160-320  | Heavier          | >420     | heaviest         |
| >320     | heaviest         |          |                  |

4.3 The overall potential ecological harm index of heavy metal $E_{rt}$

From overall potential ecological harm index of heavy metal $E_{rt}$, there is only one sample point’s $E_{rt}$ is less than 105, which belong to low ecological damage. And another sample point’s $E_{rt}$ is 105-220, which belongs to the medium of the ecological damage, the remaining 87% the sample points which belong to the serious potential ecological harm, should appeal considerable attention.

5. Conclusions

5.1 Pb and Cd pollution should be as a key object in the risk decision-making management

Content of heavy metals in upstream Bi River sediments is rather low (sample SX20-22), but in active mine activity area (begin from sample C06), content of metals in sediment increased, especially the sections flowing through the Jinding mining area. The content of Cd and Zn had been greatly influenced, the pollution degree has a certain decline from upstream to downstream, but there is a lot of concentration in downstream Yunlong section where water flow is slower. Mining activity is the source of heavy metals in watershed sediment and environment pollution has been intensifying. From potential ecological harm index of single heavy metal, the risk of Cd and Pb are the highest, which belongs to the super serious potential ecological harm degree. Potential ecological harm index of single heavy metal in the interchange of Lancang River and Bi River is 2735.00. Therefore, the Pb and Cd should be regarded as the key object in the risk decision-making management. Both have potential impact to the soil, water quality and crops.

Compare with Wang Lihong [23] draw a same conclusion by potential ecological risk assessment that Heavy metals such as Pb and Cd is high level in the ecological damage coefficient, a serious threat to river basin ecological security, the ecological and environmental governance is necessary. Zhao Xiaqing[24] use the single factor index evaluation and Nemerow composite index shows Bi river coast of farmland soil has different levels of pollution by Cd, Pb,Zn and As , which all sampling points of soil is severely polluted by Cd, most of the farmland soil is severely polluted by zinc. Zhou Hongbin [25], draw a same conclusion by soil magnetic susceptibility measurements show that most farmland soil in the basin is severely polluted by Cd and Zn, Pb pollution is mainly concentrated in the upper Bi River, the largest single pollution index is Cd. This is consistent with the heavy metal pollution in sediment.

5.2 Pay attention to the pH change on the influence of the combination state of heavy metals

Previous studies have found that except water soluble state and ion exchange state, carbonate of Pb, Zn, Cd combination state and humic acid state are also more active states, easy to transfer to water soluble state and ion exchange state [8]. Water soluble state and ion exchange state can directly enter into the filling loop, so you can put the four kinds of forms to a valid state for the environment. Heavy metal ions will have circulation in sediment and water by chemical and biological effect. The sediment will
be polluted again. They are more likely to be released under acid condition; especially the most sensitive to changes in pH carbonate combination state of metal elements. If PH of water and sediment in Bi River reduced, such as acid rain or acidic mining waste water discharge, ion exchange state and water soluble state of Pb, Cd, and Zn will increase a lot [9]. The heavy metal element content in the water will increase a large, which has huge potential harm on the Bi River basin.

5.3 For the further analysis we should focus on governance resume work

At present, as for the analysis and evaluation of Jinding mining area of heavy metal pollution, pollution to surrounding soil, water, sediment and agriculture caused by waste emissions have been analyzed. We suggested that in the future the analysis can be combined with Jinding mining area geological background and formation mechanism, further researching mining pollution; focus on how to do pollution restoration work. Suggestions should be taken from several aspects for Bi River’s heavy metal pollution in sediments. First, reduce or cut off the source of heavy metal pollution, control water quality, improve the environmental quality of sediment; Second, choose suitable pollution repair methods for Bi river basin, improve the stability of the heavy metals in sediment avoiding causing secondary pollution, and further transfer, absorb degrade and transform the heavy metal in sediments, making its concentration reduce to an acceptable level, or transform poisonous harmful heavy metals into harmless heavy metal compounds, refer to the successful cases at home and abroad, put forward appropriate repair plan according to the effect of governance and costs, hydrological features and pollution situation of Bi River.

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