Heavy Metal Contamination of Surface Water and Groundwater in and Around Gejiu Tin Mine, Southwest China

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Abstract

Heavy metal contamination due to mining activity is a global major concern because of its potential health risks to local inhabitants. The heavy metal contamination of surface water and ground water by mining activities in Gejiu tin-polymetallic mining area, Southwest China, was studied. Surface water and ground water were sampled and analyzed using AAS for Cr^{6+}, Cd, As, Hg, Cu, Pb, Zn, Se, Fe and Mn. Analysis of HCO_3^-, Cl^-, SO_4^{2-}, F^- and NO_3^- in water samples was also undertaken by ion chromatography. It was shown that none of water samples exceeded the guideline of Cr^{6+}, Se and Hg, while the contamination degree of heavy metals was Mn > Fe > Cd > Zn > Pb > As > Cu, all of which were serious contamination except mild contamination for Cu. The ground waters were polluted much worse than surface water.

Keywords: heavy metals, contamination, Gejiu tin mine, surface water, mine water

Introduction

As one of the largest and oldest tin district in the world, the Gejiu tin-polymetallic ore district (GTD) is located approximately several tens of kilometers southeast of Gejiu city, Yunnan Province, SW China. It has been mined for more than 2000 years since the Han dynasty (202 B.C. to 220 A.D.).

The study of the GTD mainly focus on deposit geology and fundamental geology formerly (Mao et al., 2008; Cheng et al., 2013), while mine environment, especially heavy metal pollution in soil, plants and water is noticed recently (Huang et al., 2014a; Huang et al., 2014b; Li et al., 2014a; Zhou, 2009l Li et al., 2014b; Qiao et al., 2014; Cai et al., 2014). However, the research of the mine water environment is still rare. In fact, carbonate strata are widespread in GTD with karst development, intensive stony desertification and shortage of water resources. Surface water and groundwater is polluted at the different levels under the influence of the intense mining, processing and smelting activities and so on.

The surface waters are sensitive to influence from mining and industrial sources which can result in the degradation of the water resources. The monitoring of the water quality, processing of data by advanced methods of statistical analysis and sophisticated wastewater and environmental management is the most effective way how to reduce adverse impact of human activities (Drozdova et al., 2014; Drozdova et al., 2015).

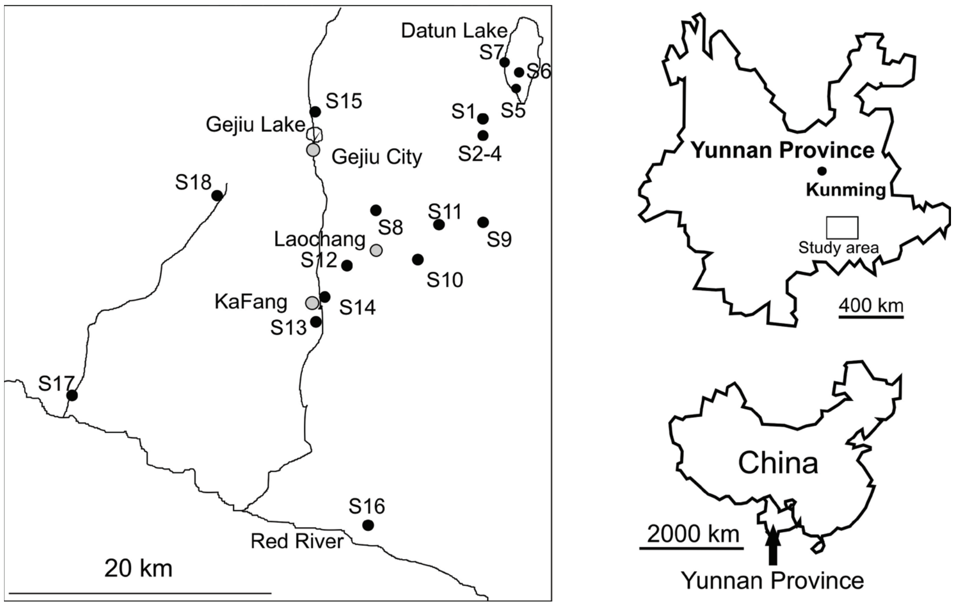

Fig. 1. Location of the collected samples

Rys. 1. Lokalizacja pobranych próbek

Study area

The study area is situated between latitudes 23°05′–23°30′ N and longitude 102°60–103°20′E. The GTD is located in the watershed between Nanpanjiang River (the upstream of the Pearl River) in the northward and Red River in the southward. The landform is karst fault block mountains at an elevation of 2000–2400 m. There are 9 streams flowing into Red River and 4 streams flowing into Lujiang River which is a tributary of Nanpanjiang River in the GTD. The streams are mainly seasonal and surface runoff is not developed. There are two lakes around the GTD, namely Datun Lake in the northeast and Gejiu Lake in the northwest.

In wide karst zones, underground runoff is developed. Precipitation and surface water can quickly change into underground runoff. The groundwater watershed is basically similar to the surface water watershed, but it was transferred to the south for 7–8 km gradually under the influence of mining. Mining area is located in the groundwater recharge area. Surface karst is exposed where placer tin ores were mined in recent years, so the surface water tend to carry a large amount of sediment and tailings flowing into adits, then mine environment is polluted and production is affected.

The GTD enjoys a plateau type subtropical monsoon climate bearing an unclear distinction between the four seasons. The mean annual temperature is 16.4°, averaging 10.1° in January and 20.5° in July. The rainy season is from May to October accounting for 80% of the total precipitation, and the dry season is from November to April of the next year. Precipitation varies with elevation, but the annual average is about 1399.02 mm in the watershed.

Gejiu tin-polymetallic ore district contains approximately 300 Mt of Sn ores at an average grade of 1% Sn, another 300 Mt of Cu ores averaging 2% Cu, and 400 Mt of Pb-Zn ores with an average grade of 7% Pb+Zn (Cheng et al., 2013). In addition, associated elements are enriched in large or middle deposits, such as Ag, W, S, As, Bi, Mo, Be, Au, and REE. The area of the GTD is about 1700 km^2, divided into East District and West District by Gejiu Fault. East District is the major area of mineralization and mining with 200 km2 and comprises five Sn-Cu-Pb-Zn polymetallic deposits, namely Malage, Songshujiao, Gaosong, Laochang and Kafang. The mineralization of West District is weak. Tin in skarns forms a significant part of the total Sn resource, and erosion of these primary deposits has produced rich alluvial concentrations, creating the basis for a historically important tin-mining industry (Chen et al., 1992).

Mining methods used in the GTD included underground and open-pit mining. According to the rough statistics, tin metal mined from GTD in the last 100 years has amounted to 103×10^4 t (from 1890 to 1949: 33.90×10^4 t; from 1949 to 2000: more than 70×10^4 t). To calculate the output of mining ores based on the highest grade (1.1%), it has added up to 100 million tons. The mining activities will have a huger impact on the environment if combined with effect of discarded low grade ores, gangue and tailings.

Tab. 1. Collected water samples physico-chemical data of GTD

Tab. 1. Dane fizykochemiczne pobranych próbek wody GTD

Sample no.	pH	SO_4^{2-} mg/L	F^- mg/L	NO_3^- mg/L	Cd mg/L	As mg/L	Cu mg/L	Pb mg/L	Zn mg/L	Fe mg/L	Mn mg/L
S5	8.25	68.525	1	7.9	0.0011	<0.001	0.003	<0.001	0.036	0.04	0.35
S6	8.22	90.115	1.1	3.82	<0.001	0.007	0.001	0.006	0.008	0.013	0.008
S7	7.67	134.395	1.9	4.509	<0.001	0.032	0.001	0.001	0.004	0.012	0.02
S8	7.59	744.76	7.69	10.594	0.008	<0.001	0.055	0.011	0.4	0.3	3.76
S11	8.27	68.71	0.51	0.81	<0.001	0.011	0.002	0.007	0.002	0.03	0.025
S12	8	425.5	1.23	0.52	<0.001	0.002	0.004	0.005	0.003	0.032	0.018
S15	8.2	84.57	0.48	8.29	<0.001	<0.001	0.003	0.004	<0.001	0.027	0.004
S16	8.13	130	3.3	5.78	<0.001	0.011	0.002	0.003	<0.001	0.015	0.022
S17	8.21	44.35	0.24	5.41	<0.001	<0.001	0.002	0.006	<0.001	0.034	0.005
S18	8.7	8.4	0.45	4.41	<0.001	<0.001	0.001	0.033	0.002	1.18	0.044
S1	8.8	60.06	0.64	8.17	0.001	<0.001	<0.001	0.002	<0.001	0.017	0.052
S2	4.22	935	35	21.26	0.063	<0.001	1.27	0.013	15.7	14.28	6.6
S3	8.26	62.35	0.052	7.64	0.001	<0.001	0.003	0.003	0.041	0.053	0.25
S4	8.25	8.961	0.09	4.11	<0.001	0.007	<0.001	0.002	0.001	0.013	<0.001
S9	6.35	994	13.28	31.294	0.095	<0.001	0.28	0.009	9.86	0.12	15.4
S10	3.37	636.9	5.1	2.52	0.102	<0.001	0.48	0.013	14.72	5.97	17.84
S13	8.8	361.9	2.4	9.32	<0.001	0.006	0.002	0.005	0.001	0.072	0.037
S14	7.47	572.4	3	0.38	0.001	0.03	0.018	0.007	0.001	0.88	1.4

Methods of investigation

Water samples were collected in and around the mine in the dry season according to surface water system, hydrogeological characteristics and pollution sources (Fig. 1). There are 10 samples for surface water (S5, S6, S7, S8, S11, S12, S15, S16, S17, S18) and 8 samples for mine water (S1, S2, S3, S4, S9, S10, S13, S14). Some mine water samples were collected from several adits drainages and abandoned adits seeps. On-site measurements included water pH, water temperature and turbidity. The source of water supplied by the waterworks is from adit clean drainage for several years.

Waters were analyzed for several elements including Cr^{6+}, Cd, As, Hg, Cu, Pb, Zn, Se, Fe and Mn in Ministry of Land and Mineral Resources Supervision and Test Center Kunming. Cr^{6+}, Cd, As, Cu, Pb, Zn, Se, Fe and Mn were analyzed by atomic absorption spectrophotometer (AAS, Shimadzu AA7000), and total Hg was was determined by F732-V mercury vapourmeter. The concentrations of HCO_3–, F–, NO_3– and SO_4– were measured by ion chromatography. Data were assessed for accuracy and precision using a quality control system integral to the analytical procedure.

Results and discussion

The results of physical and chemical analysis are given in the Table 1. Chemical data were compared with the Chinese standard for drinking water quality GB 5749-2006. Through analysis of data, it was discovered that the concentration of anions of SO_4^{2-} and F– in some samples are 2–4 times, 2–35 times, respectively higher than standard value for drinking water. Contents of Cd and Zn were 10–20 times higher than standard value, contents of Fe were 3–48 times higher and contents of Mn were up to 180 times higher than standard level for drinking water, in several samples. The concentrations of anions and heavy metals above standard level were discovered mostly in the samples collected from adits.

For assessment of water pollution, the single-factor pollution index (SPI) and comprehensive pollution index (CPI), proposed by Nemerow (1974), were used.

The SPI is an index of environmental quality of a pollutant and calculated by Ci/Si ratio. It was employed to obtain quantitative information of key pollution elements and excessive multiples. The mathematical expression is written as follows:

$$P_{ij} = C_{ij}/S_j$$

where P_{ij} is the pollution index of the heavy metal *j* in *i*-th sample. Cij is the measured contamination value of heavy metal *j* in the *i*-th sample,

Tab. 2. Descriptive statistics for physico-chemical characteristics [* DWQS – Limits for drinking water according to the Chinese standard GB 5749-2006.]

Tab. 2. Statystyki opisowe fizykochemicznych danych [*DWQS – limit dla wody pitnej według chińskiej normy GB 5749-2006]

Parameter	Unit	Max	Min	Mean	Median	St.Dev.	DWQS	SPI Range
pH		130	0	16.36	0.02	37.18	6.5～8.5	1.3-7.26
SO_4^{2-}	mg/L	44.35	0	7.28	0.14	12.72	250	2.23-3.74
F^-	mg/L	8.4	0	2.51	0.45	3.22	1	1.1-35
NO_3^-	mg/L	60.06	0	9.63	0.35	17.18	10	1.06-1.56
Cd	mg/L	935	0.01	103.29	10.17	267.57	0.005	12.6-20.4
As	mg/L	62.35	0	7.87	0.05	17.83	0.01	1.1-3.2
Cu	mg/L	8.96	0	2.68	0.05	3.4	1	1.27
Pb	mg/L	994	0.01	107.03	8.11	285.1	0.01	1.1-3.3
Zn	mg/L	636.9	0.01	68.69	4.19	182.64	1	9.86-15.7
Fe	mg/L	361.9	0	38.15	0.05	104.01	0.3	2.93-47.6
Mn	mg/L	572.4	0	53.2	0.38	164.92	0.1	2.5-178.4

Tab. 3. Assessment grade of the water samples

Tab. 3. Ocena próbek wody

Class	Scope	Water quality	Water samples
I	<1	Clean	S1, S4, S6, S7, S11, S15, S17
II	1—2	Relatively clean	S3, S12, S13
III	2—3	Mild contamination	S5, S16, S18
IV	3—5	Moderate contamination	0
V	>5	Serious contamination	S2, S8, S9, S10, S14

and S_j is the reference value of heavy metal *j*. The results of SPI are shown in the Table 2.

The CPI evaluation method gives the environmental quality index based on weighted multi-factors and not only the extreme values. The expression is written as follows:

$$Pi = \sqrt{(P^2_{ijmax} + P^2_{ijave})/2}$$

where P_i is the comprehensive pollution index of *i*-th functional area, P_{ijmax} is the reference value of a pollutant in the region, which are based on the thresholds of standards for drinking water quality (GB 5749-2006) specified by the Chinese criteria in this study.

The CPI is more reasonable to reflect the nature and degree of pollution of water environment, because it not only considers the single factor evaluation method for evaluation of pollution index of all kinds of pollutants, but also emphasizes the role of the maximum value with considering all kinds of pollutants content of the measured average and the ratio of the corresponding environmental standards set by pollutants.

Based on the SPI results, 13 factors were selected to assess the water quality including pH, SO_4^{2-}, F–, NO_3–, hardness, TDS (Total Dissolved Solids), Fe, Mn, Cd, As, Cu, Pb and Zn. The assessment results are shown in table 3.

It was shown that ten samples were clean or relatively clean. These samples were collected from rivers, lake, spring and new adit drainage. It is notable that water samples of S11 and S12 collected from tailings pond were clean and relatively clean respectively. The similar result was also shown in the research of Zhao et al. (2007).

One sample of surface water (S8) collected from tailing pond shows serious contamination. The serious contamination were determined for four samples of mine water, which were collected from abandoned adit seeps and 1800 adit drainage in Kafang and Laochang.

Conclusion

Both surface water and mining water collected from adits in Gejiu tin-polymetallic mines have been contaminated by mining activity. High concentrations of heavy metal exceeded the guideline of Chinese standards for drinking water quality with maximum values of 0.032, 0.102, 0.033, 15.7, 14.28 and 17.84 mg/L of As, Cd, Pb, Zn, Fe and Mn, respectively. One sample of ground water has mild contamination by Cu. None of water samples exceeded the guideline of Cr^{6+}, Se and Hg. In addition, mild contamination included TDS and NO_3–, moderate contamination included hardness, and serious contamination included SO_4^{2-} , F+ and pH.

The above analysis uses single-factor pollution index and comprehensive pollution index to study the environmental risk of anions and heavy metals in the surface and mining waters. The data from SPI shows that quality grade for several individual samples for pH, two anion groups (SO_4^{2-}, F–) and six heavy metals (As, Cd, Pb, Zn, Fe and Mn) are heavy polluted. Heavy pollution grade for samples from five areas, and slight pollution grade for samples from three areas, was calculated using CPI.

The all factors show that surface water is significantly affected only by F–. On the other side, the mining waters are besides anion contamination, polluted significantly by heavy metals.

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Zanieczyszczenie wód powierzchniowych i podziemnych metalami ciężkimi w kopalni Gejiu Tin, południowo-zachodnie Chiny i jej okolicach

Zanieczyszczenie metalami ciężkimi spowodowane działalnością kopalń jest światowym problemem z powodu ryzyka utraty zdrowia przez okolicznych mieszkańców. Zbadano zanieczyszczenie wód powierzchniowych oraz wód podziemnych wywołane działalnością kopalni cyny w rejonie górniczym Gejiu, południowo-zachodnie Chiny. Pobrano próbki wody powierzchniowej oraz podziemnej i zanalizowano je ze względu na obecność Cd, As, Hg, Cu, Pb, Zn, Se, Fe oraz Mn. Analizy HCO_3^-, Cl^-, SO_4^{2-}, F^- oraz NO_3^- w próbkach wody również zostały przeprowadzone za pomocą chromatografii jonowej. Ukazano, że żadna z badanych wód nie przekroczyła dopuszczalnych poziomów dla Cr^{6+}, Se oraz Hg. Jednakże poziom zanieczyszczenia metali ciężkimi tj. Mn > Fe > Cd > Zn > Pb > As > Cu był wysoki, za wyjątkiem niewielkiego przekroczenia norm dla Cu. Wody podziemne były znacznie bardziej zanieczyszczone niż wody powierzchniowe.

Słowa klucze: metale ciężkie, zanieczyszczenie, kopalnia cyny Gejiu, wody powierzchniowe, wody kopalniane