Original Research Paper

Mercury Contamination from Historic Gold Mining to Water Bodies and Soils in Zhaoyuan, Shandong, Eastern China

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ABSTRACT

To clarify the pollution status of mercury (Hg) in water bodies and soils from an old gold mining in China, we collected and analysed water samples in April 2010. The concentration of total Hg (THg) in water ranges from 0.032 to 0.225 µg/L, with average concentration as 0.078 µg/L. Among Hg species, particulate Hg (PHg) ranges from 0.021 to 0.106 µg/L, and the percentage of PHg exceeded 50 percent in most samples. Hg concentration in water is considerably lower than polluted areas by gold mining with amalgamation and Hg mining, close to the concentrations in high Hg background areas in China, but obviously higher than natural waters. THg in sediments ranges from 0.456 to 5.712 mg/kg, with a positive correlation to Hg of waters. THg of sediments in rivers shows a higher concentration than that in reservoirs. Soil Hg concentration ranges from 0.094 to 4.04 mg/kg, with geometric mean 0.36 mg/kg. Fifty percent of soil samples exceed Chinese Soil Reference (Grade II). The calculation results of the geoaccumulation index present a higher accumulation status of Hg in soils in this area. Furthermore, a strong ecological risk is found due to Hg accumulation in soils, according to the classification of assessment index of potential ecological risk levels. Results indicate that Zhaoyuan shows a certain degree of mercury pollution due to gold mining activities.

INTRODUCTION

Mercury (Hg) and its compounds, as the poisonous global pollutants, are an issue of international concern (Sather et al. 2014). The early greater event in mercury poisoning to public health appeared in Japan in 1953, and since then it has been reported in other countries. Elemental, inorganic, and organic mercury, which are mainly in the form of methyl mercury (MeHg), harm the environment and human health. A recent breakthrough in toxicology research on Hg and MeHg indicated that the population considered safe for Hg exposure before, would become the subgroup in danger of health risks from Hg exposure. Due to bioaccumulation and methylation in aquatic ecosystems, Hg pollution in water environments is one of the concerns of environmental science (Linqvist et al. 1991, Heyes et al. 2000). Specia-tion transformation of Hg in water is frequently influenced by environmental condition, which accordingly affects the methylation and toxicity in aquatic ecosystem. Hg in soil may result in the risk of human health by transfer in the food chain.

The use of mercury amalgamation for the extraction of gold from ore materials is widely utilized by non-organized prospectors in many tropical countries, including Bolivia, Brazil, Colombia, Indonesia, Peru, the Philippines, Venezuela and Vietnam. The data reported from those research works have shown a serious environmental Hg contamination in these districts. Furthermore, Hg released from gold mining activities was commonly held responsible for the Hg contamination in air, water and soil (Pfeiffer & de Lacerda 1988, Lyons et al. 1998, Domagalski 2001). Zhaoyuan, a city in Shandong Province, called "golden capital", is famous for gold production in China. Furthermore, Linglong town in Zhaoyuan possesses a long history with thousand years in gold mining and smelting. Although the gold extraction by Au-Hg amalgamation has been annulled in 1960's, the reverse effects of Hg pollution caused by mining activities, may be existing for a long time.

However, there is little information about Hg pollution in old gold mining areas so far. The present paper studies Hg contamination in water bodies and soils in the gold mining area in Zhaoyuan, to understand if historical gold mining activities resulted in any pollution to the environment in this historic gold mining area. It could provide a scientific basis for the prevention and control of Hg pollution and risk assessment of human health.

MATERIALS AND METHODS

Study area: Zhaoyuan city is located in 120°08'-120°38'E

and 37°05'-37°33'N. The study area, Linglong town, located in the northeastern Zhaoyuan city is one of the oldest gold mining areas in China. The mining activities have persisted for one thousand years, since Song Dynasty. In 1078, gold production in Zhaoyuan and the surrounding area accounted for 89% of total production in China. The area has typical temperate and monsoonal climate and four clearly distinct seasons, with average annual temperature 12.0-12.6°C and 650-850 mm of average annual precipitation. Loam is the major soil type, suitable for planting agriculture. Luoshan River originates from Luoshan Mountain, which is located in the north of Linglong, flowing through the mining area from north to south. In addition, there are several small reservoirs in this gold mining area.

Sampling procedures: Sampling procedures were conducted in April 2010. Water samples were collected from surface waters in Linglong mine, meanwhile sediments were also collected. Site 1-6 are samples from reservoirs. Site 7, 8, 9 and 10 are from upstream, middle, downstream, and junction with other rivers of Luoshan River, respectively. Site 11 is located in drainage of a current gold extraction spot and site 12 is from a pond of an old gold extraction spot.

Water samples were collected with polytetrafluoroethylene bottles, filtered and stored with borosilicate glass vessels. They were all undergone ultraclean procedure before using (Yan et al. 2003). Samples for total Hg determination was stored with 500 mL bottles, filled with purified nitric acid. 1000 mL water was filtered on-site by 0.45 μm nylon filter membrane, then 500 mL was subsampled into bottles for determining dissolved Hg. At the beginning of each filter operation, the containing device was rinsed three times with the filtrate itself. The used filter was collected in a pre-cleaned polyethylene bag for particulate Hg analysis. The folded filter membranes were put into polyethylene valve bag, and stored in freezer for particulate Hg analysis. Water samples were kept in refrigerator at 4°C and determined in two weeks.

We collected 46 topsoil samples from agricultural fields. In each spot, 6-10 subsamples were collected and mixed to one soil sample. Soil samples were air-dried, ground and sieved through 2 mm mesh for determining physical and chemical properties. The plastic or wooden tools were used in the sampling process to avoid pollution of metals. Sediment and soil samples were ground and passed through a 0.149 mm nylon sieve for analysis of total Hg concentration.

Sample treatments and determination: Mercury measured in the sediments, soil and waters was based on the procedure of cold-vapour atomic absorption spectrophotometry (CVAAS) techniques. Unacidified filtered sub-samples of 250 mL were analysed for reactive Hg. Hg as the fraction, that is reduced and therefore volatilized from solution after the addition of 0.5 mL of 10% $SnCl_2$ solution in 2.6 M HCl. The samples for total Hg and dissolved Hg were oxidated by the addition of BrCl solution for twenty-four hours, followed by addition of $NH_2OH \cdot HCl$ as reductant, and Hg^{2+} was reduced to Hg by $SnCl_2$ (Yan et al. 2003). Filters with particles were digested by adding 5 mL mixture of acids (HCl: HNO_3=3: 1) to determine particulate Hg. Hg concentrations in waters were determined by JLBG-230 Hg detector.

Sediment and soil samples were digested using the method of H_2SO_4-HNO_3-V_2O_5 described by Liu et al. (2003). Hg concentration in sediments was determined using F732-V Hg detector. Certified standard soil samples GBW07401 (GSS-1) was used to ensure precision of the measurement. The recovery of the method was in the range of 87.9%-107.2%. Statistical analysis of the data was finished by using the SPSS software package (SPSS 17.0).

RESULTS AND DISCUSSION

Mercury concentration and speciation in waters: The total Hg concentrations measured in unfiltered surface waters of Linglong gold mine varied from 0.032 to 0.225 μg/L and averaged 0.078 μg/L (Fig. 1). According to the "China Environmental Quality Standards for Surface Water" (GB 3838-2002), all samples conformed to the quality standard for grade IV (1 μg/L), and two samples exceeded the quality standard for grade III (0.1μg/L). However, Hg concentrations in these mine waters typically exceeded the 0.012 μg/L concentration, that the USEPA indicates may result in chronic effects to aquatic life (US Environmental Protection Agency 1992). Of all sites from reservoirs, total Hg concentration showed higher values in site 6 compared to the other sites. It may attribute to the position of this spot, located in the southeastern of the mining area. There was higher opportunity to accept more Hg of atmospheric precipitation under the dominant wind direction.

Total Hg concentrations were found higher in Luoshan River than reservoirs, however, concentrations among river sites showed a limited variation, which may result from the short length and mixture of the streams of this river. The highest Hg concentration was found in site 12, in which was a history of more than 30 years in gold extraction.

A comparison between total Hg concentration in Linglong mine and other areas is given in Table 1. Hg concentration in the waters in Linglong is considerably lower than some polluted areas by gold mining with amalgamation and Hg mining, such as Tongguan, Shanxi Province and Wanshan, Guizhou Province. It indicated that the annulment of gold extraction by Au-Hg amalgamation in 1960's, reduced effectively the Hg contamination in this area.

Table 1: Comparison of total mercury concentrations in waters of Linglong with other areas.

Regions		Range	Average
Polluted areas	Gold mine, Tongguan, Shanxi Province, China (Dai et al. 2004)	0.24-258.6	209.9
	Sulpher Bank, USA (Kim et al. 2004)	0.005-0.7	-[a]
High Hg background areas	Wujiang River, China (Jiang et al. 2004)	0.001-0.329	0.066
	Baihua Lake, China (Hou et al. 2004)	0.023-0.336	0.075
Natural waters	Belgian coast, Belgium Leermarkers et al. 2001)	0.0001-0.016	-
Linglong, Shandong Province, China		0.032-0.225	0.078

a. "-" denotes no data

Table 2: Physical and chemical properties of soil samples in the study area.

Properties		Range mean	Arithmetic mean	Geometric	Median	SD	CV
pH		4.50-7.68	6.19	6.13	5.93	0.89	0.15
CEC (cmol/kg)		1.22-20.88	14.40	13.64	14.52	3.46	0.24
Organic matter (%)		0.52-4.78	2.42	2.21	2.20	1.01	0.42
Particle distribution (%)	1-0.02 mm	47.02-86.18	70.43	68.26	71.14	8.23	0.12
	0.02-0.002 mm	2.13-24.36	10.22	11.28	10.93	4.53	0.44
	<0.002 mm	6.99-38.25	19.35	18.26	18.77	5.43	0.28

Table 1 shows that Hg concentration in the waters in present study is close to that in Wujiang River and Baihua Lake in Guizhou province, which are the high Hg background areas in China. However, an obvious elevation is observed when compared with natural waters (Table 1). It indicates that Linglong mine has suffered from Hg pollution to a certain extent due to the long period of gold mining activities.

Hg speciation data showed that the average value of the particulate Hg concentration was 0.043 µg/L, varying from 0.021 to 0.106 µg/L (Fig. 2).

In contrast to reservoirs, samples of river showed higher particulate Hg concentrations. The highest concentration was still found in site 12, which may be caused by frequent flow turbulence to sediments. Dissolved Hg concentrations varied from 0.011 to 0.119 µg/L, with an average concentration 0.035 µg/L, slightly lower than particulate Hg. Reactive Hg concentrations were the lowest, varying from 0.0009 to 0.0025µg/L.

In freshwaters, the distribution of mercury and methyl mercury is primarily influenced by adsorption and desorption of Hg in particles, and controlled by the oxidation reduction status of water-sediment interface. Therefore, suspended particles in freshwater systems play a key role in the migration of methyl mercury (Leermakers et al. 2001, Mason & Sullivan 1998). Of all species, particulate Hg showed a higher proportion, with average 58.6%, particularly 83% in river water. These data suggest that most of the mercury in waters from the mines is as suspended material (Gray 2000).

Reactive Hg includes mostly ionic (Hg^{2+}) and dissolved gaseous Hg (DGM), but also the Hg fraction weakly bound to inorganic and organic dissolved complexes. As the previous study (Lacerda & Goncalves 2001) reactive Hg concentrations showed the minimum proportion, ranging from 0.6 % to 6.3% of total Hg, and from 8.2% to 18.2% of dissolved Hg, respectively. This indicates that over 80% of the total dissolved Hg in these waters is strongly bound to refractory organic colloids. Correlation analysis shows the significant positive correlation between particulate Hg and total Hg concentration (r=0.867, p<0.01) (Fig. 3). It suggests that the source of Hg in waters was the suspended materials brought by atmospheric precipitation or (and) sediment disturbance. This conclusion coincides with previous studies (Jiang et al. 2004, Leermakers et al. 2001).

Mercury in sediments: Total Hg concentrations in the surface sediments ranged from 0.456 to 5.712 mg/kg, with an average of 1.575 mg/kg (Fig. 4). The values significantly exceeded the soil Hg background concentration (0.049 mg/kg) in this area (China Environmental Monitoring Station 1990). It indicates that many years of smelting and mining have resulted in a more serious Hg accumulation in environment. The Hg concentration in river sediments was found significantly higher than reservoirs, which attributed to the acceptance of more pollutants in river. In the present study area, the source of river sediments mainly included tailings of gold mining and materials brought by industrial discharges. The formation of reservoir sediments is more complicated, dealing with tailings, atmospheric precipitations,
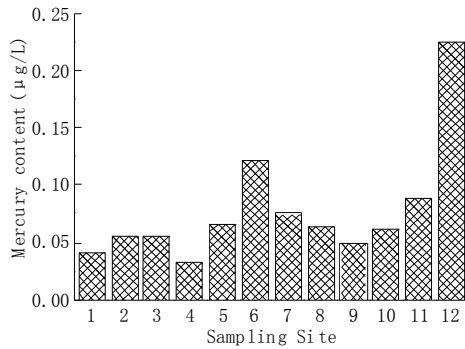
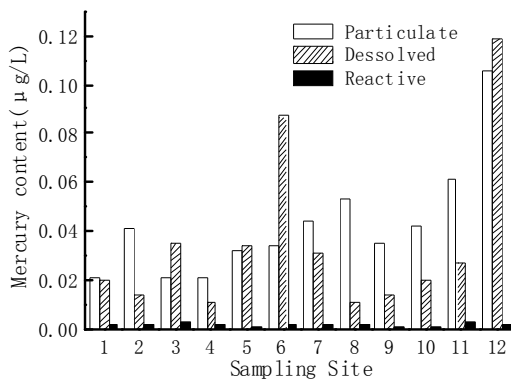Fig. 1: Total Hg concentrations of waters in gold mining area.

Fig. 2: Mercury species in waters in Linglong gold mining area.
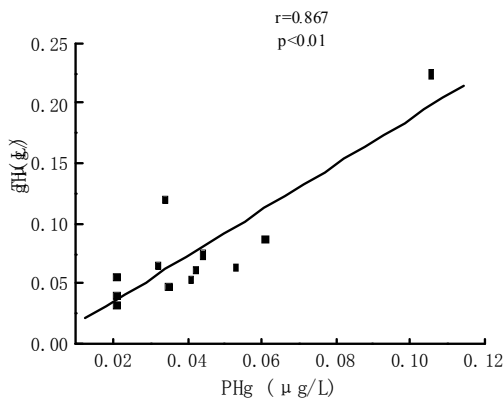

Fig. 3: Relationship between THg and PHg in water bodies.

materials of soil erosion and so on. Moreover, the existence time of reservoirs also varied, resulting in difficulty in explaining the source of sediment Hg.

Remarkably, the total Hg concentrations in Luoshan river increased first, and then decreased from upstream to downstream, due to accepting wastewater in middle and dilution of tributary downstream.

Generally speaking, Hg in sediments is the source and

sink of Hg in waters. Correlation analysis showed that Hg concentration of sediments was positively correlated to Hg of waters ($r^2=0.39$, $p=0.03$) (Fig. 5). It indicated the close relationship between Hg in sediment and water, further accounting for that the changing Hg content of water decided by the exchange between sediment and water.

Mercury in soils: Soil heavy metal pollution has adverse effects on the function of the soil ecosystem, accordingly threats the quality of agricultural products and human health. The elusiveness and toxicity of heavy metal pollutant in soil makes it a focus in the current research field of environmental science (Zhang et al. 2008, Clemente et al. 2003). The main soil type in the research area is brown soil and its physical and chemical properties are listed in Table 2. The pH values of the soil were neutral or slightly acidic, and the average pH was 6.19. The range of cation exchange capacity (CEC) varied from 1.22 to 20.88 cmol/kg, and the average CEC was 14.40 cmol/kg. Due to different geographical locations of sampling points as well as the impact from tailing stocking, the content of organic matters in soil changed greatly. The variable coefficient was 0.42. The research area was located at the sloping fields down the hill. The soil texture of the hilly areas was comparatively coarse. Besides, the content of sand particles took up a comparatively large proportion, with an average proportion of 70.43%. Overall, the soil quality of the research area was suitable for agricultural uses.

In Linglong mine, the skewed distribution of Hg concentrations in soils was observed. After the logarithmic conversion, it was in line with normal distribution (Fig. 6). Hg contents presented great dispersion, and the range was 0.094-4.04 mg/kg. The geometric mean of Hg was 0.36 mg/kg. Compared with background value in this area (China Environmental Monitoring Station 1990), Hg content of all sample points exceeded the background value. Compared with Chinese Soil Reference (Grade II), the exceeding rate was 50.0%, indicating that the gold mining and smelting have caused serious Hg pollution in the local farmland soil, which might increase the health risks of edible agricultural products for people.

Tailing stocking, leaching and dispersion of pollutants, waste water, dust spreading of exhaust gas emissions will influence the content and distribution of heavy metal pollutant. The soil nature, not only affects the bioavailability of heavy metal pollutants, but also determines the accumulation of metals in soil to a certain extent. Our research carried out the analysis of correlation between THg content and physical and chemical properties of soil at different sample points. No significant correlation was found between Hg concentrations and soil properties such as pH, OM, CEC and
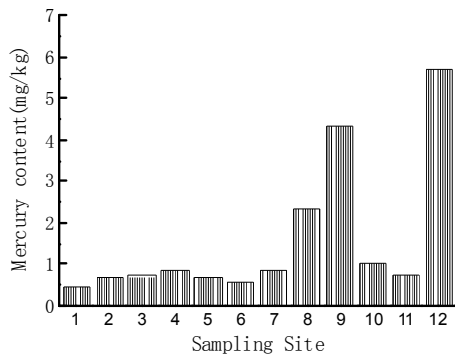
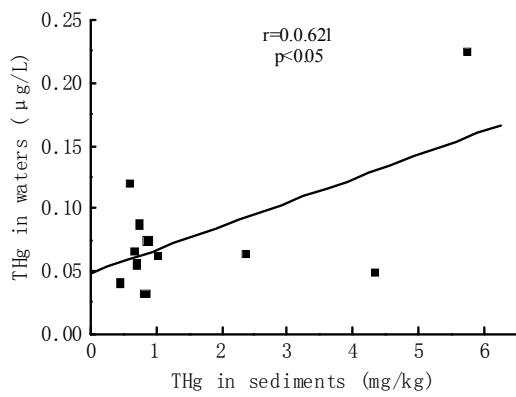Fig. 4: THg of sediments in gold mining area.

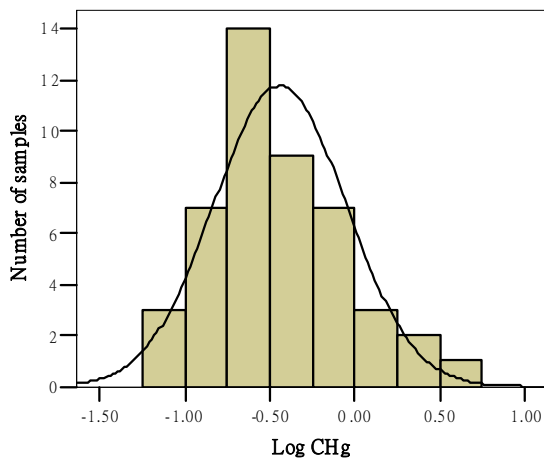r=0.0.621
p<0.05

Fig. 5: Relationship between THg in waters and sediments.

Fig. 6: Frequency distribution of soil Log C_{Hg} in study area.

Table 3: Distribution and classification of geoaccumulation index of Hg in soils samples.

Grade	Pollution level	Geoaccumulation index (I_{geo})	Number of samples
0	No pollution	≤ 0	0
1	Light	0~1	7
2	Medium	>1~2	9
3	Median-severe	>2~3	16
4	Severe	>3~4	8
5	Severe-extreme	>4~5	4
6	Extreme	>5	2

Table 4: The classification of assessment index of potential ecological risk levels.

Level of risk	A	B	C	D	E
E_r^i	≤ 40	40-80	80-160	160-320	>320
Degree of ecological risk	Slight	Medium	Strong	Severe	Extremely severe

of Hg in soil in the study area, the background values of elements in brown soil area of Shandong Province were referred to calculate the geoaccumulation index (I_{geo}). The calculation results are depicted in Table 3. The geoaccumulation indexes of Hg were mainly distributed in areas with at least medium pollution, which accounted for 84.8% of all sample points. The indexes in areas above severe pollution still accounted for 30.4%, which indicated extremely serious Hg pollution in soil.

Previous studies have shown that in the alchemical process of amalgamation, for every 1 g of gold produced, 1.2-1.5 g of mercury was discharged into the environment. The mercury in the tailings accumulated on the ground surface via processes like leaching, percolation, volatilization and deposition. The mercury may exist for thousands of years, leading to horrible mercury pollution of soil, sediments and water in the gold field (van Straaten 2000, Appleton 1999). In 1996, China quit the practice of amalgam treatment for gold metallurgy. However, the previous gold metallurgy based on indigenous methods has released a certain amount of mercury into the environment, which may exist for a long term. This has produced serious mercury pollution in gold fields.

Potential ecological risk index method was established by Hakanson using principles of sedimentology to evaluate heavy metal pollution and potential ecological risks (Hakanson 1980). This method reflects the impact of different pollutants in a certain circumstance, quantitatively identifying the degree of potential ecological risks of heavy metals, and is considered as the most widely used method to evaluate the potential ecological risks of heavy metal pol-

particle distribution.

Geoaccumulation index method was proposed by Muller (Muller 1969). This method reflects the intuitive pollution level of heavy metal pollutants as well as the accumulation degree of heavy metal pollutants in soils/sediments. Currently, it is widely used in the research field of evaluating heavy metal pollution in soil. To evaluate the accumulation

lutants. The classification criteria of ecological risk index and ecological risk index of metal pollution are shown in Table 4. We calculated the potential ecological risk index (E_r^i) of Hg. The results present that the range of E_r^i of Hg is from 83.2 to 3847.4, and the average was 344.3, showing strong ecological risks, according to the classification of assessment index of potential ecological risk levels.

CONCLUSIONS

In Linglong gold mining area, Shandong province, China, total Hg concentrations of waters ranged from 0.032 to 0.225 µg/L. Of all species of Hg, particulate Hg showed a higher proportion, and reactive Hg was the lowest. A positive correlation was found between total Hg and particulate Hg ($p<0.01$). Compared with other areas, Hg concentrations of waters in Linglong were considerably lower than polluted areas, but obviously higher than natural waters.

The Hg concentrations of sediments varied from 0.456 to 5.712 mg/kg, with a positive correlation to Hg of waters. Hg contents of the sediments in rivers were higher than that in reservoirs. Soil Hg concentrations range from 0.094 to 4.04 mg/kg and 50 percent of soil samples exceed Chinese Soil Reference (Grade II). Hg in soils shows an obvious accumulation status and strong ecological risks.

Results indicate that gold mining activities have resulted in Hg pollution in Linglong mine and more attention should be given to it.

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