



Mercury concentration and speciation in mine wastes in Tongren mercury mining area, southwest China and environmental effects

Junyao Yan^{a,b}, Chuan Wang^{a,b}, Zhiheng Wang^c, Shaochen Yang^c, Ping Li^{a,d,*}

^a State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, China

^b University of Chinese Academy of Sciences, Beijing, 100049, China

^c School of Earth Sciences, China University of Geosciences (Wuhan), Wuhan, 430074, China

^d CAS Center for Excellence in Quaternary Science and Global Change, Xi'an, 710061, China

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ABSTRACT

Mercury mines cause mercury (Hg) contamination to local environment, because mine wastes are not properly disposed during long-term large scale Hg mining activities. This study investigated Hg concentration and speciation in mine wastes collected from Tongren Hg mining area, and evaluated the impact of Hg mines subjected to different remediation measures on the surrounding environment. Total Hg (THg) concentrations in the mine wastes varied from 4.15 to 825 mg/kg, and Hg⁰ was the dominant form of Hg in the mine wastes. No obvious deformation was observed in the mineral boundaries by TEM analysis, which indicated that the smelting process was incomplete. Nanometer-scale Hg compounds were observed in the mine wastes using EDS microtopography analysis, which may pose risks for the local environment. The average concentration of total soluble Hg (TSHg) in mine waste leachates was 11.27 µg/L. The THg concentrations in surrounding surface waters varied from 0.038 to 10.6 µg/L, and THg concentrations in 21.1% of samples exceeded level V of the national standards (1 µg/L). There was a significant negative correlation between THg concentration and pH in the surface water, indicating that Hg was more mobile under acidic conditions. The total gaseous mercury (TGM) concentration above the mine waste piles varied from 13.5 to 309 ng/m³; these values are significantly lower than those recorded in previous studies. These data demonstrate that restoration and proper treatment are required for the mine waste.

1. Introduction

Mercury (Hg) and its compounds are highly toxic pollutants that can cause severe damage to human health. The toxicity of Hg is related to its chemical form. Methyl-mercury (MeHg) is the most toxic Hg compound; it has high neurotoxicity, carcinogenicity, cardiovascular toxicity, reproductive toxicity, immune system effects, and renal toxicity (Zhang et al., 2010b). Methylation can be a consequence of the activity of anaerobic microorganisms, and occurs mainly in aquatic ecosystems. The general population is primarily exposed to inorganic Hg in amalgam dental fillings, and to MeHg through consumption of contaminated aquatic products and rice (Mergler et al., 2014). The consumption of Hg-contaminated aquatic products by pregnant women may affect the IQ of newborns, and its consumption may cause an increased rate of mortality and morbidity associated with heart attacks in the non-pregnant population (Zhang et al., 2018). Workers at Hg smelters are exposed to Hg vapor through inhalation, which causes

serious damage to their renal systems (Li et al., 2008). Moreover, Hg can exist in a gaseous form at room temperature and has a long residence time in the atmosphere (0.5–1.5 years). Therefore, gaseous elemental Hg (GEM) can undergo long range transport and has been found in remote areas, including the polar regions (Aspmo et al., 2006; Driscoll et al., 2013).

China has abundant Hg resources. The Guizhou Province was a major Hg production area in China, with the highest reserves and production in the country. The Wanshan and Tongren Hg mines were the biggest Hg mines in China. Operation of the Tongren mine ceased in the 2000s because the Hg resource was exhausted and because of environmental concerns. Mercury processing in retorts is generally conducted at 600°C–700°C. At these temperatures, cinnabar (HgS) is converted into Hg vapor (Hg⁰), which is then condensed to obtain liquid Hg (Li et al., 2013). If smelting is incomplete then Hg is retained in the mine waste. Large amounts of solid mine wastes were discarded close to the mine pit without proper treatment (Qiu et al., 2005).

* Corresponding author. State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, China.
E-mail address: liping@mail.gyig.ac.cn (P. Li).

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Environmental Hg pollution caused by Hg mining has been investigated in the Wanshan and Bijiang counties. Mercury levels have been analyzed in mine waste calcines (Qiu et al., 2005), water (Zhang et al., 2010a, 2010b), riparian soils (Qiu et al., 2005; Yin et al., 2016), and ambient air (Dai et al., 2012). Large-scale Hg mining activities caused serious Hg pollution in the local environment and Hg-enrichment in agricultural crops (Horvat et al., 2003). The THg concentrations in rice and other crops in the area surrounding the Wanshan Hg mine varied from 10.3 to 1160 $\mu\text{g}/\text{kg}$, and most exceeded the National Permitted Limit of 20 $\mu\text{g}/\text{kg}$ for foods in China (Qiu et al., 2008). Rice can bioaccumulate MeHg, and it has been confirmed that rice consumption is the main pathway for MeHg exposure in the Hg mining areas of Guizhou Province, and for some inland areas of South China (Zhang et al., 2010).

Increasing attention has been paid to environmental protection and environmental health issues in China as the economy has developed. The 10-Chapter Soil Pollution Action Plan, China's third national action plan to curb pollution, provides strategies that tackle air and water pollution. Soil deterioration has been targeted as part of the objectives, which are to improve the prevention and control of pollution in China. Tongren City was listed as an area suitable for the development of comprehensive soil pollution prevention and control strategies, and a range of remediation measures was undertaken to reduce Hg emission at source, and to minimize Hg exposure risks. The aims of this study were to investigate the concentration of Hg in mine waste, surrounding water, and the atmosphere, at different mine waste piles, and to evaluate the efficacy of the remediation measures. The results provide theoretical support for cost-effective restoration measures, which will ultimately reduce Hg emissions to the surrounding environment and mitigate the health risks posed to local residents.

2. Materials and methods

2.1. Study area

The Tongren area is located within the karst landscape of the Yunnan-Guizhou Plateau. The Wanshan and Bijiang counties are typical mountainous karst regions with elevations from 205 to 1150 m above sea level (asl). The climate in the study areas is sub-tropical and humid, with an annual average temperature of 13.5°C–17.6°C and an average annual precipitation of 1110–1410 mm. The Tongren Hg mine is located in Bijiang County, and the Wanshan Hg mine is located in Wanshan County (Fig. 1). Mineralization at the Tongren and Wanshan Hg mines is primarily associated with thin-layered, laminated, fine-grained, dolomite or limestone beds of mid-Cambrian age. The wall rocks are intensively altered by silicification, dolomitization, calcification, and subordinate bituminization and pyritization (Hua and Cui, 1994). The primary ore mineral in the Hg deposits is cinnabar, with lesser metacinnabar.

The study area contains 14 mine waste piles, nine of which were selected for sampling in this study. The locations of the sampling sites are shown in Fig. 1 and detailed information about the mine waste piles is provided in Table 1. Large-scale Hg mining activities ceased in 2001. Mine wastes were stacked randomly, and most of the waste piles have been remediated in various ways. For example, curing agents were used to solidify and stabilize the mercury-contained mine wastes at the Meizixi (MZX) mine waste pile, which was then covered with soil and revegetated. However, some mine waste piles, such as the Pangxiexi (PXX) pile, are still untreated and the mine waste is exposed to rain-water and sunshine.

2.2. Sample collection

Sampling was conducted in July 2017, which was a dry period with daytime temperatures up to 35°C. A total of 22 mine waste samples were collected from nine waste piles. Each sample was composed of 3–5

sub-samples collected from different locations within a 1 m² area. The depth of sampling was about 10 cm; this depth was chosen to avoid surface oxidization (Gray et al., 2006). The mine waste samples were preserved in clean polyethylene zip-lock bags. Prior to analysis, the mine waste was air-dried, ground using a grinding machine, and passed through a minus 100-mesh sieve. Unfiltered and filtered surface water samples were collected from the rivers for THg and dissolved Hg (DHg) analysis, respectively. Nineteen water samples were collected. The water samples were preserved in centrifuge tubes, acidified with ultrapure hydrochloric acid, and sealed and packaged in double-layer bags, after which they were returned to the laboratory and stored in a refrigerator at 4 °C and protected from the light. The THg and DHg analyses were completed within 28 days. Total gaseous Hg (TGM) concentrations were measured at 52 sites with a portable RA-915 + Zeeman Hg Analyzer (Lumex, Russia) (Sholupov et al., 2004). This instrument displays the instantaneous TGM concentration at 1 s intervals; each reported data point represents the average of at least 5 min of monitoring at the site.

2.3. Analytical methods

The 22 mine waste samples were subjected to analysis for THg concentration and Hg speciation, and leaching experiments. For THg analysis, the mine waste samples were digested with a fresh mixture of HNO₃ and HCl (v:v 1:3) in a 95 °C water bath for 2 h. Then, BrCl was added and the sample was kept for 24 h to convert all forms of Hg into Hg²⁺, since HgS can also be extracted with aqua regia. An appropriate aliquot of the digested solution was then analyzed for THg using cold vapor atomic absorption spectroscopy (CVAAS, F732-S). Acidic SnCl₂ was added to the solution to reduce the Hg ions to Hg⁰ for detection. For Hg²⁺ measurement, the mine wastes were agitated at a ratio of 10:1 with 1N HCl for 18 h at room temperature, this technique liberates most Hg not bound in HgS or present as Hg⁰ (Gray et al., 2006; Bloom and Fitzgerald, 1988). The concentration of Hg⁰ was determined by a pyrolysis technique described by Biester and Scholz (1997) (Hua and Cui, 1994). Concentrations of Hg⁰ were calculated from the difference between the THg concentration obtained from mine wastes before and after heating at 180 °C for 18 h (Garcia-Sanchez et al., 2009; Wang et al., 2011). The concentrations of other Hg species in the mine waste were obtained by subtracting the Hg²⁺ and Hg⁰ concentrations from the THg concentration.

Leaching experiments were performed by shaking and rotating 2 g of mine waste with 20 mL of dilute mixed acids for 20 h in 50 mL centrifuge tubes (Li et al., 2013). The dilute mixed acid was prepared by adding 2–3 drops of mixed acid (H₂SO₄:HNO₃ = 2:1) to 1 L ultrapure water. The samples were centrifuged (7 min, 3000 RPM) and filtered through a 0.45 μm filter, after which the upper leachate was collected for measurement of the THg concentrations. The pH in the leachates was measured using a pH electrode.

Two mine waste samples with relatively high THg concentrations were selected for microscopic morphology analysis to determine the shape of Hg particles in the mine wastes. The morphology of microscopic particles in the mine waste was determined by transmission electron microscopy (TEM: Tecnai G2 F20 S-TWIN TMP) using a 200 kV field emission transmission electron microscope. This instrument is equipped with scanning and transmission analytical electron microscopy (STEM), and can collect TEM bright field and dark field images, as well as high-resolution images. Moreover, it can perform selected area electron diffraction, convergent beam diffraction, Energy Dispersive X-Ray Fluorescence Spectrometer (EDX) spectrum analysis, and high-resolution STEM atomic number analysis. Image analysis and STEM, combined with EDX point, line, and surface scans, were conducted to produce the micro-area energy spectrum analyses. The shapes, sizes, and structures of the particles were obtained using the TEM images and bright field images.

To measure THg concentrations in surface water samples, BrCl was

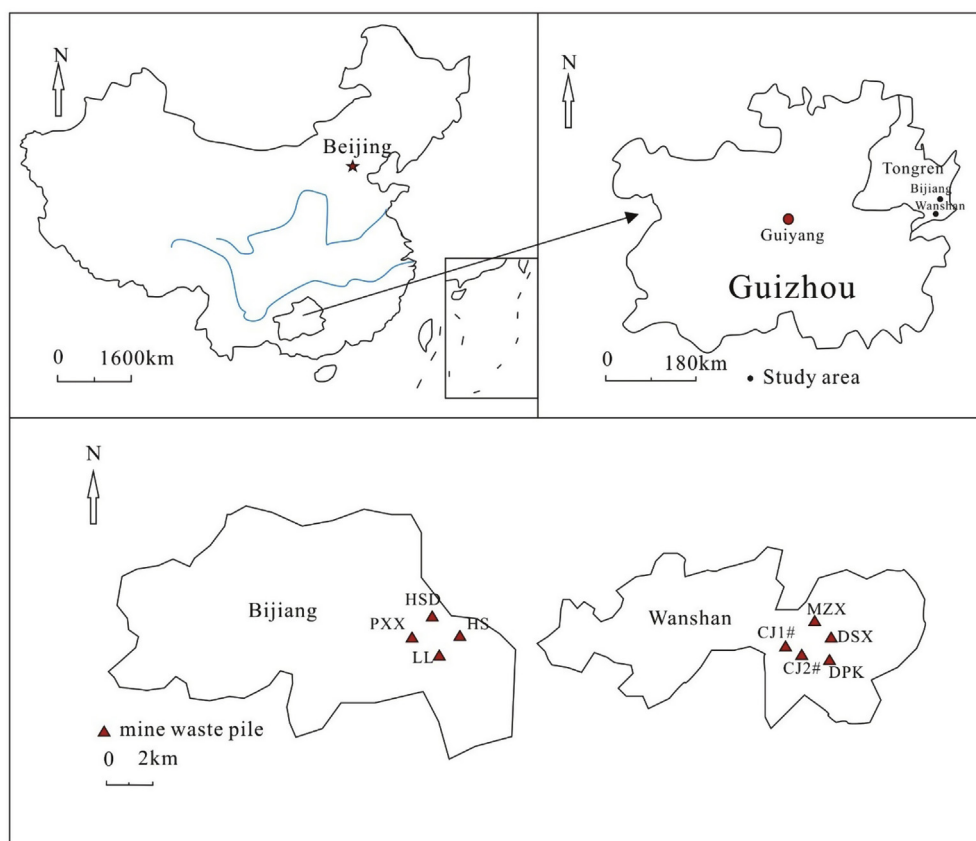


Fig. 1. Locations of mine waste piles sampled for this study, Tongren, southwest China.

added to the samples, which were left to oxidize for 24 h. The Hg ions in the solution were then reduced to Hg^0 using acidic SnCl_2 . Pre-enrichment was conducted in a gold tube and the samples were analyzed using a cold vapor atomic fluorescence spectrophotometer (CVAFS, Tekran 2500, Canada). The THg in water filtered through a $0.45\ \mu\text{m}$ filter is defined as dissolved Hg (DHg); the detection method is the same as that for THg in the unfiltered water. The particulate Hg concentration (PHg) in the water was obtained by subtracting the DHg concentration from the THg concentration. Other water parameters, including pH, DO, and conductivity, were determined using a water quality parameter meter (Leici DZB-718, China) in-situ during sampling.

2.4. Quality control

Quality control consisted of method blanks, blank spikes, certified reference materials (CRMs), and blind duplicates. For the Hg in mine wastes, blanks and matrix spikes were run once every 10 samples. The limit of determination was $0.05\ \mu\text{g/g}$ for THg in mine wastes with CVAAS, and $0.001\ \mu\text{g/L}$ for THg in surface water with CVAFS. The average measured THg concentration in CRM CC580 (marine sediment) was 138.6 ± 12.4 (S.D) mg/kg, which was in a good agreement with the certified value of 132 ± 3 mg/kg. The recoveries for matrix spikes ranged from 92% to 110%. The relative standard deviation was $\leq 5\%$ for THg analysis and $\leq 13\%$ for Hg^0 and Hg^{2+} in duplicate samples.

2.5. Data analysis

The data were analyzed using the statistical software SPSS 21. The concentrations of THg and other forms of Hg in mine wastes and water samples are reported as mean \pm S.D. (standard deviation) and the distribution of the measurements was investigated with descriptive statistics. The TGM concentrations showed a log normal distribution and are therefore described using geometric means. Correlation

coefficients were evaluated using Pearson's correlation analysis. Correlations were considered statistically significant when $p < 0.05$.

3. Results and discussion

3.1. Mine wastes

3.1.1. THg

The mine waste contained high THg concentrations (4.15–825 mg/kg). The geometric mean of the THg concentrations in the mine wastes was 49.0 mg/kg. The total mass of mine waste stored at the Wanshan and Tongren Hg mines is about 8.5 Mt (MEP, 2016) and the average density of the mine waste is $1.6\ \text{t/m}^3$; therefore there is 665.7 t of mercury stored in the mine wastes. The stored mass of each Hg species in each mining waste pile was calculated (Table 1). The highest THg concentrations, (14.3–825 mg/kg, Fig. 2), were found at the Hongshuidong (HSD) site. The concentrations obtained in our study are lower than those reported by a previous study (5.7–4400 mg/kg; Qiu et al., 2005). The discrepancy might mean that remediation projects have reduced the extent of Hg pollution in the mine wastes. Nonetheless, THg concentrations in the mine wastes analyzed for this study are still much higher than those in the local bedrock (0.35 mg/kg; Hua and Cui, 1994). The THg concentration in 50% of the mine wastes (11/22 samples) exceeded the risk screening value for soil contamination of the second type of development land (38 mg/kg; MEE, 2018), while 27.3% (6/22) of the THg concentrations exceeded the risk intervention value for soil contamination of the second type of development land (82 mg/kg; MEE, 2018). Mine wastes with high THg concentrations can release Hg into the local environment continuously through volatilization, leaching, and erosion, which poses threats to the local environment and to the local population. The THg concentrations in mine wastes varied significantly among the different piles, and even in the same pile. The variability of THg in the mine wastes suggests that the

Table 1
Basic information of the studied mine waste piles.

Region	Site	Reserves (Mt)	THg Storage (t)	Hg ²⁺ Storage (t)	Hg ⁰ Storage (t)	Affected water area (km ²)	Affected land area (ha)	Remediation project
Wanshan	Dashuixi (DSX)	2.0	172	7.49	75.3	4.13	423	Most were covered with film and soil.
	Chongjiao1# (CJ1#)	0.2	58.6	0.09	18.6	1.35	-	All fixed with cement.
	Chongjiao2# (CJ2#)	0.3	20.4	0.76	9.26	0.91	-	All covered with soil.
	Lengfengdong (LFD)	0.5	-	-	-	1.28	53	All fixed with cement.
	Meizixi (MZX)	0.3	5.36	2.37	4.27	4.06	133	Fixed with curing agent, covered with soil and vegetation, retaining walls and leaching pond were built.
Bijiang	Hongshuidong& Houshan (HSD & HS)	1.0	123	2.19	45.6	3.33	173	Partially immobilized with cement, most were uncovered.
	Lula (LL)	1.4	193	7.01	78.8	1.33	91	Most were covered with soil.
	Pangxiexi (PXX)	2.8	214	4.66	105	3.33	240	No treatment.

Data were adopted from Special Plan of Mercury Pollution Control in Tongren City by Technology Center of Solid Waste and Chemicals Management, Ministry of Environmental Protection (MEP) (2016).

Hg extraction process was not efficient.

3.1.2. Hg speciation

3.1.2.1. Hg²⁺. The concentration of Hg²⁺ in the mine wastes varied from 0.07 to 20.6 mg/kg and the percentage of Hg²⁺ relative to THg was 5.3% (Fig. 3). The geometric mean of the Hg²⁺ concentration in the mine wastes was 1.59 mg/kg, therefore Hg²⁺ storage in the mine wastes was estimated to be 21.6 t. The fraction of Hg²⁺ is taken to represent the proportion of active Hg in the mine wastes. There was no significant correlation between the concentrations of Hg²⁺ and THg in the mine wastes, because of the relatively low Hg²⁺ concentrations in the mine wastes. The Hg²⁺ concentrations reported here are much lower than those in mercury mines in the Terlingua district, Texas, USA (Mariposa, Study Butte, Mariscal, and Terlingua mine), where the average was 180 mg/kg, and the range was 1.5–2,100 mg/kg (Gray et al., 2006). The significant differences in Hg²⁺ concentrations between Wanshan/Tongren and Texas may be attributable to differences in climate. The study area is warm and humid with abundant precipitation so Hg²⁺ may be leached from the mine waste more quickly at Tongren than in Texas (Li et al., 2013).

The proportion of Hg²⁺ relative to THg was relatively low, but Hg²⁺ is more active than other forms of Hg and can be leached into the surface water when rainwater erodes the waste piles. The Hg²⁺ can be converted readily into more toxic MeHg by microorganisms under anaerobic conditions.

3.1.2.2. Hg⁰. The concentration of Hg⁰ in the mine waste varied from 1.55 to 271 mg/kg. The geometric mean of the Hg⁰ concentrations in the mine wastes was 21.9 mg/kg, and Hg⁰ storage in the mine waste was estimated to be 298 t. High proportions of Hg⁰ relative to THg in the mine wastes were observed, with a mean of 46.0%. A significant positive correlation was observed between Hg⁰ and THg in the mine wastes (r² = 0.82, p < 0.01). During Hg extraction in retorts, cinnabar is converted into Hg vapor at high temperature and liquid Hg is obtained by condensation. However, a substantial amount of Hg⁰ can be absorbed by the mine waste inside the retort. The Hg⁰ in the mine waste can evaporate into the atmosphere, which poses serious environmental risks on a global scale, because Hg vapor can undergo long-range transport.

The results obtained in this study are comparable to those reported for Hg mines in China (0.22–79 mg/kg; Li et al., 2013), but are significantly higher than those reported for mine wastes at the Texas Hg mine (USA), where Hg⁰ in most samples is below the limit of detection (0.005 mg/kg). The discrepancy might be related to the difference in climate between Tongren and Texas. The climate in Texas is dry and hot, so the Hg⁰ in the mine wastes would be emitted into the atmosphere relatively quickly (Gray et al., 2006). Conversely, the climate in Tongren is cool and mild; therefore, release of the Hg⁰ would be slow and a substantial proportion would remain in the mine wastes.

3.1.2.3. Other Hg. The total concentration of other Hg species in the mine wastes ranged from 2.28 to 552 mg/kg. These species accounted for a large proportion of the THg in the mine wastes, with an average of 46%. The high proportion of other Hg species indicates that the mine waste contains a substantial amount of residual HgS. This result is consistent with values of 0.23–500 mg/kg reported for wastes from other Chinese Hg mines (Li et al., 2013).

3.1.3. Micromorphology analysis

A combination of results from EDS and TEM revealed the morphology and three-dimensional distribution of Hg in the mine wastes (Fig. 4). The minerals showed fine crystals with clearly delineated boundaries even after the retorting extraction process. The grains were symmetrical and showed no significant deformation. These characteristics indicate that the Hg ores were not sufficiently smelted and that cinnabar micro-particulates remained to cause the high THg

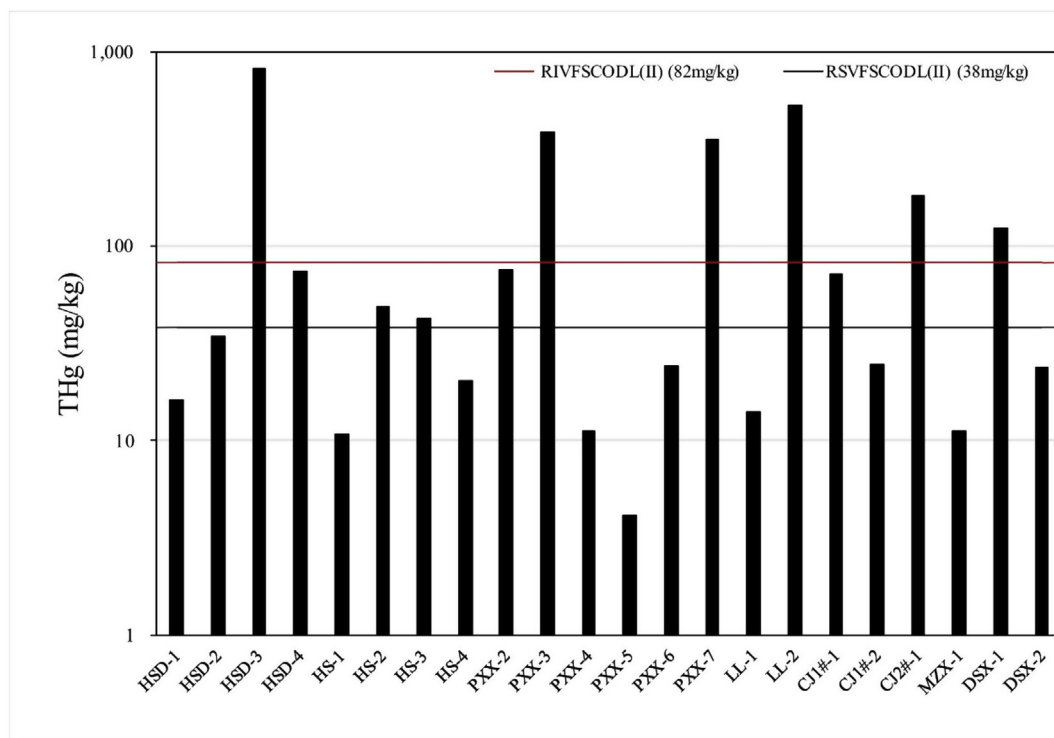


Fig. 2. Concentrations of THg in mine waste collected from the Tongren and Wanshan Hg mines
 *"RSVFSCODL (II)": "Risk Screening Values for Soil Contamination of Development Land (Second type of land); "RIVFSCODL (II)": "Risk Intervention Values for Soil Contamination of Development Land (Second type of land).

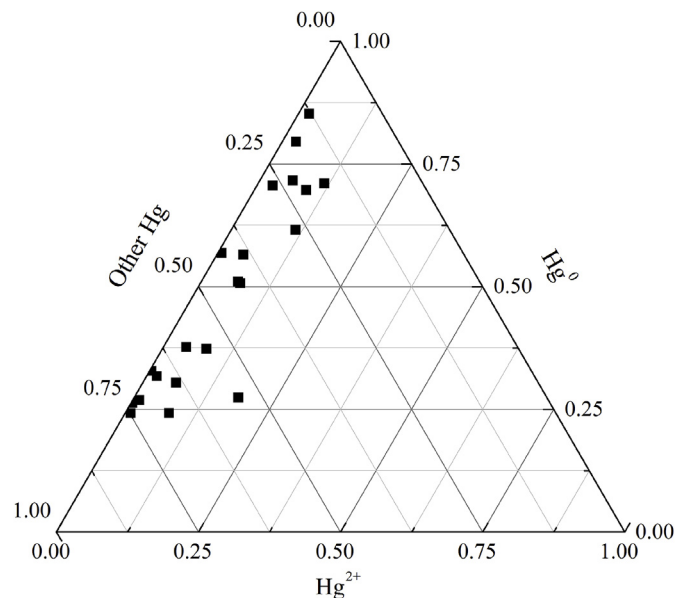


Fig. 3. Triangle diagram showing Hg speciation distributions in mine waste.

concentrations in the mine waste.

As much as 55% of the Hg in epigenetic pyrite from Carlin-type gold deposits, is in the form of metacinnabar nanoparticles (Manceau et al., 2018). According to the results of energy spectrum analysis (Fig. 4a–c), Hg in the Tongren mine wastes occurred mainly as Hg oxide and Hg sulfide. The commonest gangue minerals observed in the mine wastes were dolomite, silicate minerals, calcite, and quartz, with accessory calcium oxide, Hg oxide, Hg sulfide, iron oxide, and pyrite.

The Hg in unroasted Hg ores is mainly in the form of cinnabar (99%), with a minor proportion of β -HgS (1%). In the mine waste, Hg is

present as β -HgS (52%), α -HgS (42%), and $HgCl_2$ (6%) (Yin et al., 2013). Sulfidation is generally considered to be an important process associated with Hg deposition. Other Hg species (e.g., MeHg, Hg^0) can be transformed into Hg sulfide, which can reduce Hg migration, methylation, and bioaccumulation (Chen et al., 2018). While HgS has low mobility and solubility, and is less harmful to the surroundings than other Hg species, it can still dissolve, albeit slowly (Jonsson et al., 2012). The Hg in mine waste from Wanshan and Tongren was mostly held by nanometer-scale Hg compounds. Interaction between these nanoscale Hg compounds and dissolved organic matter (DOM) promotes the dissolution of the nanoscale Hg (Ravichandran et al., 1998, 1999). Nanoparticles of HgS can be methylated, and methylation rates are similar to those of dissolved Hg^{2+} , and higher than methylation rates for HgS microparticles (Zhang et al., 2014). The size of Hg crystals with microstructures ranged from several nanometers to tens of nanometers; there was little evidence of remnant crystal morphology (Fig. 4). Therefore, nanoscale HgS, and other forms of nanoscale Hg in mine wastes, pose risks to the local environment. Further studies are needed to explore the mechanisms through which these particles form, and their environmental impacts.

3.1.4. Leaching experiments

The mean concentration of total soluble Hg (TSHg) in the mine waste leachates was 11.3 $\mu g/L$ (range = 0.029–193 $\mu g/L$). Overall, 5% of the TSHg concentrations exceeded the national standard for hazardous waste of 100 $\mu g/L$, while 50% exceeded Grade V levels (1 $\mu g/L$) according to the National Surface Water Quality Standard (Onsanit et al., 2012).

The pH of the leachates ranged from 6.41 to 9.95 with a mean of 9.67, which is consistent with the pH of the surface water that leaches from the mine waste piles. Most of the leachates were alkaline, which is attributed to interaction with the alkaline host rock (Zhang et al., 2004).

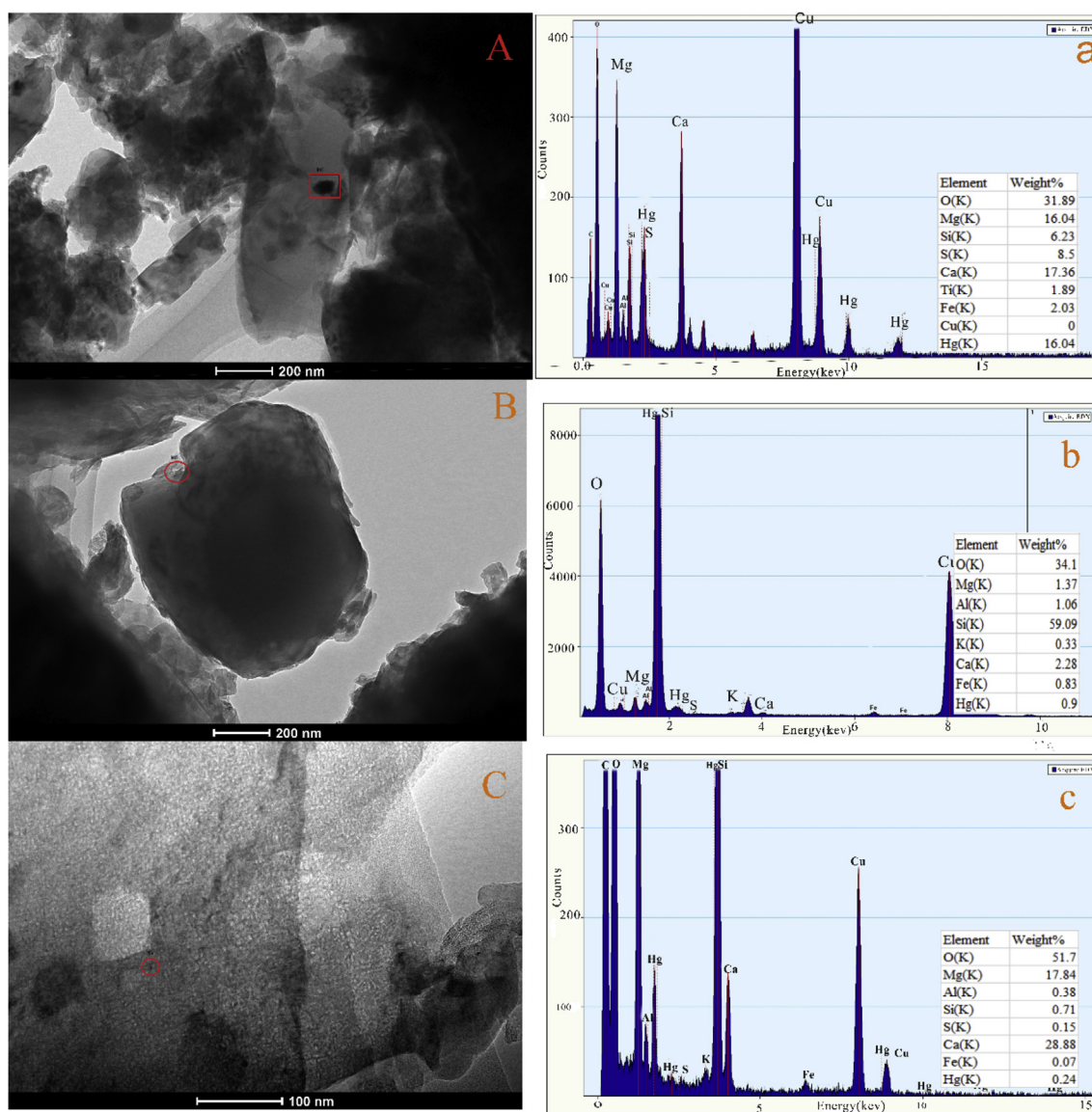


Fig. 4. Bright field images of mine wastes containing Hg (A, B, C) and corresponding energy spectra (a, b, c).

3.2. Surface water

The concentration of THg in the surface water that flowed through the mine wastes ranged from 0.038 to 10.6 $\mu\text{g/L}$. The results of this study are consistent with previous reports from the Wanshan Hg mine, where Hg in surface waters ranged from 0.019 to 12 $\mu\text{g/L}$ (Qiu et al., 2009). The concentration of THg in the surface water collected from different mine waste piles varied significantly (Fig. 6). The THg concentration in the surface water from MZX was much lower than that at other waste piles, which is attributed to effective remediation measures. The MZX mine waste pile was mixed with a curing agent, covered with soil and re-vegetated, and retaining walls and a leaching pond were constructed. In contrast, other mine waste piles were remediated using only vegetation or cement. This result indicates that proper treatment can effectively reduce the release of Hg into the aquatic environment. However, the THg concentrations obtained in this study are still elevated compared with background values, which are mostly < 0.010 $\mu\text{g/L}$, and indicate environmental accumulation of Hg (Aspmo et al., 2006). Surface water concentrations were compared with national environmental quality standards for surface water. Of the THg concentration measurements, 21.1% exceeded level V (1 $\mu\text{g/L}$) and 73.7% exceeded level III (0.1 $\mu\text{g/L}$). In spite of this Hg pollution, the surface waters are

still used for irrigation of paddy fields in the downstream. The highest THg concentrations were measured in samples from the HSD waste pile, and the elevated concentrations are tentatively attributed to the relatively low pH (6.94) in the surface water at this site. The Wanshan Hg mine is at a relatively high elevation, and is located upstream of four major rivers — the Xiaxi, Aozhai, Huangdao, and Gaolouping rivers. With distance increasing, the THg concentrations in the surface water declined, consistent with the results of previous studies (Qiu et al., 2009). The decline indicates that the mine wastes are significant sources of Hg pollution for the surface waters. The results of this study confirm that the mine waste contains high concentrations of water-soluble Hg compounds, which can be leached into surface waters by the interaction of rainwater with the mine waste (Kim et al., 2004). With distance increasing, the particulate matter is deposited in sediments and THg concentrations decrease. It is also notable that the THg concentrations in the surface water are comparable to the TSHg concentrations in mine waste leachates (Fig. 5), consistent with the results of previous findings (Li et al., 2013).

The concentrations of DHg ranged from 0.013 to 6.66 $\mu\text{g/L}$, and the highest value (6.66 $\mu\text{g/L}$) was obtained at the HSD site where the highest THg concentration was observed. A significant positive correlation was observed between THg and DHg concentrations in the

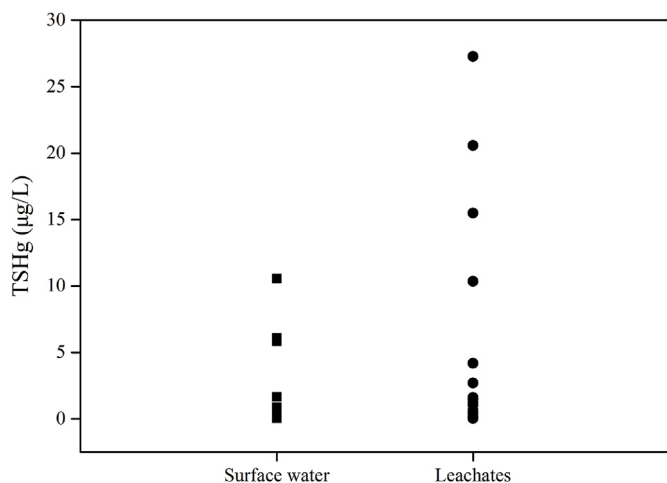


Fig. 5. Comparison of THg in surface water with TSHg in leachates.

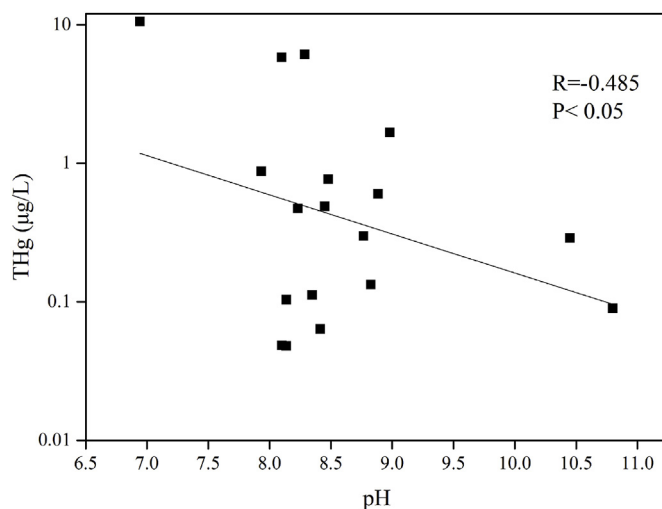


Fig. 7. Concentrations of THg in surface water versus surface water pH.

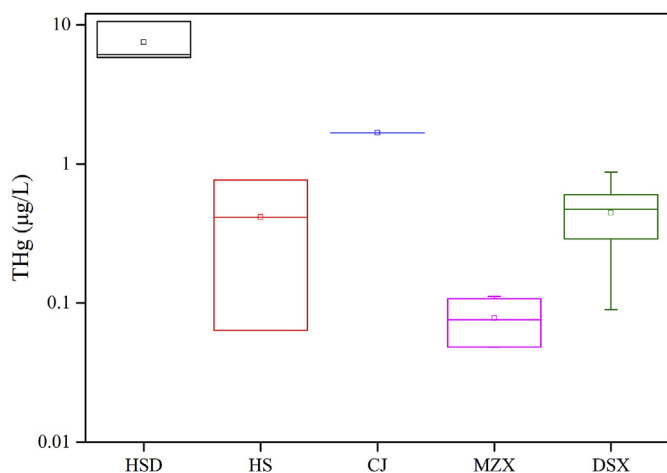


Fig. 6. Concentrations of THg in surface water collected from the Tongren and Wanshan Hg mines in July 2017.

surface water samples ($r^2 = 0.96$, $p < 0.01$), and DHg accounted for an average of 53% of the THg. It is possible that the high pH of the water drives conversion of DHg to PHg. However, continuous weathering and leaching of mine waste with high THg concentrations may also increase the DHg in the surface waters (Qiu et al., 2009). Moreover, DHg can transform into MeHg, which poses a threat to aquatic ecosystems.

The concentration of PHg in the surface waters varied from 0.00089 to 3.89 µg/L, and the percentage of PHg relative to THg ranged from 6.19% to 78.7%, with a mean value of 46.9%. The sampling work was carried out during a drought period, so Hg in the surface water was mainly present as dissolved species, rather than bound to transported particulate matter.

The pH of the surface water in the study area was alkaline with a range of 6.9–10.8. As discussed above, the bedrock in the study area is composed of limestone and other carbonate-rich rocks, which dissolve to produce high pH surface water. A significant negative correlation ($r = -0.485$, $p < 0.05$) between THg concentration and pH in the surface waters was observed (Fig. 7). High THg concentrations were observed in low pH surface waters, which indicates that acidic conditions enhance the solubility of Hg in the surface water (Gray et al., 2003). Therefore, alkaline conditions (high pH) mitigate Hg contamination in the surface water.

3.3. Atmosphere

The concentration of TGM in ambient air over the mine waste piles ranged from 13.5 to 309 ng/m³, which is elevated compared with the background global value (1.5–1.6 ng/m³; Kim et al., 2005) and TGM at Guiyang (8 ng/m³; Feng and Qiu, 2008). The results from Tongren indicate that the mine wastes are a significant source of Hg emissions to the atmosphere. The TGM concentrations documented in this study are much lower than those recorded by a previous study conducted in the Wanshan area (17–2100 ng/m³; Dai et al., 2012), which confirms that there were significant impacts from artisanal Hg mining activities during the sampling period. The TGM concentrations were spatially variable. The highest TGM concentrations (49.4–309 ng/m³) were observed at the PXX site (Fig. 8), where no remediation treatments have been carried out. The LL and CJ sites were covered with vegetation at the time of sampling, and the TGM at these sites were much lower. These findings indicate that mine wastes release Hg into the atmosphere continuously, even after the cessation of large-scale Hg mining activity. Conversely, remediation treatments can effectively reduce Hg fluxes from the interface between mine waste and air.

Gaseous Hg can be transported on a global scale and may pose threats to the global environment (Aspmo et al., 2006; Driscoll et al., 2013). Therefore, Hg emissions from mine wastes should be strictly controlled to reduce environmental risks. The results presented in this

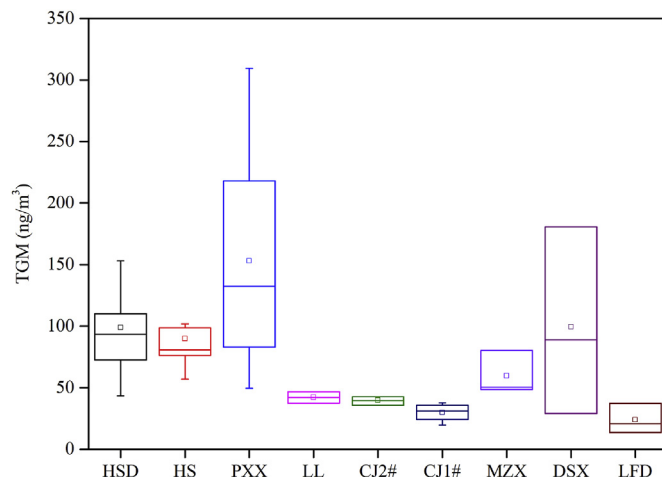


Fig. 8. Concentrations of TGM in the atmosphere above the mine waste piles in July 2017.

study can be used to improve the design of remediation measures applied to mine waste piles in Hg mining areas. Fixing with cement in conjunction with the addition of soil and revegetation can significantly reduce emissions of Hg to the atmosphere.

4. Conclusion

The mine wastes contained high concentrations of THg, and Hg⁰ was the dominant Hg species. The concentrations of THg, and Hg speciation in the mine wastes, varied widely among the different Hg mine waste piles. The mine waste is a major source of Hg pollution to local aquatic ecosystems and the atmosphere. Remediation treatments can significantly reduce release of Hg from mine waste to surface waters and the atmosphere. However, the efficacy of different remediation measures varied. Remediation techniques should be optimized to mitigate the release of Hg to local environments. Long-term monitoring is needed to evaluate environmental risks in Hg mining areas.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2019.05.008>.

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