



Gold mining related mercury contamination in Tongguan, Shaanxi Province, PR China

Xinbin Feng ^{a,*}, Qianqin Dai ^{a,b}, Guangle Qiu ^a, Guanghui Li ^{a,b},
Lei He ^c, Dingyong Wang ^{a,c}

^a State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry,
Chinese Academy of Sciences, Guiyang 550002, China

^b Graduate School of Chinese Academy of Sciences, Beijing 100049, China

^c College of Resources and Environment, Southwest University, Chongqing 400716, China

Available online 27 September 2006

Abstract

Elemental Hg–Au amalgamation mining practices are used widely in many developing countries resulting in significant Hg contamination of surrounding ecosystems. The authors examined for the first time Hg contamination in air, water, sediment, soil and crops in the Tongguan Au mining area, China, where elemental Hg has been used to extract Au for many years. Total gaseous Hg (TGM) concentrations in ambient air in the Tongguan area were significantly elevated compared to regional background concentrations. The average TGM concentrations in ambient air in a Au mill reached 18,000 ng m⁻³, which exceeds the maximum allowable occupational standard for TGM of 10,000 ng m⁻³ in China. Both total and methyl-Hg concentrations in stream water, stream sediment, and soil samples collected in the Tongguan area were elevated compared to methyl-Hg reported in artisanal Au mining areas in Suriname and the Amazon River basin. Total Hg concentrations in vegetable and wheat samples ranged from 42 to 640 µg kg⁻¹, all of which significantly exceed the Chinese guidance limit for vegetables (10 µg kg⁻¹) and foodstuffs other than fish (20 µg kg⁻¹). Fortunately, methyl-Hg was not significantly accumulated in the crops sampled in this study, where concentrations varied from 0.2 to 7.7 µg kg⁻¹. © 2006 Elsevier Ltd. All rights reserved.

1. Introduction

Mercury is a metal that is toxic to living organisms and is one of few pollutants where ingestion of contaminated food has led to human deaths (NAS, 1978). Since the industrial revolution, human activities have released significant amounts of Hg to surrounding environments. Due to its volatility, Hg

may be transported in the atmosphere over long distances once it is released into the environment (Schroeder and Munthe, 1998). Therefore, the release of Hg to the environment by human activities can seriously contaminate local environments, but may also adversely affect the regional and global environment. Studies have demonstrated that elevated concentrations of methyl-Hg in fish from remote lakes in Northern America and Scandinavia has resulted from long-range transport and deposition of Hg (Verta, 1990; Watras and Frost, 1989; Lindqvist et al., 1991; Rask and Metsala, 1991).

* Corresponding author. Tel.: +86 851 5891356; fax: +86 851 5891609.

E-mail address: fengxinbin@vip.skleg.cn (X. Feng).

Environmental problems related to the use of elemental Hg for recovery of Au and Ag have been known since Roman times (Lacerda and Salomons, 1998). Small-scale or artisanal Au mining is popular in developing countries because it involves the use of simple processes generally by a few individuals to recover particulate Au. Since the 1980s, a resurgence of artisanal Au mining in many countries has led to Hg pollution of terrestrial and aquatic ecosystems, but such mining is especially prevalent throughout South America (Brazil, Bolivia, Columbia, Venezuela, Peru, Ecuador, French Guiana, Guyana and Suriname), China, Russia, the Philippines, Indonesia, Thailand, Tanzania and Mexico (Lacerda and Salomons, 1998). As a result of the highly toxic nature of Hg, its release into highly sensitive and diverse tropical rainforest ecosystems has been the focus of abundant research throughout South America (Malm et al., 1990; Aula et al., 1994; Maurice-Bourgoin et al., 1999; Guimarães et al., 2000; Lechler et al., 2000; Richard et al., 2000; Frery et al., 2001; Mol et al., 2001; Gray et al., 2002; Pestana and Formoso, 2003). Local Hg contamination related to Au mining activities has also been reported in Africa and Asia (Limbong et al., 2003; Taylor et al., 2005). It is estimated that about 1/3 of the annual Au production in China was related to the use of Hg amalgamation techniques during the 1980s and 1990s (Gunson, 2004). In the last decade, many studies have been conducted to investigate human health effects to Au miners from different provinces in China (Wang et al., 1999; Xi et al., 1996; Wang, 2001; Duan et al., 2001; Zhong and Lou, 2000; Guan et al., 2002; Zhang et al., 1999), but only a few studies addressing the source of the associated Hg contamination have been conducted (Lin et al., 1997; Dai et al., 2003; Gunson, 2004). There are basically two types of Au extraction processes using Hg in China, large-scale mining and small-scale (artisanal) mining. Generally, during large-scale Au mining in China, elemental Hg is efficiently recovered, however, Hg loss is estimated to be 0.68 g of elemental Hg per g of Au produced (Qi, 1997). Conversely, Hg loss is high during artisanal Au mining in China, and is estimated to be about 15 g of elemental Hg for each g of Au recovered (Qi, 1997). The annual production of Au in China from artisanal mining generally constituted about 16% of the Au produced using amalgamation techniques during the 1980s and 1990s (Qi, 1997). In 1995, the consumption of elemental Hg

in Au mining activities throughout China was estimated to be about 400 tons and the amount of elemental Hg lost to surrounding environments was estimated to be 107 tons (Feng, 2004). Estimates indicate that about 120 tons of elemental Hg was lost to the environment in Tongguan from 1980 to 2003 (Dai, 2004). Although artisanal Au mining activities have been officially prohibited in China since 1996, a few illegal mines presently are operating in some remote areas. In addition, there is significant Hg contamination remaining in ecosystems surrounding areas of past Au mining, and these areas remain largely unstudied. In this paper, the first Hg concentrations in ambient air, stream water, stream sediment, soil, and some crops in the Tongguan area, Shaanxi Province, China are reported.

2. Study area

Tongguan, which is the third largest Au-producing county in China, is located in eastern Shaanxi Province ($34^{\circ}23'–34^{\circ}40'N$ and $110^{\circ}09'–110^{\circ}25'E$), northwestern China (Fig. 1). The Au production in Tongguan from 1980 to 2003 reached 56.25 tons (Dai, 2004). Tongguan is situated in the Loess Plateau, and its average elevation is 1500 m above sea level. It has a typical temperate zone terrestrial monsoon arid climate. The average annual rainfall is 625.5 mm, and the average annual temperature is 13 °C.

According to local records, Au mining was first initiated in Tongguan about 900 a ago (Dai, 2004). About 72 abandoned ancient Au mines are known in the Tongyu, Haochayu, Taiyu, and Dongtongyu areas (Fig. 1). Since 1965, the Geological Survey of Shaanxi Province has initiated extensive exploitation of Au in this area. Large-scale Au mining and smelting activities began in 1975. Presently, there are 29 large Au mining companies involving 6000 workers in Tongguan. Generally, elemental Hg is used by these companies for extraction of Au. To date, at least eight million tons of tailings have been produced from mining in this area, and the average Hg concentration in the tailings is approximately 630 mg kg^{-1} , which is significantly elevated compared to the average Hg concentration in original Au ores, which is 0.069 mg kg^{-1} (Dai, 2004). The annual Au production reaches 2.5–3.0 tons in the Tongguan area (Dai, 2004). The Au processing mills are distributed along several streams that are tributaries of the

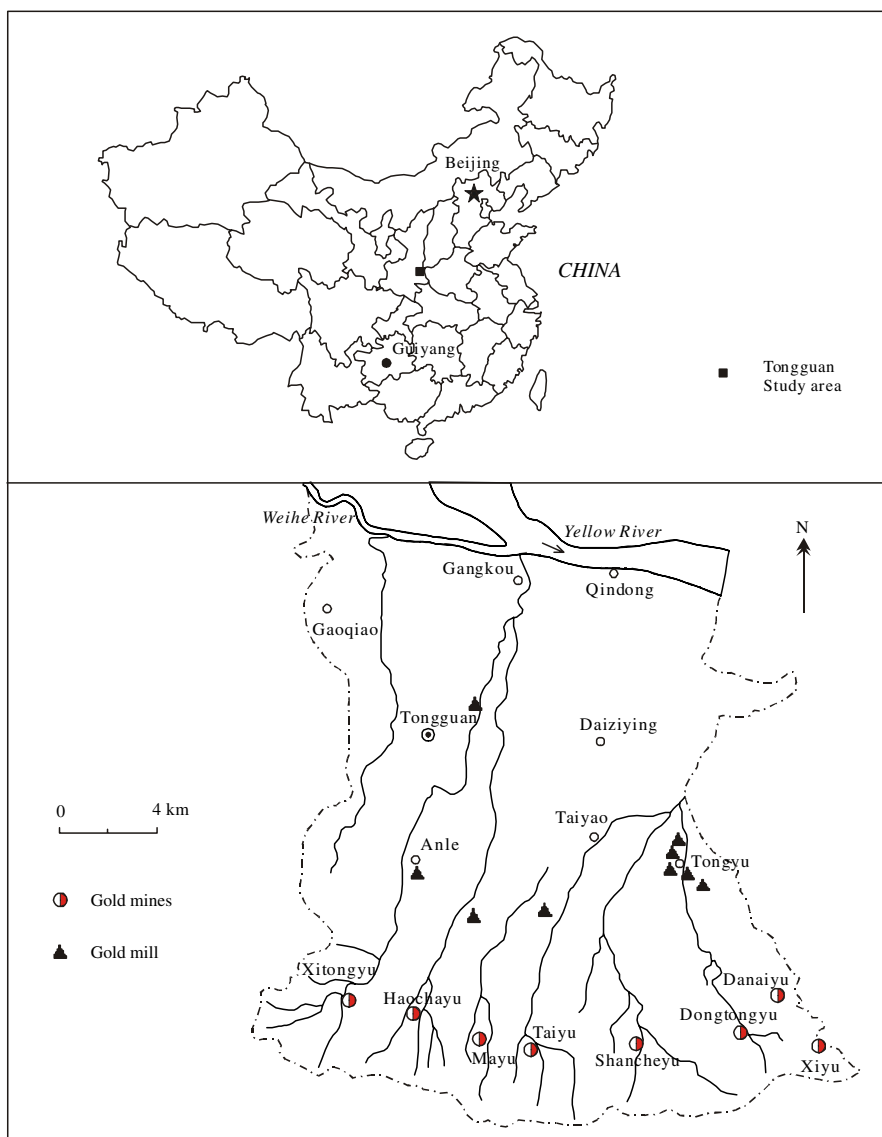


Fig. 1. The location of the Tongguan study area.

Yellow River (Fig. 1) and waste water from these mills is directly discharged into these streams. During the 1980s and 1990s, artisanal Au mining activities were popular in the region and more than 15,000 people were involved in Au mining activities in which elemental Hg was used widely for Au extraction. Artisanal Au mining activities mainly occurred along the streams in Tongguan. Artisanal Au mining in Tongguan has declined significantly since the Chinese ban of such activities in 1996, but there are presently a few artisanal Au mines still operating.

3. Sampling and analytical methods

3.1. Air samples

The concentrations of total gaseous Hg (TGM), which is mainly Hg⁰ in the ambient air in the Tongguan area, were monitored using a RA-915+ automated Hg vapor detector made by LUMEX (Russia). The instrument is a real time Hg detector, which is based on the Zeeman cold vapor absorption spectrometry technique with a time resolution of 1 s. The instrument is calibrated with an internal

Hg vapor source. The detection limit of the instrument is 0.3 ng m^{-3} . Air measurements for Hg was taken at 40 sites (Fig. 2). The average TGM concentrations in 30 s were recorded in a portable computer, and at each site the measurements were carried out for at least for 10 min. The average TGM concentrations in the ambient air at each site were calculated based on 10-min measurements.

3.2. Sampling and analysis of surface water samples

Stream water sampling locations are shown in Fig. 3. All samples were filtered on-site with a $0.22\text{-}\mu\text{m}$ membrane filter, collected in acid pre-cleaned Teflon bottles, and 0.4% (v/v) of sub-boiling, distilled ultra-pure HCl acid was added within 24 h of collection. Field blanks were also collected on-site by adding ultra-pure Milli-Q water in sample bottles. Collection, storage, and preservation techniques of samples followed US EPA Method 1631 (US EPA, 1999). Total Hg concentrations were determined within 28 days of sampling using operationally defined methods for species of reactive, dissolved and particulate Hg in water, where a dual stage Au-amalgamation method and cold vapor atomic fluorescence spectrometry (CVAFS) detection was

used (Qiu et al., 2006). Total dissolved Hg and particulate forms of methyl-Hg in water were determined following distillation and ethylation processes and gas chromatograph-cold vapor atomic fluorescence spectrometry (GC-CVAFS) detection using US EPA Method 1630 (US EPA, 2001). Dissolved organic C (DOC) concentrations in water samples were analyzed using a high temperature combustion method. The detection limit for total Hg was 0.30 ng L^{-1} and for methyl-Hg was 0.050 ng L^{-1} . Recoveries on matrix spikes of methyl-Hg in water samples were in the range of 88–108%.

3.3. Sampling and analysis of sediment and soil samples

At each surface water sample site, a representative sediment sample (Fig. 3) was also collected using a pre-cleaned plastic shovel. In addition, 27 soil samples were collected in the study area. At each site, sediment and soil samples were composited from 3 to 5 sub-samples collected from several localities within an area of 1 m^2 . All soil and sediment samples were collected and stored in sealed polyethylene bags to avoid cross contamination. In the laboratory, all samples were air dried, ground in a ceramic disc mill,

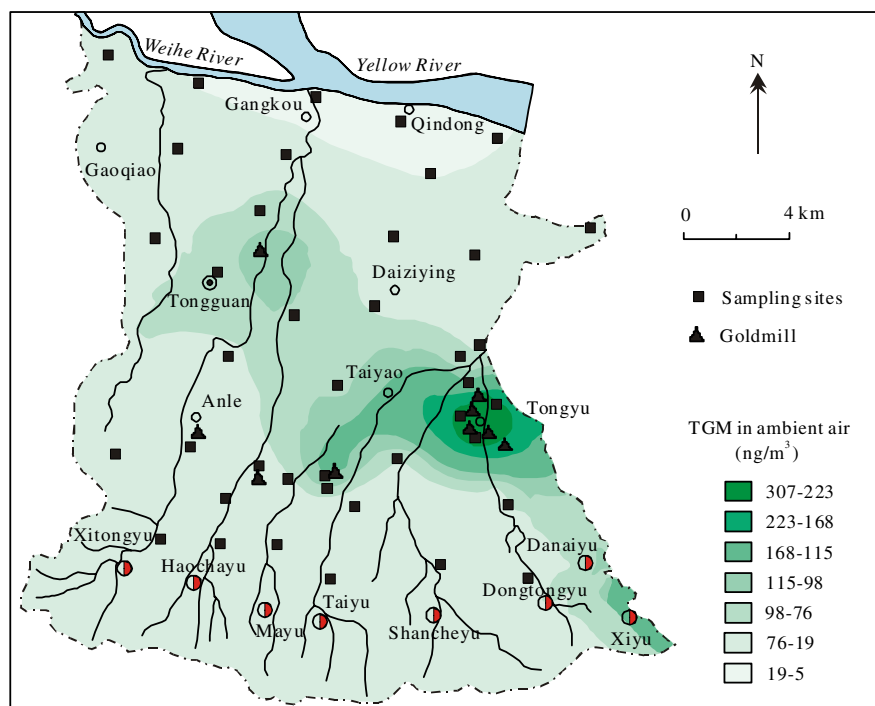


Fig. 2. Localities of atmospheric sample sites and the spatial distribution of TGM concentrations in ambient air in the Tongguan Au mining area.

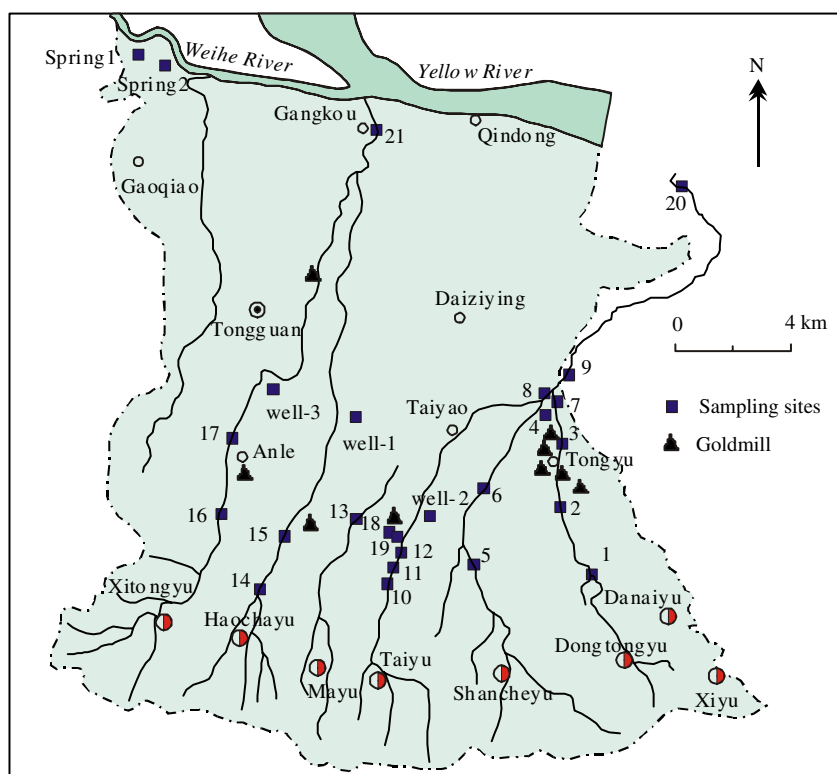


Fig. 3. Localities of water samples collected in the Tongguan Au mining area.

Table 1
Location and Hg concentrations in crop samples collected in the Tongguan area

Sample no.	Sample type	Corresponding soil sampling site	Total Hg ($\mu\text{g kg}^{-1}$)	Methyl-Hg ($\mu\text{g kg}^{-1}$)
1	Mung bean seed	9	63	7.7
2	Mung bean skin	9	190	2.2
3	Cowpea seed	10	84	7.0
4	Cowpea skin	10	240	1.1
5	Mung bean seed	13	42	2.9
6	Mung bean skin	13	190	0.6
7	Whole pumpkin	14	280	1.9
8	Pulp of pumpkin	14	490	1.2
9	Cowpea	14	170	4.3
10	Potato	16	160	2.6
11	Potato	17	52	0.9
12	Kidney bean	18	640	0.8
13	Wheat	21	180	1.0
14	Wheat	11	170	1.1
15	Wheat	19	140	1.1
16	Wheat	4	110	1.0
17	Wheat	22	140	0.5
18	Wheat	Near the Yellow River	83	0.2
Chinese guidance limit for vegetables			10	
Chinese guidance limit for foodstuffs other than fish			20	

and sieved to 100 μm . Sample aliquots of the prepared soil and sediment were digested with a mixture acid of HCl/HNO₃ (HCl/HNO₃ of 3:1) for total Hg analysis. A separate aliquot of the prepared soil or

sediment sample was digested using HNO₃ followed by a solvent extraction and coupled ethylation technique for methyl-Hg determination (Liang et al., 2004). Quality control for the Hg and

methyl-Hg determinations was addressed with method blanks, blank spikes, certified reference materials (GBW07405; CRM580), and blind duplicates. Limits of determination were 0.01 ng g^{-1} for total Hg and 0.003 ng g^{-1} for methyl-Hg, respectively, in both soil and sediment samples. The average total Hg concentration of the geological standard GBW07405 was $0.30 \pm 0.01 \text{ mg kg}^{-1}$ ($n = 5$) with a range from 0.29 to 0.31 mg kg^{-1} , which is comparable with the certified value of $0.29 \pm 0.04 \text{ mg kg}^{-1}$. An average methyl-Hg concentration of $70.6 \pm 0.6 \text{ ng g}^{-1}$ ($n = 7$) with a range from 69.0 to 72.1 ng g^{-1} was obtained from CRM580 with the certified value being $70.2 \pm 3 \text{ ng g}^{-1}$. The relative percent difference was $<8.5\%$ for total Hg obtained from analysis of duplicates of soil and sediment samples.

3.4. Sampling and analysis of crop samples

Crops such as mung bean (*Phaseolus aureus* Roxb.), cowpea (*Vigna sesquipedalis* Koern.), pumpkin (*Cucurbita moschata* Duch.), tomato (*Solanum tuberosum* L.), kidney bean (*Phaseolus vulgaris* L.) and wheat (*Triticum aestivum* L.) were collected from farms around mined areas. Generally, the crop samples were collected at sites where water and soil samples were collected (Fig. 3, Table 1). In the laboratory, all crop samples were air dried, ground in a ceramic disc mill, and sieved to $100 \mu\text{m}$. Total and methyl-Hg concentrations in crop samples were analyzed using the same method as soil and sediment samples stated in Section 3.3. Recoveries on matrix spikes of methyl-Hg in crop samples were in the range of 83–120%.

4. Results and discussion

4.1. TGM concentrations in ambient air

Data indicate that TGM concentrations of ambient air inside a Au large mill in the Tongguan area

were highly elevated ranging from 5600 to 33,000 ng m^{-3} , averaging 18,000 ng m^{-3} (Table 2), which exceeds the maximum allowable occupational standard for TGM concentrations in China, which is 10,000 ng m^{-3} . The TGM concentrations measured inside this Tongguan Au mill are comparable to those reported in an artisanal Au mill in Venezuela, where the average TGM concentrations reached 21,600 ng m^{-3} (Pamela et al., 2001). Workers in the Tongguan Au mills were exposed to potentially high concentrations of Hg vapor. Additional work is needed to evaluate the health effects of Hg exposure to these workers.

TGM concentrations in ambient air decreased gradually with increasing distance from the Au mills in the Tongguan area (Table 2). However, greater than 1000 m downwind from the Au mills, the average TGM concentration was 29 ng m^{-3} , which is significantly higher than the average TGM concentration of 8.4 ng m^{-3} in the air collected from the city of Guiyang (Fig. 1), which is polluted with coal combustion emissions (Feng et al., 2004). The only significant Hg contaminant in the Tongguan area is emissions from the Au mines, thus the Au mining activities are the clear source of elevated TGM in ambient air in this region.

Using geo-statistical analysis and geographic information system (GIS) techniques coupled with ambient air Hg data, elevated TGM concentrations were found in the vicinity of active large Au mills in the Tongguan area (Fig. 2). Two large Au mills in the southwestern part of Tongguan, near Anle (Fig. 2), were not in operation when the TGM measurements were made, and as a result of this inactivity, the TGM concentrations in ambient air around these two Au mills were significantly lower than the active Au mills. There were also a few artisanal Au mills scattered in Tongguan, but TGM concentrations around these mills were much lower than those found around large Au mills. This observation demonstrates that large Au mills are the most significant Hg source of TGM in the Tongguan area.

Table 2

Statistical summary of TGM concentrations in ambient air of different regions in the Tongguan Au mining area (ng m^{-3})

Sampling zone	Range	Average	SD	N^a
Inside a large Au mill	5600–33,000	18,000	7400	36
100–200 m from Au mills	58–1500	390	270	164
200–500 m from Au mills	9–250	77	39	235
>1000 m from Au mills	7–66	29	13	236
Control site ^b	1–6	2	1	41

^a Each sample represents the average of 10 min sampling with individual samples in a time resolution of 30 s.

^b The control site was located near the Yellow River, upwind from the Au mills.

At a sampling site upwind from the Au mills, located adjacent to the Yellow River, an average TGM concentration of 2 ng m^{-3} in the ambient air was found. This Yellow River TGM concentration is similar to that of the global atmospheric background in the Northern Hemisphere of $1.5\text{--}2.0 \text{ ng m}^{-3}$ (Ebinghaus et al., 2002).

4.2. Mercury in surface water and sediment

Dai et al. (2003) reported reactive, dissolved, particulate, and total Hg concentrations in surface water samples collected from sampling sites 1–17 (Fig. 3) during the cold and dry season from October 28 to November 05, 2002. Additional water samples were collected in July 2003 during the warm, high precipitation season. The Hg data for all of these water samples are listed in Table 3. Reactive Hg concentrations in the stream water samples collected in the cold season varied from 6.9 to 700 ng L^{-1} with a geometric mean of 56 ng L^{-1} , and during the warm season reactive Hg varied from 12 to 1200 ng L^{-1} with a geometric mean of 48 ng L^{-1} (Table 3). Dissolved Hg concentrations in stream water samples collected in the

cold season varied from 110 to 3100 ng L^{-1} with a geometric mean of 410 ng L^{-1} , and from 75 to 1800 ng L^{-1} with a geometric mean of 250 ng L^{-1} during the warm season. Particulate Hg was the dominate Hg species in the stream water samples and during the cold season varied from 130 to $260,000 \text{ ng L}^{-1}$ with a geometric mean of 3600 ng L^{-1} , but was higher varying from 330 to $880,000 \text{ ng L}^{-1}$ with a geometric mean of 6100 ng L^{-1} during the warm season. Total Hg concentrations in the cold season stream water samples ranged from 240 to $260,000 \text{ ng L}^{-1}$ with a geometric mean of 4800 ng L^{-1} , whereas stream water collected in the warm season varied from 400 to $880,000 \text{ ng L}^{-1}$ with a geometric mean of 6900 ng L^{-1} (Table 3). The concentrations of all Hg species in stream water at all Tongguan sample sites from both sampling campaigns were significantly elevated compared to total Hg concentrations reported from worldwide background rivers and lakes that range from 0.1 to 5.0 ng L^{-1} (Nriagu, 1990; Lindqvist et al., 1991), and also significantly higher than total Hg concentrations ($0.1\text{--}2.6 \text{ ng L}^{-1}$) reported in water collected near artisanal Au mining areas in Suriname and the Amazon River basin (Gray et al.,

Table 3
Mercury concentrations in surface water samples collected in different seasons in the Tongguan Au mining area (ng L^{-1})

Sampling site	Reactive Hg		Dissolved Hg		Particulate Hg		Total Hg	
	Cold season ^a	Warm season	Cold season ^a	Warm season	Cold season ^a	Warm season	Cold season ^a	Warm season
1	16	42	190	250	2600	14,000	2800	14,000
2	23	30	150	130	23,000	2900	23,000	3000
3	370	130	1200	420	2300	1400	3500	1800
4	35	23	300	79	190	1300	490	1400
5	9.0	17	120	220	150	980	260	1200
6	8.4	13	110	75	130	330	240	400
7	510	55	1600	200	13,000	280,000	15,000	280,000
8	680	1200	3100	1600	260,000	2400	260,000	4000
9	310	210	1200	570	100,000	520,000	100,000	520,000
10	56	27	230	150	75,000	2000	75,000	2200
11	35	50	1000	190	440	2300	1500	2500
12	15	n.a.	740	n.a.	960	n.a.	1700	n.a.
13	6.9	20	300	170	890	410	1200	580
14	22	58	130	240	3500	2900	3600	3100
15	700	30	1100	310	19,000	15,000	20,000	15,000
16	86	41	220	170	890	1000	1100	1200
17	45	12	240	180	8500	11,000	8700	12,000
18	n.a.	23	n.a.	190	n.a.	530	n.a.	720
19	n.a.	19	n.a.	150	n.a.	2500	n.a.	2700
20	n.a.	170	n.a.	1800	n.a.	520,000	n.a.	520,000
21	n.a.	200	n.a.	500	n.a.	880,000	n.a.	880,000
Geomean	56	48	410	250	3600	6100	4800	6900
SD	250	270	790	470	65,000	240,000	66,000	240,000

^a Data from Dai et al. (2003).

Table 4
Total Hg and methyl-Hg concentrations in sediment samples collected in the Tongguan area

Sample no.	Total Hg (mg kg ⁻¹)		Methyl-Hg (μg kg ⁻¹)	
	Cold season	Warm season	Cold season	Warm season
1	65	20	4.3	0.40
2	34	150	30	12
3	1200	20	28	0.20
4	4.7	1.4	3.2	0.10
5	27	160	2.4	7.8
6	13	10	0.60	0.80
7	n.a.	8.8	n.a.	0.40
8	n.a.	16	n.a.	4.7
9	11	8.8	0.30	0.50
10	28	94	0.20	3.0
11	77	80	2.0	8.3
12	n.a.	n.a.	n.a.	n.a.
13	n.a.	60	n.a.	7.4
14	56	11	0.60	2.5
15	n.a.	15	n.a.	2.4
16	n.a.	44	n.a.	2.1
17	n.a.	0.90	n.a.	3.5
18	n.a.	10	n.a.	0.80
19	n.a.	76	n.a.	4.4
20	n.a.	50	n.a.	8.1
21	n.a.	60	n.a.	2.6
Geomean	38	22	2.0	1.9
SD	370	47	11	3.5

2002; Nriagu, 1992). These data indicate that present large-scale and past artisanal Au mining activities have contaminated surface water with Hg in the Tongguan area. The most contaminated sites (e.g., sites 7, 9, 17, 20) are located downstream from large-scale Au mills, and this Hg contamination (total Hg concentrations ranging from 8700 to 520,000 ng L⁻¹) is due to waste water discharge from the Au mills into the streams. High total Hg concentrations in water samples 1, 2, 5, 6, 10, 11, 12, 14, 15 and 16 ranging from 240 to 23,000 ng L⁻¹ (Table 3) collected upstream from the Au mills were mainly derived from sediment contamination during past artisanal Au mining activities (Table 4). In general, reactive and dissolved Hg concentrations in water samples collected during the cold season were higher than those collected in the warm season, but particulate Hg concentrations were higher in the warm season (Table 3). The warm season concurs with the rainy season in the Tongguan region. High precipitation in the warm season diluted both reactive and dissolved Hg in surface water samples collected in this study. However, warm season high precipitation increased the stream discharge resulting in re-suspension of sediment particulates, and consequently, increased particulate Hg concentrations in stream water.

Table 5
Methyl-Hg concentrations in surface water samples collected in the warm season in Tongguan Au mining area

Sampling site	Dissolved methyl-Hg (ng L ⁻¹)	Particulate methyl-Hg (ng L ⁻¹)	Total methyl-Hg (ng L ⁻¹)	DOC (mg L ⁻¹)	Particulate matter (mg L ⁻¹)
1	1.7	4.2	6.0	0.94	290
2	5.0	12	17	1.1	330
3	1.2	4.1	5.3	2.6	13
4	0.30	1.6	2.0	2.2	4.6
5	0.60	0.50	1.1	1.8	7.4
6	1.2	0.70	1.9	1.7	9.1
7	2.3	14	17	1.6	7600
8	1.0	230	230	5.6	31
9	1.1	38	39	1.7	6600
10	0.80	3.7	4.4	0.73	6.6
11	0.80	0.90	1.7	2.1	9.7
12	n.a.	n.a.	n.a.	n.a.	n.a.
13	2.8	0.60	3.4	3.2	9.1
14	1.3	1.0	2.3	0.88	120
15	1.2	2.0	3.2	1.1	87
16	2.7	0.50	3.2	1.3	8.3
17	0.70	30	31	2.6	7100
18	1.8	0.60	2.5	1.9	4.6
19	1.8	1.3	3.2	3.7	38
20	0.80	250	250	4.1	7100
21	3.5	70	74	1.7	1600
Geomean	1.3	4.5	7.9	2.1	85
SD	1.1	72	72	1.2	2900

Total Hg concentrations in water samples collected in this study greatly exceeded the 12 ng L^{-1} Hg standard recommended by the US Environmental Protection Agency to protect against adverse chronic effects to aquatic life (US EPA, 1992), and in most cases, also exceeded the 1000 ng L^{-1} international drinking water standard for Hg recommended by the World Health Organization (WHO, 1971). However, stream water in Tongguan area is not generally used for drinking water due to high particulate matter contents in the water.

Dissolved, particulate and total methyl-Hg concentrations in warm season water samples varied from 0.3 to 5.0 ng L^{-1} , 0.5 to 250 ng L^{-1} , and 1.1 to 260 ng L^{-1} , respectively (Table 5). Methyl-Hg concentrations in surface water samples collected in the Tongguan area were also elevated compared to those reported in artisanal Au mining areas in

Suriname and the Amazon River basin, which ranged from 0.05 – 3.8 ng L^{-1} (Gray et al., 2002; Nriagu, 1992; Lacerda and Salomons, 1998; Maurice-Bourgoin et al., 1999; Hylander et al., 2000; Lechler et al., 2000). High methyl-Hg concentrations and particulate matter were found in stream water collected from sampling sites 20 and 21, which were close to the confluence with the Yellow River (Table 5). This may imply that the surface water in the Tongguan area carries significant methyl-Hg to the Yellow River, posing a potential threat to this ecosystem. Dissolved Hg concentrations in water correlated significantly with DOC, with a correlation coefficient (r^2) of 0.4904 ($p < 0.01$) (Fig. 4) indicating that DOC may play an important role in partitioning of Hg between particulate and dissolved Hg (Turner et al., 2001). No significant correlation

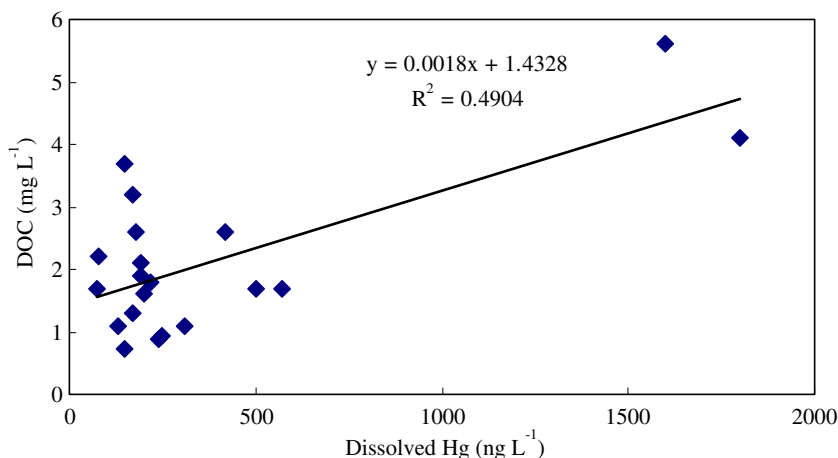


Fig. 4. Correlation between dissolved Hg concentrations and DOC in surface water samples collected in the warm season in the Tongguan area.

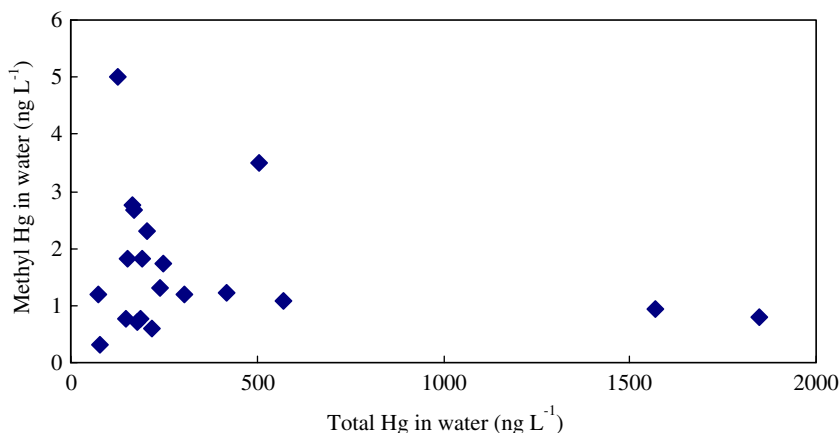


Fig. 5. Correlation between methyl-Hg and total Hg in surface water samples.

concentrations in surface water was observed (Fig. 5), indicating that total Hg is not the most important factor governing Hg methylation processes in surface water.

Total Hg concentrations in sediment collected in the cold and warm seasons varied from 4.7 to 1200 mg kg⁻¹, and 0.90 to 160 mg kg⁻¹, respectively

(Table 4). These total Hg concentrations are significantly higher than those reported from background sites, which is 0.2 mg kg⁻¹ (Förstner and Wittmann, 1983; Hacon et al., 1990), and is also higher than the 0.056 mg kg⁻¹ average total Hg concentration for the upper crust (Wedepohl, 1995). Total Hg concentrations in sediment in the Tong-

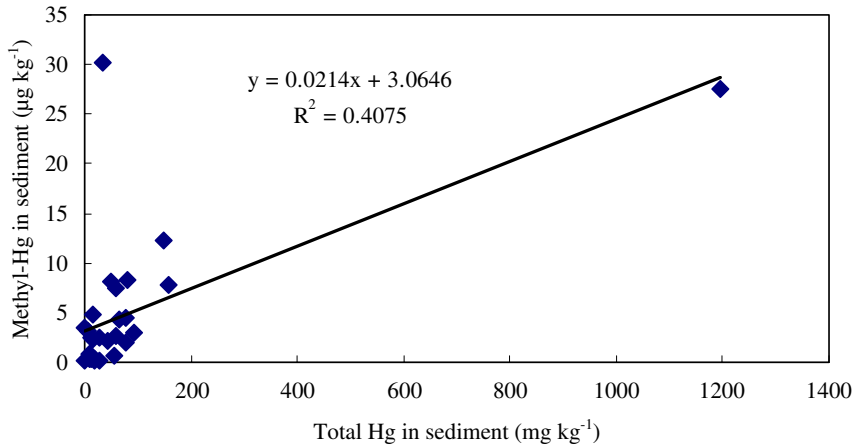


Fig. 6. Correlation between methyl-Hg and total Hg in sediment samples.

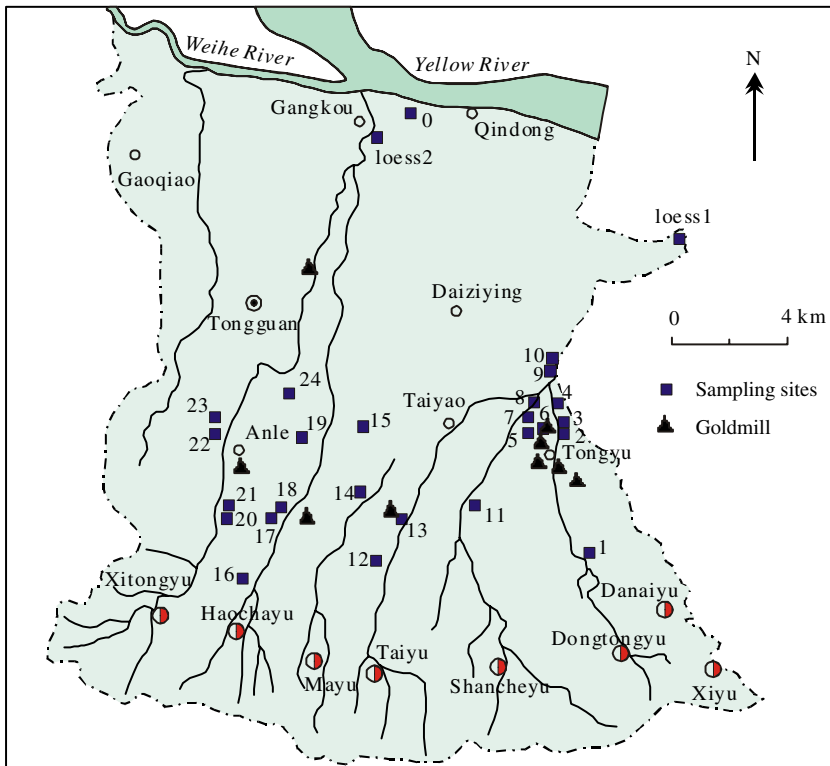


Fig. 7. Localities of soil samples collected in Tongguan Au mining area.

guan Au mining area were also higher than those reported in a past Au mining areas in Nevada, USA, which varied from 0.3 to 42 mg kg⁻¹ (Blum et al., 2001; Miller and Lechler, 2003), and artisanal Au mining areas in Suriname, which varied from 0.11 to 0.15 mg kg⁻¹ (Gray et al., 2002). Past Au mining activities in the Tongguan region have resulted in Hg contamination to sediment ecosystems in this area.

Methyl-Hg concentrations in stream sediment samples collected in the cold and warm seasons ranged from 0.20 to 30 µg kg⁻¹, and 0.10 to 12 µg kg⁻¹, respectively (Table 4). These methyl-Hg concentrations are significantly higher than those reported from a past Au mining area in Nevada, USA (Stamenkovic et al., 2004), which varied from 0.03 to 2.98 µg kg⁻¹, and those reported in artisanal Au mines in Suriname and the Amazon River basin, which ranged from <0.02 to 1.4, and 0.07 to 1.9 µg kg⁻¹, respectively (Gray et al., 2002; Nriagu, 1992; Lacerda and Salomons, 1998; Maurice-Bourgoin et al., 1999; Hylander et al., 2000; Lechler et al., 2000). A significant correlation between methyl-Hg and total Hg in sediment ($r^2 = 0.4075$, $p < 0.01$) was found (Fig. 6). This study demonstrates that active Hg methylation processes occurred in the sediment of streams in the Tongguan area. Fortunately, there are few fish in these streams, limiting methyl-Hg accumulation in aquatic food chains.

4.3. Mercury in surface soil and crop

Soil samples collected from control sites 0, loess 1 and loess 2 were located in the northern part of Tongguan, a few km upwind from Au mills (Fig. 7). Total Hg (0.3–0.9 mg kg⁻¹) and methyl-Hg (0.1 µg kg⁻¹) concentrations in these soil samples were significantly lower than those collected close to the Au mills (Table 6). However, total Hg concentrations in these three control soil samples were elevated compared to the reported regional background total Hg concentrations in soil of 0.02 to 0.04 mg kg⁻¹ (Chinese Environmental Monitoring Center, 1992). Total Hg in these samples was most likely derived from atmospheric Hg deposition. Soil samples collected in the vicinity of Au mills were significantly contaminated with Hg as indicated by total Hg concentrations ranging from 0.9 to 76 mg kg⁻¹ (Fig. 6). Although methyl-Hg only constituted less than 0.6% of the total Hg in soil samples collected from the Tongguan area, methyl-Hg concentrations ranged from 0.40 to

Table 6
Total Hg and methyl-Hg concentrations in soil samples collected in Tongguan Au mining area

Sample no.	Total Hg (mg kg ⁻¹)	Methyl-Hg (µg kg ⁻¹)
Loess 1	0.4	0.1
Loess 2	0.3	0.1
0	0.9	0.1
1	9.9	4.7
2	1.3	7.2
3	1.3	4.2
4	4.7	13
5	11	5.9
6	7.1	16
7	2.5	13
8	0.9	3.2
9	1.7	6.1
10	1.0	2.7
11	9.6	9.5
12	58	2.3
13	5.0	5.4
14	10	9.3
15	6.0	7.5
16	76	7.1
17	3.2	1.8
18	44	0.5
19	9.4	1.1
20	21	2.2
21	18	2.9
22	2.3	0.4
23	2.5	0.7
24	19	5.9
Geomean	4.7	2.5
SD	18	4.3

16 µg kg⁻¹, which are comparable to those observed in the Wanshan Hg mining district ranging of 0.13 to 23 µg kg⁻¹ (Qiu et al., 2005). Surface soil in the Tongguan Au mining area is significantly contaminated with Hg, but total Hg and methyl-Hg concentrations in soil do not correlate (Fig. 8). Methyl-Hg concentrations are elevated in some soil samples (up to 9.5 µg kg⁻¹, Table 6) indicating that Hg methylation is active in these soils.

Total Hg and methyl-Hg concentrations were measured in a few crop samples collected in Tongguan area (Table 1). Total Hg concentrations in vegetable and wheat samples ranged from 42 to 640 µg kg⁻¹, all of which significantly exceed the Chinese guidance limit for vegetables (10 µg kg⁻¹) and foodstuffs other than fish (20 µg kg⁻¹). More studies are needed to evaluate the health effects of consuming foods in this area with such highly contaminated Hg. Fortunately, methyl-Hg was not generally accumulated in these crop samples, where concentrations varied from 0.2 to 7.7 µg kg⁻¹ (Table 1).

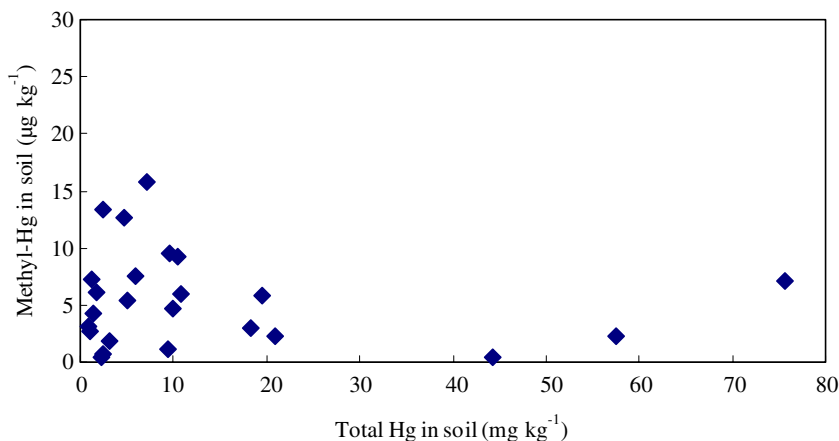


Fig. 8. Correlation between methyl-Hg and total Hg in soil samples.

5. Conclusions

Long-term and large-scale Au mining activities using elemental Hg amalgamation techniques in Tongguan, Shaanxi have resulted in local ecosystem Hg contamination. TGM concentrations in large-scale Au mills were highly elevated, exceeding the maximum allowable TGM concentrations for occupational exposure recommended in China. Workers in these Au mills were exposed to concentrations of Hg vapor with potential adverse effects to human health. Generally, TGM concentrations in ambient air in the Tongguan area were significantly higher than global background TGM concentrations reported in the Northern Hemisphere. Controls are needed to reduce Hg emissions from Au extraction processes. Stream water, stream sediment and soil collected in this study were found to be highly contaminated with Hg and methyl-Hg, suggesting that Hg methylation is active in ecosystems in the Tongguan area. Data shown here indicate that vegetables and wheat grown in this area may be also contaminated with Hg and that potential exposure of Hg to humans consuming such foods in this area needs further study.

Acknowledgment

This research was financed by the Chinese Academy of Sciences through a key innovation project (KZCX3-SW-443) and by Natural Science Foundation of China (405320514).

References

- Aula, I., Braunschweiler, Leino, T., Malin, I., Porvari, P., Hatanaka, T., Lodenius, M., Juras, A., 1994. Levels of mercury in the Tucuruí Reservoir and its surrounding area in Para, Brazil. In: Watras, C.J., Huckabee, J.W. (Eds.), *Mercury Pollution: Integration and Synthesis*. CRC Press, Boca Raton, Florida, pp. 21–40.
- Blum, M., Gustin, M.S., Swanson, S., Donaldson, S.G., 2001. Mercury in water and sediment of Steamboat Creek, Nevada: implications for stream restoration. *J. Am. Water Res. Assoc.* 37, 795–804.
- Chinese Environmental Monitoring Center, 1992. *Soil Environmental Background Value of Elements in the People's Republic of China*. China Environmental Science Press, Beijing, pp. 1–87 (in Chinese).
- Dai, Q., 2004. Environmental geochemistry study of mercury contamination from gold mining areas by amalgamation technique in China—a case study from Tongguan county of Shaanxi Province. Master's Thesis, Institute of Geochemistry, Chinese Academy of Sciences.
- Dai, Q., Feng, X., Qiu, G., Jiang, H., 2003. Mercury contaminations from gold mining using amalgamation technique in Xiaoqinling Region, Shanxi Province, PR China. *J. Phys.* 107, 345–348.
- Duan, S., Liu, X., Li, H., Yuan, Z., 2001. A survey of health impact from mercury of miner in a gold mining workshop. *Henan J. Prevention Medicine* 12, 358–359 (in Chinese).
- Ebinghaus, R., Kock, H.H., Coggins, A.M., Spain, T.G., Jennings, S.G., Temme, Ch., 2002. Long-term measurements of atmospheric mercury at Mace Head, Irish west coast, between 1995 and 2001. *Atmos. Environ.* 36, 5267–5276.
- Feng, X.B., 2004. Mercury pollution in China – an overview. In: Pirrone, N., Mahaffey, K.R. (Eds.), *Dynamics of Mercury Pollution on Regional and Global Scales: Atmospheric Processes and Human Exposures Around the World*. Springer Publishers, Norwell, MA, USA, pp. 657–678.
- Feng, X., Shang, L., Wang, S., Tang, S., Zheng, W., 2004. Temporal variation of total gaseous mercury in the air of Guiyang, China. *J. Geophys. Res.* 109, D03303. doi:10.1029/2003JD00415.
- Förstner, U.W., Wittmann, G.T.W., 1983. *Metal Pollution in the Aquatic Environment*. second ed.. Springer-Verlag, Berlin.
- Frery, N., Maury-Brachet, R., Maillot, E., Deheeger, M., de Merona, B., Boudou, A., 2001. Gold-mining activities and

- mercury contamination of native Amerindian communities in French Guiana: key role of fish dietary uptake. *Environ. Health Perspect.* 109, 449–456.
- Gray, J.E., Labson, V.F., Weaver, J.N., Krabbenhoft, D.P., 2002. Mercury and methylmercury contamination related to artisanal gold mining, Suriname. *Geophys. Res. Lett.* 29, 2105. doi:10.1029/2002GL015575.
- Guan, M., Xue, G., Li, X., Fu, X., 2002. Epidemiological survey of mercury pollution in a gold mine. *Chinese J. Public Health Eng.* 1, 146–148 (in Chinese).
- Guimarães, J.R.D., Roulet, M., Lucotte, M., Mergler, D., 2000. Mercury methylation along a lake-forest transect in the Tapajos river floodplain, Brazilian Amazon: seasonal and vertical variation. *Sci. Tot. Environ.* 261, 91–98.
- Gunson, A.J., 2004. Mercury and artisanal small scale gold mines in China. Master's Thesis, Univ. British Columbia, Canada.
- Hacon, S., Lacerda, L.D., Pfeiffer, W.C., 1990. Riscos e conseqüências do uso do mercúrio. Rio de Janeiro: FINEP/CNPq.
- Hylander, L.D., Meili, M.m., Oliveira, J., Silva, E., Guimaraes, J.R.D., Araujo, D.M., Neves, R.P., Stachiw, R., Barros, A.J.P., Silva, G.D., 2000. Relationship of mercury with aluminum, iron, and manganese oxy-hydroxides in sediments from the Alto Pantanal, Brazil. *Sci. Total Environ.* 260, 97–107.
- Lacerda, L.D., Salomons, W., 1998. Mercury from Gold and Silver Mining: A Chemical Time Bomb? Springer-Verlag, Berlin.
- Lechler, P.J., Miller, J.R., Lacerda, L.D., Vinson, D., Bonzongo, J.C., Lyons, W.B., Warwick, J.J., 2000. Elevated mercury concentrations in soils, sediments, water and fish of the Madeira River basin, Brazilian Amazon: a function of natural enrichments? *Sci. Total Environ.* 260, 87–96.
- Liang, L., Horvat, M., Feng, X.B., Shang, L.H., Li, H., Pang, P., 2004. Re-evaluation of distillation and comparison with HNO₃ leaching/solvent extraction for isolation of methylmercury compounds from sediment/soil samples. *Appl. Organometal. Chem.* 18, 264–270.
- Limbong, D., Kumampung, J., Rimper, J., Arai, T., Miyazaki, N., 2003. Emissions and environmental implications of mercury from artisanal gold mining in north Sulawesi, Indonesia. *Sci. Total Environ.* 302, 227–236.
- Lindqvist, O., Johansson, K., Aastrup, M., Anderson, A., Bringmark, L., Hovsenius, G., Hakanson, L., Iverfeldt, A., Meili, M., Timm, B., 1991. Mercury in the Swedish environment—recent research on causes, consequences and corrective methods. *Water Air Soil Pollut.* 55, 1–261.
- Lin, Y., Guo, M., Gan, W., 1997. Mercury pollution from small gold mines in China. *Water Air Soil Pollut.* 97, 233–239.
- Malm, O., Pfeiffer, C., Souza, C., Reuther, R., 1990. Mercury pollution due to gold mining in the Madeira River basin, Brazil. *Ambio* 19, 11–15.
- Maurice-Bourgoin, L., Quiroga, I., Guyot, J.L., Malm, O., 1999. Mercury pollution in the upper Beni River, Amazonian basin: Bolivia. *Ambio* 28, 302–306.
- Miller, J.R., Lechler, P.J., 2003. Importance of temporal and spatial scale in the analysis of mercury transport and fate: an example from the Carson River system, Nevada. *Environ. Geol.* 43, 315–325.
- Mol, J.M., Ramlal, J.S., Lietar, C., Verloo, M., 2001. Mercury contamination in freshwater, estuarine, and marine fishes in relation of small-scale mining in Suriname, South America. *Environ. Res. A* 86, 183–197.
- NAS, 1978. An Assessment of Mercury in the Environment. National Academy of Sciences, Washington, DC.
- Nriagu, J.O., 1990. Human influence on the global cycling of trace metals. *Paleogeog. Paleoclim. Paleoecol.* 82, 113–120.
- Nriagu, J.O., 1992. Mercury pollution in Brazil. *Nature* 356, 389.
- Pamela, L.D., Maritza, R., Christopher, M.R., Charles, A.M., Jenkins, F.M., 2001. Occupational exposure to airborne mercury during gold mining operation near El Callao, Venezuela. *Internat. Arch. Occup. Environ. Health* 74, 206–212.
- Pestana, M.H.D., Formoso, M.L.L., 2003. Mercury contamination in Lavras do Sul, South Brazil: a legacy from past and recent gold mining. *Sci. Total Environ.* 307, 125–140.
- Qi, X., 1997. Development and application of an information administration system on mercury. Master's Thesis, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China (in Chinese).
- Qiu, G., Feng, X., Wang, S., Shang, L., 2005. Mercury and methylmercury in riparian soil, sediments, mine-waste calcines, and moss from abandoned Hg mines in east Guizhou province, southwestern China. *Appl. Geochem.* 20, 627–638.
- Qiu, G., Feng, X., Wang, S., Shang, L., 2006. Environmental contamination of mercury from Hg-mining areas in Wuchuan, northeastern Guizhou, China. *Environ. Pollut.* 142, 549–558.
- Rask, M., Metsala, R., 1991. Mercury concentrations in northern pike, *esox lucius* L., in small lakes of Evo area, Southern Finland. *Water Air Soil Pollut.* 56, 369–378.
- Richard, S., Arnoux, A., Cerda, P., Reynouard, C., Horeau, V., 2000. Mercury levels of soils, sediments and fish in French Guiana, South America. *Water Air Soil Pollut.* 124, 221–244.
- Schroeder, W.H., Munthe, J., 1998. Atmospheric mercury—an overview. *Atmos. Environ.* 32, 809–822.
- Stamenkovic, J., Gustin, M.S., Marvin-Dipasquale, M.C., 2004. Distribution of total and methyl mercury in sediments along Steamboat Creek (Nevada, USA). *Sci. Total Environ.* 322, 167–177.
- Taylor, H., Appleton, J.D., Lister, R., Smith, B., Chitamwebwa, D., Mkumbo, O., Machiwa, J.F., Tesha, A.L., Beinhoff, C., 2005. Environmental assessment of mercury contamination from the Rwanagasa artisanal gold mining centre, Geita District, Tanzania. *Sci. Total Environ.* 343, 111–133.
- Turner, A., Millward, G.E., Le Roux, S.M., 2001. Sediment-water partitioning of inorganic mercury in estuaries. *Environ. Sci. Technol.* 35, 4648–4654.
- US EPA, 1992. Water quality standards; establishment of numeric criteria for priority toxic pollutants; states' compliance; final rule, US EPA. *Federal Register* 40 CFR Part 131, 57 (246), 60,874–60,916.
- US EPA, 1999. Method 1631, Revision B: Mercury in water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. United States Environmental Protection Agency, 1–33.
- US EPA, 2001. Method 1630: Methyl mercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS. Draft January 2001. US Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303), 1200 Pennsylvania Avenue NW, Washington, DC 20460, 1–41.

- Verta, M., 1990. Mercury in Finnish forest lakes and reservoirs: anthropogenic contribution to the load and accumulation in fish. Publications of the Water and Environment Research Institute, National Board of Waters and the Environment. Finland. No. 6.
- Wang, S., 2001. An investigation of health impact of mercury to miners in a gold mining workshop. *Occup. Health* 17 (11), 20–25 (in Chinese).
- Wang, W., Shui, C., Du, W., 1999. An investigation of health impact of mercury to miners in a gold mining workshop. *China Public Hyg.* 15, 432–435 (in Chinese).
- Watras, C.J., Frost, T.M., 1989. Little rock lake: perspectives on an experimental approach to seepage lake acidification. *Arch. Environ. Contam. Toxicol.* 18, 157–165.
- Wedepohl, K.H., 1995. The composition of the continental crust. *Geochim. Cosmochim. Acta* 59, 1217–1232.
- WHO, 1971. International Standards for Drinking Water, third ed. World Health Organization, Geneva, Switzerland.
- Xi, S., Chen, M., Weng, Z., Ma, Q., Zhu, M., Xu, H., 1996. An investigation of mercury poisoning in a gold mining workshop. *Labor Med.* 13, 92–93 (in Chinese).
- Zhang, C., Zhang, X., Chang, Z., 1999. Mercury pollution of gold extraction from gold mercury compound in Henen province Xiaoginling gold mineral belt. *J. Geol. Hazards Environ. Preser.* 10 (2), 18–23 (in Chinese).
- Zhong, G., Lou, J., 2000. A survey of occupational risk of mercury in gold mine. *J. Sichuan Continuing Educ. College MS* 19 (1), 61–62 (in Chinese).