



Mercury distribution and speciation in water and fish from abandoned Hg mines in Wanshan, Guizhou province, China

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ABSTRACT

Concentrations of total mercury (Hg^{T}), methylmercury (MeHg), and its speciation in water samples as well as fish collected from abandoned Hg mines in Wanshan, Guizhou province, China, were measured to show regional dispersion of Hg contaminations that are not well known. High Hg^{T} and MeHg^{T} (total methylmercury) concentrations obtained in waters from mining areas, ranged from 15 to 9300 ng/l and 0.31 to 25 ng/l, respectively. MeHg^{T} were not correlated with Hg^{T} , whereas, peak values in both cases were in accord with high concentrations of particulate fraction, which appeared to be enhanced during high-flow regime with ratios reaching to 99%. Elevated Hg concentrations in the particulate form indicated that particles released from Hg mining tailings (calcines) might be an important pathway of Hg to the aquatic system. The concentrations of total Hg in fish muscle were elevated ranging from 0.061 to 0.68 mg/kg, but MeHg were generally low ranging from 0.024 to 0.098 mg/kg with a mean ratio of 28%. The concentrations and distribution patterns of Hg in aquatic systems suggested derivation from historic Hg mining sites in the Wanshan area.

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1. Introduction

Hg mining is an important anthropogenic source of Hg pollution in the environment. At most Hg mining sites, surface waters are usually highly contaminated with Hg released from mine tailings, commonly termed calcines. The input of Hg to waters is of great concern because of the production of MeHg that is a highly toxic and biomagnified Hg form. Hence the precise knowledge of Hg content and its fractions in aquatic systems is essential to evaluate the Hg cycling within Hg mining sites.

The Wanshan Hg mine in Guizhou province, southwestern China, was the largest Hg producing area in Asia. Mining at Wanshan was initiated in 221 B.C., but ceased in 2001 due to lower demand for Hg and increasing environmental concerns. The primary concern about the Hg mine is the large quantities of calcines disposed on lands and in creeks in Wanshan. Between 1949 and early 1990s, for instance, approximately 130 million tons of calcines had been dispersed into adjacent ecosystem (Liu, 1998). The calcines introduced by cinnabar ores heating processing usually have Hg concentrations 2–3 orders of magnitude greater than the background concentrations of regional soil and sediment (Qiu et al., 2005). Those abandoned and untreated mine tailings continue releasing Hg by mechanical dispersion into surrounding environmental compartments, such as water, soil, and sediment.

Geochemical studies relating Hg contamination to the local environment in Wanshan were recently reported. Concentrations of Hg^{T} in water emanating from calcines were reported to be up to the range of 580–10,580 ng/l (Feng et al., 2003; Horvat et al., 2003). Some results showed that the historic Hg mining had a strong impact on agricultural crops. The Hg^{T} levels of between 10.3–1120 $\mu\text{g}/\text{kg}$ and up to 170 $\mu\text{g}/\text{kg}$ in MeHg were found in rice seeds (Horvat et al., 2003; Feng et al., 2008; Qiu et al., 2008).

The present work focuses on speciation of Hg in the aquatic system impacted by Hg mining in Wanshan. The information on the concentration, speciation, and distribution of Hg in water has been presented. Preliminary results on Hg concentrations in fish inhabited the aquatic system are also discussed.

2. Materials and methods

2.1. Study sites

Wanshan is hilly and karstic, with the highest elevation of 1149 m above sea level in the midwest decreasing to the lowest elevation of 270 m above sea level in the east. It has a sub-tropical humid climate characterized by abundant precipitation and mild temperature. The annual average rainfall is 1200–1400 mm. Most of the Hg mines and retorts in Wanshan are scattered in valleys in the highest midwest (Fig. 1).

The major rivers in the study area include the Xiaxi, Aozhai, Huangdao and Gaolouping Rivers with their headwaters originating

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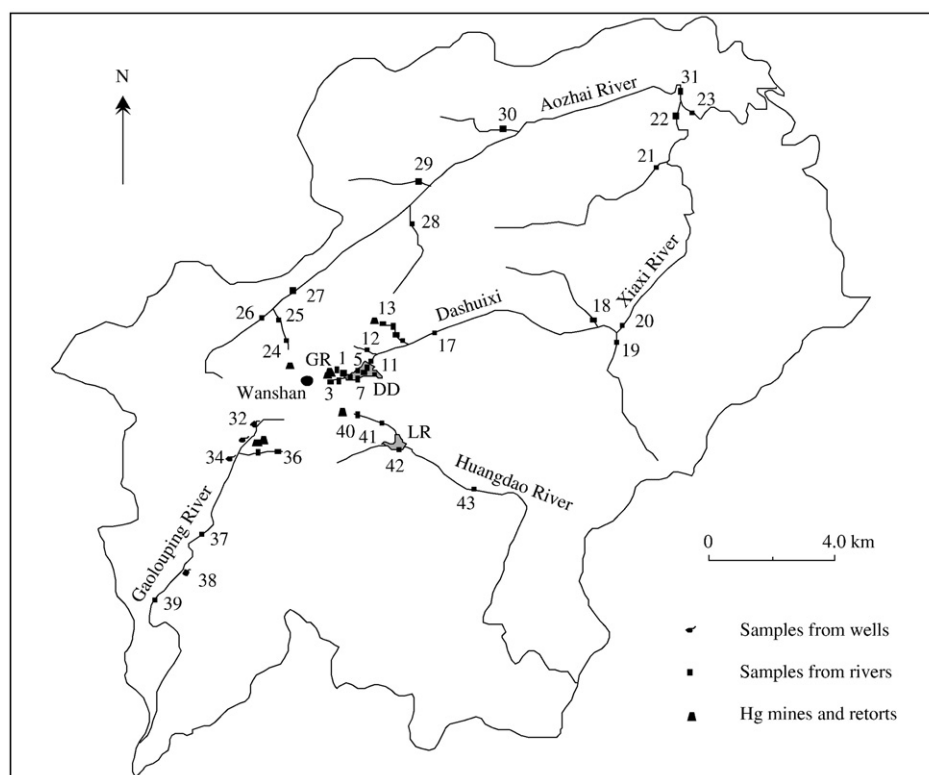


Fig. 1. Map of the sampling locations in Wanshan.

from Hg mining sites. Large quantities of rejected materials of waste rocks, low-grade ores, and calcines are found in their upstream banks and/or flood plains. The upper tributary of the Xiayi River, named Dashuixi, flows through an area where the largest Hg processing facility, Guizhou Retort (GR), and other historic Hg retorts are distributed. A large reservoir, Dashuixi Dam (DD) that was built to receive drainage and mine-wastes discharged from the GR, lies in the same area. The Dam was also a temporary fish fostering site deployed by farmers. Another big reservoir, Longjiang Reservoir (LR), is located in the upstream of the Huangdao River, which was also designed to receive mining drainage. Sources of water for the upper stream of the Gaolouping River, which is characterized by lots of domestic wells along its upstream's bank, are the combination of drainages of the wells and mine discharge through surrounding calcines. Geological outcrops in the drainage basin comprise limestone, dolomite, and sandstone with intercalated shale.

2.2. Sample collection

Water samples were taken during base-flow and high-flow regimes and the sampling locations were shown in Fig. 1. Samples were collected with polyethylene-gloved hands either into an acid-cleaned 500 ml Teflon bottle (for dissolved Hg measurements) or directly into an acid-cleaned 100 ml borosilicate-glass bottle (for total and reactive Hg measurements). After collection, samples for dissolved Hg measurements were immediately filtered with 0.45 μm Millipore membrane filters using a borosilicate-glass filtration apparatus. Samples were acidified in the field, immediately after collection or filtration, by adding 0.4% (v/v) of high-purity HCl.

Fish samples were collected from Dashuixi Dam during a high-flow regime. Only a sort of grass carp (*Ctenopharyngodon idella Valenciennes*), which were raised when they were fry by farmers but grown naturally, were sampled. In the field, fish samples were labeled and placed in polyethylene bags and temporarily stored at +4 °C in a refrigerator. In

the laboratory, muscle samples were carefully removed from fish and stored in polyethylene vials, then stored deep-frozen (−25 °C). Before sample aliquots were taken for analysis, a homogeneous mass of muscle tissue was obtained with a sterilized glass plate using a clean scalpel.

2.3. Sample analyses

Hg^T and MeHg were determined in water and fish samples using cold-vapor atomic fluorescence (CVAFS). Measurement of Hg^T followed U.S. EPA Method 1631, and analysis of MeHg followed U.S. EPA Method 1630 (U.S. EPA, 1999, 2001).

Hg speciation in water samples was operationally defined according to the steps in treating of samples as follows. Reactive Hg (Hg^R) includes Hg species reduced by SnCl₂ to Hg⁰ and was directly determined by SnCl₂ reduction on acidified samples. Hg^T and its dissolved fraction (Hg^D) were determined by SnCl₂ reduction following BrCl oxidation. A detailed description of the method of Hg speciation was given elsewhere (Bloom and Creclius, 1983; Horvat et al., 1987, 1991, 2002). Samples collected during high-flow regime were also determined for MeHg concentration, and MeHg^T and MeHg^D (dissolved fraction) were analyzed by NaBEt₄ ethylation following distillation, Tenax trapping, and GC-CVAFS detection (Horvat et al., 1993; Liang et al., 1994, 1996). The particulate fraction of either Hg^P or MeHg^P was obtained by subtracting dissolved fraction from the Hg^T and MeHg^T, respectively.

Hg^T and MeHg in fish samples were analyzed as follows. An appropriate aliquot of homogeneous mass of fish muscle (typically 0.5–1.0 g for Hg^T; 0.1–0.5 g for MeHg) was weighed out into a 25 ml borosilicate bottle for Hg^T and a 30 ml Teflon vial for MeHg, respectively. For Hg^T analysis, add 10 ml of a mixture of HNO₃ and H₂SO₄ (8:2, v/v), then heated in an oven at 95–140 °C for 2 h for digestion. For MeHg analysis, added 2 ml of 25% KOH–methanol into the vial, then capped and heated in an oven at 75 °C for 3 h for digestion. After digestion, MeHg was back-extracted from the solvent phase into water prior to aqueous phase ethylation.

Quality assurance and quality control of Hg^T and MeHg analysis were assessed using duplicates, method blanks, matrix spikes, and reference material (TORT-2). The relative standard deviation was <9%, and the relative percentage difference of sample duplicates was <5.4%. Recoveries on matrix spikes of MeHg in water samples were in the range of 88–108%. Mean MeHg concentration of $0.153 \pm 0.0024 \mu\text{g/g}$ ($n = 5$) was obtained from TORT-2 with a certified value of $0.152 \pm 0.013 \mu\text{g/g}$. Limits of determination were 0.02 ng/l for Hg^T and 0.009 ng/l for MeHg in water samples, and 0.013 ng/g for Hg^T and 0.002 ng/g for MeHg in fish samples.

3. Results and discussion

3.1. Hg^T and speciation in waters

3.1.1. Spatial distribution and variation

3.1.1.1. Hg^T . Concentrations of Hg^T determined in two surveys widely ranged from 15 to 9300 ng/l, reflecting impacts of mine tailings

Table 1
Mercury and its speciation in surface waters in Wanshan, Guizhou, China (ng/l).

ID	Location	Hg^T		Hg^D		Hg^P		Hg^R	
		Base-flow	High-flow	Base-flow	High-flow	Base-flow	High-flow	Base-flow	High-flow
<i>Xiaksi River</i>									
1	Creek	1700	5900	31	33	1600	5900	6.3	5.7
2	Creek	4500		34		4400		7.1	
3	Creek	3100		87		3000		34	
4	Creek	810	830	110	23	700	810	40	4.1
5	Reservoir	1800	2500	26	16	1800	2500	7.2	3.1
6	Reservoir	490		22		470		6.8	
7	Reservoir	1100		22		1100		6.8	
8	Reservoir	300		19		280		5.4	
9	Reservoir	260		20		240		4.4	
10	Reservoir	200		25		170		4.7	
11	Creek	430	1500	32	24	400	1500	14	20
12	Tributary	60	1100	15	57	45	1100	2.1	1.0
13	Drainage	280	3800	23	48	260	3800	1.0	1.8
14	Pond	620	4700	86	46	530	4600	8.5	4.2
15	Pond	710	3600	88	52	620	3500	11	2.2
16	Creek	1300	1700	430	45	880	1700	400	8.1
17	Creek	350	870	42	20	310	850	5.3	8.9
18	Tributary	22	730	17	92	4.5	640	5.3	18
19	Tributary	15	81	14	13	1.4	68	1.6	1.9
20	River	38	180	17	16	21	160	2.5	3.7
21	Tributary	27	35	17	19	9.6	16	1.5	0.80
22	River	37	46	28	15	9.0	31	2.5	0.60
23	River	20	110	13	16	6.9	91	2.0	2.2
<i>Aozhai River</i>									
24	Creek	87	870	26	20	61	850	4.0	2.2
25	Creek	260	740	52	20	210	720	3.1	3.1
26	Creek	64	570	24	11	40	560	3.7	1.2
27	Creek	26	840	17	19	8.9	820	2.3	1.2
28	Tributary	24	43	21	17	3.2	26	1.9	1.6
29	Tributary	33	38	23	20	10	18	1.2	2.5
30	Tributary	21	46	19	25	2.0	21	1.8	0.69
31	River	27	34	17	22	9.6	12	1.8	1.1
<i>Gaolouping River</i>									
32	Well	58	1500		35		1400	14	2.4
33	Well	270	3500		58		3400	230	8.5
34	Well	66	600		27		570	43	1.6
35	Pond	67	1000		21		930	26	11
36	Creek	160	3900		140		3700	16	79
37	Creek	42						8.8	
38	Well	350	1800		65		1700	320	12
39	River	47						5.2	
<i>Huangdao River</i>									
40	Creek	2000	9300	93	52	1900	9200	15	31
41	Creek	6200		410		5800		390	
42	Reservoir	1700	780	24	17	1700	760	2.8	2.1
43	River	410	1100	23	20	390	1100	3.3	5.4

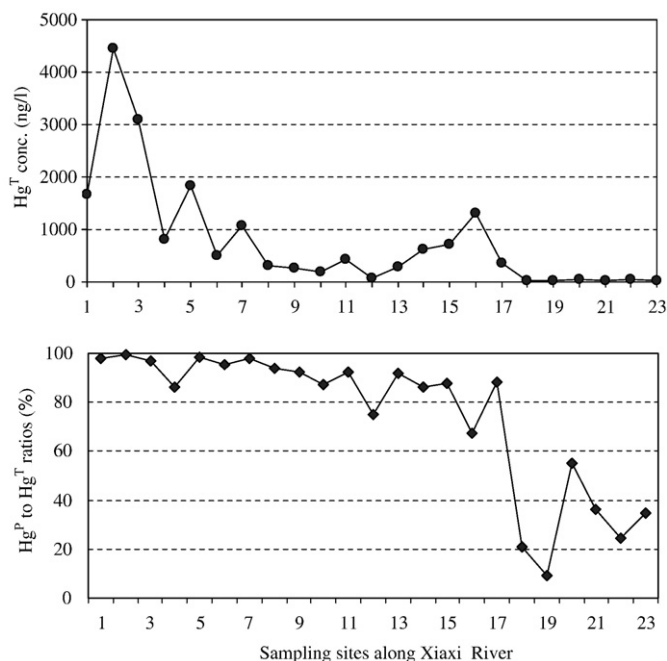


Fig. 2. Mercury and its speciation distribution in samples along Xiaksi River during base-flow regime in Wanshan.

spatially distributed along rivers (Table 1). Peak values of Hg^T were observed at the upper tributaries of the Lonjiang Reservoir, where historic Hg retorts and huge quantities of calcines are located. Similar results were found in Dashui Creek and upstream of Aozhai and Gaolouping Rivers. Those high values of Hg^T decreased sharply in downstream waters and tributaries isolated from mining sites. The Hg^T in Dashui Creek during base-flow condition in December, for instance, declined from upstream with mean value of 1100 ng/l (samples 1–17) to downstream of 26 ng/l (samples 18–23) (Fig. 2). Similarly, low levels of Hg^T were found in downstream tributaries of Aozhai River (samples 28–30).

Exceedingly high values of Hg^T in upper streams reacted with calcines could be attributed to the abundant water-soluble Hg compounds in those tailings (Kim et al., 2000, 2004). This suggested that, therefore, calcines are a primary source of Hg to waters in the Wanshan Hg mining sites. The high levels of Hg in calcines (Qiu et al., 2005) may be considered a primary impact factor for Hg concentrations in water systems in the region. On the other hand, the constant low values of Hg^T in downstream tributaries might be, presumably, characteristic of the background Hg concentrations for the aquatic system. Sources of Hg in those tributaries can be attributed to accumulative inputs from host Hg-bearing rock by weathering and/or leaching processes.

3.1.1.2. Hg^P . The range of Hg^P concentrations in water samples varied from 1.4 to 9200 ng/l, and displayed a similar trend to that of Hg^T . Samples collected from upper streams reacted with calcines presented abnormally high levels of Hg^P , and usually constituted large portions of the Hg^T (67–99%). A significant positive correlation between Hg^P and Hg^T was observed ($r^2 = 0.998$, Fig. 3), which confirmed that high Hg-contaminated waters in Hg mining areas were attributed to inputs of Hg-contaminated particles eroded from calcines heaps (Rytuba, 2000).

Similar to Hg^T spatial variation, Hg^P in downstream and tributaries decreased sharply as well. The Hg^P fraction accounted for only 9.1% of Hg^T in sample 19 during the base-flow regime. This likely was due to the suspended particulate matters decreasing within the downstream and the different Hg sources for the tributaries isolated from Hg mining sites.

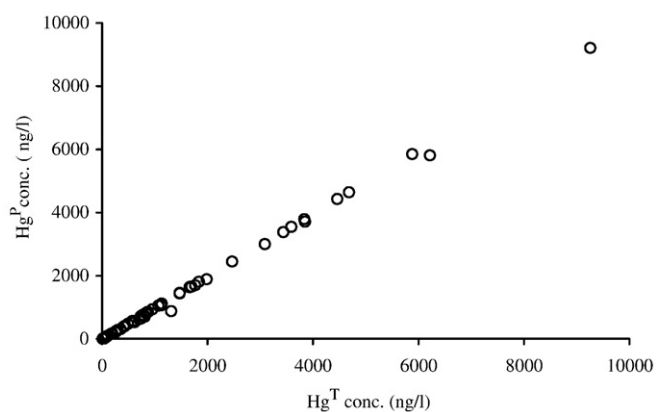


Fig. 3. The relationship between Hg^T and Hg^P in water samples in Wanshan.

3.1.1.3. Hg^D . The range of Hg^D concentrations varied from 11 to 430 ng/l. The peak value of Hg^D as high as 430 was obtained in sample 16, which reacted with leaches released from nearby calcines. Similarly, the sample 41 that was directly impacted by the tailings presented elevated Hg^D concentrations as well. Those observations indicated that sources of Hg^D in waters were most likely the calcines that contained unstable and water-soluble Hg compounds (Kim et al., 2000, 2004; Gray et al., 2002, 2003). The Hg^D concentrations in samples from downstream and tributaries were low, but high ratios of Hg^D to Hg^T were obtained, which comprised up to 90% in sample 19 during the base-flow regime. This might indicate different sources of Hg in those aquatic systems.

Generally, inputs of water discharges from nearby calcines heaps might explain the high Hg^D concentrations. However, significant quantities of alkali minerals (i.e. CaO, MgO) that composed of calcines (Wu and Liu, 2002; Zhang et al., 2004) produced high pH in water as shown in Table 2, which could cause Hg^D to transform into Hg^P , thus resulting in high ratios of Hg^P in contaminated water samples in Hg mining sites. But Hg released from host Hg-bearing sulfide ores by weathering/leaching processes might contribute to the high ratios of Hg^D in downstream tributaries.

3.1.1.4. Hg^R . The Hg^R concentrations constituted a small fraction of Hg^T in water samples and always matched high ratios of Hg^D , which varied from 0.60 to 400 ng/l. A positive relationship between Hg^R and Hg^D was found ($r^2=0.93$). Generally, the Hg^R represents the Hg substrate available for methylation, Hg^0 formation, and other conversion processes (Mason and Fitzgerald, 1990).

3.1.1.5. Dashuixi Dam. Hg^T concentrations were spatially variable within the Dam. High Hg^T were observed at the sites where entrances of streams are located (locations 5–7), while samples from other sites (locations 8–10) contained slightly low Hg^T . This spatial variation might be related to the nature of suspended particles released from upstream mining tailings. The immediate inputs from upstream usually conveyed large portions of particles either in fine or coarse fractions. While moving within reservoir, most coarse fractions deposited quickly, thus resulted in a sharp decrease in Hg^T . However, different distribution patterns were observed in Hg^D and Hg^R . Mercury concentrations of both species constantly ranged from 19 to 26 ng/l and 4.7 to 7.2 ng/l, respectively.

As shown in Table 1, in addition, samples collected from above and within the reservoir exhibited elevated levels of Hg (locations 5–10), but samples from downstream of the Dam (location 11) contained low level of Hg^T . This might indicate that Dashuixi Dam acted as a sink of Hg in long term.

3.1.1.6. Wells. Mercury in unfiltered groundwater collected from domestic wells along Gaolouping River was also measured in this

Table 2
Methylmercury in surface waters in Wanshan, Guizhou, China (ng/l).

ID	Location	MeHg ^T	MeHg ^D	MeHg ^P	pH
<i>Xiixi River</i>					
1	Creek	2.9	0.98	1.9	8.9
4	Creek	0.31	0.081	0.23	7.0
5	Reservoir	1.7	1.2	0.52	7.6
11	Creek	7.6	0.31	7.3	6.8
12	Tributary	0.72	0.36	0.36	8.2
13	Drainage	1.2	0.69	0.51	8.7
14	Pond	1.6	0.45	1.1	8.2
15	Pond	0.48	0.45	0.031	11
16	Creek	1.1	1.0	0.12	11
17	Creek	0.39	0.22	0.17	7.5
18	Tributary	0.51	0.32	0.21	7.6
19	Tributary	0.80	0.68	0.12	7.6
20	River	22	6.0	16	7.6
21	Tributary	1.1	0.84	0.26	9.4
22	River	1.7	0.36	1.3	9.6
23	River	0.85	0.16	0.69	9.0
<i>Aozhai River</i>					
24	Creek	0.44	0.21	0.23	8.8
25	Creek	0.79	0.36	0.43	8.8
26	Creek	1.63	0.43	1.2	8.4
27	Creek	0.74	0.37	0.37	8.3
28	Tributary	0.56	0.23	0.33	8.6
29	Tributary	0.59	0.35	0.24	8.1
30	Tributary	0.42	0.19	0.23	8.7
31	River	0.52	0.51	0.011	8.7
<i>Gaolouping River</i>					
32	Well	0.44	0.42	0.022	7.1
33	Well	0.44	0.19	0.25	7.0
34	Well	0.34	0.26	0.081	7.1
35	Pond	1.5	0.21	1.3	8.9
36	Creek	3.3	0.65	2.6	12
38	Well	25	3.1	22	7.1
<i>Huangdao River</i>					
40	Creek	3.5	0.31	3.2	7.6
42	Reservoir	0.95	0.43	0.52	7.8
43	River	1.1	0.31	0.79	7.7

*MeHg in samples collected in high-flow season.

study (Table 1). High Hg^T concentrations were obtained, ranging from 58 to 970 ng/l. The Hg^R presented as dominant fraction with ratios ranging from 64 to 91%. Those elevated Hg concentrations in wells might indicate that the groundwater system was contaminated.

3.1.2. Temporal distribution and variation

Water samples usually represent information under particular hydrological conditions during periods of sampling (Horvat et al.,

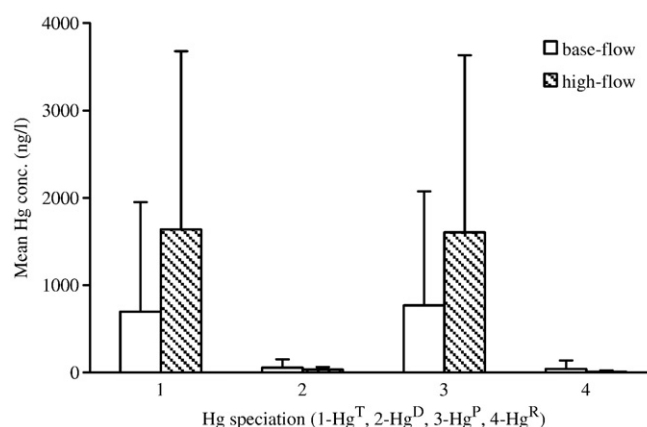


Fig. 4. The temporal variations of mercury and its speciation in water samples in Wanshan.

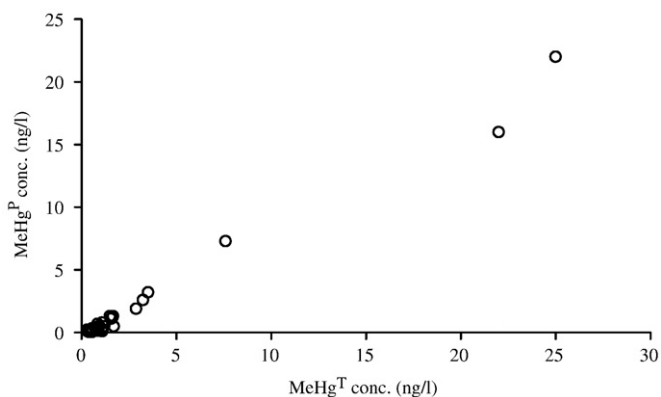


Fig. 5. The relationship between MeHg^{T} and MeHg^{P} in water samples in Wanshan.

2003). Mercury species in water samples from the Wanshan Hg mining region in the base-flow and high-flow regimes were shown in Fig. 4.

Concentrations of Hg^{T} in samples from the high-flow regime were higher than that of samples from the base-flow regime. The mean value of Hg^{T} in the high-flow season was almost about 2 times higher than that of the base-flow season. In both cases, Hg^{P} constituted a large portion of the total. However, variations of Hg^{T} in samples from downstream became slight between the high-flow and base-flow seasons, which were probably attributed to low levels of Hg^{P} in samples. Abundant precipitation in high-flow season in Wanshan may increase the input of Hg-rich particles in runoff, and as such, resulted in high levels of Hg^{T} in waters during the season.

Hg^{D} concentrations in samples from high-flow season were lower than that of samples from base-flow season. A similar trend was found in levels of Hg^{R} in samples from different seasons. Those observations reflected temporal variations in runoff associated Hg contamination from historic Hg mines.

3.2. MeHg in waters

MeHg^{T} concentrations in water samples ranged from 0.31 to 25 ng/l, MeHg^{D} from 0.080 to 6.0 ng/l, and MeHg^{P} from 0.010 to 22 ng/l (Table 2). Samples within contaminated sections usually contained MeHg^{T} values of >1.0 ng/l, but with most of ratios less than 1.0%. A peak value of 7.6 ng/l was found at the outlet of Dashuixi Dam (location 11). Samples from far distance away from Hg mining sites and tributaries downstream always contained low MeHg^{T} . However, an abnormally high concentration of 22 ng/l in MeHg^{T} was recorded in the sample 20 from downstream 10 km (location 20). In

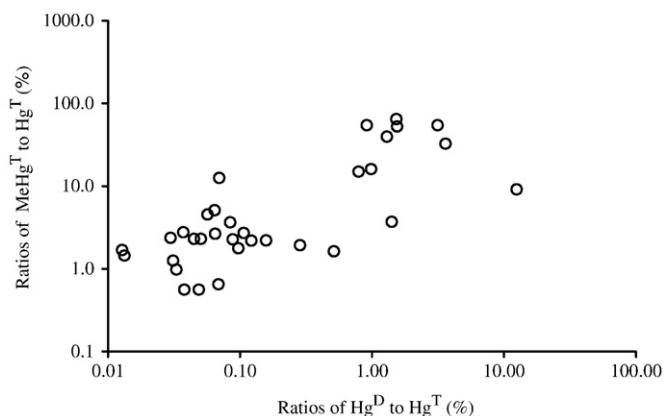


Fig. 6. The relationship of ratios between ratios MeHg^{T} to Hg^{T} and Hg^{D} to Hg^{T} in water samples in Wanshan.

Table 3

Comparison of Hg concentrations in waters in Wanshan with the results reported in recent literature (ng/l).

Location	Hg^{T}	Hg^{D}	MeHg^{T}
Alaska Hg mines, USA ¹	0.1–2500	1.3–50	0.01–1.2
Nevada Hg mines, USA ²	2.1–2107	2–56	0.039–0.92
Almadén Hg mines, Spain ^{3,4}	7.6–20,300		0.41–30
Idrija Hg mines, Slovenia ^{5,6}	2.8–322	0.03–134	0.01–0.6
California Hg mines, USA ^{7–10}	2–45,000	0.2–140	<0.003–47
Palawan Quicksilver Mine, Philippines ¹¹	120–31,000	8–30,000	<0.02–3.1
Langmchang Hg mines, China ^{12,13}	25–7020	<3–1300	
Wuchuan Hg mines, China ¹⁴	22–362	8.2–75.7	0.21–5.7
Tongren Hg mines, China ¹⁵	92–2300		2.6–7.9
Wanshan Hg mines, China ¹⁶	15–9300	11–430	0.31–25

Refs: ¹Gray et al. (2000).

²Bonzongo et al. (1996).

³Berzas Nevado et al. (2003).

⁴Gray et al. (2004).

⁵Horvat et al. (2002).

⁶Hines et al. (2000).

⁷Ganguli et al. (2000).

⁸Domagalski (2001).

⁹Thomas et al. (2002).

¹⁰Rytuba (2000).

¹¹Gray et al. (2003).

¹²Xiao et al. (2003).

¹³Qiu et al. (2006b).

¹⁴Qiu et al. (2006a).

¹⁵Li et al. (2008).

¹⁶This study.

the sample, MeHg^{T} ratios to Hg^{T} reached to 12.5%, which was higher than that of previously documented values of MeHg in Hg mining sites (Gray et al., 2002; Horvat et al., 2003; Qiu et al., 2006a). The possibility of a substantially external MeHg contribution might need to be considered in the region.

The fraction of MeHg^{P} in samples constituted a large portion of MeHg^{T} , reaching to 96%. A positive linear correlation between MeHg^{T} and MeHg^{P} in water samples was observed ($r^2 = 0.986$, Fig. 5). This indicated that MeHg produced in Wanshan was readily combined onto particles. There is no correlation between MeHg^{T} and Hg^{T} , whereas, the ratios of MeHg^{T} to Hg^{T} were significantly correlated with the ratios of Hg^{D} to Hg^{T} ($r^2 = 0.57$, Fig. 6), confirming that Hg^{D} is favorable for methylation.

Previous studies showed that water pH may affect MeHg distribution in water body (Ullrich et al., 2001). In the present study, elevated MeHg in water samples were related to pH values of 6.5–7.5, while the samples that had high pH values always contained low levels of MeHg^{T} . These observations indicated that the alkaline nature of Wanshan aquatic systems, which might result in inactive abilities of bacteria, would likely limit MeHg production.

Our analytical data for both Hg^{T} and MeHg in waters in this study were comparable to the results of waters from other Hg mining areas (Table 3). Stream waters impacted by calcines in Coast Range Hg

Table 4

Mercury and methylmercury in fish in Wanshan, Guizhou, China (mg/kg, wet weight).

ID	Hg^{T}	MeHg	% MeHg
ws1	0.68	0.050	7.4
ws2	0.11	0.098	93
ws3	0.40	0.035	8.8
ws4	0.28	0.059	21
ws5	0.34	0.031	8.9
ws6	0.38	0.090	24
ws7	0.061	0.032	52
ws8	0.25	0.062	25
ws9	0.27	0.073	27
ws10	0.19	0.024	13
ws11	0.26	0.083	32
ws12	0.29	0.084	29

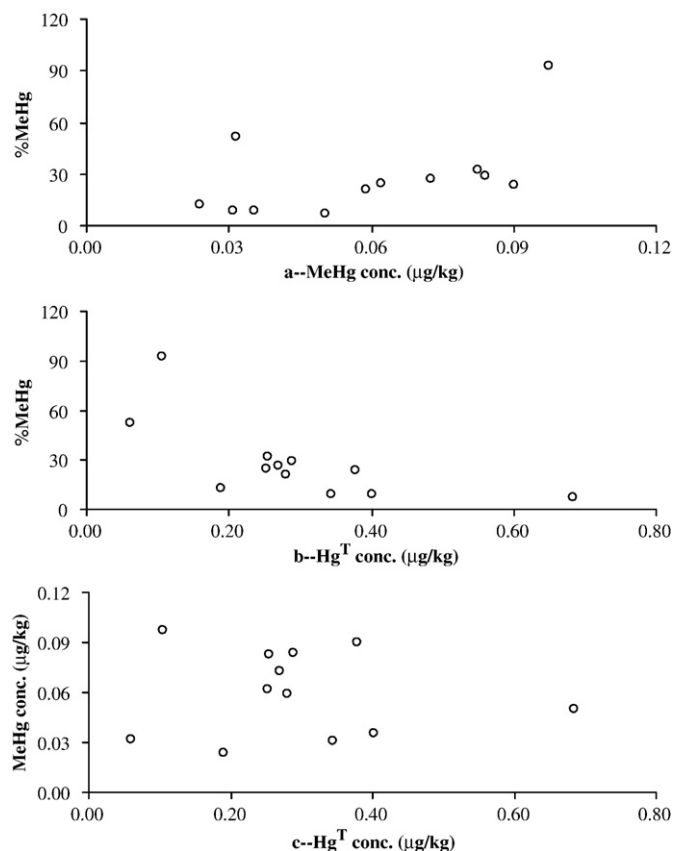


Fig. 7. The relationships between MeHg and Hg^T in fish in Wanshan (a—relationship between ratios of MeHg to Hg^T and MeHg concentrations; b—relationship between ratios of MeHg to Hg^T and Hg^T concentrations; c—relationship between MeHg and Hg^T).

mines, California, and in Palawan Quicksilver Hg mine, Philippines, exhibited as much as 45,000 and 31,000 ng/l in Hg^T, respectively (Rytuba, 2000; Gray et al., 2003). High MeHg concentration as high as 30 ng/l in stream water collected from the Almadén Hg mine, Spain was observed (Gray et al., 2004). Similar to our results, the creek waters impacted by the drainage through calcine tailings all indicate highly elevated concentrations of Hg, which confirms that the calcine tailings contained numerous soluble Hg compounds is the most significant Hg contamination source in Hg mining areas. The elevated Hg concentrations in waters, especially the MeHg, may lead to Hg accumulation in biota that inhabited the aquatic systems, in the long term, pose a great human health concern. Therefore, the calcine tailings in those sites must be appropriately discarded and the mine runoff from those calcine tailings should be collected and not be used as water sources for irrigation or any domestic use.

3.3. Hg^T and MeHg in fish

Concentrations of Hg^T in fish muscles were in the range of 0.061–0.68 mg/kg wet wt and MeHg of 0.024–0.098 mg/kg wet wt (Table 4). Although fish from Dashuixi Dam contained Hg concentrations of up to 0.68 mg/kg in Hg^T, the average Hg^T level of 0.29 mg/kg in fish does not exceed the Nation's guideline of 0.30 mg/kg as an acceptable level of Hg in fish.

The MeHg to Hg^T ratios were markedly different, but most of which were less than 35% with a mean value of 28%. Only a sample was found to exhibit a high MeHg to Hg^T ratio of 93% (Sample ws2, Table 4). Similar results for low MeHg to Hg^T ratios were reported in the juvenile fish that inhabited more time near Hg-contaminated sediments (Lasorsa and Allen-Gil, 1995). Our results also showed that MeHg to Hg^T ratios in fish were negatively correlated with Hg^T

concentrations ($r^2=0.44$) and weakly correlated with MeHg concentrations ($r^2=0.27$) in Wanshan (Fig. 7).

Obviously, factors such as species, age, sex, and feeding habit of fish may influence MeHg ratios. A lack of any correlation between MeHg and Hg^T in fish suggests that factors besides Hg concentration are impacting fish MeHg. Given the limitations of the data available, however, no consideration can be given to reasons for unusually low MeHg fraction in fish from Dashuixi Dam in Wanshan.

Results for Hg^T in fish from Wanshan were comparable to those of fish collected from Alaska Hg mines, but MeHg concentrations were lower (Gray et al., 2000). High average ratios (generally more than 90%) of MeHg to Hg^T were found in samples in the Alaska Hg mining area. Further investigation is needed to determine the reasons for low MeHg to Hg^T ratios in fish muscles from present study.

4. Conclusions

Analyses of Hg concentrations in waters showed a high degree of contamination in the Wanshan Hg mining area. Sources of contamination were most likely the calcines that were dumped and introduced into river banks during historic mining activities. The intensive erosion of Hg-contaminated particles, which occurred in conjunction with mine drainage, runoff, and leaches leaching from the calcine heaps, constituted the main factor leading to the Hg load into the system. Though inorganic Hg species dominated in water samples and the ratios of MeHg to Hg^T were generally low, elevated concentrations of MeHg in certain water samples were found. The reservoirs built to receive mine-waste drainage behaved as a terminal sink, occurring by sedimentation removal of Hg. Despite that the aquatic system in Wanshan was heavily Hg-contaminated, domestic fish inhabited in reservoirs exhibited low MeHg concentrations, probably due to its special feeding habit.

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