



Fractionation, distribution and transport of mercury in rivers and tributaries around Wanshan Hg mining district, Guizhou Province, Southwestern China: Part 2 – Methylmercury

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ABSTRACT

Water samples were collected during normal flow (2007) and during a drought period (2008) from five rivers and tributaries draining the Wanshan Hg mining district, Guizhou, China. Unfiltered methylmercury (MeHg) as well as particulate and dissolved fractions of MeHg (P-MeHg, D-MeHg) were measured to assess the spatial and temporal variation of MeHg contamination in the local river system. Most locations (about 80%) displayed higher MeHg concentrations during drought period than during normal discharge conditions. Concentrations of MeHg during the drought period ranged from <0.035 to 11 ng L⁻¹ (geometric mean: 0.43), while during normal flow the concentrations ranged from <0.035 to only 3.4 ng L⁻¹ (geometric mean: 0.21). Concentrations of MeHg were positively correlated with total Hg (THg) concentrations ($R^2 = 0.20\text{--}0.58$, $P < 0.001$) and inversely related to distance from the calcines, during both sampling periods ($R^2 = 0.34$ and 0.23 , $P < 0.001$, for low and normal flow, respectively) indicating that calcines may be important sources of MeHg to the downstream environment. Approximately 39% of MeHg was bound to particulates and the rest was transported in the dissolved phase along stretches of the entire river, which was different from THg, as this was mainly transported bound to particulates (commonly more than 80%).

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1. Introduction

Mercury is an element of environmental concern because of its accumulative and persistent nature; however, its ecological and toxicological effects are strongly dependent on its chemical form (Clarkson, 1998). Methyl Hg, is more toxic to living organisms than inorganic Hg. Methyl Hg is effectively taken up by aquatic biota with bioconcentration factors ranging from 10^4 to 10^7 (Stein et al., 1996). Inorganic Hg may, under certain conditions, be transformed to MeHg (Boening, 2000). Understanding Hg-methylation processes and the biogeochemistry of MeHg are therefore of particular importance and have received considerable attention (Ullrich et al., 2001).

Mining and retorting of Hg-bearing ore are significant sources of Hg to downstream aquatic systems. Drainage from abandoned mines and seepage water from mine-waste calcines have high concentrations of both THg and MeHg (Gray et al., 2003, 2004; Rytuba, 1997, 2000; Rytuba and Enderlin, 1999). Extremely high concen-

trations of MeHg were observed in mine-waste calcines of the Almaden mining district, Spain, ranging from <0.2 to 3100 $\mu\text{g kg}^{-1}$ (Gray et al., 2004). Documenting Hg cycling in the environment around Hg mining areas is therefore important for assessing potential threats to local human health and fauna (Fitzgerald and Clarkson, 1991; Wolfe et al., 1998).

The Wanshan Hg mining region was the largest Hg producing area in China (Qiu et al., 2005). Approximately 22,000 tons Hg, 6000 tons of cinnabar and large quantities of mine wastes were produced at Wanshan (Liu, 1998). Between 1949 and the early 1990s in the Wanshan Hg mining region, approximately 125.8 million tons of calcines and 20.2 billion m³ of Hg-containing exhaust gas were dispersed into the adjacent ecosystems (Liu, 1998). Severe Hg-contamination has been reported in various environmental compartments, including river water, sediments and vegetation (Feng et al., 2003; Feng and Qiu, 2008; Horvat et al., 2003; Qiu et al., 2005, 2009; Li et al., 2008). Exposure of the local population to MeHg through ingestion of contaminated rice has also been documented (Feng et al., 2008). Rivers receiving seepage from Hg mine wastes might transport both inorganic Hg and MeHg to downstream environments, increasing the area adversely impacted by

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mine wastes. Previous studies (Horvat et al., 2003; Qiu et al., 2005, 2009; Li et al., 2008; Feng et al., 2003; Feng and Qiu, 2008) have mostly focused on contaminated sites close to mine wastes. Hence, an investigation of the speciation and dispersion of THg and MeHg in the aquatic system around the Wanshan Hg mining district is needed to assess the extent of the Hg-contamination in the region.

Results from this study detail MeHg concentrations in the river systems draining the Wanshan Hg mining area. In a companion paper (Zhang et al., 2010) the THg concentrations in the river

systems draining the Wanshan Hg mine area are also documented.

2. Materials and methods

2.1. Study area

The Wanshan area is a typical mountainous and karstic terrain with elevations ranging from 205 to 1150 m asl. The region has a

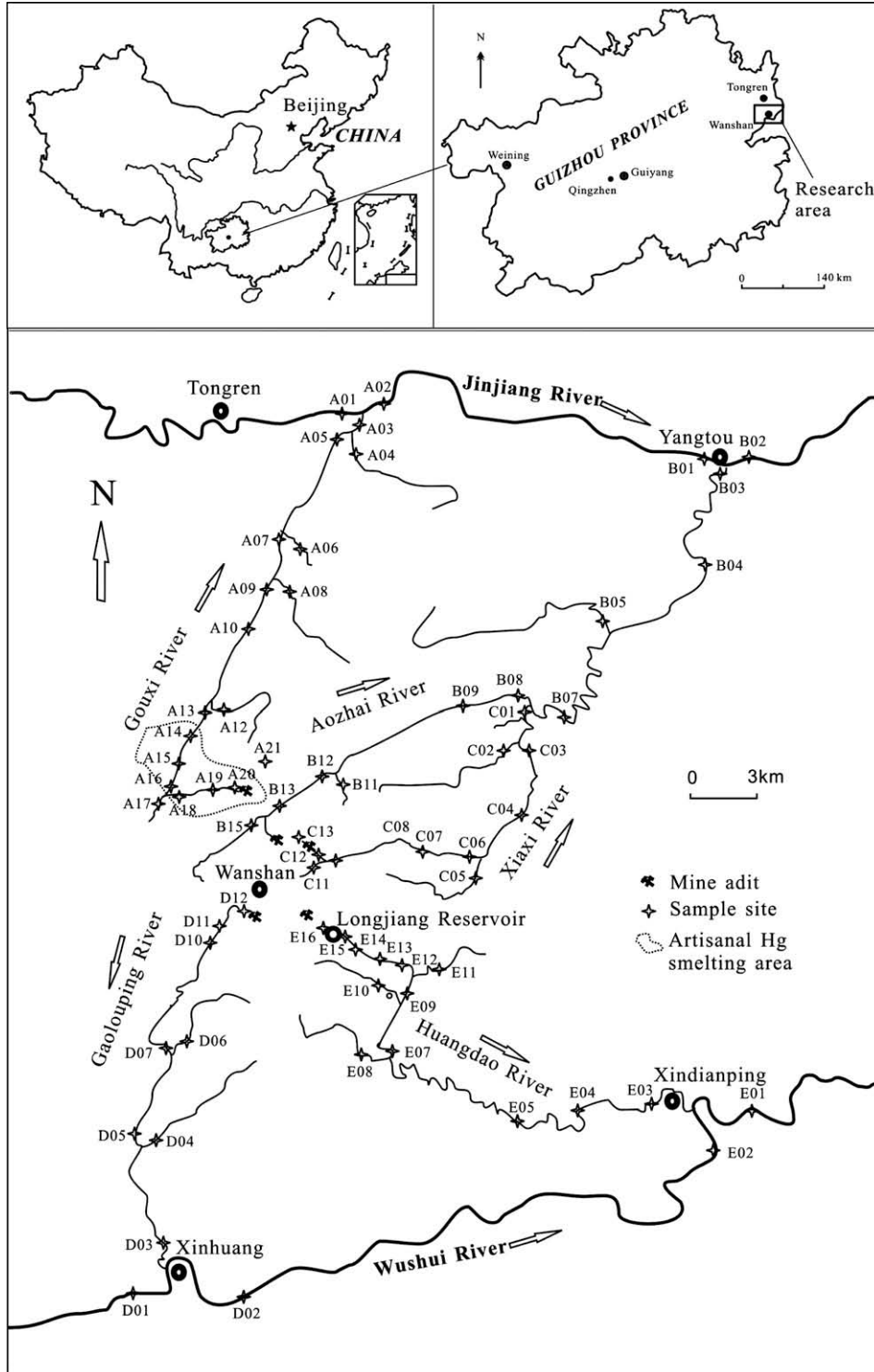


Fig. 1. Map of the sampling locations in Wanshan Hg mining district, Guizhou Province, China.

sub-tropical humid climate characterized by abundant precipitation and a mild temperature. The annual average rainfall is between 1200 and 1400 mm and the annual mean temperature is 17 °C.

The region has five major river valleys, and all have or have had considerable Hg mining and retorting activities. Large scale Hg production activities ceased in 2001, but small scale artisanal Hg production was still in operation in one of the valleys (Gouxu) at the time of sampling (2007 and 2008). A large number (around 50) of very simple furnaces were observed along the banks of the upper parts of the river. In the other four valleys (Aozhai, Xiaxi, Gaolou, and Huangdao) (Fig. 1) Hg mining and retorting were abandoned in 2001.

The five major rivers flow for 22–34 km from the upstream sites, where the mines are located, to the confluence with two bigger rivers, the Jinjiang and Wushui Rivers.

2.2. Sample collection

Sampling campaigns were conducted in August 2007 (normal flow period) and June 2008 (drought period), sampling locations are shown in Fig. 1. Sampling started downstream near the confluence with the Jinjiang and Wushui Rivers, and progressed upstream, with the five main rivers sampled within 24 h.

A duplicate set of samples were collected at each site; one unfiltered sample was stored in a 200 mL borosilicate glass bottle for measurement of unfiltered MeHg, and the other was filtered in situ with a 0.45 µm polyvinylidene fluoride filter (millipore) for measurements of D-MeHg. Before fieldwork, the borosilicate glass bottles were rigorously pre-cleaned by heating for at least 45 min in a muffle furnace at 500 °C. During collection, the filtration equipment and sample bottles were rinsed three times with river water prior to filling. Water samples for Hg species analysis were preserved by adding 0.4% (v/v) of distilled ultra-pure HCl within 24 h. Sample bottles were tightly capped and placed into double plastic bags and stored in clean coolers (4 °C) until processing and analysis. Collection, storage and preservation techniques of samples strictly followed USEPA Method 1631 (USEPA, 1999).

2.3. Sample analyses

Methyl Hg concentrations were determined in all samples, and the D-MeHg was also characterized in samples collected during the

drought period. For the latter samples, the P-MeHg was obtained by subtracting the dissolved fraction from the MeHg concentration. Water samples were distilled, ethylated, and analyzed by cold vapor atomic fluorescence spectrometry (CVAFS) for MeHg analysis (Horvat et al., 1993; Liang et al., 1994, 1996). A 45 mL sample aliquot was placed in a Teflon® distillation vessel in an Al heating pan and distilled at 125 °C for 3–4 h. The distillate then underwent aqueous phase ethylation with the stepwise addition of 0.2 mL 2 M sodium acetate and 0.1 mL 1% sodium tetraethylborate, followed by purging with N₂ onto a Tenax® trap (Guo et al., 2008). Methyl Hg was then desorbed with heating onto an isothermal GC column for peak separation and analyzed by CVAFS (Brooks Rand Model III). Total suspended solids (TSS) were obtained by filtering a 1.5 L sample through a pre-weighed 0.45 mm cellulose filter. The filters were oven-dried at 40 °C to constant weight.

Quality assurance and quality control of MeHg analysis were assessed using duplicates, method blanks and matrix spikes. The relative standard deviation was less than 8%, 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 83–115%. The limit of determination for MeHg in water samples was 0.035 ng L⁻¹, three times the standard deviation of blanks. The average concentration (and range) of MeHg in field blanks was 0.021 ng L⁻¹ (0.012–0.027 ng L⁻¹).

3. Results and discussion

3.1. Unfiltered MeHg

As shown in Fig. 2a–c, water samples collected from the five rivers in the Wanshan Hg mining area contained highly variable MeHg concentrations ranging from <0.035 to 11 ng L⁻¹ (geometric mean 0.43 ng L⁻¹) during the drought period and from <0.035 to 3.42 ng L⁻¹ (geometric mean 0.21 ng L⁻¹) during the normal flow period. These data are comparable to a previous report (Qiu et al., 2009) on MeHg in Wanshan (0.31–25 ng L⁻¹) which was mainly conducted in a limited area within about 4 km from Hg mine wastes during a high flow period (August 2004), and slightly higher than MeHg values from a river system elsewhere in Guizhou Province (range: 0.062–0.24 ng L⁻¹) (He et al., 2008). Most selected sampling locations (around 80%) had higher MeHg concentrations during low flow than under normal flow conditions, which may be due to less dilution during the drought period.

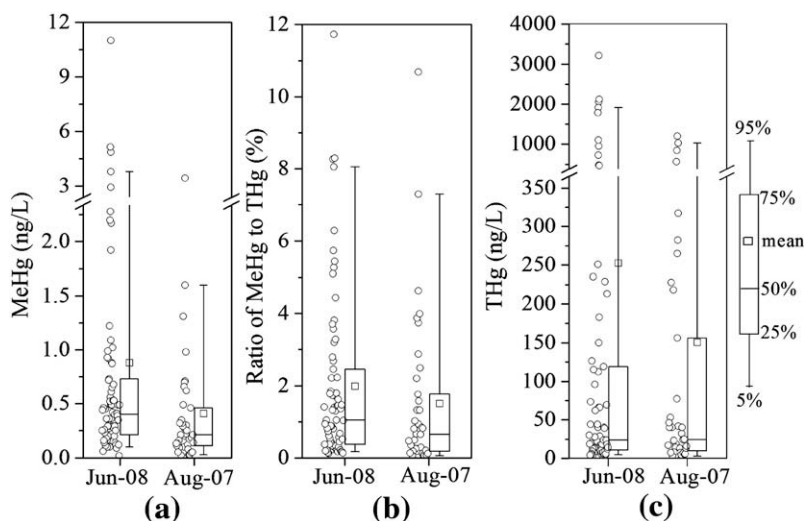


Fig. 2. Statistical chart of MeHg concentrations (a), ratio of MeHg to THg (%MeHg) (b), with THg concentrations (c) in water samples collected from Wanshan Hg mining district.

The average and range of MeHg concentrations in samples from tributaries, devoid of direct impacts of mining activities, were similar to background concentrations in the Wanshan area (average: 0.42 ng L^{-1} , range: $0.22\text{--}0.88 \text{ ng L}^{-1}$). Concentrations were similar to background concentrations 8–18 km downstream from calcines (Fig. 3a–d). This was further downstream than was reported for THg concentrations (Zhang et al., 2010), where background concentrations were observed 6–8 km downstream from the mine wastes. A rapid decline in the THg concentration was most likely due to Hg binding to particulates (Zhang et al., 2010).

The MeHg concentrations in Hg-contaminated upstream areas were significantly (ANOVA, $P < 0.01$) higher than that in less-impacted downstream areas. As shown in Table 1, the geometric mean (and range) in upstream areas was $1.0 (0.12\text{--}11) \text{ ng L}^{-1}$; the mean (and range) in less-impacted downstream areas was only $0.32 (<0.035\text{--}0.88) \text{ ng L}^{-1}$, which was close to or below the local background value ($0.42 (0.22\text{--}0.88) \text{ ng L}^{-1}$). This suggested that the surface water in Wanshan impacted by MeHg released from the mine wastes was limited.

Of the five rivers, the geometric mean (and range) of MeHg concentrations in the Huangdao River ($0.68 (<0.035\text{--}5.2) \text{ ng L}^{-1}$) was slightly higher than in other rivers (Gouxi: $0.39 (0.099\text{--}1.9) \text{ ng L}^{-1}$; Aozhai: $0.22 (0.11\text{--}0.42) \text{ ng L}^{-1}$; Xiaxi: $0.49 (0.088\text{--}11) \text{ ng L}^{-1}$; Gaolouping: $0.46 (0.14\text{--}2.3) \text{ ng L}^{-1}$). Higher THg concentrations in the Huangdao River relative to the other streams were also found (Zhang et al., 2010). The Huangdao River catchment has a longer history and larger scale of Hg mining and retorting compared to the other rivers.

In three rivers (Gaolouping, Gouxi and Xiaxi), MeHg concentrations decreased with distance from the mine wastes, and reached moderately low concentrations (below 1.0 ng L^{-1}) within 3.0 km downstream. In the Huangdao River, the MeHg concentrations did not fall to background concentrations until 16 km downstream due to heavier Hg-contamination in its upstream reaches. In the Aozhai River, THg concentrations were generally below 50 ng L^{-1} with no significant difference between upstream and downstream; likewise no difference in MeHg concentrations was observed along the length of the stream. A significant correlation between MeHg concentrations and distance downstream from mine wastes was observed ($R^2 = 0.23$ and 0.34 , $P < 0.001$). These results indicated that mine wastes from the Hg mining and processing of ore material are important sources of MeHg. Moreover, this implies that Hg-methylation may occur within the mine wastes.

Qiu et al. (2005) reported high amounts of both THg ($5.7\text{--}4400 \text{ mg kg}^{-1}$) and MeHg ($0.17\text{--}1.1 \text{ } \mu\text{g kg}^{-1}$) in mine-waste calcines in Wanshan. Extremely high concentrations of MeHg were observed in calcines of the Almaden mining district, Spain, varying from <0.2 to $3100 \text{ } \mu\text{g kg}^{-1}$ (Gray et al., 2004). High MeHg concentrations in mine-waste calcines were also reported from the Palawan Hg mine area ($0.13\text{--}3.2 \text{ } \mu\text{g kg}^{-1}$) in the Philippines (Gray et al., 2003), and the Nevada Hg mine area ($<0.035\text{--}96 \text{ } \mu\text{g kg}^{-1}$) in the USA (Bonzongo et al., 1996; Gray et al., 2002). This study also suggested mine-waste calcines in Wanshan were important sources of MeHg to the downstream environment. Generally, historical mine-waste calcines (retorted ore) produced by inefficient roasting of Hg ore contain abundant soluble Hg compounds, such as the elemental Hg and Hg salts (e.g. calomel), which is likely to be leached from calcines, carried downstream, and potentially methylated (Gray et al., 2004; Kim et al., 2000, 2004).

Methyl Hg concentration in aquatic systems is not a simple function of inorganic Hg concentration (Kelly et al., 1995). Methyl Hg is primarily produced by microbes through in situ methylation and therefore MeHg concentrations are related to environmental conditions that promote the activity of Hg-methylating bacteria and increase the bioavailability of Hg, including temperature, pH, microbiology, organic material, redox conditions and sulfide (Ullrich et al., 2001). However, in Wanshan there were significant positive correlations between concentrations of MeHg and all species of inorganic Hg, during both sampling periods ($R^2 = 0.20\text{--}0.58$, $P < 0.001$) (Fig. 4a–d). These correlations were mainly generated because the concentrations of both THg and MeHg, were highly elevated just downstream of the mine waste sites (Fig. 5). The correlation between THg and MeHg may be, therefore, just a co-variation, especially in the contaminated upstream areas, and the concentrations of both fractions in the water are determined by common governing environmental factors, i.e. factors that control

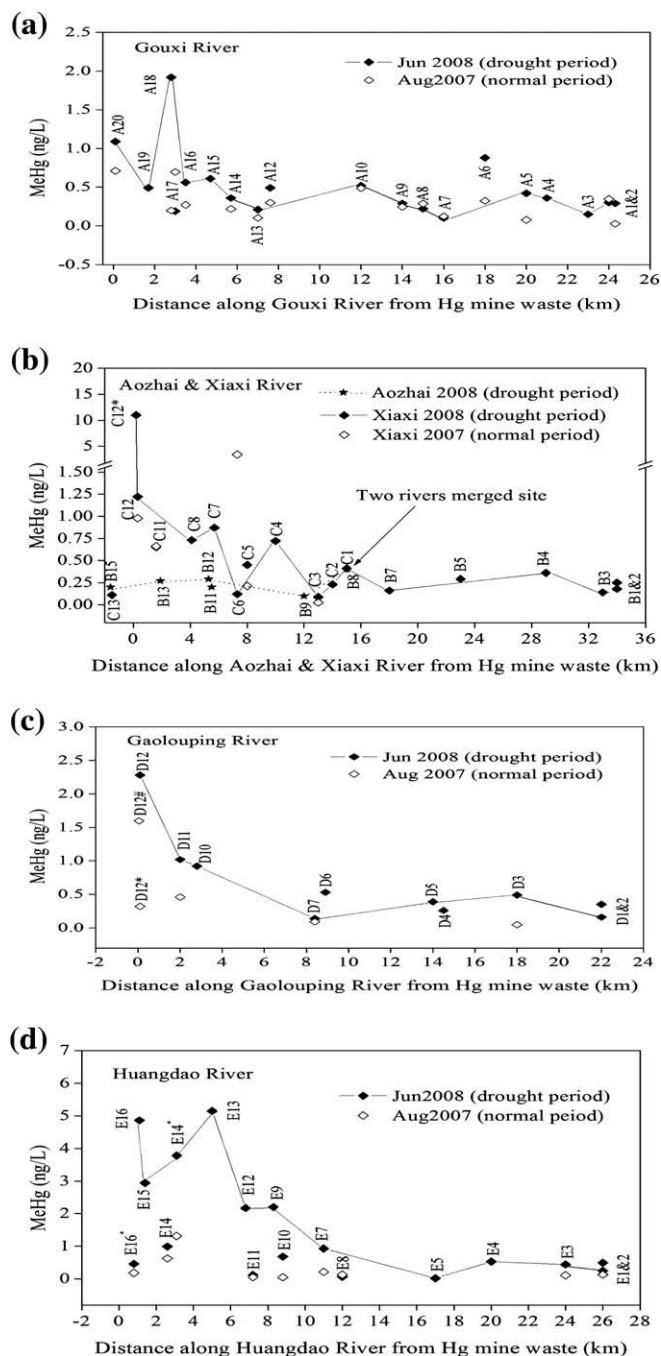


Fig. 3. Distribution of MeHg in water samples along all rivers (a – Gouxi, b – Aozhai and Xiaxi, c – Gaolouping, d – Huangdao) from Wanshan Hg mining district. (Sample locations such as “E3” are also shown; data of samples not in the main rivers are also included, but not connected with lines; the distance from Hg mine waste is given as “0” on the X axis.)

Table 1
Concentration of different MeHg species (ng L⁻¹) and ratios of different MeHg fractionation (%) during low flow period (June 2008) in Hg-contaminated area and less-impacted area in Wanshan, respectively.

	Hg-contaminated areas (with THg ≥ 50 ng L ⁻¹) (N = 26)					Less-impacted areas (with THg < 50 ng L ⁻¹) (N = 44)				
	Min	Max	Mean	SD	Distribution	Min	Max	Mean	SD	Distribution
MeHg	0.12	11	1.02 ^b	2.3	Log-normal	<0.035	0.88	0.32	0.18	Normal
MeHg ^a	<0.035	3.4	0.41 ^b	0.21	Log-normal					
P-MeHg	<0.035	8.5	0.40 ^b	2.0	Log-normal	<0.035	0.59	0.077 ^b	0.13	Log-normal
D-MeHg	0.087	2.7	0.45 ^b	0.65	Log-normal	<0.035	0.73	0.14 ^b	0.15	Log-normal
D-MeHg/MeHg	6.6	93	61	26	Normal	11	95	61	25	Normal
P-MeHg/MeHg	7.1	93	39	26	Normal	5.4	89	39	25	Normal
MeHg/THg	0.12	1.7	0.35 ^b	0.35	Log-normal	0.13	12	2.0 ^b	2.6	Log-normal
MeHg/RHg	0.37	37	3.7 ^b	7.8	Log-normal	0.33	90	13 ^b	20	Log-normal
D-MeHg/DHg	0.24	16	1.4 ^b	3.4	Log-normal	0.11	35	2.3 ^b	5.9	Log-normal
P-MeHg/PHg	0.021	0.67	0.16 ^b	0.20	Log-normal	0.10	74	1.6 ^b	14	Log-normal

^a Data measured in normal flow period, August 2007, not divided into Hg-contaminated areas and less-impacted areas.

^b Geometric mean.

the release and dilution of both THg and MeHg from the upstream pollution source.

Methyl Hg content of sediment profiles from the Huangdao and Xiayi Rivers (0–40 cm depth), collected at sites about 400–600 m downstream of Hg mine wastes, ranged from 3.0 to 20 μg kg⁻¹ (Qiu et al., 2005). Though Hg-methylation is known to occur in aquatic surface sediments (0–2 cm) (Ullrich et al., 2001), sediments in the river streambed consisted mainly of pebbles, with a scarce amount of fine material. Hence this was likely a minor source for MeHg, compared to the upstream mine waste heaps.

Riparian rice paddies are abundant along all five rivers and most of these fields are irrigated with the contaminated river water. The soils in the rice paddies were severely Hg-contaminated and had elevated MeHg concentrations, possibly due to Hg-methylation in the paddy soil (Qiu et al., 2005). Methyl Hg produced in these soils may leach back to the river during the rainy season. However, moderate downstream MeHg concentrations suggested that this was only a minor source.

A relatively high MeHg concentration (0.88 ng L⁻¹) was recorded in a tributary (A06) with no apparent upstream anthropogenic Hg source and with low THg concentration (14 ng L⁻¹). This was possibly due to favorable microbial activity conditions in the side valley during the drought period, which promoted in situ MeHg production (Ullrich et al., 2001).

3.2. Ratio of MeHg to THg (%MeHg)

Methyl Hg accounted for up to 11% and 12% (geometric mean: 0.59% and 1.04%) of the THg (%MeHg) in the water samples during normal and low flow conditions, respectively (Fig. 2b). These ratios are close to or higher than previously documented values from other Hg mining sites (Ganguli et al., 2000; Hines et al., 2000; Gray et al., 2002, 2003; Horvat et al., 2003; Qiu et al., 2006). In addition to an overall higher %MeHg during the drought period, about 70% of the samples had relatively higher MeHg during the low flow period than during normal flow.

The ratio of MeHg to THg in upstream areas was significantly (ANOVA, $P < 0.01$) lower than that in downstream areas, which was similar to the ration of MeHg to RHg (Table 1). Methyl Hg accounted for up to 37% and 90% (geometric mean: 3.7% and 13%) of the RHg in upstream and downstream areas, respectively. A significant correlation was observed between RHg and MeHg ($R^2 = 0.20$ – 0.40 , $P < 0.001$, Fig. 4d). Usually, RHg represents the Hg substrate available for methylation, Hg⁰ formation, and other conversion processes (Mason and Fitzgerald, 1990).

Interestingly, the ratio of MeHg to THg (%MeHg) was positively correlated with distance from Hg mine wastes ($R^2 = 0.36$,

$P < 0.001$). Similar results have been reported in other Hg-contaminated fluvial systems (Hines et al., 2000; Bonzongo et al., 2006). There was hence a significant negative correlation between %MeHg and THg during both sampling periods ($R^2 = 0.82$ and 0.52 , low and normal flow, respectively, $P < 0.001$) (Fig. 6). Similar data from studies in the Nevada Hg mining area, USA (Bonzongo et al., 1996), and the Wuchuan Hg mining area, China (Qiu et al., 2006), were found to be in a good agreement with the present data ($R^2 = 0.82$ and 0.52 , respectively, $P < 0.001$) (Fig. 6).

An inverse relationship between %MeHg and THg concentrations may indicate that MeHg decreased less rapidly downstream than THg in Hg-contaminated areas. However, in less-impacted downstream areas, this might be due to the increased in situ MeHg production. For example, MeHg concentrations in the Aozhai and Gaolouping Rivers declined to background concentrations at downstream sites, and then slightly increased again until the streams merged into the main rivers (Fig. 3b and c). Furthermore, THg in less-impacted downstream areas was close to or below local background values and decreased slowly or was relatively stable in most downstream sites before merging into the main rivers (Zhang et al., 2010). Hence, an increased %MeHg may suggest in situ MeHg production in less-impacted downstream sites in Wanshan.

Schaefer et al. (2004), addressed the inverse relationship between %MeHg and THg concentrations, and attributed this to increased MeHg degradation rates in more Hg-contaminated waters. The authors suggested that in strongly Hg-contaminated surface waters, the amount of MeHg that accumulates is limited by high rates of reductive de-methylation by Hg resistant bacteria. In environments with low concentrations of THg, where microbial communities are not adapted to Hg, the concentration of bioavailable Hg may be insufficient to induce the expression of Hg-resistance operons that regulate reductive de-methylation. In the present study, this may also explain why the %MeHg in the contaminated upstream area (geometric mean = 0.35%) was significantly ($P < 0.01$) lower than that in less-impacted areas (geometric mean = 2.0%) (Table 1).

The ratio of particulate Hg (PHg) to THg (%PHg) and the ratio of dissolved Hg (DHg) to THg (%DHg) were also determined. Results indicated that %PHg was inversely correlated with %MeHg ($R^2 = 0.33$ – 0.43 , $P < 0.001$, Fig. 7a). Conversely, %DHg was positively related to %MeHg ($R^2 = 0.32$ – 0.43 , $P < 0.001$, Fig. 7b). Qiu et al. (2009), observed a similar result in waters in Wanshan, and suggested that a high %DHg may be favorable for Hg-methylation. However, in the present study, this may be limited in downstream areas, while in upstream areas this result may also be due to faster settling of Hg-contaminated particles, resulting in the %PHg decreasing faster with distance from mine wastes than %DHg.

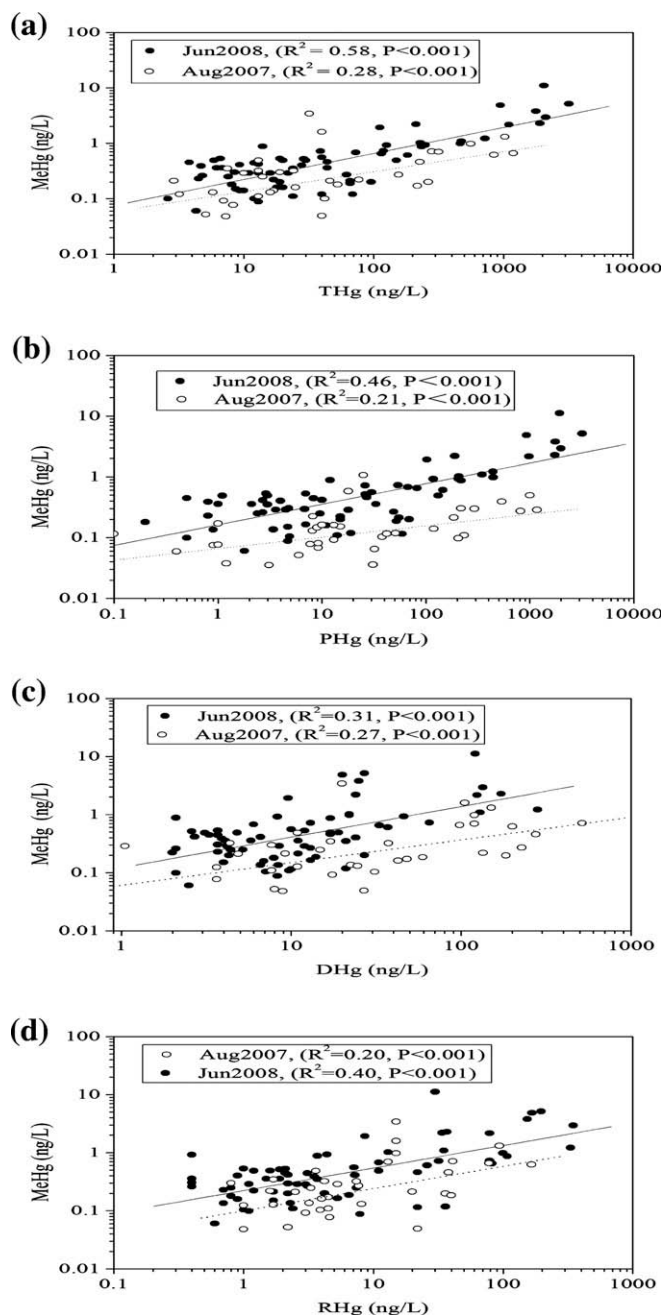


Fig. 4. Relationship between MeHg concentrations and different speciation of inorganic Hg concentrations (a – THg, b – PHg, c – DHg, d – RHg) in water samples from Wanshan Hg mining district (inorganic Hg data from Zhang et al. (2010)).

3.3. D-MeHg and P-MeHg

Dissolved-MeHg and P-MeHg concentrations ranged from <0.035 – 2.7 ng L^{-1} (geometric mean: 0.22) and <0.035 – 8.46 ng L^{-1} (geometric mean: 0.14), respectively (Table 1). Similar to MeHg concentrations, the highest values of both D-MeHg and P-MeHg in all rivers were recorded at locations downstream from the mine wastes, and both were inversely related to distance from Hg mine wastes ($R^2 = 0.25$ and $0.30, P < 0.001$). This suggested the main source of MeHg in waters in Wanshan was likely the Hg mine wastes.

A correlation between MeHg or P-MeHg concentrations and TSS was not observed, suggesting that TSS was not a governing factor for MeHg distribution and transport. On average the P-MeHg ac-

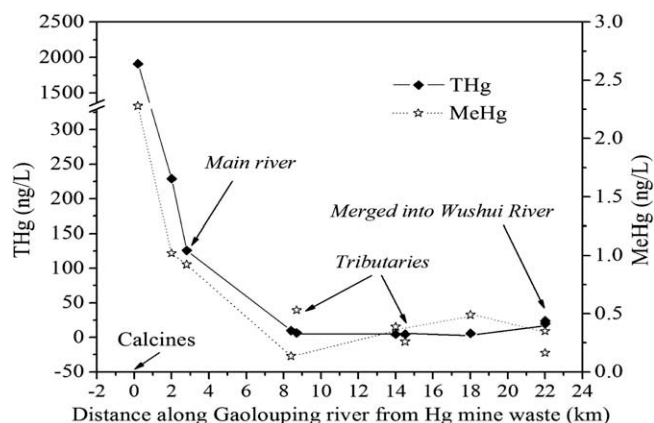


Fig. 5. Example of concentrations of THg and MeHg in water samples collected in June 2007 (drought period) impacted by calcines in Wanshan Hg mining district.

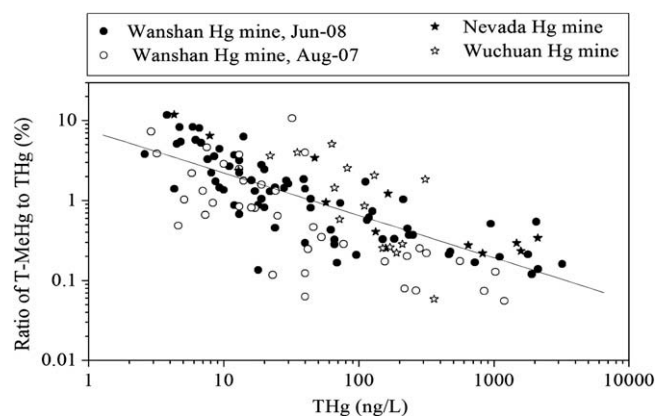


Fig. 6. Comparison of relationship between THg and %MeHg (ratio of MeHg-THg) in water samples collected from Wanshan Hg mining district with those from other Hg mine areas (Wanshan Hg mine, China, this study; Nevada Hg mine, USA, Bonzongo et al. (1996); Wuchuan Hg mine, China, Qiu et al. (2006)).

counted for only 39% of the MeHg, with no clear trends between upstream and downstream reaches of the streams (Table 1). This result was different from THg, which consisted of more than 80% particulate fractions in upstream reaches. This indicated that THg and MeHg in the Wanshan region have somewhat different main transport mechanisms: THg was depended on particulate transport, while MeHg was mainly (61%) governed by de-sorption from particulates into the dissolved phase. Methyl Hg concentrations were strongly positively correlated to both D-MeHg and P-MeHg concentrations ($R^2 = 0.70$ – $0.76, P < 0.001$) (Fig. 8), indicating that the partitioning may be controlled by an equilibrium reaction.

One way to describe the distribution of Hg between dissolved and particulate fractions is through a distribution constant. The partitioning coefficient, K_d for THg and MeHg in surface water is defined as $[Cu-Cf]/[TSS]/[Cf]$ (where Cu and Cf are the unfiltered and filtered surface water concentrations). The geometric mean of K_d for MeHg in Wanshan was only 0.23 (0.0067–17), with no significant difference between upstream and downstream. This suggested that MeHg in these sites does not strongly bind to particulate matter and transport is mainly dependent on the dissolved phase. This was different from the K_d of THg, which was significantly ($P < 0.01$) higher upstream (geometric mean: 2.3) compared to less-impacted downstream areas (geometric mean: 0.43). In upstream areas, THg was mainly bound to particles, while downstream THg was in both particulate- and dissolved phases (Zhang et al., 2010).

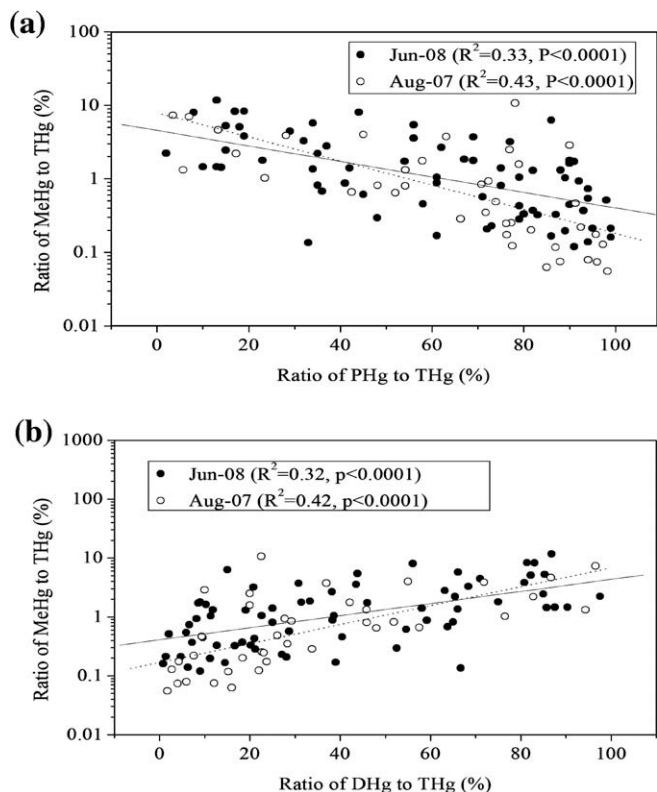


Fig. 7. Relationship between %MeHg (ratio of MeHg to THg) and %DHg (Ratio of DHg to THg) (a) with relationship between %MeHg and %PHg (ratio of PHg to THg) (b) in water samples collected from Wanshan Hg mining district.

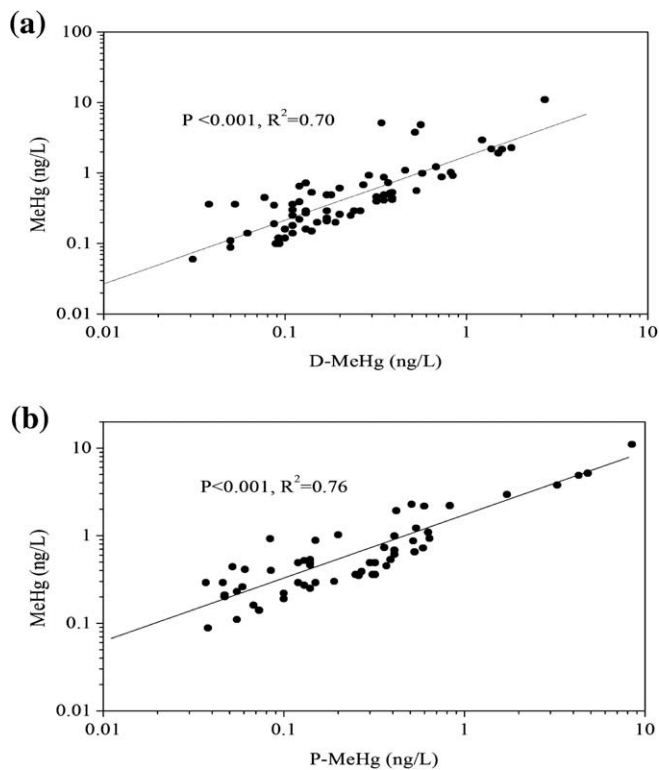


Fig. 8. Relationship between MeHg and P-MeHg (a) with MeHg and D-MeHg (b) in water samples collected from Wanshan Hg mining district.

No significant correlation was observed between K_d (THg) and TSS ($R = -0.35$, $P > 0.05$). K_d (MeHg), however was negatively re-

lated to TSS ($R = -0.71$, $P < 0.001$), which has been observed by others (Hurley et al., 1995; Babiarz et al., 2001), and explained by the “particle concentration effect,” that is, as TSS increased, a higher proportion of metals associated with the colloidal particles (<0.45 mM) was counted with the dissolved fraction, lowering K_d (Benoit, 1995).

The ratios of D-MeHg to DHg and P-MeHg to PHg are also summarized in Table 1. Geometric mean (and range) of the ratio of D-MeHg to DHg in upstream sites was 1.4% (0.24–16%), which was slightly lower compared to downstream sites (2.3%, 0.11–35%, $P > 0.05$). The ratio of P-MeHg to PHg, was significantly lower upstream compared to downstream, with a geometric mean (and range) of 0.16% (range: 0.021–0.67%) and 1.6% (0.10–74%), respectively ($P < 0.05$). This was consistent with the ratio of MeHg to THg (%MeHg) discussed above. The extremely high ratios (e.g. $>10\%$) for D-MeHg to DHg or P-MeHg to PHg were all recorded in the downstream area and/or tributaries with very low THg (e.g. <10 ng L⁻¹). This may reflect the enhanced Hg-methylation effect in less-impacted environments, as discussed above (Schaefer et al., 2004).

4. Conclusions

High concentrations of MeHg in water samples show that the aquatic system around the Wanshan Hg mine was severely MeHg-contaminated. Mercury methylation appears to occur in the mine-waste calcines, where it is released through seepage water and transported downstream. Mine-waste calcines were, therefore, considered to be the main source of MeHg. Methyl Hg concentrations during the drought period were significantly higher than during the normal flow period. This was mainly due to less dilution of the seepage water from the calcines, rich in MeHg, during the drought period. Generally, MeHg transport in Wanshan was mainly (60%) governed by de-sorption from particulates into the dissolved phase. This differs from THg, which was mainly transport by adsorption to particles (80%).

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