Mercury pollution in Guizhou, Southwestern China — An overview

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ABSTRACT
Mercury (Hg) is a global pollutant and poses a worldwide concern due to its high toxicity. Guizhou province is recognized as a heavily Hg-polluted area in China due to both the special geochemical background and human activities. Here an integrated overview of current knowledge on the behavior of Hg in environments, as well as human health risk with respect to Hg contaminations in Guizhou was presented. Two key anthropogenic Hg emission sources in Guizhou were coal combustion and metals smelting, which dominantly contributed to the high levels of Hg in local ecosystems and high fluxes of Hg deposition. The annual Hg emission from anthropogenic sources ranged between 22.6 and 55.5 t, which was about 6.3–10.3% of current total Hg emissions in China. Meanwhile, Hg Hg-enriched soil in the province serves an important natural Hg emission source to the ambient air. The local environment of Hg mining and zinc smelting areas are seriously contaminated with Hg. It is demonstrated that rice growing in Hg Hg-contaminated soil can accumulate methylmercury (MeHg) to a level to pose health threat to local inhabitants whose staple food is rice. Local inhabitants in Hg mining areas are exposed to Hg through inhalation of Hg vapor and consumption of rice with high level of MeHg. Rice intake is indeed the main MeHg exposure pathway to local inhabitants in Hg mining areas in Guizhou, which is contrary to the general point of view that fish and fish products are the main pathway of MeHg exposure to humans.

MeHg is recognized as the most toxic Hg form to humans. It can be generated from ionic Hg in environments by organisms under appropriate conditions such as reducing environments (Grieb et al., 1990; Choi and Bartha, 1994; Ebinghaus et al., 1994). Because of its accumulative and persistent characteristics in biota, MeHg has a strong ability of bioaccumulation in the food chain, resulting in fish tissues more than 10⁶ times higher than ambient water MeHg concentrations (WHO, 1990; US EPA, 1997a). In this sense, an important transformation in Hg cycle is the conversion of inorganic Hg to MeHg.

Guizhou province (N24°30′–29°13′′, E103°1′–109°30′′; Fig. 1) is located in southwestern China with an elevation of 1100 m above sea level and a land area of 176,000 km². Its climate...
represents a typical subtropical humid monsoon with an average annual temperature of 15 °C and a precipitation of 1100–1400 mm. Guizhou is a typically karstic topography. The bedrocks in the province are limestone and dolomite.

From the perspective of the global plate tectonics, Guizhou province is situated in the center of the circum-Pacific mercuriferous belt (Qiu et al., 2006a; Gustin et al., 1999). Therefore, Guizhou is one of the world’s important Hg production centers. So far, at least 12 large and super-large Hg mines have been discovered in the province (e.g. Wanshan, Wuchuan, Lanmuchang, and Danzhai, etc.) and the locations of all Hg mines are shown in Fig. 1. The total reserves of cinnabar deposits in the province reached 80,000 t of metal Hg and represented 80% of the total in China (Qu, 2004). A long-term of 3000 years Hg mining activities have experienced in Guizhou and introduced significant quantities of gangues and mine tailings (calcines), which are uncontrolled stockpiled near the abandoned Hg processing sites and retorts. Between 1949 and early 1990s in the Wanshan Hg mining areas, for instance, approximately 125.8 million tons of calcines and 20.2 billion cubic meters of Hg-contained exhaust gas had been dispersed into the adjacent ecosystems (Liu, 1998). The gangue and calcine piles are continuing releasing Hg to the environment, causing serious Hg contamination. As a result, the crops produced in Hg

Fig. 1 – Map of Guizhou and typical anthropogenic Hg emission sources.
mining areas contained elevated Hg (Qiu et al., 2008; Feng et al., 2008), posing health threat to the local inhabitants.

Guizhou is one of the major coal production centers and coal consumers in China. Approximately 80% of total energy consumption in the province resulted from coal combustion (Tan et al., 1997, 2000). Currently, more than 50 million tons of coals were combusted annually for both industrial and domestic purposes, and most coals were used without cleaning or flue gas controls (Tang et al., 2007). Due to the special geochemical background, Hg concentrations in coal from Guizhou are elevated compared to coal produced in other provinces in China (Feng et al., 2002). Therefore, a large quantity of Hg is released from coal combustion in Guizhou, resulting in Hg contamination to the ambient air and the local environment.

Guizhou is also an important artisanal Zn smelting center. Large quantities of artisanal Zn smelting workshops were scattered in northwestern parts of the province (i.e. Hezhang, and Weining). Artisanal Zn smelting using indigenous methods experienced at least hundreds years in Guizhou (Fig. 1). Hg is an important associate element in zinc ores, and during zinc smelting processes a large quantity of Hg is released to the environment, resulting in serious Hg contamination to the local environment (Feng et al., 2004a, 2006; Li et al., 2008).

In addition, Guizhou has a unique State-owned chemical plant, Guizhou Organic Chemical Plant (GOCP), which used Hg as a catalyst for acetaldehyde producing. Drainages released from the GOCP through direct and/or river discharges contributed to significant Hg contaminations to the local ecosystems. The total loss of Hg into environments estimated by the GOCP was about 134.6 t within 30 years of operation of the company.

Hg pollution problems in Guizhou have drawn a great attention to the scientific communities in China and over the world. A number of studies have been diverted to understand the emission, transport, and cycling of Hg in the environment in Guizhou and the health impacts to humans. This paper is mainly aimed at summarizing the state of art of knowledge on the emission, transport, and cycling of Hg in the environment in Guizhou, China and the status of Hg pollution in the environment in China has been reviewed by Jiang et al. (2006) and Zhang and Wong (2007).

2. Anthropogenic Hg emissions in Guizhou

Recent estimates of anthropogenic total Hg emissions to the atmosphere in China suggested that the total anthropogenic Hg emissions in China reached 536 t in 1999, which constituted about 1/4 of the total emissions over the world (Streets et al., 2005). It is pointed out that Guizhou is one of the most important Hg emission regions. Contributions estimated from the province ranged between 22.6 and 55.5 t yr⁻¹, which was about 6.3–10.3% of current total anthropogenic Hg emissions in China (Wang et al., 2000; Streets et al., 2005; Wu et al., 2006; Zhang and Wong, 2007).

2.1. Emission from coal combustion

Coal combustion is an important source category of anthropogenic Hg emissions to the atmosphere worldwide. Guizhou stands out in coal-related Hg emissions primarily due to high high-Hg contents in raw coals and numerous combustion facilities without pollution control facilities (Feng et al., 2002; Tang et al., 2007).

An investigation of 48 crude coal samples collected from 4 coal production centers in Guizhou provided a high average Hg concentration of 0.53 mg/kg, ranging from 0.10 to 2.67 mg/kg (Feng et al., 2002). Zhang et al. (2004b) introduced a wide range of 0.04–10.5 mg/kg Hg in coals from southwestern Guizhou. An extremely high value of 12.1 mg/kg was reported in an anthracite coal sample from Xingren, in southwestern Guizhou (Dai et al., 2006). Coal Hg contents in Guizhou were higher compared with other regions in China, which ranged from 0.02 to 0.44 mg/kg on average (Wang et al., 2000; Streets et al., 2005).

High levels of Hg contents in raw coals were predominantly attributed to the high background of Hg in bed rocks in Guizhou, which is in the center of the circum-Pacific global mercuriferrous belt (Gustin et al., 1999). Since the majority of commercial coal produced in Guizhou is not washed to remove heavy metal contaminants, Hg contents in commercial coal should be identical to the crude coal.

Hg emission rates and speciation profiles depend greatly on the combustion and pollution control techniques employed in the facilities. Statistical data for coal consumption suggested that large-scale coal-fired power plants, industrial sectors, and domestic users consumed about 30%, 48%, and 22% of the total coal consumption in Guizhou, respectively. Using a mass balance technique, Tang et al. (2007) estimated that Hg emission factors of a small industrial coal-fired boiler without and with flue gas desulphurization (FGD) systems was were 66% and 26% of total Hg presented in coal, respectively. Hg emission factors of a large coal-fired power plant with electrostatic precipitators (ESPs) systems was were up to 85% of total Hg presented in coal, which could be decreased to 43% in the case of FGD systems employed. Those data suggested that 56% of Hg emission from coal combustion in Guizhou was released as Hg⁰, 33% as Hg²⁺, and 13% as Hg⁴⁺, respectively, which were comparable to the estimated values of China by Streets et al. (2005).

Using above-estimated Hg emission factors, Tang et al. (2007) estimated that the annual emission of total Hg into atmosphere from coal combustion in Guizhou steadily increased from 5.8 t in 1986 to 26.4 t in 2006 (Fig. 2). However, Streets et al. (2005) reported an even higher value of 39 t of total Hg in Guizhou in 1999, with 18.2 t of Hg⁰, 11.1 t of Hg²⁺, and 9.5 t of Hg⁴⁺, respectively. It is obvious that the coal consumption

Fig. 2—Mercury emission from coal combustion in Guizhou from 1986 to 2006 (data from Tang et al., 2007).
increased significantly with the rapid economic development. With the implementation of “Go West” policy, more coal coal-fired power plants are planned to be constructed in Guizhou by 2010, and by then the total coal consumption will be doubled compared to the current consumption. New regulations in China will force all newly built coal coal-fired power plants to install both ESP and FGD, which will significantly reduce Hg emission from coal burning (Tang et al., 2007).

2.2. Emission from Zinc smelting

Hg emission from refining of Zn is another important anthropogenic source (Nriagu and Pacyna, 1988; Pai et al., 2000). Most compounds of Hg will be decomposed to Hg0 at temperatures greater than 700–800 °C (Lindqvist, 1986; Schroeder and Jackson, 1985), thus at high temperatures of Zn smelting (~1000 °C), nearly all of Hg occurring in Zn ores will be converted to Hg0 and emitted to the ambient air with the exhaust gas.

Zinc ores produced in Guizhou contain high high-Hg concentrations. Feng et al. (2004a) reported an average Hg concentration of 66.8 mg/kg in sulfide ores from Hezhang. Li et al. (2008) found Hg concentrations in carbonate Zn ores from Weining ranged from 1.06 to 87.1 mg/kg, with an average of 13.4 mg/kg, which was similar to the results found in oxide ores from Hezhang (Feng et al., 2004a). Elevated Hg concentrations in both sulfide Zn ores and oxide Zn ores occurred in those areas were probably contributed to the high-background Hg concentrations in bedrocks in the circum-Pacific global mercuriferous belt.

Using a mass balance method, Feng et al. (2004a) estimated the average Hg emission factors from artisanal Zn smelting in Hezhang to be 155 and 79 g Hg t⁻¹ of Zn produced from sulfide ores and oxide ores, respectively. Similar to the emission factor from oxide ores in Hezhang, an average Hg emission factor from carbonate ores in Weining was 75 g Hg t⁻¹ of Zn produced (Li et al., 2008). The average Hg emission factor from sulfide ores was almost two times higher than that of oxide ores. However, compared to the value reported in the literature, which was 25 g Hg t⁻¹ of Zn produced in developing countries (Nriagu and Pacyna, 1988), Hg emission factors of artisanal Zn smelting in Hezhang and Weining were significantly higher.

Emission factors of Hg from smelting facilities strongly depend on Hg concentrations in Zn ores and efficiencies of Hg removal by air pollution control equipments. No pollution devices were applied for artisanal zinc smelting activities. The amount of Hg remained in bottom ash from combustion chambers was estimated to be less than 5% of total Hg in Zn ores during artisanal Zn smelting processes (Li et al., 2005).

Using above-estimated Hg emission factors, annual Hg emissions from artisanal Zn smelting in Hezhang from 1989 to 2001 were estimated to be a few metric tons (Fig. 3). The maximum annual Hg emission was 7.1 t in 2000, which was comparable to the annual Hg emission from coal combustion in Guizhou in 1995 (Feng et al., 2002). It highlights that artisanal Zn smelting is an important regional atmospheric Hg emission source.

2.3. Emission from artisanal Hg mining in Guizhou

Since the beginning of 21st century, all large large-scale Hg mining activities in Guizhou province have ceased mainly due to lack of profits for the mining companies. However, the market for Hg demand has been increasing since China started to restrict importing Hg from Europe and other regions a few years ago. Consequently Hg prices in the market went up sharply recently, which stimulated the revival of small scale (artisanal) Hg activities using indigenous methods in Guizhou province. Especially the artisanal Hg mining activities using indigenous method have extensively existed in Wuchuan areas, northeastern Guizhou province, China. Wuchuan is one of the most important Hg production areas in Guizhou province. The large-scale mining activities ceased in 2003 because of the increasing environmental concerns. But small scale smelting activities which are classified as illegal and forbidden by the local government are still in operation in this area. The Hg ore (cinnabar) was crushed and then heated to 700–800 °C to produce Hg vapor that condensed in cooling wooden barrel, which contained water (Li et al., 2008). Because the simple smelting processes are without any environmental protection measures, the Hg emission factors (the proportion of Hg in ore is released to the ambient air) ranged from 6.9% to 32.1% and the annual Hg emission from artisanal Hg smelting activities was up to 3.7 to 9.6 t in Wuchuan area (Li et al., 2006a,b).

3. Hg emissions from natural sources in Guizhou

3.1. Emission from Hg Hg-enriched soil in Guizhou

In Hg mine areas, soil Hg concentrations are usually elevated by 2–4 orders of magnitude compared to the national background value of 0.038 mg/kg mainly due to Hg mineralization processes. Hg emissions from Hg-enriched substrates may, therefore, serve as an important natural emission source in Guizhou.

A field examination of Hg emissions by Wang et al. (2005) showed that in the Lanmuchang Hg mines, Southwestern Guizhou, Hg emission from soil was the main source of Hg in the ambient atmosphere. An average Hg emission flux of 19.9 mg/m² per year was obtained and within a total area of 2.9 km², the annual Hg emission reached ~3.54 kg Hg, indicating that soil is a strong Hg emission source to the ambient air. The average Hg emission fluxes from soil in
Wanshan Hg mines ranged from 1.42 to 243.7 mg/m² per year (Wang et al., 2007a), while the average Hg emission flux reached 1.23 mg/m² per year in Wuchuan Hg mines (Wang et al., 2007b).

3.2. Emission from natural soil

Due to high-Hg levels of geological baseline, natural soils in Guizhou are usually enriched in Hg. In situ total gaseous Hg (TGM) exchange fluxes between air and soil surface were intensively measured in Guiyang and Hongfeng reservoir area (Feng et al., 2005; Wang et al., 2004). Results showed that Hg emission fluxes from natural soil reached 9.64 µg/m²·year, which was almost one order of magnitude higher than the value used to estimate Hg emission from the soil in the global mercuriferous belts. The annual Hg emission from natural soil in Guiyang reached 0.41 t, which constituted an important atmospheric Hg source in the ambient air of Guiyang.

3.3. Emission from natural water

Hg exchange between air and water surfaces is recognized to be of significance in global biogeochemical cycling of Hg (Lindqvist et al., 1991; Mason et al., 1994). Since the Baihua reservoir was seriously contaminated with Hg released from the GOCP (Yan et al., 2008), an annual Hg emission from the reservoir to ambient air is estimated to be 0.75 kg, constituting 3% of total Hg in water body of the reservoir (Feng et al., 2004b). The Hg emission from water surfaces of the Baihua reservoir is considered to be an important local atmospheric Hg sources.

4. Atmospheric Hg pollution and deposition

4.1. Hg in ambient air

Significant Hg emissions from anthropogenic and natural sources resulted in high levels of atmospheric Hg in Guizhou. An average TGM concentration in ambient air in Guiyang was 11 ng/m³ in 1996 and 13 ng/m³ in 1999 (Feng et al., 2002). An investigation on TGM distribution in ambient air in Guiyang from November 2001 to November 2002 showed that an annual average TGM concentration was 8.4 ng/m³, with a seasonal distribution pattern descending from winter, spring, fall to summer (Feng et al., 2004c). Those values were significantly elevated compared to the global continental background values of North hemisphere which varied from 1.5 to 2.0 ng/m³ (Schroeder et al., 2001; Ebinghaus et al., 2002a; Lamborg et al., 2002). The seasonal TGM distribution pattern in Guiyang could be attributed to different amounts of coal combustion between cold and warm seasons.

In Lannuchang Hg mine, highly elevated TGM concentrations in ambient air varied from 35.2 ng/m³ (7.9–353.8 ng/m³) in cold season to 111.2 ng/m³ (12.7–468.0 ng/m³) in warm season (Wang et al., 2005). Recently, atmospheric Hg levels in ambient air near artisanal smelting retorts in Wuchuan exhibited values of 17.8–1101.8 ng/m³ (Wang et al., 2007a). The highest value of 12,222 ng/m³ was measured at an artisanal Hg smelting site at the prevailing wind direction. Even at considerable distance of 5–10 km in a downwind direction from the smelting retorts, high air Hg levels of 50.5–56.3 ng/m³ were observed as well. A significant correlation \( R^2 = 0.98 \) between air Hg concentrations and distances from artisanal Hg smelting sites was observed (Wang et al., 2007b), and the study indicated that air Hg concentrations decreased exponentially with distance between sampling sites and Hg smelting areas.

Air Hg concentrations in Hg mines were much elevated by 2–4 orders of magnitude compared to the values observed in pristine areas in Europe and North America, which was 1.5–2 ng/m³ (Ebinghaus et al., 2002b; Poissant et al., 2005).

Zinc smelting process also resulted in high concentrations of Hg in the ambient air. A study conducted in Weinig exhibited a high average air concentration of TGM of 124 ng/m³ on an average of 24 measurements around a zinc smelting workshop (Li et al., 2008).

4.2. Hg deposition

Large Hg emissions can lead to marked Hg depositions (Carpi, 1997; Nadim et al., 2001). Using moss bag technique, Hg deposition fluxes in Guizhou were investigated (Xiao et al., 1998; Tan et al., 2000). Total annual depositions ranged from 336 to 2340 µg/m² and the annual wet deposition ranged from 144 to 1404 µg/m². The highest annual total Hg deposition of 2340 µg/m² was as much as 42 times of the deposition flux measured at a reference site (Tan et al., 2000). Xiao and Ikihara (1998) reported that the annual total Hg deposition to Fanjing Mountain Nature Reserve was 115 µg/m², of which the dry deposition was of >50%. Recently, annual wet deposition fluxes of total Hg from five monitoring sites in rural areas of Guizhou were reported to be 34.7 µg/m² in 2006 (Guo et al., 2008). Those data in Guizhou were much higher than the value of 9.3 µg/m²/a reported in North America (NADP, 2007).

An investigation on the precipitation showed that total Hg concentrations in rain ranged from 10.3 to 90.6 ng/L with an average of 33 ng/L in Guiyang in 1996 (Feng et al., 2002). Similar results were found in 2006, which ranged from 7.5 to 149.1 ng/L with an average of 49.2 ng/L (Guo et al., 2008). Since Guiyang is impacted by acid rain caused by coal combustion (Shen et al., 1993), high levels of Hg in precipitation could be contributed to the Hg emission from coal combustion in the region.

5. Hg contamination to the environment from anthropogenic activities

5.1. Hg contamination from zinc smelting

In Hezhang, top soils were sampled along a valley from upwind direction of the artisanal zinc smelting workshops to the downwind direction. It is shown that total Hg concentrations in top soils decreased exponentially with the distance from Zn smelting areas, and dropped dramatically at upwind direction (Feng et al., 2006). This indicated that contaminations of Hg in top soils were mainly derived from the deposition of atmospheric Hg emitted from Zn smelting.

Local surface waters were also seriously contaminated with Hg due to Zn smelting. An average total Hg concentration
in the surface water in Hezhang reached 138 ng/L and was higher than the values observed in local springs and wells (Feng et al., 2004a). Apart from the deposition of Hg species that emitted from Zn smelting, smelting residues were also the primary source of Hg contamination to the surface water systems.

5.2. **Hg contamination from cinnabar mining**

Although large-scale state owned Hg mining activities were completely shut down in 2004, large quantities of illegal artisanal Hg mining activities are still operating in Wuchuan. Long-terms of Hg mining and the artisanal Hg mining activities resulted in significant quantities of piles and spoil heaps of calcines, which are dumped in stream banks and flood plains and are continuing to impact the local environments.

5.2.1. **Hg levels in mine tailings (calcines)**

High concentrations of total Hg in mine tailings, up to 4400 mg/kg, were observed in Wanshan (Qiu et al., 2005). Results from leaching experiments on calcines identified the existence of soluble reactive Hg compounds (Li et al., 2008b), suggesting that the introduction of Hg-contaminated tailing materials into river systems could release Hg species (i.e. soluble reactive Hg) to water. Studies showed that Hg phases in calcines, which usually include elemental Hg, metacinnabar, and Hg sulfates and chlorides (Kim et al., 2000, 2004), mainly depend on the efficiency of roasting techniques (Gray et al., 2002, 2003, 2004).

MeHg concentrations in calcines ranged from 0.17 to 3.9 µg/kg (Qiu et al., 2005, 2006a). Those data were comparable to the values reported in the Palawan Quicksilver Mine (Gray et al., 2003), but were 10–1000 times lower than the levels of 96–3100 µg/kg found in Nevada and Almadén (Gray et al., 2002, 2004). Qiu et al. (2005) concluded that low MeHg in calcines in Guizhou might be linked with the low microbial activities during sampling campaign in winter.

As both speciation and mobility of Hg in tailing materials are mostly unknown, determining solid phase Hg binding forms and aqueous phase Hg mobility in tailings is essential to estimate the potential for Hg transformation processes and to evaluate the environmental risks.

5.2.2. **Hg levels in soil**

Mining operations generally increased the mobilization of Hg through the smelting activities and the deposition of mine tailings and thus resulted in elevated Hg levels in soils. Hg concentrations in soils from Hg mines varied in wide ranges from background levels to several hundreds mg/kg. At the Wanshan Hg mine, Hg concentrations in surface soils could be as much as 790 mg/kg (Qiu et al. 2005). At a site of 24 km downstream from the Wuchuan mine, soils alongside river banks were still heavily contaminated with Hg and Hg concentration reached 24 mg/kg (Qiu et al., 2006a).

The distribution of Hg in a soil profile impacted by a large-scale Hg smelter was investigated in Wuchuan by Qiu et al. (2006a). Results showed that total Hg concentrations were the highest in the surface soil, ranging from 6.5 to 17 mg/kg, and decreased to a low level of 0.48 mg/kg at a depth of 45 cm. This indicated that Hg species deposited onto the soil surface can be transported downward so that anomalous Hg values can extend to depths of about 50 cm.

Elevated MeHg levels as high as 23 µg/kg in soil was found in Wanshan (Horvat et al., 2003). Similar results were reported in soils from Wuchuan, which ranged from 0.69 to 20 µg/kg (Qiu et al., 2006a). However, studies showed that MeHg concentrations in rice paddies were usually higher than those of cornfields (Qiu et al., 2005, 2006a) due to its favorable environment for methylation of Hg (Hines et al., 1999). Hg Hg-contaminated irrigating water and the anaerobic conditions most likely contributed to the high concentrations of MeHg in rice paddies. High levels of MeHg in paddies may result in MeHg exposure to humans through the food chain.

Although soils from Hg mining areas have elevated levels of MeHg, no significant correlation between MeHg and total Hg were found as shown in Fig. 4. However, ratios of MeHg to total Hg were lower in Hg mining areas compared to the background sites in un-mineralized areas. This might be because an enzyme-catalyzed microbial demethylation reaction breaks the Hg-C bond to produce Hg(II) and CH₄ (Summers, 1986), thus preventing high concentrations of MeHg from accumulating in these soils (Hines et al., 1999).

5.2.3. **Hg levels in surface water**

Total Hg concentrations in surface water emanating from calcines in Wanshan were reported to be up to 10,580 ng/L (Horvat et al., 2003). Concentrations of total Hg in surface water collected from Wanshan, Lamuchang and Wuchuan varied from 24.8 to 7020 ng/L (Feng et al., 2003; Qiu et al., 2006a,b). A geochemical study showed that the drainages from calcines had pH value of 10.6–11.8, containing high dissolved Hg concentrations of 300–1900 ng/L (Zhang et al., 2004a). This indicated that the reaction between water and calcines increased the concentrations of Hg in mine drainage and was an important process, which controls the release and transport of Hg from mine sites into the streams.

A positive correlation between total Hg and suspended substances in surface water samples was found in Fig. 5. This suggested that Hg associated with particulate material was an important vector for Hg migration from the abandoned Hg mine sites (Horvat et al., 2003; Qiu et al., 2006a,b). In temperate climates, the source of mass loading was from Hg mine

Fig. 4—The relationship between total Hg and MeHg in surface soils from Guizhou Hg mines (data from Horvat et al., 2003; Qiu et al., 2005, 2006b).
tailings and the transport of Hg from mine sites occurred primarily in particulate forms (Qiu et al., 2006a). Besides the atmospheric Hg deposition and the influx of soil-derived Hg, most of Hg found in streams is attributed to the erosion of tailings material. Hence, the secondary sources of the toxic forms of Hg can be transported to great distances from the original sources.

The fate of Hg transported downstream is controlled primarily by the biogeochemical conditions which affect the mobility of Hg. Studies revealed that the high concentrations of MeHg in downstream watersheds were associated with significant quantities of inorganic Hg emitted from those abandoned Hg mines (Horvat et al., 2003; Qiu et al., 2006a). The relationship between total MeHg and dissolved MeHg in surface water was shown in Fig. 6. This significant positive correlation indicated that the dissolved fraction dominated MeHg levels in stream waters from the Hg mining areas.

Hg concentrations in waters in Hg mining areas were much higher than those found in other aquatic systems that had been investigated in other parts of Guizhou (Jiang et al., 2004; Hou et al., 2004; He et al., 2006). Aquatic systems are of great interest due to the possibility of Hg transformation and accumulation in the food chain. Moreover, these contaminated stream waters are used by the local farmers to irrigate the rice paddy fields, which could result in further Hg contamination to soil compartment. The chemical speciation, fractionation and availability of Hg in sediments could be useful to understand the fate of Hg within the systems and thus need to be investigated.

Table 1 – Total Hg and MeHg concentrations in plant samples collected from Guizhou Hg mining areas

<table>
<thead>
<tr>
<th>Sample</th>
<th>THg (mg/kg)</th>
<th>MeHg (µg/kg)</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moss</td>
<td>0.98–95</td>
<td>0.19–20</td>
<td>Qiu et al. (2005)</td>
</tr>
<tr>
<td></td>
<td>2.1–182</td>
<td>0.57–149</td>
<td>Li et al. (2008b)</td>
</tr>
<tr>
<td>Rice</td>
<td>0.0091–0.55</td>
<td>0.019–1.12</td>
<td>Qiu et al. (2006a, 2008)</td>
</tr>
<tr>
<td></td>
<td>0.011–0.57</td>
<td>0.010–0.19</td>
<td>Horvat et al. (2003)</td>
</tr>
<tr>
<td></td>
<td>0.0018</td>
<td>0.011–0.57</td>
<td>Feng et al. (2008)</td>
</tr>
<tr>
<td></td>
<td>0.065</td>
<td>0.011–0.20</td>
<td>Cheng et al. (2006)</td>
</tr>
<tr>
<td>Corn</td>
<td>0.089–0.57</td>
<td>0.47–0.69</td>
<td>Qiu et al. (2006a, 2008)</td>
</tr>
<tr>
<td>Tobacco</td>
<td>0.02–0.76</td>
<td>0.12–1.6</td>
<td>Horvat et al. (2003)</td>
</tr>
<tr>
<td>Cole</td>
<td>0.011–0.20</td>
<td>0.017–1.3</td>
<td>Feng et al. (2008)</td>
</tr>
<tr>
<td>Cabbage</td>
<td>0.0018</td>
<td>0.011–0.20</td>
<td>Cheng et al. (2006)</td>
</tr>
<tr>
<td>Potato</td>
<td>0.018</td>
<td>0.008–0.18</td>
<td>Horvat et al. (2003)</td>
</tr>
<tr>
<td>Capsicum</td>
<td>0.18</td>
<td>0.011–0.20</td>
<td>Feng et al. (2008)</td>
</tr>
</tbody>
</table>

5.2.4. Hg levels in plants

Only a few studies were conducted to evaluate the environmental impacts and the potential hazards related to Hg contamination in plants (Table 1). In Hg mining areas, a significant amount of Hg can be concentrated in the foliar portion of the plants, which confirmed that plants uptake Hg via absorption of atmospheric Hg by leaves (Ericksen et al., 2003). Levels of Hg up to 18 mg/kg occurred in green cabbages (B. oleracea) grown in Hg-contaminated soils in Lammuuchang Hg mining area (Qiu et al., 2006b), where atmospheric Hg concentrations were elevated mainly due to Hg emissions from Hg Hg-enriched soil (Wang et al., 2005).

Moss obtaining nutrients through atmospheric route can be used as a bio-indicator of air pollution of Hg (Carpi et al., 1994; Calasans and Malm, 1997; Fernández et al., 2000). A significant amount of Hg can be concentrated in mosses in Hg mining areas, reaching up to 95 mg/kg (Qiu et al., 2005; Li et al., 2008b). Qiu et al. (2005) clearly demonstrated a significantly positive correlation between atmospheric Hg concentrations and total Hg concentrations in moss. The elevation of Hg concentrations in moss samples collected in Wanshan and Wuchuan Hg mining areas indicated that Hg mining activities have resulted in serious Hg contamination to the ambient air.

Though inorganic Hg species predominated in most of Hg-enriched plants, high levels of MeHg in rice (Oryza sativa L.) grown in Hg mining areas were reported (Horvat et al., 2003; Feng et al., 2008; Qiu et al., 2006a, 2008). It is demonstrated that total Hg concentrations in almost all agriculture crops exceeded the national guidance limit for foodstuff other than fish that is 20 µg/kg for food and 10 µg/kg for vegetables recommended by the Chinese National Standard Agency (Feng 2008).
et al., 2008). However, it is clearly demonstrated that only rice could assimilate and accumulate MeHg in its edible portion in a high level, and MeHg concentration in rice can be as high as 174 µg/kg (Qiu et al., 2008). The Hg-contaminated water (Horvat et al., 2003; Feng et al., 2003) for irrigation the soil and the anaerobic conditions created by the seasonal flooding during rice growing period may contribute to the high methylation ability in paddy soils. Qiu et al. (2005) observed that Me–Hg concentrations in soil samples from rice paddy field were generally higher than those in cornfield in Wanshan Hg mining area. However, the mechanism of rice tissue to uptake MeHg probably through its roots is still unclear.

5.3. Hg contamination from the GOCP and other plants

The GOCP, which used Hg-based technology till 1997, is located at the upper reaches of the Baimia reservoir. The GOCP went into operation in 1980, and about 160 t of Hg had been consumed since then. From 1980 to 1985, drainages from the GOCP were directly discharged to the environment without any treatment, which seriously contaminated the surrounding environments with Hg, especially the Baimia reservoir.

High average concentrations of total Hg in water samples from the Baimia reservoir were found up to 73.4 ng/L (Yan et al., 2005). Data reported by Yan et al. (2008) showed that the highest total Hg concentration of 39 mg/kg in sediments was obtained in the upstream of the Baimia reservoir, which is located immediately downstream of the GOCP. However, high high-Hg concentrations and strong variations with depth were observed in the sediment cores collected in a downstream part of the Baimia reservoir. Two strong peaks could be distinguished at 14 cm and 22 cm in the sediment cores, respectively. In more recent sediments, however, concentrations of Hg decreased toward the surface of the sediment, which corresponding the reducing discharging Hg from the company. The study testified exceedingly high high-Hg levels in the historical records provided by sediment cores.

Yasuda et al. (2004) demonstrated that the paddy fields downstream of GOCP receiving the waste water from GOCP were seriously contaminated with Hg. The average total Hg concentration was 15.73±42.98 mg/kg, which were significantly elevated compared to the average value of 0.11±0.05 mg/kg in the control area nearby (Yasuda et al., 2004). Horvat et al. (2003) reported that Hg concentrations in soil in Quingzhen is the closest to the GOCP but the levels reached background concentrations at a distance of several km. Even though the major source of Hg in this area is inorganic Hg, it was observed that active transformation of inorganic Hg to organic Hg species (MeHg) takes place in water, sediments and soils. The concentration of Hg in rice grains can reach up to 87.8 µg/kg of total Hg of which 41.4 µg/kg was in MeHg form, and the percentage of Hg as MeHg varied from 32.9 to 52.8% (Horvat et al., 2003).

Recently, an investigation on the spatial and temporal distribution of MeHg in the Hongfeng reservoir, which was impact by a coal-fire power plant, showed that MeHg concentrations significantly increased from 0.053 to 0.92 ng/L in hypolimnion in summer season, suggesting strong MeHg productions in water column. The outflow of reservoir was rich in MeHg, which was 5.5 times higher than those in the inflow (He et al., 2006, 2008). This study indicated that MeHg-enriched water from the anoxic hypolimnion in reservoir can be a potential MeHg contamination source to the downstream ecosystems.

6. Hg exposure pathways and human health risk

The human health risk assessment of Hg exposure in Hg mining areas was conducted by several studies. In Wuchuan, the average hair total Hg and MeHg for smelting workers were 69.3 and 2.32 mg/kg, respectively, and were significantly higher than those in a control group, which were 0.78 mg/kg for total Hg and 0.65 mg/kg for MeHg, respectively. (Li et al., 2008a). Urinary Hg levels ranged from 22.6 to 4577 mg/kg creatinine for the exposed workers and from 1.0 to 17.4 mg/kg creatinine for the unexposed subjects (Sakamoto et al., 2007; Li et al., 2008a). Total Hg concentrations in urine and hair showed a significant correlation in the exposed group (r=0.62), indicating an adhesion of Hg vapor to hair (Sakamoto et al., 2007). Total tremor intensity and frequency-specific tremor intensities at 1–6 and 10–14 Hz of the exposed workers were significantly higher than the unexposed subjects (Iwata et al., 2007). Studies clearly demonstrated that symptoms included finger and eyelid tremor, gingivitis and typical dark-line on gums were observed in six workers (Li et al., 2008a). These indicated that physical impairments occurred and the workers were heavily exposed to Hg vapor during the process of cinnabar roasting.

Feng et al. (2008) reported that concentrations of total Hg and MeHg in hair samples collected from residents from three villages in Wanshan Hg mining area ranged from 0.6 to 58.5 mg/kg and 0.2 to 5.6 mg/kg, respectively. However, hair Hg levels in samples from a control site were quite low, ranging from 0.32 to 1.7 mg/kg in total Hg and 0.26 to 1.1 mg/kg in MeHg, respectively. As mentioned above, MeHg tends to accumulate in rice, which is a staple food for the local residents, and MeHg-contaminated rice consumption could represent a social and economic problem. Recent experiments on rats’ 20-day exposure to rice from Wanshan revealed an inducible lipid peroxidation in rat’s brain, liver, and kidney tissue, exhibiting an increase of c-jun mRNA (Cheng et al., 2005, 2006). A study of 98 persons from Wanshan showed a significant correlation (r=0.65, p<0.01) between hair MeHg concentrations and daily MeHg intake through rice consumption (Feng et al., 2008). Official statistical data showed that for the rural populations in Guizhou, the amount of fish and rice consumed per person per year varied from 0.22 to 0.31 kg, and from 140 to 153 kg, respectively (Bureau, 2006). Hence, rice provides more caloric input than fish and other single food. This indicated that rice is an important MeHg exposure route for residents in Wanshan and the main human exposure to MeHg via food consumption is rice rather than fish. Generally, the inhabitants in Wanshan Hg mining area are exposed to Me–Hg to a certain level. However, they are not under a serious health risk. Hair Me–Hg concentrations of the inhabitants in Wanshan Hg mining area were much lower than the thresholds for onset of neurological symptoms in human body recommended both.
by WHO (1990) and National Research Council (2000). Nevertheless, some female participants may exceed the tolerable intake levels of Me–Hg for pregnant women established by USEPA (1997b). Thus, rice intake in Hg mining areas in Guizhou may pose a health risk of Me–Hg exposure to local inhabitants.

7. Summary

Coal combustion and metals smelting (i.e. Hg and Zn smelting) were two key sources for Hg pollution in environments in Guizhou. High values of Hg deposition fluxes were found even in rural areas in the province. Residents in the vicinity of smelting areas could be exposed to high levels of Hg vapor through the inhalation due to high levels of Hg vapor in the ambient air. In Hg mining areas, rice consumption is a main exposure pathway of MeHg to the local populations.

Though a number of studies are summarized in an effort to understand Hg pollution status in Guizhou, these studies showed an important knowledge gap concerning identification and quantification of Hg compounds, which are known to be dominant components of Hg chemistry (Ullrich et al., 2001). In addition, an accurate assessment of molecular-level speciation of Hg contained in environmental compartments, which is a main parameter governing Hg mobility, toxicity, and bioavailability (Brown et al., 1999), is necessary to determine for the remediation actions that should be taken. There is also an urgent need for the better understanding of the fate of Hg in the atmosphere, as well as in aquatic ecosystems. Moreover, long-term effects of consuming MeHg-contaminated rice should be scrutinized to assess the risk of human exposures.

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