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Environmental contamination and risk assessment of mercury from a historic mercury mine located in southwestern China

Yonghua Li

Abstract A field survey of mercury pollution in environmental media and human hair samples obtained from residents living in the area surrounding the Chatian mercury mine (CMM) of southwestern China was conducted to evaluate the health risks of mercury to local residents. The results showed that mine waste, and tailings in particular, contained high levels of mercury and that the maximum mercury concentration was 88.50 $\mu g\ g^{-1}$. Elevated mercury levels were also found in local surface water, paddy soil, and paddy grain, which may cause severe health problems. The mercury concentration of hair samples from the inhabitants of the CMM exceeded 1.0 $\mu g\ g^{-1}$, which is the limit recommended by the US EPA. Mercury concentrations in paddy soil were positively correlated with mercury concentrations in paddy roots, stalks, and paddy grains, which suggested that paddy soil was the major source of mercury in paddy plant tissue. The average daily dose (ADD) of mercury for local adults and preschool children via oral exposure reached 0.241 and 0.624 $\mu g\ kg^{-1}$ body weight per day, respectively, which is approaching or exceeds the provisional tolerable daily intake. Among the three oral exposure routes, the greatest contributor to the ADD of mercury was the ingestion of rice grain. Open-stacked mine tailings have resulted in heavy mercury contamination in the surrounding soil, and the depth of appreciable soil mercury concentrations exceeded 100 cm.

Keywords Mercury · Heavy metals · Exposure pathway · Average daily intake dose · Mining activity

Introduction

A significant body of research on mercury (Hg) has been performed because of its adverse impacts on public health and environmental quality (Horvat et al. 2003; Taylor et al. 2005; Appleton et al. 2006; Feng et al. 2006; Qiu et al. 2006; Zheng et al. 2007; Kim and Jung 2012). Currently, the global input of anthropogenic mercury to the environment is estimated to be 2,000–2,200 ton yr^{-1} (Seigneur et al. 2004), 12 % of which is derived from the mining–refining industry (Han et al. 2006). Once released into the environment, mercury is redistributed between and within the environmental compartments. Therefore, mercury is an acute environmental problem due to its bioaccumulative and persistent characteristics in the ecosystem, especially within agro-ecosystems.

Blood, urine, and hair have been successfully used as biomarkers to reflect the health risks of mercury exposure (Adimado and Baah 2002; Mortada et al. 2002). Hair in particular is a suitable indicator for estimating long-term mercury exposure (McDowell

Y. Li (✉)
Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China
e-mail: yhli@igsnrr.ac.cn

et al. 2004; Yasutake et al. 2004). Although preliminary investigations of the daily intake (DI) of mercury via several types of exposure routes have been performed (Taylor et al. 2005; Feng et al. 2006), most DIs used in mercury assessments related to populations affected by mercury contamination have been based on fish and other seafood, which accumulate mono- and dimethylmercury in fatty tissues. Studies in areas where seafood consumption does not represent the main exposure route, such as those surrounding inland mercury mines, have been rare. For people who live in inland areas, the consumption of fish or shellfish is not common; therefore, other pathways for exposure, such as freshwater consumption, grain and vegetable intake, and inhalation, may contribute to the mercury DI of inland residents. A quantitative understanding of the mechanism by which each pathway contributes to mercury exposure is essential for developing effective mitigation strategies, especially for residents living in contaminated sites and adjacent areas in southwestern China, where remediation efforts are constrained by costs or other factors and nutritional challenge may exacerbate exposure outcomes.

Within the context outlined above, the main objectives of this study were as follows: (1) to delineate mercury contamination in a historic mercury mining area located in southwestern China by analyzing soil, mine waste, water, paddy plant tissue, rice grain, and human hair and (2) to assess the health risk of mercury pollution via oral exposure to inhabitants in the vicinity of the area.

Materials and methods

Study area

The Chatian mercury mine (CMM) has been one of the largest producers of mercury in China, producing approximately 10 % of the total national production of mercury, which supplies both domestic demands and exports. The CMM is located in the town of Chatian, southwestern China, at 27°46′00″–27°47′30″ north latitude and 109°20′30″–109°21′10″ east longitude (Fig. 1). The area has a subtropical humid monsoon climate, and the annual average temperature and rainfall are 13–18 °C and 1,100–1,500 mm, respectively. Mining activities in the area date back to the Qin

Dynasty (221 BC), but only in the early 1950s were its mines rediscovered, and an intensive mining activity was started. Between the late 1950s and the early 1990s, for instance, approximately 150 ton yr^{-1} of mercury had been produced from the CMM. Because of an increasing health concern about mercury and the importance of decline of its price, the mines in the CMM were abandoned gradually until the late 1990s. However, long-term mining operations, random tailing disposal, and poor governmental control have resulted in heavy mercury pollution. The emission of metallic mercury from the CMM and the adjacent area has become one of the largest and most serious environmental problems in southwestern China in recent decades (Horvat et al. 2003; Li et al. 2009).

Sampling and preparation

In the fall of 2005, a total of 158 samples (29 soil samples, 14 mine waste samples, 13 water samples, 72 paddy tissue samples, 15 rice grains, and 15 human hairs) were collected within the CMM. The soil samples included 18 paddy soils and 11 profile soils. To study mercury translocation and accumulation in paddy soil–paddy plant systems, 18 sets of paddy plant tissues (including paddy roots, paddy stalks, paddy leaves, and paddy grains) and corresponding paddy soils were sampled. A soil profile below a historic mine tailing pile was sampled to determine the impact of slag piles on the migration and distribution of mercury. At the tested soil profile site, intensive sampling was performed to a depth of 110 cm, and 11 samples were collected at 10-cm intervals using a cylindrical auger. The hand auger was drilled into the soil and removed, and the resulting sample was carefully cut into 10 cm sections. Mine wastes were also collected from discarded piles. In total, 13 water samples were tested, including 4 drinking water samples from mountain streams and 9 irrigation water samples, which were obtained from reservoirs, ponds, and ditches. Moreover, 15 sets of hair and rice grain samples were collected from local adult inhabitants to evaluate the health response of the residents to mercury exposure. All of the solid samples were sealed in polyethylene bags to avoid cross-contamination. The sampling sites of the CMM are shown in Fig. 1.

In the laboratory, the soil and mine waste samples were air-dried, ground, and separated using a 150-mesh sieve. Water samples were filtered in situ
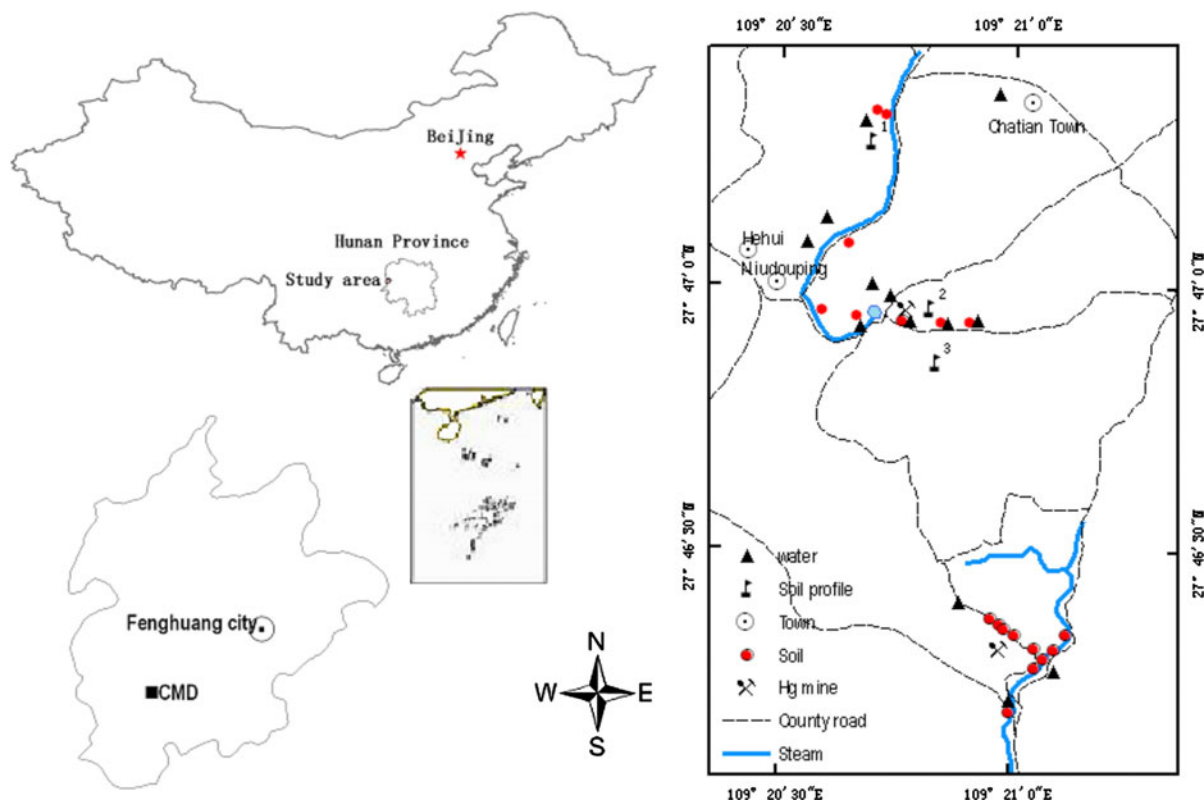
Fig. 1 Sampling locations in the CMM

through a 0.45 μm precleaned cellulose membrane filter, added to 1 % (v/v) HCl, and stored at 4 °C prior to analysis. Paddy plants were rinsed several times using flowing demineralized water to remove external attached soil particles. Subsequently, the plants were separated into 4 parts (root, stalk, leaves, and paddy grain without the hull, i.e., brown rice) and were cut into small pieces. All of the plant samples were oven-dried at 40 °C for 48 h, ground, sieved to less than 50 μm, thoroughly mixed, and stored in sealed polyethylene bottles. Each hair sample was washed with nonionic detergent, tap-water, and demineralized water. The washed samples were air-dried at room temperature in a dust-free area and were cut into pieces smaller than 1 cm in length prior to storage or digestion.

Sample analysis

All of the reagents used in this study were of analytical-reagent grade. For the dilutions, high-purity

demineralized water provided by a Milli-Q Plus filter apparatus (Millipore Inc., USA) was used.

For the total mercury analysis, the appropriate amounts of prepared soil and mine waste were collected for digestion, which was performed using a water bath containing a mixture of HCl-HNO$_3$ (9:1 in v/v) (Horvat et al. 1991; Qiu et al. 2006). Dry hair samples, rice grains, and different tissues from paddy plants were digested in a water bath with a fresh mixture of HNO$_3$/H$_2$SO$_4$ for the total mercury analysis (Horvat et al. 1991). The total mercury content of mine waste, soil, water, paddy tissue, rice grains, and human hair samples was determined using cold vapor atomic absorption spectrometry (CV-AAS). For quality assurance and quality control (QA/QC), method blanks, certified reference materials (CRMs), and blind duplicates were used during analyses. CRMs obtained from China National Standard Materials Research Center including soil (GBW07404), water (GBW08603), bush branches and leaves (GSV-1), and human hair (GSH-1). The analytical results of mercury in the CRMs were in good agreement with the

certified values, with RSDs in range from 2.32 to 12.58 %. The recovery of mercury on spiked samples varied from 87 to 110 %, and the relative percent difference in the total mercury content of duplicate samples was less than 11 %.

The following soil properties were also tested: pH (the ratio of soil to Milli-Q water is 1:2.5, W/V) and soil organic matter (OM), according to the conventional methods issued by ISSCAS (1978), and the grain size of the soil was determined by laser-diffraction analysis (Mastersizer 2000, Malvern, UK).

Exposure assessment

In the exposure assessment stage, the average daily dose [ADD, $\mu g\ kg^{-1}$ of body weight (BW) per day] was used to quantify mercury exposure from water, rice grain consumption, and other pathways. The following equation was used in the exposure assessment (US EPA 1992):

$$ADD = [C \times IR \times ED]/[BW \times AT]$$

where C is the mercury concentration in the environmental sample (e.g., soil, rice grain, water in $\mu g\ kg^{-1}$, $\mu g\ kg^{-1}$, $\mu g\ L^{-1}$, etc.), IR is the ingestion rate ($kg\ day^{-1}$, $L\ day^{-1}$), ED is the exposure duration (day), BW is body weight (kg), and AT is the time period over which the dose is averaged (day). The total ADD was equal to the sum of ADDs via various exposure routes.

Results

Mercury levels in mine wastes

In the CMM, mine wastes, such as tailings and waste rock, are usually stocked in piles on the ground without a proper disposal system. Similar to most mercury mines, the mine waste from the CMM exhibited a high mercury concentration (Table 1). The concentration of mercury in mine waste ranged from 0.47 to 88.50 $\mu g\ g^{-1}$, which was 5.88–1 106 times higher than the crustal average mercury content of 0.08 $mg\ kg^{-1}$ suggested by Habashi (1997). In general, mining and ore processing techniques have greatly increased the surface area of mercury-containing mine wastes, thus facilitating the interaction of mercury phases with surface and rain water (Kim et al. 2000). As surface and/or rain water passes through the highly permeable piles, it can leach and mobilize mercury in both the dissolved and particulate phase. This process is particularly enhanced at mines where acid mine drainage increases the degree of leaching (Kim et al. 2000). The elevated mercury levels for these mine wastes suggest that significant amounts of mercury can be released into surrounding compartments, including soil and surface water.

Mercury levels in surface water

Overall, the mercury concentrations of surface water samples collected from the CMM ranged from 0.09 to 9.92 $\mu g\ L^{-1}$ (Table 1), which is lower than the reported concentration at a mercury mine located in Almadén, Spain (water mercury: 0.01–20.30 $\mu g\ L^{-1}$) (Berzas Nevado et al. 2003) and the Palawan Quicksilver mine (Philippines, water mercury: 0.12–31.00 $\mu g\ L^{-1}$) (Gray et al. 2003) but is comparable to those found at the Wanshan mercury mine in China (water mercury: 0.02–10.58 $\mu g\ L^{-1}$) (Horvat et al. 2003). Nevertheless, the mercury concentrations determined in surface water in the CMM, specifically the maximum observed values, were higher than those found at mercury mines located in Idrija, Slovenia (water mercury: 0.00–0.32 $\mu g\ L^{-1}$) (Horvat et al. 2002), Nevada, USA (water mercury: 0.001–2.11 $\mu g\ L^{-1}$)

Table 1 Mercury concentration in mine waste samples and surface water samples from the CMM

	Sample size	Maximum	Minimum	Mean	Standard deviation
Mine wastes ($\mu g\ g^{-1}$)					
Tailings	8	88.50	0.47	22.20	34.76
Waste rock	6	33.80	6.01	19.27	13.94
Surface water ($\mu g\ L^{-1}$)					
Drinking water	4	0.18	0.09	0.14	0.05
Irrigation water	9	9.92	0.15	2.84	3.51

(Bonzongo et al. 1996), and Alaska, USA (water mercury: 0.00–2.50 µg L^{-1}) (Gray et al. 2003).

The mercury concentrations of irrigation water samples varied greatly and showed remarkable heterogeneity in the CMM. Almost all of the irrigation water samples exceeded the national guidelines for mercury in agricultural water in China (1 µg L^{-1}). Compared to irrigation water, the concentrations of mercury in drinking water were much lower and ranged between 0.09 and 0.18 µg L^{-1}. However, because this water was derived from the CMM, which contains a high geochemical background of mercury, these values were greater than the national guidelines for mercury in drinking water in China (0.05 µg L^{-1}). As a result, the local population is exposed to mercury through the consumption of drinking water as well as crops and vegetables that are irrigated using contaminated surface water.

Vertical distribution of mercury in soil

The enrichment factor (EF), which is the ratio between the content of an element in any given horizon and that of the parent rock, was used to describe the mobility of mercury in the soil profile, as proposed by Rahn and McCafrfrey (1979). The formula is as follow:

$$EF = (X_s/I_s)/(X_r/I_r)$$

where X_s and I_s represent the contents of element X and immobile element I in the soil sample, respectively, while X_r and I_r represent those in the parent rock.

Martínez Cortizas et al. (2003) developed this approach to estimate the extent of heavy metal migration and enrichment in soil profiles. In the current study, because the soil was too deep and soil profile was too shallow to reach the parent rock, the deepest layer (100–110 cm) was used as the substitute. The enrichment factor of mercury in any given horizon is calculated by using Ti as the stable element (Table 2).

A maximum mercury concentration of 640 µg g^{-1} was observed in the topsoil (0–10 cm) below the stacked tailings. However, the mercury enrichment factor abruptly decreased from 23.7 in topsoil to 11.2 in the subsoil (10–20 cm), which indicated that open-stacked tailings without proper disposal led to heavy mercury pollution in the surrounding soil. With respect to the mobility of mercury, the enrichment factor decreased with an increase in the depth of the soil profile (Table 2). However, at a depth of 90–100 cm, the soil horizon still contains elevated levels of mercury (the mercury enrichment factor remained constant at 1.2), which suggested that mercury has migrated downward to at least 100 cm depth in the soil profile.

Mercury levels in paddy soil–paddy plant systems

The mercury concentration in paddy soil and paddy plant tissue is shown in Fig. 2. The concentration of mercury in paddy soil ranged from 3.90 to 55.70 µg g^{-1}, which exceeded the benchmark value of Grade II Environmental Quality for Soils in China (0.5 µg g^{-1}). The amount of mercury in paddy soil

Table 2 Analysis result of mercury enrichment factor (EF) and some soil physicochemical parameters in the tested soil profile

Layer (cm)	Hg (µg g^{-1})	Ti (µg g^{-1})	Enrichment factor[a]	pH	OM (µg g^{-1})	Sand (%)	Silt (%)	Clay (%)
0–10	640.0	4,455	23.7	8.23	18.0	36.43	58.61	4.96
10–20	300.0	4,416	11.2	8.38	12.9	40.90	54.13	4.97
20–30	134.0	4,583	4.8	8.16	16.8	37.08	58.68	4.24
30–40	190.0	4,641	6.8	8.30	13.8	36.36	58.38	5.26
40–50	170.0	4,304	6.5	8.55	13.6	41.23	53.62	5.15
50–60	131.0	4,670	4.6	8.51	16.0	25.22	67.14	7.64
60–70	97.5	4,606	3.5	8.62	16.9	27.19	66.50	6.31
70–80	150.0	4,782	5.2	8.68	15.9	39.96	55.32	4.72
80–90	68.6	4,729	2.4	8.60	11.9	47.53	49.26	3.21
90–100	35.0	4,817	1.2	8.51	7.8	32.78	61.90	5.32
100–110	28.0	4,617	1.0	8.48	5.5	25.99	61.17	6.84

[a] EF = $(Hg_s/Ti_s)/(Hg_r/Ti_r)$, where Hg_s and Ti_s represent the contents of Hg and Ti in the given soil layer, respectively, while Hg_r and Ti_r represent those in the 100–110 cm soil layer

varied considerably due to anthropogenic disturbances. The concentration of mercury abruptly decreased as the distance from the mine increased, especially in soil located upstream of the mine well. The mercury concentration in paddy grains varied between 10 and 150 ng g^{-1} based on dry weight (DW), and the average mercury content was 30.6 ng g^{-1} (DW). Among the paddy grain samples, the mercury content of 11 samples exceeded the maximum permissible level of mercury for grain in China [20 ng g^{-1} (DW)].

Table 3 showed a comparison of our results with several earlier reports on mercury concentrations in rice grains. As can be seen, mercury in rice commonly consumed in China averages 0.58 ng g^{-1} (range,

Fig. 2 Mercury concentration in paddy plant tissue and corresponding paddy soil

0.02–31 ng g^{-1}; Qian et al. 2010), whereas a value of 5.21 ng g^{-1} was reported for commercial rice from Italy (Horvat et al. 2003). The mean value of mercury concentrations found in the CMM rice grains is 52.8 and 5.9 times above the Chinese and Italian background value, respectively, indicating that rice grains from the CMM are at higher risk of mercury exposure. Actually, mercury in rice grains from the CMM in general is much higher than reported concentrations in mercury polluted areas from Philippines, such as the Manila mercury mines (range, 3.08–3.61 ng g^{-1}; Maramba et al. 2006) and Mt. Diwata gold mining areas (range, 9–58 ng g^{-1}; Appleton et al. 2006), but is comparable to those found in Wanshan, China (range, 4.9–214.7 ng g^{-1}; Feng et al. 2008) and Wuchuan, China (range, 6.0–113.0 ng g^{-1}; Li et al. 2008), especially concerning the mean values. Nevertheless, the mean concentration found in the studied area is higher than concentrations found in Zhejiang e-waste recycling areas, China (range, 15.6–68.4 ng g^{-1}; Fu et al. 2008) and Jiangsu rural-industrial zone, China (range, 1–13 ng g^{-1}; Cao et al. 2010).

The average concentration of mercury in different paddy plant tissues displayed the following trend: paddy roots > paddy leaves > paddy stalks > paddy grains. Significant positive correlations ($p < 0.05$) were observed between mercury in paddy roots, paddy stalks, paddy grains, and paddy soil (Table 4), which implied that the paddy soil was the major source of mercury in paddy roots, stalks, and grains. However, statistically significant correlations between mercury in paddy leaves and paddy soil were not observed. This
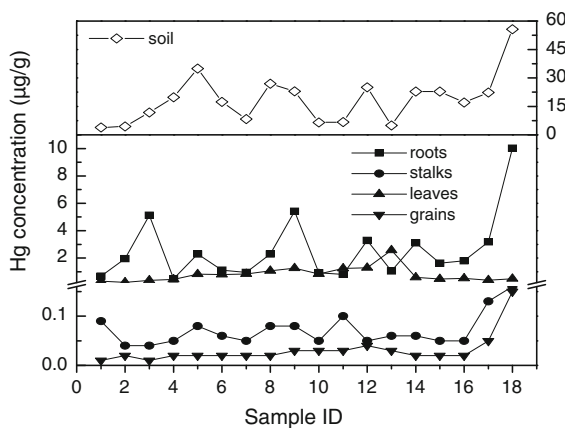
Table 3 Comparison of mercury concentrations in rice grains collected from the CMM with other results reported in the recent literature

Locations	Range [ng g^{-1} (DW)]	Mean [ng g^{-1} (DW)]	References
Commercial rice from Italy	NA	5.21	Horvat et al. (2003)
Commercial rice from China	0.02–31	0.58	Qian et al. (2010)
Manila abandoned Hg mines, Philippines	3.08–3.61	3.35	Maramba et al. (2006)
Mt. Diwata gold mining areas, Philippines	9–58	21	Appleton et al. (2006)
Wanshan Hg-mining areas, Guizhou, China	4.9–214.7	36.2	Feng et al. (2008)
Wuchuan Hg-mining areas, China	6.0–113.0	26.8	Li et al. (2008)
E-waste recycling areas, Zhejiang, China	15.6–68.4	22	Fu et al. (2008)
Jiangsu rural-industrial zone, China	1–13	5.7	Cao et al. (2010)
CMM, China	10–150	30.6	This study

NA not available

Table 4 Correlation matrix of mercury concentration in paddy soil and paddy plant tissue

	Soil	Roots	Stalks	Leaves
Roots	0.74*			
Stalks	0.60*	0.57*		
Leaves	–0.16	–0.15	–0.07	
Paddy grains	0.71*	0.79*	0.75*	–0.07

Correlation is significant at the * $p < 0.05$ level; sample size is 18

indicates that the uptake and retention of mercury in paddy leaves is influenced by a number of factors, of which the concentration of mercury in paddy soil may only be one of the variables. Our findings are similar to the results illustrated by Horvat et al. (2003) who found mercury concentrations in rice from two stations in Wanshan and Quingzhen with similar concentrations of mercury in paddy soil but distinct differences in mercury concentrations in paddy plant. Because the amount of mercury in paddy leaves was greater than that of paddy stalks, paddy leaves also absorbed particle-bound mercury from the atmosphere through foliage stomata exchange as well as via a soil source (Patra and Sharma 2000). A large amount of mercury is emitted into the atmosphere during mining. For example, Horvat et al. (2003) demonstrated that the mercury content of the atmosphere at the Guizhou mercury mine was 500–1,500 ng m^{-3}.

Mercury in hair

Hair analysis is a valuable indicator for estimating long-term heavy metal exposure, especially for cadmium, lead, and mercury (Mortada et al. 2002). The average concentration of mercury in the hair of Chinese citizens is estimated to be 1.36 μg g^{-1} (Qin 2004). In the present study, the mercury content of residents from the CMM ranged between 1.04 and 10.32 μg g^{-1}, and the average concentration was 3.73 μg g^{-1}. In total, 87 % (13/15) of the residents possessed a hair mercury concentration greater than 1.36 μg g^{-1}, thereby indicating that residents in the CMM may suffer from severe health problems caused by mercury exposure. Moreover, of the hair samples that were tested for mercury content, all were found to exceed 1.0 μg g^{-1}, which is the limit recommended by the US EPA (Hightower and Moore 2003).

Discussion

ADD of mercury via oral routes

Generally, oral routes to ADD include drinking water intake, grain products intake, fish and meat intake, fruit and vegetable intake, soil ingestion and pica, etc. (US EPA 1997). Given that the CMM is a poor area of southwestern China and very far from any lake and ocean. Those people who live in the CMM eat rare amount of fish, meat, fruit, and vegetable (3, 22, 20, and 125 g day^{-1} based on fresh weight, respectively) (FBS 2008); however, rice grain is a staple food and provided more calories than any other single food (FBS 2008). Previous studies indicated that meat and vegetables contained very low methylmercury compared to rice grain in mercury mining area in southwestern China (Feng et al. 2008). In the present study, data on mercury in fish, meat, fruit, and vegetable in the CMM are not available; nevertheless, it is reasonable to assume that drinking water intake, rice grain intake, and soil ingestion are the major oral routes to the ADD of mercury in inhabitants in the CMM.

The joint FAO/WHO Expert Committee on Food Additives recommends that the provisional tolerable weekly intake (PTWI) of mercury should be 3.3 μg kg^{-1} BW per week (namely 0.47 μg kg^{-1} BW per day) (UNEP 2002). The average daily drinking water intakes for adults and children were considered to be 2 and 1 L person^{-1} day^{-1} (US EPA 1991), respectively, while the average adult and preschool child BW were considered to be 60 and 16 kg, respectively, as used in previous studies (Fu et al. 2008; Li et al. 2008). Therefore, the ADD of mercury via drinking water consumption by local adults and children is 0.005 and 0.009 μg kg^{-1} BW per day, respectively.

As rice grain is a staple food for daily consumption in China, especially in the region of our study site, mercury in rice grain may contribute a major part to the total ADD. Based on the national survey of nutrition and health of Chinese people (Wang 2005), average daily consumption of rice grain is 402 g for a general adult; according to field investigation on local resident's diet, 200 g day^{-1} is a conservative estimate of the mean rice grain ingestion for local preschool children. Therefore, local adults and children would receive an ADD of mercury from rice grain that is 0.205 and 0.383 μg kg^{-1} BW per day, respectively.

The incidental oral ingestion of contaminated soil was considered to be another important pathway for heavy metal absorption, especially for preschool children with regular hand-to-mouth activity. According to the US EPA, a soil intake is 200 mg day^{-1} for children (US EPA 2002) and 100 mg day^{-1} for adults (US EPA 1997) through inadvertent ingestion; however, certain researchers use lower levels of soil ingestion for adults (Edward et al. 1997). In the present study, 100 mg day^{-1} was used as the direct soil ingestion rate for adults due to their participation in regular farming activities, such as the plowing, weeding, and fertilizing of paddy plots. Therefore, the ADD of mercury via soil ingestion by local preschool children reached 0.232 µg kg^{-1} BW per day, which is greater than that of adults (0.031 µg kg^{-1} BW per day).

The total ADD of mercury via oral routes, including drinking water, rice grain ingestion, and incidental soil ingestion, was calculated to be 0.241 µg kg^{-1} BW per day for adults and 0.624 µg kg^{-1} BW per day for preschool children (Table 5), which approaches or exceeds the PTDI recommended by the joint FAO/WHO Expert Committee on Food Additives (0.47 µg kg^{-1} BW per day). Among the aforementioned exposure routes, rice grain ingestion contributed 85 and 61 % of the total ADD of mercury for adults and preschool children, respectively, which indicated that rice grain ingestion is the primary pathway of mercury exposure to humans in the CMM. Although obvious health problems have not been observed in the CMM, long-term exposure to mercury through the regular consumption of rice grain and the incidental oral ingestion of soil may pose a potential health risk.

Mercury migration through the soil profile

In general, when mercury in forest soil originates from a deposition or polluted water, mercury does not move downward through soil profile but primarily remains in the topsoil (Sterckeman et al. 2000; Feng et al. 2006; Ettler et al. 2007). However, the mercury concentrations of the tested soil profile in the CMM were indicative of a high vertical mobility, thereby allowing us to draw a different conclusion. Soil horizons in the tested soil profile were enriched in mercury with respect to the deepest soil horizon concentration (23.7–1.2 times higher). The observed increase in the mercury concentration with depth could be attributed to inputs from tailings due to weathering, eluviation, and downward migration. Previous study (He et al. 1995) indicates that the hydrothermal fluids in the CMM are characterized by high Cl$^-$ and low SO$_4^{2-}$ concentrations (Cl$^-$: 34.03–64.87 g L^{-1}, 46.44 g L^{-1} in average; 2.88–42.24 g L^{-1}, 20.16 g L^{-1} in average); thus, mercury may have immigrated as Hg$_2$Cl$_2$ and HgCl$_4^{2-}$ rather than HgS when the mercury ore was formed (Varekamp and Buseck 1984; He et al. 1995). Hg$_2$Cl$_2$ is less thermodynamically stable than HgS, and the solubility products of HgS and Hg$_2$Cl$_2$ are 1.0×10^{-53} and 4.1×10^{-23}, respectively. Therefore, Hg$_2$Cl$_2$ becomes more active when the Cl$^-$ content is high (Hahne and Heiss 1974). Brandon et al. (2001) demonstrated that Cl$^-$ greatly extends the area of stability of Hg$^+$ and Hg$_2^{2+}$ ions and that Hg$_2$Cl$_2$ and HgCl$_4^{2-}$ ions form in Hg–Cl–H$_2$O systems. Thus, during long-term weathering in hot, wet environments, the mercury present in Cl-rich tailings likely combines with Cl$^-$ to form HgCl$_2$, HgCl$_4^{2-}$, or HgClOH, which

Table 5 Daily mercury intake of local inhabitants via oral routes

Pathway	Parameter	Average mercury content	ADD (µg kg^{-1} BW per day)
Drinking water by adults	2 L	0.14 µg L^{-1}	0.005
Drinking water by preschool children	1 L	0.14 µg L^{-1}	0.009
Rice ingestion by adults	402 g day^{-1}	30.6 ng g^{-1}	0.205
Rice ingestion by preschool children	200 g day^{-1}	30.6 ng g^{-1}	0.383
Soil ingestion by adults	100 mg day^{-1}	18.59 µg g^{-1}	0.031
Soil ingestion by preschool children	200 mg day^{-1}	18.59 µg g^{-1}	0.232
Total ADD for adults			0.241
Total ADD for preschool children			0.624

Body weight (BW) for adults and preschool children is 60 and 16 kg per person, respectively

can migrate downward through the soil profile. The amount of mercury in different soil layers showed slight fluctuations due to variances in the physico-chemical characteristics of the soil profile, such as high silt and sand contents (Table 2), which facilitate mercury movement (Sterckeman et al. 2000).

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