Human Exposure To Methylmercury through Rice Intake in Mercury Mining Areas, Guizhou Province, China

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The toxicity of methylmercury (Me-Hg) has caused widespread public human concern as a result of several widely publicized disasters. Me-Hg is highly toxic, and the nervous system is its principal target tissue for humans. Although the general population is primarily exposed to Me-Hg through contaminated fish and marine mammals, in Hg mining areas a long history of mining activities can produce serious Hg pollution to the local environment. In a study of 98 persons from the Wanshan Hg mining area, hair Me-Hg levels indicated Me-Hg exposure. Rice, the staple food of the local inhabitants also showed high total Hg (T-Hg) and Me-Hg levels. The geometric mean concentration of T-Hg and mean concentration of Me-Hg in rice samples collected from 3 villages in Wanshan Hg mining area were 36.2 (ranging from 4.9 to 214.7), and 8.5 (ranging from 1.9 to 27.6) μg/kg, respectively, which were significantly elevated compared to the rice samples collected from a reference area, where the mean T-Hg and Me-Hg concentrations were 7.0 (3.2–15.1) and 2.5 (0.8–4.3) μg/kg, respectively. Pork meat, vegetable, and drinking water samples collected in Wanshan Hg mining area contained highly elevated T-Hg, but very low levels of Me-Hg. The relationships between the estimated rice Me-Hg intake and hair Me-Hg levels ($r = 0.65$, $p < 0.001$) confirmed rice with high Me-Hg levels indeed was the main route of Me-Hg exposure for the local residents in the Wanshan Hg mining area. From our study, we can conclude that the main human exposure to Me-Hg via food consumption is not restricted to fish, but in some cases in mining areas of China to frequent rice meals.

Introduction

Outbreaks of severe poisoning in Japan, Iraq, and elsewhere in the last century revealed important characteristics of Me-Hg action in humans (*1, 2*). Me-Hg crosses the blood−brain and placental barriers without hindrance to reach its principal target tissue, the brain (*3*). Because Me-Hg compounds are no longer used as fungicides, the principal and probably sole route of human exposure is currently believed to be through consumption of fish, fish products, and marine mammals (*3, 4*). Many studies have found that Me-Hg concentrations in human hair show a positive correlation with fish consumption (*5–7*).The long-range atmospheric transport of Hg, and in certain areas, the effects of acid rain and water impoundment, have led to "blacklisting" of thousands of lakes in North America and North Europe because the fish exceeded the state or Federal health guidelines for Me-Hg (*8, 9*). Tremendous efforts have been devoted to understanding the relationship of Hg deposition rate and Me-Hg concentrations in fish in North America and Europe.

China is rich in Hg and the reserve of Hg ranks third in the world. The most important Hg production center in China is Guizhou province. From the perspective of global plate tectonics, Guizhou province is situated in the circum-Pacific mercuriferous belt (*10*), and so far 12 large or superlarge Hg deposits have been discovered in the province. The known reserve of cinnabar deposits in the province, approximately 80,000 tons of metal Hg, represents approximately 78% of the total in China (*11*). Due to the long history of Hg mining activities, the local environment, especially soil in the farmlands in Hg mining areas in Guizhou, has been seriously contaminated with Hg (*10–15*). Relatively high concentrations of both T-Hg (up to 569 μg/kg) and Me-Hg (up to 144 μg/kg) have been reported in the rice samples collected from Wanshan Hg mining areas, Guizhou province, China (*12*). The official statistical data showed that for the rural population in Guizhou province the amount of fish and rice consumed per person per year varied from 220 to 310 g and from 140 to 153 kg from 2000 to 2005, respectively, and rice is the staple food which provides more caloric input than any other single food (*16*). Therefore, rice eating may constitute an important source of Me-Hg exposure for local residents in Hg mining areas in Guizhou province, China. The current study was designed to investigate the relationship between the human Me-Hg exposure and rice intake in Hg mining areas, Guizhou province, China. To the best of our knowledge, human Me-Hg exposure through rice intake has not been reported previously in the study areas.

Materials and Methods

Study Area. Wanshan Hg mining area and one control site (Changshun) were selected for our study. The Wanshan Hg deposit located in the eastern part of Guizhou province, southwestern China (Figure 1), was ranked as the largest Hg producing district in China. Mining activities at Wanshan were initiated in the Qin Dynasty (221 B.C.), but large-scale (*10*) mining activities officially ceased in 2001. Due to a recent Hg price increase in the market of China, small-scale or artisanal Hg smelting activities revived a few years ago in the Wanshan area. This long history of mining activities has resulted in serious Hg contamination to the local environment and adjacent ecosystems, including contamination to air, water, soil, sediment, and organisms (*10–12, 15, 17, 18*). It is interesting to notice that all Hg adits and historical retorts are situated upstream of rivers in the region as shown in Figure 1. Significant quantities of calcines and gangues have been produced in spoil heaps around the Hg adits and historical retorts, which constituted the primary Hg contamination sources to the environment downstream of the rivers. The rice paddies are located immediately downstream

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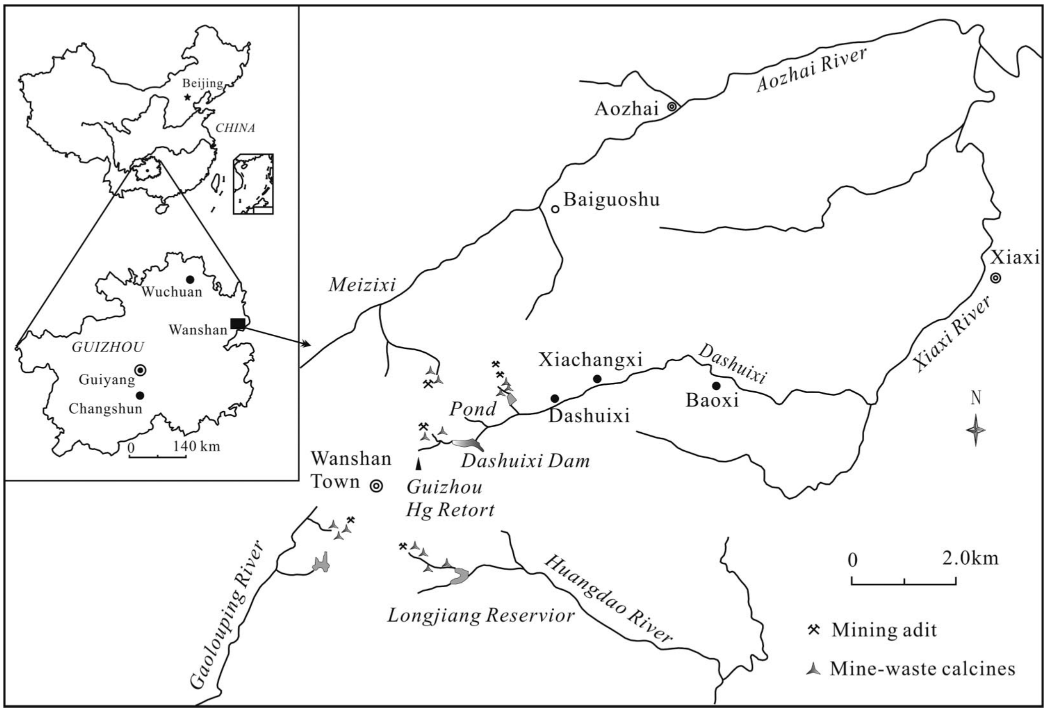

FIGURE 1. Locations of the study areas in Guizhou province, China.

of the calcine pile (See Figure S1, Supporting Information). Our previous study demonstrated that the riparian soil which is the base for the rice paddy field in the Wanshan Hg mining area has been seriously contaminated with Hg and the total Hg concentrations in the riparian soil varied from 5.1 to 790 mg/kg (*10*). About 49,000 inhabitants live along the Huangdao, Xiaxi, Aozhai, and Gaolouping rivers, and basically they live on the foods they produce from their own land. Residents from Dashuixi (DSX), Xiachangxi (XCX), and Baoxi (BX) villages, which are situated about 1.5, 3, and 5 km downstream of the calcine pile shown in Figure 1, respectively, were chosen for the Me-Hg exposure study. According to the information from the local communities, the total numbers of inhabitants in DSX, XCX, and BX villages are 206, 120, and 200, respectively. For comparison, residents in Changshun (CS) village were selected as the control group because there are no Hg contamination sources in that area. CS is located in the south of Guizhou Province and is about 90 Km away from Guiyang, the Capital of Guizhou province (Figure 1). The majority of the populations in Wanshan and CS are minority nationalities, and people from the two study areas have similar traditional customs, making them favorable for the comparison purposes. The local residents in the study areas seldom eat fish and rice is the staple food which provides more calories than any other single food (*16*).

Sample Collection. The sampling campaign in Wanshan Hg mining area was conducted in December 2006. The only criterion to select the participants was that they had not left their home during the previous 3 months. We managed to select 30, 25, and 43 participants in DSX, XCX, and BX villages, respectively, for our survey. The recruitment strategy for our survey was to include as many participants as possible. Since most young people in these villages went out to do labor work in cities and some farmers refused to participate in the investigation, as a matter of fact these numbers of participants were the maximum numbers we could recruit from each village. The numbers of participants in each village constituted 15%, 21%, and 22% of the total populations of DSX, XCX, and BX, respectively. Basically they were farmers, but some of the participants were occasionally involved in artisanal Hg smelting activities, which is basically illegal. We asked all participants to fill in a questionnaire including information on age, weight, profession, the history of involvement of artisanal Hg smelting activity, dental fillings, smoking and alcohol drinking habits, illness, and food consumption such as average daily intakes of rice, vegetables, meat, and fish. The food consumption information (g/day) was provided by the housewives based on the monthly and/or annual food consumption by the whole family. It is difficult to estimate water consumption for each participant, so that we used the daily water consumption of average Chinese people of 2 L to estimate Me-Hg exposure through drinking water. Hair samples were cut with stainless steel scissors from the occipital region of the scalp of each participant, bundled together with scrip, placed and sealed in polyethylene bags, properly identified, and taken to the laboratory for analysis. Raw rice and vegetable samples were collected from each participating family. All rice and vegetables consumed by the local residents were cultivated from their own land. The commonly consumed vegetables in Wanshan Hg mining area are Chinese mustard (*B. chinensis* L.), radish leaves (*Raphanus sativus* L.), Chinese cabbage (*B. campestris* L.), and carrot (*Daucus carota* L.). The raw samples of Chinese mustard, radish leaves, Chinese cabbage, and carrot were collected from the family of each participant. Three to four replicate drinking water samples were collected from the public well in each village (there is only one public well in each village) to assess possible Me-Hg exposure from drinking water. Water samples were filled in precleaned borosilicate glass bottles, and 0.4% (v/v) of sub-boiling distilled ultrapure HCl acid was added within 24 h. Field blanks were also prepared by adding Milli-Q water in sampling bottles. Collection, storage, and preservation of samples rigorously followed U.S. EPA Method 1631 (*19*). Since the local residents do not often eat meat, we managed to collect only a few raw (pork) meat samples from each village. Because some participants from DSX and XCX villages were involved in artisanal Hg smelting activities, urine samples from all participants from these two villages were also collected. The urine samples were collected in precleaned plastic centrifugal tubes, hermetically sealed, and stored at 4 °C until analysis. The sampling campaign in CS was carried out in June 2005.

TABLE 1. Statistical Age Distribution of Male and Female Participants from Four Investigated Villages

	number of male participants				number of female participants				
	age groups				age groups				
	<20	20–45	>45	all ages	<20	20–45	>45	all ages	total number
DSX	1	4	12	17	1	2	10	13	30
XCX	0	4	4	8	0	1	16	17	25
BX	0	11	10	21	1	9	12	22	43
CS	0	7	5	12	0	8	4	12	24

There are no major seasonal variations of food consumptions for farmers in Guizhou because the rice is the staple food and the rice they consumed is produced by their own land. Therefore, even though there were about 1.5 years between the sampling conducted in Wanshan Hg mining area and the control site, no temporal bias was expected to occur in the Me-Hg exposure study. We selected 24 participants from CS as the control group. Hair samples were collected from each participant and rice samples were also collected from the family of the participants for Hg analysis and daily Hg intake estimation in CS. For comparison, urine samples were also collected. A questionnaire was utilized to collect information on residential history, occupational history, dietary habits, life style (smoking habit and alcohol drinking), and health history.

The present study obtained ethics approval from the Institute of Geochemistry, Chinese Academy of Sciences. All participants were required to sign a consent form.

Analytical Methods. The portion of hair within 1−3 cm from the scalp was selected for Hg analysis. Hair samples were washed with nonionic detergent, distilled water, and acetone, and dried in an oven at 60 °C overnight. Rice and vegetable samples were air-dried, crushed, and sieved to 150 meshes. Hair, vegetable, meat, and rice samples were digested in a water bath (95 °C) with a fresh mixture of HNO_3/H_2SO_4 (v/v 4:1) for T-Hg analysis (*19*). T-Hg concentrations in these samples were determined by BrCl oxidation, $SnCl_2$ reduction, purge, gold trap, and cold vapor atomic fluorescence spectrometry (CVAFS). For Me-Hg analysis, prepared hair, rice, meat, and vegetable samples were digested using KOH−methanol/solvent extraction technique (*20, 21*). Me-Hg contents in these samples were measured using aqueous ethylation, purge, trap, and GC-CVAFS detection. T-Hg concentrations in water samples were analyzed within 28 days after sampling using dual-stage gold amalgamation method and CVAFS detection according to U.S. EPA Method 1631 (*19*). Me-Hg in waters was analyzed using distillation and ethylation processes and GC-CVAFS detection following U.S. EPA Method 1630 (*22*). The daily average Me-Hg exposures to the participants in the Wanshan Hg mining area through foods and water consumption were simply computed by multiplying the average Me-Hg concentrations in foods or water by the daily average consumption of the corresponding foods or water. The relative contribution of Me-Hg exposure from each food category was calculated by dividing Me-Hg exposure from each food category by the total Me-Hg exposure. T-Hg concentrations in urine were determined by cold vapor atomic fluorescence spectrometer (CVAFS) or cold vapor atomic absorption spectrometry (CVAAS).Urinary creatinine (U-Cr) contents were analyzed with a Hitachi 7170A automatic analyzer. To take hydration and urinary flow rate into account, the assessment of U-Hg as a biomarker for exposure to mercury vapor was adjusted by creatinine excretion. The results of urine T-Hg concentrations are given in mg/kg creatinine (mg/kg Cr). Information on QA/QC of our measurement data is available in the Supporting Information.

TABLE 2. Mercury Concentrations (mg/kg) in Hair of Inhabitants from Four Villages in Guizhou

		min	max	mean	SD	*N*	distribution pattern
DSX	THg	2.1	58.5	7.3[a]	11.6	30	log-normal
	MeHg	0.8	5.6	2.8	1.4	30	normal
XCX	THg	0.6	6.5	1.9[a]	1.2	21	log-normal
	MeHg	0.2	3.6	1.3	0.7	21	normal
BX	THg	1.0	9.7	2.3[a]	1.8	43	log-normal
	MeHg	0.5	3.5	1.5	0.7	43	normal
CS	THg	0.32	1.72	0.75	0.28	24	normal
	MeHg	0.26	1.1	0.62	0.23	24	normal

[a] Geometric mean.

Results and Discussion

Hair Hg Levels. Table 1 summarizes the age and gender information of the participants from DSX, XCX, BX, and CS villages. All participants are of Miao nationality, and most participants were only graduated from preliminary school or were illiterate. Concentrations of T-Hg and Me-Hg in the hair samples collected from DSX, XCX, BX, and CS residents are summarized in Table 2. Me-Hg constituted 42.4 ± 23.3%, 61.9 ± 19.1%, 62.2 ± 18.5%, and 82.7 ± 13.3% of the T-Hg in hair samples collected in DSX, XCX, BX, and CS, respectively. The mean T-Hg and Me-Hg concentrations in hair samples collected from the Wanshan Hg mining area were significantly higher than those from the control site. This indicated that the residents in Wanshan Hg mining area presented higher levels of T-Hg and Me-Hg.

The mean T-Hg and Me-Hg concentrations in the hair samples of DSX residents were significantly higher than those of XCX and BX residents in Wanshan Hg mining areas. The hair T-Hg and Me-Hg levels indicated the residents in DSX were more seriously exposed to both mercury vapor and Me-Hg than the residents in XCX and BX.

The correlations between hair T-Hg and hair Me-Hg concentrations for the participants selected from the 4 villages are listed in Table S1 (Supporting Information). It is interesting to note that no significant correlation ($r = 0.01$, $p > 0.05$) was observed for DSX residents, but significant correlation was obtained for XCX ($r = 0.86$, $p < 0.01$), BX ($r = 0.77$, $p < 0.01$), and CS ($r = 0.87$, $p < 0.01$) residents. According to the information from the questionnaires, 60% (18 out of 30) of participants from DSX, one participant from XCX, and no participants from BX and CS were involved in artisanal (small-scale) Hg smelting activities. A previous study (*23*) demonstrated that the artisanal smelting workers in Guizhou were exposed to mercury vapor through inhalation, and as a result the T-Hg concentrations in hair and urine were significantly elevated. The statistical summary of urine T-Hg concentrations for the participants from DSX, XCX, and CS villages is listed in Table S2 (Supporting Information). Urine T-Hg concentrations were significantly elevated for the participants from DSX village compared to the groups from XCX and CS villages. Therefore, the significant elevation of hair T-Hg for the participants from DSX village probably resulted from Hg

TABLE 3. Mercury Concentrations in Rice from the Study Villages in Guizhou, China (μg/kg, Dry Weight)

		min	max	mean	SD	N	distribution pattern
DSX	THg	21.1	191.9	58.5[a]	39.9	25	log-normal
	MeHg	7.5	27.6	14.6	4.7	25	normal
XCX	THg	10.0	66.9	21.3[a]	16.8	18	log-normal
	MeHg	3.3	10.2	5.7	1.9	18	normal
BX	THg	4.9	214.7	33.1[a]	57.4	27	log-normal
	MeHg	1.9	14.7	4.0[a]	3.0	27	log-normal
CS	THg	3.2	15.1	7.0	2.8	24	Normal
	MeHg	0.80	4.3	2.5	1.2	24	Normal

[a] Geometric mean.

vapor exposure during the involvement of artisanal Hg smelting activities. Moreover, it is noted from Table S2 that urine T-Hg concentrations from some participants in DSX and XCX villages exceeded 50 mg/kg Cr which is the threshold for the onset of symptoms for mercury vapor exposure to occupational workers recommended by WHO (*24*). The health impacts to these participants need to be urgently scrutinized.

It is the limitation of our study that we included a number of participants who were involved in Hg mining activities in Wanshan Hg mining area while no Hg miners were included in the control group. This may add a confounding factor that may be difficult to adjust for using statistical techniques. However, we believe that the inclusion of some Hg miners in the Wanshan Hg mining area will not affect the outcome of our study on Me-Hg exposure through food consumption to local inhabitants in Wanshan Hg mining area. First of all, even though some participants were occasionally involved in artisanal Hg smelting activities, they still had the same lifestyle and habits as the other farmers so that they had the same Me-Hg exposure through food consumption. Moreover, mercury vapor exposure during mining activities will not affect the Me-Hg exposure through food consumption for these participants because the pathways of mercury vapor and Me-Hg in human body are totally different and independent of each other (*24, 25*).

Me-Hg concentration in the scalp hair is a good bioindicator of the dose of human Me-Hg exposure (*25*). The principal and probably sole route of human exposure is currently believed to be through consumption of fish, fish products, and marine mammals (*3, 4*). Due to the special food habits, the ordinary farmers in Guizhou province seldom eat fish and fish products. All participants from the 4 villages reported that they did not have any fish meals during the last 3 months before our sampling. However, hair Me-Hg concentrations of the residents in DXS, XCX, and BX were elevated compared to those of CS residents, which demonstrated that the residents in Wanshan Hg mining area are exposed to Me-Hg through a route other than fish consumption.

Food Hg Levels. The concentrations of T-Hg and Me-Hg in the rice samples collected from the 4 villages are listed in Table 3. The average T-Hg concentrations in rice from the 3 villages in Wanshan Hg mining area exceeded the national guidance limit for foodstuff other than fish which is 20 μg/kg recommended by the Chinese National Standard Agency (*26*). However, T-Hg concentrations in rice from CS were below the Chinese national guidance limit for rice. Me-Hg constituted 27.2 ± 13.7% (7.9–65.9%), 30.8 ± 18.8% (6.1−72.3%), 17.7 ± 16.8% (2.4–75.1%), and 40.8 ± 24.2 (9.6–88.3%) of T-Hg in rice samples collected from DSX, XCX, BX, and CS villages, respectively.

Two independent sample tests of nonparametric statistical analyses (SPSS 11.5) were performed for both T-Hg and Me-

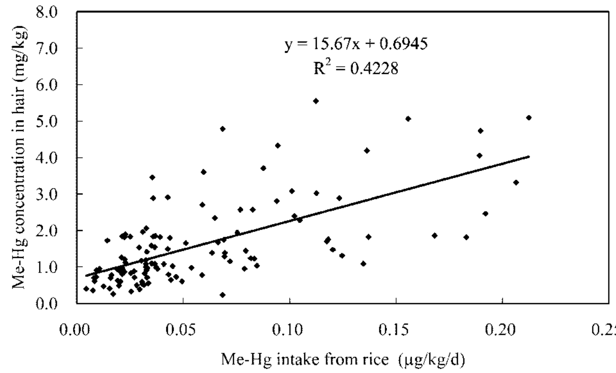

FIGURE 2. Correlation between hair Me-Hg concentrations and Me-Hg intake from rice for all participants in the four studied villages.

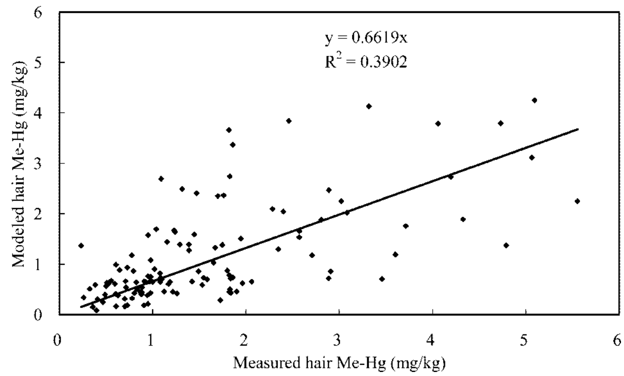

FIGURE 3. Correlation between the modeled hair Me-Hg concentrations and the measured hair Me-Hg concentrations for all participants in the four studied villages.

Hg concentrations in rice samples collected in different villages. The T-Hg and Me-Hg concentrations in rice samples collected from DSX were significantly higher than those from XCX ($p < 0.001$ for both T-Hg and Me-Hg) and BX ($p < 0.005$ for T-Hg, $p < 0.001$ for Me-Hg). Because DSX is located closer to the smelting residue heaps, rice was more seriously polluted by Hg. The T-Hg and Me-Hg concentrations in rice from the 3 villages in Wanshan Hg mining areas were significantly higher than rice samples collected from the control site CS ($p < 0.001$ for both T-Hg and Me-Hg).

Our results were comparable to those of other studies obtained in both Wanshan and Wuchuan Hg mining areas by Horvat et al. (*12*) and Qiu et al. (*13*). The results indicate that rice produced in Hg mining areas in Guizhou province show high accumulation abilities of Me-Hg. The Hg contaminated water (*12, 15*) for irrigation, soil, and the anaerobic conditions created by the seasonal flooding during the rice-growing period may contribute to the high methylation ability in paddy soils. Qiu et al. (*10*) observed Me-Hg concentrations in soil samples from a rice paddy field were generally higher than those in a cornfield in Wanshan Hg mining area. However, the mechanism of rice tissue to uptake Me-Hg probably through its roots is still unclear.

Hg concentrations in pork meat, vegetables, and drinking water samples collected from DSX, XCX, and BX villages in Wanshan Hg mining area are listed in Tables S3, S4, and S5 (Supporting Information), respectively. T-Hg concentrations in pork meat samples varied from 7.5 to 564.6 μg/kg with a mean value of 215.8 μg/kg. Five out of seven pork meat samples had T-Hg concentrations exceeding the national guidance limit for foodstuff other than fish, which is 20 μg/kg recommended by the Chinese National Standard Agency (*26*). However, Me-Hg concentrations in pork meat samples were very low and the average value was 0.85 μg/kg (ranging

TABLE 4. Me-Hg Intakes (in μg/kg/d) and the Relative Contribution of Me-Hg Intakes (Values in Brackets in %) from Different Exposure Routes for Inhabitants in the Three Villages in Wanshan Mercury Mining Area

	source of intake	min	max	mean	SD	*N*
DSX	rice	0.035(91.6)	0.21(99.2)	0.12((97.5)	0.048(1.8)	30
	meat	0.001(0.6)	0.002(5.3)	0.002(1.5)	0.0003(0.9)	30
	vegetables	0.0003(0.2)	0.009(5.8)	0.001(1.1)	0.001(1.1)	30
	drinking water	0.0002(0.001)	0.0004(0.01)	0.0002(0.003)	0.0001(0.002)	30
	total	0.038	0.214	0.123	0.048	
XCX	rice	0.019(84.2)	0.085(98.0)	0.049(94.1)	0.02(3.5)	21
	meat	0.001(1.4)	0.002(6.2)	0.001(3.3)	0.0003(1.3)	21
	vegetables	0.0002(0.5)	0.006(12.4)	0.001(2.6)	0.001(2.9)	21
	drinking water	0.0001(0.003)	0.0003(0.02)	0.0002(0.008)	0.00005(0.003)	21
	total	0.021	0.086	0.051	0.019	
BX	rice	0.01(81.1)	0.14(98.5)	0.04(93.5)	0.03(3.4)	43
	meat	0.001(1.0)	0.004(12.2)	0.001(4.4)	0.0004(2.4)	43
	vegetables	0.0001(0.3)	0.002(6.7)	0.001(2.1)	0.0004(1.4)	43
	drinking water	0.0001(0.001)	0.0002(0.01)	0.0001(0.005)	0.00002(0.003)	43
	total	0.013	0.139	0.043	0.026	

from 0.05 to 3.43 μg/kg). Due to serious Hg contamination to the environment from Hg mining activities, the food supplies for the livestock such as pigs are also seriously contaminated with inorganic Hg, resulting in the elevated T-Hg concentrations in pork meat in Wanshan Hg mining area. Vegetable samples collected from DSX, XCX, and BX villages also contained elevated T-Hg. T-Hg concentrations in vegetable samples from DSX, XCX, and BX villages varied from 5 to 1890 μg/kg (wet weight) with a mean value of 346 μg/kg, from 4 to 266 μg/kg (wet weight) with a mean value of 87 μg/kg (wet weight), and from 4 to 738 μg/kg (wet weight) with a mean value of 109 μg/kg (wet weight), respectively. The average T-Hg concentrations in vegetables collected from DSX, XCX, and BX significantly exceeded the national guidance limit for vegetables, which is 10 μg/kg recommended by the Chinese National Standard Agency (*26*). However, Me-Hg concentrations in vegetable samples were very low, and varied from 0.04 to 0.51 μg/kg (wet weight) with a mean of 0.10 μg/kg in DSX, from 0.02 to 0.51 μg/kg (wet weight) with a mean of 0.11 μg/kg in XCX, and from 0.03 to 0.18 μg/kg (wet weight) with a mean of 0.08 μg/kg in BX, respectively. Me-Hg concentrations constituted only a very small portion of T-Hg (less than 0.83%) in vegetables in Wanshan Hg mining area. Drinking waters in these 3 villages also contained high levels of T-Hg, and the average concentrations were 66.9, 55.5, and 25.6 ng/L in DSX, XCX, and BX, respectively. However, Me-Hg constituted only less than 0.3% of T-Hg in drinking water as shown in Table S5 (Supporting Information).

It should be noted that in general it is believed that rice does not pose a significant source of Me-Hg exposure to humans compared to fish or/and other aquatic products consumption. However, the residents in Wanshan Hg mining area rarely eat fish due to their traditional living custom, and rice is their staple food. Therefore, rice with high Hg levels in the study areas needs to be evaluated as to whether it may be posing a significant source of Me-Hg exposure to the local residents.

Relationship between Rice Me-Hg Intake and Hair Me-Hg Levels. Inorganic Hg on the one hand is much less toxic to humans compared to Me-Hg (*27*), and on the other hand the absorption rate of inorganic Hg in food by the human body is about 7% (*27, 28*), much less than that of Me-Hg which is about 95% (*29*). Thus, even though the residents in Wanshan Hg mining area are exposed to significantly higher levels of inorganic Hg than Me-Hg through food consumption due to high level of T-Hg present in foods, the effects of Me-Hg exposure to human still remain a health concern in that area. Of course, the health effects of high levels of Hg vapor exposure to artisanal Hg smelters also need to be scrutinized (*23*).

In this study we selected those residents who stayed in the study areas during the previous 3 months and always consumed the rice planted by themselves to collect hair samples to evaluate Me-Hg exposure. According to the daily rice consumption data provided by the participants, and Me-Hg concentrations in rice, we calculated daily Me-Hg intakes for all participants in DSX, XCX, BX, and CS villages. A significant correlation ($r = 0.65$, $p < 0.01$) between hair Me-Hg concentrations and daily Me-Hg intakes from rice for all participants was observed as shown in Figure 2. This indicates that rice may be an important Me-Hg exposure route for residents in the Wanshan Hg mining area.

The evidence indicates that the accumulation and excretion of Me-Hg in humans, measured in terms of hair or blood levels, can be represented by a single-compartment model (*29, 30*). The steady-state Hg concentration in blood (C) in μg/L is related to the average daily dietary intake (in μg Hg per kg body weight per day) as shown in the following equation (*1*) (*29, 30*):

$$C = \frac{d \times A \times f \times bw}{b \times V} \quad (1)$$

where d represents daily Me-Hg intake in μg/ kg/d; A is the absorption factor which is assumed to be 0.95; f is the absorbed dose found in blood and the value is 0.059; bw is the body weight (60 kg); b is the elimination constant (0.014); and V is the blood volume (5 L).

Using eq 1, Me-Hg concentrations in blood were obtained by the average daily dietary intake. Furthermore, the hair/blood concentration ratio is frequently cited as 250:1 expressed as mg/kg hair Hg to μg/L of blood Hg (*29, 30*). Thus, the modeled hair Me-Hg concentrations were also obtained according to the estimated Me-Hg intake from rice consumption. We observed a significant correlation ($r = 0.62$, $p < 0.01$) between the modeled hair Me-Hg and the measured hair Me-Hg for all participants in the 4 villages as shown in Figure 3, even though the slope is 0.66. Since a large uncertainty is associated with the current model (for example, the ratio used by the model between the hair Hg versus blood is 250 but ranged from 140 to 370 (*31, 32*), or roughly +48%/−45%), the slope of 0.66 is within the uncertainty of the model. This further reinforced that rice intake could be the main Me-Hg exposure route to the residents in Wanshan Hg mining area.

We calculated the Me-Hg intakes (in μg/kg/d) and the relative contribution of Me-Hg intakes to the participants in DSX, XCX, and BX, and the statistical results are listed in Table 4. It is obvious that rice consumption is the main route of Me-Hg exposure to all participants from the 3 villages. This is because Me-Hg concentration in rice is much higher than in other foods and rice is eaten much more frequently for it is the staple food. Rice intake constituted 97.5% (91.6–99.2%), 94.1% (84.2–98.0%), and 93.5% (81.1–98.5%) of the total Me-Hg exposure to participants in DSX, XCX, and BX, respectively. This certainly confirmed that rice with high Me-Hg levels was undoubtedly the main route of Me-Hg exposure for residents in Hg mining areas in Guizhou Province, China.

Potential Health Effects of Me-Hg Exposure in Wanshan Hg Mining Area. Hair Hg threshold for showing onset of neurological symptoms in the human body is 50–125 mg/kg (*29*). The threshold for the onset of symptoms for Me-Hg is recognized to be 10–14 mg/kg in maternal hair (*33*). Tolerable intake levels of Me-Hg for pregnant women are decided by each country and the authorities concerned, taking safety into consideration. The Joint Food and Agriculture Organization of the United Nations (FAO)/WHO Expert Committee on Food Additives (*34*) established a provisional tolerable weekly intake (PTWI) for MeHg to 1.6 μg Hg/kg bw/week (0.23μg Hg/kg bw/day, equivalent to a hair mercury concentration of about 2.3 mg/kg) using an uncertainty factor 6.4. The United States Environmental Protection Agency (USEPA) (*29*) set the limit to 0.1 μg Hg/kg bw/day (equivalent to a hair mercury concentration of 1.0 mg/kg) as reference dose (RfD) using an uncertainty factor of 10.

Generally, the inhabitants in Wanshan Hg mining area are exposed to Me-Hg to a certain level. However, they are not under the 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 (*29*) and the National Research Council (*33*). Nevertheless, some female participants may exceed the tolerable intake levels of Me-Hg for pregnant women established by USEPA (*30*) as shown in Table 4. Thus, rice intake in Hg mining areas in Guizhou may pose a health risk of Me-Hg exposure to local habitants.

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Supporting Information Available

QA/AC section and Hg distribution in pork meat, vegetables, drinking water. This material is available free of charge via the Internet at http://pubs.acs.org.

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