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Understanding the excretion rates of methylmercury and inorganic mercury from human body via hair and fingernails

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ABSTRACT

Effective biomarkers are necessary to better understand the human mercury (Hg) exposure levels. However, mismatched biomarker sampling method causes extra uncertainty in assessing the risk of Hg exposure. To compare the differences between hair and fingernail, and further understand the excretion rates of methylmercury (MeHg) and inorganic mercury (IHg) via hair and fingernails, the total mercury (THg), MeHg, and IHg concentrations in paired hair and fingernail samples were investigated through paired samples collected from two typical mining areas, Wanshan mercury mine area (WMMA) and Hezhang zinc smelting area (HZSA). The positive correlation in THg, MeHg, and IHg concentrations (p <0.01) between hair and fingernail samples indicated that those two biomarkers can be corrected in application of assessing human Hg exposure. Compared to fingernails, the hair was suggested to be a more sensitive biomarker as the concentration of THg, MeHg and IHg were 2 ∼ 4 times higher than those in fingernails. Furthermore, the amounts of THg, MeHg, and IHg excreted via hair were 70 ∼ 226 times higher than that excreted via fingernails, and the hair plays a more important role than fingernails in the excretion of Hg from human bodies. Present study therefore provides some new insights to better understand the fate of human assimilated Hg.

Introduction

Mercury (Hg) is a globally distributed heavy metal (Obrist et al., 2018). Anthropogenic activities (e.g., coal burning, metal mining, and chlorine-alkali production) have increased the amount of Hg cycling in the environment by a factor of 3 ∼ 5 since the mid-1800s (AMAP/UNEP, 2008). Hg released into the aquatic system can be transformed into methylmercury (MeHg), a neurotoxin that can be bioaccumulated and biomagnified in food webs (Hsu-Kim et al., 2018). Consumption of fish products is known as the major MeHg exposure pathway to the global population (Al-Majed and Preston, 2000;

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Mergler et al., 2007). Recent studies suggested that consumption of rice grown in Hg polluted areas can be another important MeHg exposure pathway for some inland populations who seldomly eat fish (Feng et al., 2008; Zhang et al., 2010a).

The toxicity of Hg to humans depends on its chemical speciation. Up to 95% MeHg in diet can be absorbed in the gastrointestinal tract after ingestion, however, only about 20% of inorganic Hg (IHg) in diet can be absorbed by the human body (Clarkson, 2002). After ingestion, Hg enters into the blood and is transported to various body tissues. Most IHg is deposited in the kidney and eliminated via urine and feces (Clarkson, 2002). MeHg can accumulate into scalp hair, and MeHg level in hair is often used to monitor human MeHg exposure (WHO, 1990; Sakamoto et al., 2015; Wang et al., 2021). Besides urine and hair, previous studies suggested that fingernail/toenail could also reflect Hg exposure in the human body (Adimado and Baah, 2002; Rees et al., 2007; Sakamoto et al., 2015; Specht et al., 2020; Salcedo-Bellido et al., 2021). Fingernail/toenail, as a non-invasive biomarker of human Hg exposure, is an excellent option for biomonitoring isolated/remote populations due to easy storage, and an alternative solution to hair for those men with very short hair (WHO, 2008). However, so far studies using fingernails remain very scarce due to the less accessibility compared to hair. THg concentration reflected in fingernails may be difficult to distinguish exogenous Hg contamination or the Hg accumulated by ingestion, which is necessary to conduct the study of Hg species in fingernails to systematically test whether it is a good biomarker of MeHg or IHg exposure. Besides, current studies on the excretion pathways of Hg is mainly focusing on urine and feces (Clarkson, 2002; WHO, 2008), studying the excretion of Hg via hair and nails help understanding the fate of Hg in human bodies. Indeed, only one previous study gave a rough estimate of the daily excretion of MeHg via hair (Magos and Clarkson, 2008), but the Hg species in fingernails and the Hg excretion via fingernails has not been quantified, which highlights the necessity to establish the excretion rate when compared to other biomarkers.

In recent years, Hg pollution was considered as one of the major environmental problems in China, especially in Hg polluted areas (Feng et al., 2008; Yin et al., 2013). Many previous studies indicated that residents, living in the Hg polluted areas, exposed to elevated levels of both MeHg and IHg via direct measurements of biological samples, such as hair, urinary and blood (Li et al., 2008a; Li et al., 2008b; Li et al., 2015a; Li et al., 2015b; Liang et al., 2015). As high Hg background in Hg polluted areas, the phenomenon and mechanism about human exposure can be more explicit than that in other areas. Therefore, Wanshan Hg mining areas (WMMA) together with Hezhang zinc smelting area (HZSA) were selected as the study areas to investigate the appropriateness of using fingernails as a biomarker for Hg exposure risk assessment. Here, we collected paired hair and fingernail samples from residents living in two typical Hg polluted areas in Guizhou province, SW China. Both of the two areas were contaminated with Hg at different levels. The WMMA is China's largest Hg mine, and long-term mining caused high levels of THg to the local environment such as atmosphere (17 ∼ 2,100 ng/m^3), soils (THg: 5.1 ∼ 790 μg/g), sediments (90 ∼ 930 μg/g), waters (1.9 ∼ 12,000 ng/L) (Qiu et al., 2005; Zhang et al., 2010c; Dai et al., 2012). The HZSA is of concern for its artisanal zinc smelting history in the last decade and its elevated THg levels in waters (12 ∼ 691 ng/L) and soils (0.14 ∼ 0.86 μg/g) (Feng et al., 2004; Feng et al., 2006). Previous studies in WMMA showed that the residents in this area are co-exposed to MeHg and IHg through food consumption (Zhang et al., 2010a; Li et al., 2015a). Residents in HZSA have a similar diet structure to WMMA, however, THg and MeHg levels in food are different in the two areas due to the different Hg background in two areas. For staple food-rice in WMMA, which is locally grown, the THg and MeHg were 1.9 ∼ 214.7 ng/g and 1.9 ∼ 37.6 ng/g, respectively (Feng et al., 2008). While, the consuming rice in HZSA has much lower THg (3.97 ± 2.33 ng/g) and MeHg concentrations (1.37 ± 1.18 ng/g) due to nearly all of the consuming rice in HZSA were purchased from markets (Xu et al., 2020). Quite different THg and MeHg levels in food with the same diet structure can undoubtedly cause different THg and MeHg exposure levels for residents in WMMA and HZSA.

In this study, through measuring the THg and MeHg concentration in the collected paired hair and fingernail samples, we aimed to test the hypothesis of whether fingernails can serve as a good biomarker of Hg in human bodies. Furthermore, considering that hair and fingernails are also excretion pathways of Hg, thus, the mass of MeHg and IHg excretion through hair and fingernails are estimated.

1. Materials and methods

1.1. Study area

WMMA is located in the eastern Guizhou province, SW China (Fig. 1). Long-term Hg mining activities have led to a mass of gangues and waste calcines near the abandoned Hg processing sites. These materials act as significant contamination sources of Hg to the local environment, although Hg mining activities have been officially ceased (Yin et al., 2013). HZSA is located in the western Guizhou province, SW China (Fig. 1). Artisanal Zn smelting activities had lasted for a few decades in HZSA until these activities were banned in 2004. In HZSA, a huge amount of wastes were piled along rivers and valleys after long-term artisanal Zn smelting, which served as an important Hg source to the local environment (Feng et al., 2004).

In July 2016 and August 2017, paired hair and fingernail samples were collected from 218 local residents at 8 sites in WMMA and 2 sites in HZSA (Fig. 1). The adult participants were randomly selected. The basic information of participants (e.g., gender, age, weight, occupation, smoking, and drinking habits) were collected as summarized in Table 1. All participants ($N = 218$) signed the consent before the survey, and this study followed the ethics approval from the Institute of Geochemistry, Chinese Academy of Sciences (IGCAS).

Hair samples were cut from the occipital region of the scalp using stainless steel scissors, bundled with strips of scrip, and preserved in sealed bags. Fingernail samples were also collected from the participants, correspondingly. No permed and dyed hair samples and polished fingernail samples were sampled. The samples were sealed in polyethylene bags, labeled, and delivered to the laboratory. All fingernail and hair samples were washed in the sequence of acetone-water-water-water-acetone with the assistance of ultrasound (each wash took 10

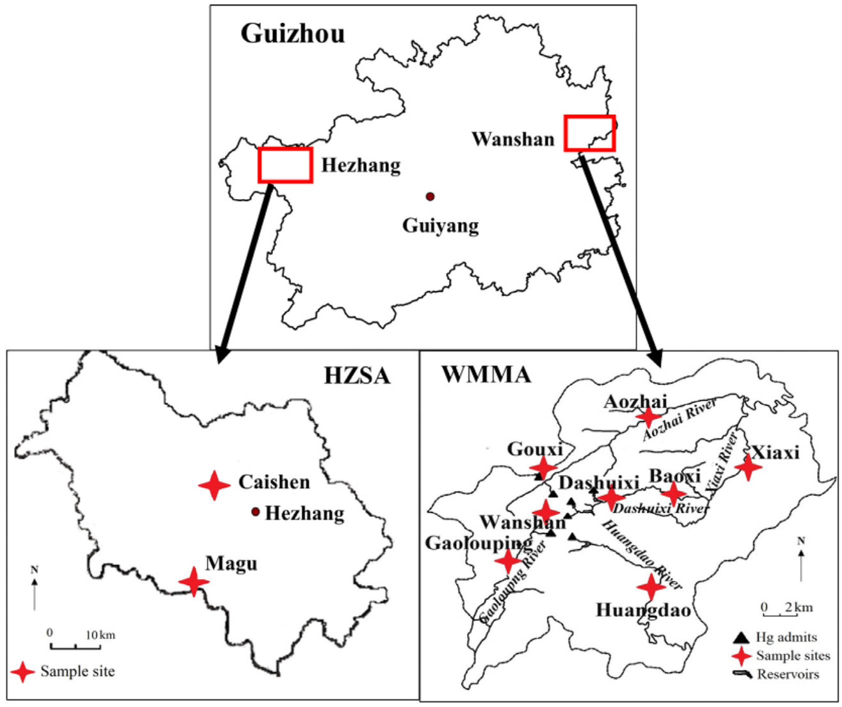

Fig. 1 – Study area and sampling sites.

minutes) (Li et al., 2008b). Then, all the samples were dried in an oven overnight at 40°C, cut into small pieces with stainless steel scissors for homogenization before THg and MeHg analysis.

1.2. *THg and MeHg concentration analysis*

For THg analysis, approximately 0.01 g sample was digested with 5 mL of HNO_3/H_2SO_4 (v/v, 4/1) at 95°C in a water bath for 3 hr until the sample was completely dissolved (Feng et al., 2008). Then, the solutions were determined by BrCl oxidation, $SnCl_2$ reduction, purge, gold trap, and cold vapor atomic fluorescence spectrometry (CVAFS) (MERX, Brooks Rand) following the method by Li et al. (2008b). For MeHg analysis, about 0.01 g sample was digested with 10 mL of 30% HNO_3 solution left overnight at 60°C for 12 hr (Hammerschmidt and Fitzgerald, 2005). Then, the digestions were buffered with sodium acetate at pH 4.9, ethylated in a borate glass bottle, and detected by GC-CVAFS (MERX, Brooks Rand) (Li et al., 2008b). The detection limit of MeHg was 0.0006 µg/kg. The IHg concentration of each sample was calculated by THg minus MeHg (Li et al., 2015a; Li et al., 2015b; Xu et al., 2020).

Quality assurance (QA) and quality control (QC) included certified reference material (NIES-13, human hair), sample duplicates, method blanks, matrix spikes. The measured THg concentration for NIES-13 was 4.3 ± 0.2 µg/g (SD, $N = 6$), which agreed well with the certified value (4.4 ± 0.2 µg/g) and yielded THg recoveries of 92% to 107%. The measured MeHg concentration of NIES-13 was 3.7 ± 0.2 µg/g (SD, $N = 6$), which agreed well with the certified value (3.8 ± 0.2 µg/g) and yielded MeHg recoveries of 95% to 102%. The relative standard deviation (RSD) of sample duplicates was within 10%.

1.3. *Excretion rates of Hg through hair and fingernails*

We estimated the excretion rates (ER) of THg, MeHg, and IHg via hair and fingernails based on the following equations:

$$ER_{Hg} = C_{Hg} \times M \quad (1)$$

where ER refers to the excretion rates of Hg via hair and fingernails (µg/day); C_{Hg} is the Hg concentration in hair or fingernails (µg/g); M is the mass of growth (g/day); The M of hair and fingernails, termed M_{hair} and $M_{fingernail}$ can be calculated using the following equations:

$$M_{hair} = GR_{hair} \times A \times r_{hair} \times N_{hair} \quad (2)$$

$$M_{fingernails} = GR_{fingernails} \times W \times T \times r_{fingernails} \times N_{fingernails} \quad (3)$$

where GR is the growth rate of hair and fingernails (cm/month), A is the cross-sectional area of hair (cm²); W and T are the average width and thickness of fingernails, respectively; ρ_{hair} and $\rho_{fingernails}$ refer to the density of hair and fingernails (g/cm³), respectively; N_{hair} and $N_{fingernails}$ are the amounts of hair and fingernails per person, respectively. According to previous studies, for Asian adults, the average GR for hair is ~ 1 cm/month (about 0.03 cm/day), the average ρ_{hair} is ~ 1.30 g/cm³, the average A for hair is ~ 5.24×10^{-5} cm² and the average N_{hair} is ~ 1.0×10^5 (Kishimoto and Nakazawa, 2017; Robbins, 2012). Regarding the fingernails, for Asian adults, the average GR is ~ 0.3 cm/month (about 0.01 cm/day), the average $\rho_{fingernails}$ is ~ 1.34 g/cm³, and the average W and T for fingernails are ~ 1.0 cm and ~ 4.9×10^{-2} cm, respectively (Yan et al., 2005; Baraldi et al., 2015).

Table 1 – Basic information of the study population in WMMA and HZSA.

Studyareas	N	Gender		Age (years)	Weight (kg)	Occupation	Smokers	Alcohol drinkers	Hair		Fingernails	
		Male	Female						THg (μg/g)	MeHg (μg/g)	THg (μg/g)	MeHg (μg/g)
WMMA	N = 185	N = 131	N = 54	58	56	N = 18	N = 85	N = 64	2.80	1.24	0.99	0.35
				21 ~ 88	35 ~ 94				(0.36 ~ 997.7)	(0.18 ~ 29.5)	(0.13 ~ 108.4)	(0.03 ~ 5.26)
HZSA	N = 33	N = 23	N = 10	51	60.5		N = 20	N = 14	0.17	0.08	0.08	0.01
				20 ~ 76	46 ~ 77				(0.09 ~ 0.39)	(0.01 ~ 0.20)	(0.02 ~ 0.19)	(0.01 ~ 0.05)

Age, weight, and Hg concentration values are reported as median(range); Occupation refers in particular to mercury miners; N references to sampling numbers.

1.4. Statistical analysis

Data Statistical analysis was performed using Microsoft Excel 2016, IBM SPSS 22.0, R 4.0.2, and Origin Pro 8.5 (Origin Lab, USA) for Windows. The characteristics of age, weight, hair, and fingernail Hg concentrations were described in median values. Kolmogorov-Smirnov test was used to analyze the normality of the data. Correlation tests were computed according to the Spearman correlation analysis. The multivariate analysis of gender, age, weight, habits (smoking and ethanol drinking), and Hg concentrations were analyzed using Non-parametric MANOVA.

2. Results and discussion

2.1. THg, MeHg and IHg levels in hair

Results of THg, MeHg, and IHg concentrations in hair and fingernail samples collected from WMMA and HZSA, are summarized in Table 1 and Fig. 2. The hair THg concentrations in the WMMA range from 0.36 to 998 μg/g, with a median value of 3.09 μg/g. In general, the hair THg concentrations in WMMA are similar to those reported in other Hg mining areas but much higher than those reported in non-Hg mining areas in China (Table 2). The high hair THg concentrations, accomplished with the high Hg levels in the local atmosphere (17 ~ 2100 ng/m^3), soils (THg: 5.1 ~ 790 μg/g), sediments (90 ~ 930 μg/g), waters (1.9 ~12,000 ng/L) and rice (4.9 ~ 214 ng/g) (Qiu et al., 2005; Feng et al., 2008; Zhang et al., 2010c; Dai et al., 2012), indicating a high risk of Hg to the WMMA residents. In WMMA, eighteen participants involved or history involved in Hg mining activities, and the THg concentration of these Hg miners are significantly high (2.2 ~ 998 μg/g, median: 10.5 μg/g), which may attribute to exposure of Hg vapor through inhalation (Li et al., 2011a). The hair THg concentration in the HZSA range from 0.10 to 0.39 μg/g, with a median value of 0.18 μg/g, which are lower than the values for hair samples from the WMMA and other polluted sites of China (Table 2), indicating a low health risk of Hg exposure for the residents in HZSA. The phenomenon is the same as that in a previous study (Kong et al., 2021), which found blood Hg in HZSA is lower than background values, which may be due to the lack of Hg-contaminated food sources in HZSA, and the staple food-rice was purchased from the market.

The hair MeHg concentration in the WMMA range from 0.18 to 29.5 μg/g, with a median value of 1.26 μg/g, and the hair MeHg concentration in Hg miners has no obvious difference with general population (non-occupational population) ($p > 0.05$). The hair MeHg concentrations in WMMA and other mining areas are compatible with those reported for fish consumers in China (Table 2). The high hair MeHg concentrations in the WMMA and other mining areas in China have been explained by the fact that consumption of rice grown in Hg contaminated soil in mining areas (Feng et al., 2008). Hg methylation readily occurs in rice paddies, and rice can accumulate a substantial amount of MeHg from paddy soils (Meng et al., 2010; Zhang et al., 2010b; Meng et al., 2011). Consumption of rice serves as a major MeHg exposure pathway to the residents in the WMMA (Feng et al., 2008). The hair MeHg concentrations

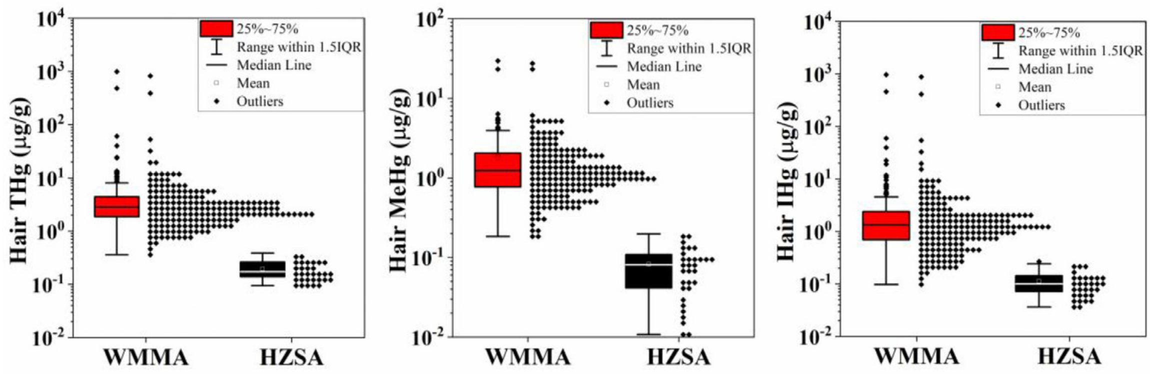

Fig. 2 – THg, MeHg, and IHg concentrations in hair samples in WMMA and HZSA.

Table 2 – Hair THg and MeHg concentrations in different areas of China

Study area	Hair THg (μg/g)	Hair MeHg (μg/g)	Description	Reference
Wuchuan, Guizhou, China	0.45 ~ 93.1	0.45 ~ 4.21	Hg mining area	(Li et al., 2008b)
Shaanxi, China	4.3 (1.6 ~ 12.6)	0.35 (0.04 ~ 0.9)	Hg mining area	(Jia et al., 2018)
Hangzhou, Zhejiang, China	1.4 (0.1 ~ 22.8)	0.2 (0.003 ~ 1.2)	fluorescent Lamp factory	(Liang et al., 2015)
Guizhou, China	0.24 (0.08 ~ 11.9)	0.12 (0.03 ~ 0.75)	Coal-fired power plant	(Wang et al., 2021)
Guizhou, China	0.33 (0.10 ~ 2.92)	0.18 (0.06 ~ 0.92)	Commercial gold mine	
Huludao, Liaoning, China	0.43 (0.05 ~ 3.25)		Zn smelting area	(Zheng et al., 2011)
Changshun, Guizhou, China	0.78 ± 0.28	0.65 ± 0.25	Background area	(Feng et al., 2008)
Pearl River Delta, Guangdong, China	0.39 ± 0.25	0.22 ± 0.10	Urban area	(Shao et al., 2013)
	1.78 ± 0.84	0.93 ± 0.46	Fishing village	
Hainan, China	0.91 (0.057 ~ 4.81)		Coastal area	(Liu et al., 2014)
Qingdao, Shandong, China	0.49 (0.05 ~ 5.40)	0.26 (0.05 ~ 3.31)	Fish-eating areas	(Wang et al., 2021)
Zhoushan, Zhejiang, China	0.8 ~ 29.9	0.3 ~ 9.5	Fishing village	(Cheng et al., 2009)
Chongqing, China	0.42 ± 0.43	0.23 ± 0.32	Three Gorges Reservoir area	(Xie et al., 2021)
WMMA	3.09[a] (0.36 ~ 998)	1.26 [a] (0.18 ~ 29.5)	Hg mining area	This study
HZSA	0.18[a] (0.10 ~ 0.39)	0.06 [a] (0.01~ 0.20)	Zn smelting area	This study

[a] reported as median value.

in the HZSA range from 0.01 to 0.20 μg/g, with a median value of 0.06 μg/g. In comparison to WMMA, rice is not commonly grown in the HZSA due to low temperature and the lack of water resources there. The low MeHg concentrations in the HZSA hair samples may be explained by the fact their staple food is rice, which is all purchased from markets as we mentioned above, and the widely-grown potatoes were in low Hg levels (Peng et al., 2018). The potatoes showed low THg levels (3 ~ 26 ng/g) (Feng et al., 2006; Peng et al., 2018), therefore, they should not cause significant Hg exposure to the local residents. This should lead to low MeHg exposure to the HZSA residents because rice from Chinese markets has much lower THg and MeHg concentrations than the maximum limit of THg in food (20 ng/g) recommended by the Chinese National Food Safety Standard (Xu et al., 2020).

In WMMA, the MeHg% fractions in hair range from 1% to 93%, with a median value of 41%, and the MeHg% fractions in hair samples of Hg miners (median: 24%) are lower than the general populations (median: 50%). In HZSA, the MeHg% fractions of hair in the HZSA range from 8% to 72%, with a median of 35%. These values in WMMA and HZSA are consistent with previous results on rice consumers, but much lower than those (>80% of hair THg) of fish-consuming people (WHO, 1990). This is due to that fish also contain a high fraction of MeHg (normally >80%) in their muscles. Compared to fish consumers, the lower hair MeHg% were attributed to the fact that the majority of Hg in rice and vegetables are in the form of IHg, and dietary intake is the main route of IHg exposure for local residents (Li et al., 2015a). Indeed, the IHg concentrations in hair samples from WMMA and HZSA range from 0.10 to 968 μg/g (median: 1.44 μg/g) and 0.04 to 0.27 μg/g (median: 0.10 μg/g), with IHg% of 7% ~ 99% and 28% ~ 92%, respectively. These values are similar to the low IHg% values in rice or vegetables (24.9% to 92.6%) (Feng et al., 2008; Qiu et al., 2008). While the MeHg% fractions of Hg miners in WMMA are much lower than that of the general population, which may attribute to the higher hair IHg concentration caused by Hg vapor exposure, since Hg inhalation has been reported as the major fraction (97.4%) of IHg exposure for the Hg miners (Li et al., 2011a; Li et al., 2011b).

2.2. *THg, MeHg, and IHg levels in fingernails*

The THg and MeHg in fingernails collected from WMMA range from 0.13 to 108 μg/g and from 0.03 to 5.26 μg/g, with median values of 1.02 μg/g and 0.36 μg/g, respectively (Fig. 3), much

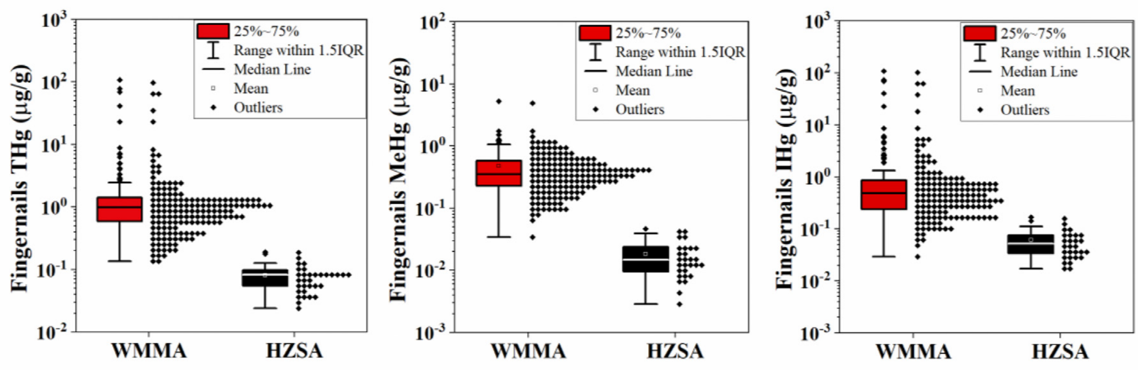

Fig. 3 – THg, MeHg, and IHg concentrations in fingernails samples in WMMA and HZSA.

Table 3 – Fingernails THg and MeHg concentrations in different areas in the world.

Study area	Fingernails THg (μg/g)	Fingernails MeHg (μg/g)	Description	Reference
Mansoura, Egypt	0.87 ± 0.30		Dental amalgam fillings users	(Mortada et al., 2002)
Peshawar, Pakistan	2.35 ± 1.2		Dental amalgam fillings users	(Gul et al., 2016)
Ankobra river basins, Ghana	0.18 ~ 10.0		Small-scale gold mine areas	(Adimado and Baah, 2002)
Tano river basins, Ghana	0.13 ~ 22.9			
Scotland	5.25 ± 20.60		Dentists	(Ritchie et al., 2004)
	0.32 ± 0.30		University employees and students	
Tehran, Iran	3.56 ± 0.53		Dentists	(Zolfaghari et al., 2007)
	0.39 ± 0.06		Students	
Ubon Ratchathani, Thailand,	2.40 ± 9.06		Intensively agricultural areas	(Wongsasuluk et al., 2018)
Kumamoto, Japan	0.55 (0.43 ~ 0.73)		Early pregnancy woman	(Sakamoto et al., 2015)
	0.50 (0.43 ~ 0.59)		Parturition woman	
WMMA	1.02[a] (0.13 ~ 108)	0.36[a] (0.03 ~ 5.26)	Hg mining area	This study
HZSA	0.07[a] (0.02 ~ 0.19)	0.02[a] (0.003 ~ 0.05)	Zn smelting area	This study

[a] reported as median value.

higher than the general population without significant Hg exposure worldwide (Table 3). The THg in fingernails of Hg miners (median: 1.81 μg/g) are higher than that of the general population (median: 0.96 μg/g) in WMMA ($p < 0.05$), and comparable to that dental amalgam fillings users and dentists (Table 3). Whereas the MeHg in fingernails of Hg miners (median: 0.42 μg/g) are consistent with the general population (median: 0.35 μg/g, $p > 0.05$) in WMMA, showing a similar pattern with hair Hg concentration. In HZSA, ranges of THg and MeHg in fingernails are 0.02 ~ 0.19 μg/g (median: 0.07 μg/g) and 0.003 ~ 0.05 μg/g (median: 0.02 μg/g), respectively, much lower than WMMA and other polluted sites of the world (Table 3). Generally, in two study areas, the THg and MeHg concentrations of fingernails are obviously lower than those of hair samples. However, for the reason why higher THg and MeHg obtained in hair rather than fingernails, it may be attributed to that hair contains higher levels of cysteine and (SH)-groups than fingernails as cysteine and (SH)-groups have a strong affinity to Hg in organisms (Marshall, 1983; Barba et al., 2010).

Interestingly, positive correlations in THg (WMMA: $r^2 = 0.59$, $p < 0.01$; HZSA: $r^2 = 0.63$, $p < 0.01$), MeHg concentration (WMMA: $r^2 = 0.53$, $p < 0.01$; HZSA: $r^2 = 0.44$, $p < 0.01$) can be observed between paired hair and fingernail samples in both areas (Fig. 4). As hair is recognized as an effective biomarker of THg and MeHg exposure levels in human bodies, the strong positive correlations in Fig. 4 suggest that fingernails can be another useful biomarker of THg and MeHg exposure to human bodies, in addition to hair. Moreover, the slope of hair over fingernail in WMMA is higher than that in HZSA, indicating that the fingernails are more sensitive to high Hg levels. The MeHg% fractions in fingernails collected from WMMA and HZSA range from 1% to 86% (median: 34%) and from 5% to 56% (median: 21%), respectively. This is similar to those observed in hair samples, suggesting a substantial fraction of Hg in fingernails is in the form of IHg. The calculated IHg concentration in fingernail samples collected from WMMA and HZSA range from 0.03 to 108 μg/g (median: 0.55 μg/g) and from 0.02 to 0.17 μg/g (median: 0.05 μg/g), respectively, which are lower than that in hair samples collected in the same area. A positive correlation in IHg concentrations can be observed between paired hair and fingernail samples in both areas (WMMA: $r^2 = 0.56$, $p < 0.01$; HZSA: $r^2 = 0.61$, $p < 0.01$) (Fig. 4), indicating that fingernails may also be an effective biomarker of IHg exposure in the human body. THg, MeHg, and IHg in hair and fingernails show no association with age, weight, smoking, and drinking habits in both areas. However, in WMMA, mercury miners showed significant higher THg and IHg levels in hair and fingernails, compared to people with different occupations ($p < 0.001$). Meanwhile, compared to females, males have

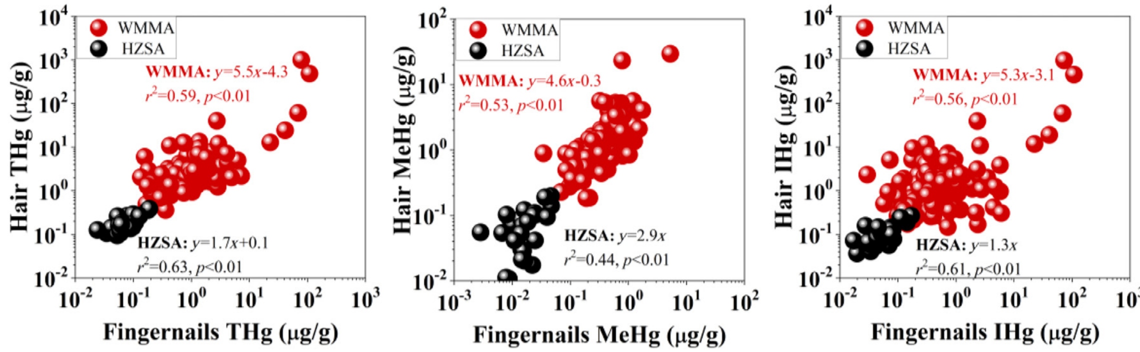

Fig. 4 – Relationships between hair THg and fingernails THg, between hair MeHg and fingernails MeHg, and between hair IHg and fingernails IHg in the WMMA and HZSA.

significant higher THg and IHg levels in hair and fingernails ($p < 0.01$), perhaps due to a substantial number of the males investigated in this study are mercury miners.

Ratios of the hair to fingernails Hg are estimated in this study, which can be used to estimate hair Hg levels if hair or fingernails Hg measurements are unavailable for the study population. The hair to fingernails THg ratio and the hair to fingernails MeHg ratio are 3.0:1 and 3.4:1, respectively, in WMMA, and are 2.3:1 and 4.1:1, respectively, in HZSA. In WMMA, compared to females, males showed significant hair to fingernails ratio of THg and MeHg ($p < 0.01$). Meanwhile, mercury miners showed higher hair to fingernail THg ratio than other populations ($p < 0.05$). However, in HZSA, the hair to fingernail THg ratio and MeHg ratio show no association with gender, age, weight, and habits (smoking and ethanol drinking). Therefore, the higher ratio of hair to fingernails Hg of males in WMMA may attribute to intake more Hg-contaminated food and exposure to Hg vapor originating from the Hg mining works. The hair contains higher levels of cysteine and (SH)-groups than fingernails, which may cause more Hg prefer to be concentrated in hair.

2.3. Evaluation of the excretion rates of Hg by hair and fingernails

Considering that hair and fingernails are effective ways of Hg excretion from the human body, the excretion rates (ER) of THg, MeHg, and IHg via hair and fingernails were estimated in this study. The calculated ER_{THg}, ER_{MeHg}, and ER_{IHg} values via hair for the residents in WMMA are 0.65 μg/day, 0.28 μg/day and 0.30 μg/day, which are 103, 127 and 100 times higher than that via fingernails, respectively. The calculated ER_{THg}, ER_{MeHg}, and ER_{IHg} values via hair for residents in HZSA are 0.04 μg/day, 0.02 μg/day, and 0.02 μg/day, which are 76, 199, and 70 times higher than that via fingernails, respectively. Those results indicated that hair plays a more important role than fingernails in the excretion of Hg from the human body. Previous studies reported that the urine Hg concentration in WMMA was about 22.1 ± 27.6 μg/L (Du et al., 2021). In HZSA, no urine Hg concentration has been reported yet. In HZSA, the hair THg concentration and diet structure are similar to those in Changshun, Guizhou, which was usually selected as a background site (Feng et al., 2008; Du et al., 2021). Thus, urine Hg concentration (0.98 ± 1.53 μg/L) of the residents in Changshun, Guizhou is employed to estimate the excretion rates of Hg via urine in HZSA. Assuming that excretion of urine is 1522 mL/day (Burnieret al., 2020), the excretion rates of Hg via urine are 33.2 μg/day and 1.5 μg/day in WMMA and HZSA, respectively, which are much higher than that via hair and fingernails.

For the Hg miners in WMMA, the ER_{THg}, ER_{MeHg}, and ER_{IHg} values via hair are 2.41 μg/day, 0.34 μg/day, and 1.62 μg/day, which are 207, 128, and 226 times higher than that via fingernails, respectively. The ER_{MeHg} values of Hg miners via hair are equal to the general population (0.27 μg/day), while the ER_{THg} and ER_{IHg} values are 4 ∼ 5 times higher than that of general population (ER_{THg}: 0.60 μg/day, ER_{IHg}: 0.29 μg/day). Moreover, The ER_{THg}, ER_{MeHg}, and ER_{IHg} values via hair and fingernails show no association with age, weight, and habits (smoking and ethanol drinking), while the ER_{THg} and ER_{IHg} of males in WMMA are higher than that the females, indicating that people who are occupationally exposed to Hg vapor could excrete more IHg via hair.

It should not be ignored that hair treatment (washing, dying, or waving) may involve the release of Hg from hair or absorption of Hg from chemicals (Dakeishi et al., 2005); and the hair of residents may live with different atmospheric Hg, which will also bias the estimate of the ER of hair.

3. Conclusions

As a bioaccumulative neurotoxin, Hg poses a potential threat to human health. Finding an effective biomarker is always beneficial to evaluate the human Hg exposure risk. In this study, fingernails share a similar distribution pattern in the two studied areas, which is supported by the positive correlations in THg, MeHg, and IHg concentrations between paired hair and fingernails, suggesting that fingernails can be another useful biomarker of Hg exposure to humans. Hair has a higher Hg concentration than fingernail, indicating that hair is more sensitive to Hg. However, when reflecting short-term human Hg exposure levels, hair may have a degree of variability if not strictly cut hair from the occipital region of the scalp. While the fingernail is replaced by a new one in about 3 ~ 6 months, which seems to be more time-sensitive than hair. This study therefore provides us an alternative biomarker for evaluating human Hg exposure levels. We further proved that hair plays a more important role than fingernails in the excretion of Hg from the human body. While urine could also substantially excrete Hg, which needs to be quantified in these areas.

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