Environment International 107 (2017) 47–54

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Dietary human exposure to mercury in two artisanal small-scale gold mining communities of northwestern Colombia

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ARTICLE INFO

Keywords:
Methylmercury
Chocó department
Fish consumption
Gold mining
Hg-amalgamation

ABSTRACT

Artisanal and small-scale gold mining (ASGM) is the largest anthropogenic source of mercury pollution worldwide, posing a grave threat to human health. The present study identifies current levels of mercury in the human population from mining areas of the Chocó Department, Colombia, through total mercury (THg) and methylmercury (MeHg) measurements in human hair. Mercury exposure of the local population was assessed in two towns affected by ASGM and was related to different variables of interest. Concentrations of THg in human hair ranged from 0.06 to 17.54 ppm and the mean value for the subjects under study was 2.48 ppm. Men had significantly higher levels than women in both towns (3.29 ppm vs. 0.77 ppm). Fish consumption was related to a marked increase of THg in hair, with mean values close to five times higher in frequent fish consumers (5–7 times/week) than in non-fish consumers (4.80 ppm vs. 0.90 ppm). A multiple linear regression model was fitted successfully ($R = 0.671$) and reveals that gender, fish consumption and location of residence were significant indicators of Hg levels in hair, while no significant relationship was found for age. Approximately 60% of subjects tested had THg levels that exceeded the U.S. Environmental Protection Agency reference dose of 1.0 ppm, while 25% surpassed that of the World Health Organization (2.2 ppm).

1. Introduction

Mercury (Hg) releases from artisanal and small-scale gold mining (ASGM) is estimated to be about 1400 t/year (UNEP, 2013), making it the largest global demand sector for Hg and the largest source of Hg pollution in Colombia (De Miguel et al., 2014; García et al., 2015). This country is the highest per capita Hg polluter in the world (Cordy et al., 2011), mainly in the areas of Antioquia, northwestern Bolivar and western Chocó. Emissions of Hg from ASGM reported for 2010 were more than twice those reported for 2005 (UNEP, 2013) and gold production using Hg for extraction increased by over 300% between 2006 and 2010 (BGS, 2012). In Colombia, small-scale miners have relocated to Chocó from other mining regions to escape violence and gold-based money laundering (Tubb, 2015). As gold prices have risen, gold production in Chocó has increased from 2000 kg/year over the period of 2005–2008 to 25,627 kg/year from 2010 to 2012 (SIMCO, 2015). Gold production was 14,547 kg in 2015 and the region has become the second largest gold producer in Colombia, while simultaneously having the worst indicators of poverty, violence, and malnutrition (Tubb, 2015).

Mining and amalgamation methods used in the gold mining industry are highly variable. The separation of Au-Hg and gold melting procedures, together with the fate of contaminated tailings, define the extent of Hg discharge to the environment (Meech et al., 1998). During gold mining, when metallic Hg is used to produce gold-Hg amalgams, small amounts can be washed out along with the unwanted tailings or sediments. Heating the amalgam volatizes the Hg, leaving behind gold ore with some residual Hg. ASGM releases Hg into the environment in its metallic form during amalgamation and as Hg vapour during the burning process; therefore mercury is easily distributed into the air, soil, water, and sediments (UNEP, 2013). Once mercury reaches open waterways, it can be transformed (methylated) into methylmercury (MeHg) by biotic or abiotic processes. Bioaccumulation and biomagnification of transformed mercury into food chains poses a significant human health risk (Clarkson, 1993). Populations in ASGM regions are exposed to Hg from gold mining activities through two main

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http://dx.doi.org/10.1016/j.envint.2017.06.011
Received 7 February 2017; Received in revised form 31 May 2017; Accepted 12 June 2017
Available online 26 June 2017

routes: occupational and environmental exposure through inhalation of Hg-contaminated air and/or ingestion of contaminated food. Individuals working in, or living near, gold shops or processing centres where the amalgam is heated can thus be heavily exposed to elemental Hg vapour, often to degrees that exceed the World Health Organization (WHO) limit of 200 ng/m^3. In northwestern of Colombia, areas near these facilities have reported Hg levels in the air exceeding the WHO limit by 10 to 1000 times (Cordy et al., 2011, 2013; Schmidt, 2012; García et al., 2015).

Environmental human exposure to Hg occurs through the consumption of fish (i.e. MeHg) and is evaluated by THg concentration analysis in hair. Scalp hair is the preferred biomarker for Hg over blood (McDowell et al., 2004; Legrand et al., 2005; Díez, 2009), since it is non-invasive, and because MeHg accumulates in the hair at a concentration usually around 300 times higher than in blood (WHO, 1990). Once incorporated in the hair, MeHg can provide a reasonable history of the ingestion of contaminated food (WHO, 1990). The majority of the THg in human hair is already methylated, with MeHg accounting for the 70–80% of hair THg (Cernichiari et al., 1995), and therefore, THg is a proxy for MeHg concentrations. On the other hand, THg concentrations in urine are commonly used as a measure of Hg vapour (Clarkson and Magos, 2006).

It has been reported that the Hg released during gold-mining activities contaminates freshwater bodies and riverside populations in some zones of northwestern Colombia (Olivero et al., 2002; Marrugo-Negrete et al., 2008a, 2008b; Olivero-Verbel et al., 2011; Marrugo-Negrete et al., 2013). The Department of Chocó, is recognised for its high biodiversity, hosting between 60 and 70% of the total number and variety of species of plants and animals in the world (Rangel, 2004; CONPES, 2012; Restrepo, 2013). This region is also important in terms of freshwater sources, which are essential for water supplies and for obtaining diverse species of fish: two key elements for the survival of riverine communities. However, information about the impact of mining practices on the population in Chocó, where extensive gold mining is taking place, remains scarce. Our study focused on analysing the effect of transformation metallic mercury used in the ASGM operations into MeHg, which is usually the main form of Hg found in fish (Veiga and Baker, 2004). Furthermore, the aim of this study was to provide scientific data on the levels of THg and MeHg in populations from the Chocó region. Finally, we will relate these values with the main risk factors including fish consumption, age, gender and location of residence, i.e. two municipalities of the mining district of San Juan, where many artisanal miners are achieving high rates of gold recovery.

2. Materials and methods

2.1. Study area

The study was conducted in Tadó and Unión Panamericana, two municipalities located in the Department of Chocó in western Colombia, where the climate is a tropical rainforest climate and rainfall occurs throughout the year (Fig. 1). These localities were selected because they are important gold mining towns within the department of Chocó, with a high number of goldminers and workers in gold shops (CODECHOCÓ, 2012). The dietary habits of the inhabitants of these regions are influenced by a marked preference of fish consumption, especially fish species obtained from important water sources, such as Quito River and San Juan River, and also in widespread water pools created by the interruption of natural drainage due to mining activities.

2.2. Hair collection and analysis

Human hair samples were collected between September and November of 2015 in the mining district of San Juan, in two municipalities: Tadó (27 subjects) and Unión Panamericana (54 subjects) located 30 km from each other. All participants were randomly selected and fully informed about the purposes and limitations of the study and provided written consent in Spanish. The study protocol was approved by the Ethics Committee of the Health Department from University of Córdoba-Colombia. Artisanal miners, *entable* (processing centre) operators, fishermen, homemakers, farmers and students participated in the study, aged between 7 and 60 years. All of the people studied appeared to be healthy and none had congenital anomalies. We collected 81 samples, of which 55 (68%) were males and 26 (32%) females.

A questionnaire was filled through individual interviews conducted by survey staff to collect information on the age, gender, place of residence, and dietary habits. The questionnaire included relevant questions about the habitual intake of fish, with questions focusing on the weekly number of times they consume fish during the past 6 months and the type of fish. Frequency responses of fish intake were recorded as: never, 1–2 times per week, 3–4 times per week and 5–7 times per week. The intake of different types of fish was determined by asking about the intake of specific fish species. The common carnivores species are: mojarra (*Caquetaia kraussii*), moncholo (*Hoplias malabaricus*) and bagre (*Pseudoplatystoma magdaleniatum*), whereas the non-carnivores fish species are cachama (*Colossoma macropomum*), tilapia (*Oreochromis spp*), bocachico (*Prochilodus magdalenae*), and barbudo (*Rhamdia quelen*).

Samples were taken from the inferior occipital region, very close to scalp, the proximal and distal zones of the samples with respect to the cranium were identified and the samples were stored in properly labelled sealed envelopes for transport to the laboratory (Olivero-Verbel et al., 2011; Marrugo-Negrete et al., 2013). Great care was taken to avoid contamination of the samples during collection. Plastic gloves were used throughout sampling. Once in the laboratory, the hair samples were washed with neutral detergents, rinsed with distilled water, dried at room temperature and stored in a desiccator. This cleaning procedure was performed for removing dust and oily or greasy material, because it has been demonstrated that washing hair even with EDTA or reagents with sulfhydryl groups like L-cysteine does not remove a significant percentage of exogenously adsorbed Hg (Li et al., 2008; Morton et al., 2002; Drasch et al., 2001).

Hair samples (30–50 mg) were digested with a 2:1 v/v mixture of H_2SO_4/HNO_3 at 100–110 °C for 2 h, and analysed for THg, following the methodology of atomic absorption spectroscopy in cold vapour (Marrugo-Negrete et al., 2013). The analysis was conducted in a Thermo Electron AAS series 4 (Thermo Electron Corporation, United Kingdom). The limit of detection (three standard deviations of the mean of ten blank measurements) was 100 ng/g. Certified reference materials for quality control were used. The measured THg concentrations in the certified material for hair (CRM-397 from Community Bureau of Reference, certified value = 12.3 ± 0.5 ppm dry wt. and IAEA-086 from International Atomic Energy Agency, certified value = 0.573 ± 0.039 ppm, dry wt.) were 11.8 ± 0.31 ppm dry wt. and 0.533 ± 0.021 ppm dry wt., respectively. The percentage recovery for CRM-397 was 95.9% and for IAEA-086 was 95.7%.

For measurements of MeHg in hair, about of 100 mg of sample were weighed and subjected to alkaline digestion in the presence of L-cysteine. Subsequently, the mixture was acidified and extracted twice with toluene. The aqueous phase was taken and re-extracted with toluene. The obtained phase was analysed by gas chromatography (Model Perkin Elmer Autosystem XL) coupled with electron capture detection (GC-ECD) (Pinedo-Hernández et al., 2015). The limit of detection was 200 ng/g calculated from the standard deviation of ten blanks. The measured MeHg concentration in the certified material for hair was 0.279 ± 0.034 ppm dry wt., which is in good agreement with the certified value (IAEA-086, 0.258 ± 0.022 ppm, dry wt.). The percentage recovery was 108%.

2.3. Statistical analysis

Mercury concentration data did not followed a normal distribution

Fig. 1. Map of the department of Chocó where are shown the two localities considered in this study.

and previous transformation did not normalise them; thus, it was necessary apply a Kruskal-Wallis analysis. The differences between the established groups were tested for significance using ANOVA and Kruskal-Wallis tests. A Sperman's (r_s) correlation test was used to establish associations between variables. The box lengths are defined as the interquartile range and outliers are defined with values of 1.5 box lengths from the upper edge of the box. Extremes are defined with values of 3 box lengths from the upper edge of the box. Multiple linear regression (MLR) analysis using a non-automated stepwise method was used to assess the relation between the covariates. All statistical analyses were conducted with the IBM SPSS Statistics, version 23. Statistical significance was defined as $P < 0.05$.

3. Results

3.1. Population studied

THg concentrations in hair from males, females and the whole studied population, are shown in Table 1. The average concentration in the whole group is 2.48 ppm (range 0.06–17.54 ppm) but males have significantly higher average THg (3.29 ppm, 0.60–17.54 ppm) than females (0.77 ppm, 0.06–1.80 ppm) ($P = 0.005$). On the other hand, the subjects living in Tadó (1.30 ± 1.15 ppm) show significantly different THg concentrations than those subjects from Unión Panamericana (3.07 ± 4.35 ppm) ($P = 0.043$). The male groups showed higher values in Unión Panamericana (4.14 ± 4.99 ppm) than in Tadó (1.67 ± 1.19 ppm). Likewise, the mean value in the female group from Unión Panamericana (0.93 ± 0.48 ppm) was significantly higher than in Tadó (0.41 ± 0.21 ppm) (Fig. 2).

When the hair THg concentrations were divided by age groups (adult and non-adult) no significant ($P > 0.05$) increase in THg was observed with age. The mean and median of ages for all individuals was 38 years: the youngest being 7 years old and the oldest being 80 years old. No significant differences ($P = 0.257$) were found between male and female groups for age. However, we found a positive significant association between age and THg among the whole tested population. The Spearman correlation coefficient for these two variables was found to be $r_s = 0.220$ ($P = 0.048$), which is indicative of a significant correlation between them.

3.2. Fish consumption

Frequency of fish consumption was classified into four qualitative categories for simpler analysis: never ($N = 4$); 1–2 times per week ($N = 26$) (low); 3–4 times per week ($N = 35$) (medium), and 5–7 times per week ($N = 16$) (high). In both villages, fish was consumed 1 to 2 times per week by 32% of the population, from 3 to 4 times per week by 43% and from 5 to 7 times per week by 20%; only 5% did not eat fish in the past half year. The THg levels stratified in terms of fish consumption are presented (Fig. 3a and b). The results showed that there is a marked increase in mean values of THg in hair with fish consumption: the mean THg increased from never to high consumption levels from 0.90 ppm and 4.80 ppm, respectively. The median THg level in hair for the whole population ($N = 81$) is 1.16 ppm, and the highest median level of 2.73 ppm is reported for the highest consumption level ($N = 16$), whereas people that were in the three lower categories have median levels of 0.92 (never, $N = 4$), 0.99 (low, $N = 26$) and 1.13 ppm (medium, $N = 35$) (Fig. 3a). Hence, there were statistically significant differences between never, low and medium groups. THg contents for the highest category is five-times higher than levels in hair of the lower, and ANOVA and Kruskal-Wallis tests showed significant differences. Moreover, people that ate 5 or more fish meals per week had significantly higher levels compared to the other categories.

Fig. 3b shows THg contents in hair from either gender for the fish consumption categories. As can be seen, the male group showed significantly higher THg concentrations in hair than the female group in categories low (1.63 ppm vs. 0.63 ppm) ($P = 0.002$), medium (3.46 ppm vs. 0.71 ppm) ($P = 0.000$), and high (5.97 ppm vs. 1.32 ppm) ($P = 0.042$).

MeHg concentrations in hair for groups with a higher frequency of fish consumption (categories medium and high) are shown in Table 1. The mean concentration for a group of 35 volunteers was 2.67 ppm

Table 1
Description of variables of interest by area and concentrations of THg (ppm) and MeHg (ppm) in hair of residents from Tadó and Unión Panamericana.

	Both localities (*N* = 81)	Tadó (*N* = 27)	Unión Panamericana (*N* = 54)
Gender, male, N (%)	55 (68)	19 (70)	36 (67)
Age, year, mean ± SD	38 ± 17	29.3 ± 12.7	42.3 ± 17.3
Fish consumption, N (%)			
Never	4 (5)	2 (2)	3 (3)
Low: 1–2 times/week	26 (32)	11 (14)	15 (18)
Medium: 3–4 times/week	35 (43)	4 (12)	25 (31)
High: 5–7 times/week	16 (20)	4 (5)	23 (15)
THg, mean ± SD, (median)			
All participants	2.48 ± 3.69 (1.16)	1.30 ± 1.15 (0.81)	3.07 ± 4.35 (1.20)
Range (min-max)	0.06–17.54	0.06–4.88	0.20–17.54
Female	0.77 ± 0.48	0.41 ± 0.21	0.93 ± 0.48
Male	3.29 ± 4.25	1.67 ± 1.19	4.14 ± 4.99
MeHg, mean ± SD, (median)			
All participants	2.70 ± 3.64 (1.14)	0.76 ± 0.44 (0.55)	3.27 ± 3.97 (1.27)
Range (min-max)	0.31–13.7	0.31–1.39	0.32–13.7
Female	0.78 ± 0.45 (0.64)	0.40 ± 0.11 (0.36)	0.98 ± 0.42 (1.09)
Male	3.36 ± 4.02 (1.36)	0.98 ± 0.41 (1.09)	3.93 ± 4.29 (1.86)
Fish consumption. Category medium (3–4 times/week); *N* = 23			
MeHg, mean ± SD			
All participants	2.70 ± 3.07	0.79 ± 0.47	2.63 ± 3.56
Range (min-max)	0.31–11.58	0.31–1.39	0.46–11.58
Female	0.57 ± 0.29	0.40 ± 0.11	0.83 ± 0.27
Male	2.49 ± 3.37	1.08 ± 0.40	2.89 ± 3.75
Fish consumption. Category high (5–7 times/week); *N* = 12			
MeHg, mean ± SD			
All participants	3.90 ± 4.44	0.58	4.20 ± 4.52
Range (min-max)	0.32–13.65		0.32–13.65
Female	1.05 ± 0.50	ND	1.05 ± 0.50
Male	5.32 ± 4.88	0.58	6.00 ± 4.85

ND: no data.

(range 0.31–13.65 ppm). Among category medium, the mean concentration was 2.70 ppm (range 0.31–11.58 ppm) and for the highest consumptive group the mean concentration was 3.90 ppm (range 0.32–13.65 ppm). The mean amount of MeHg, as a percentage of THg, for all the samples was 77% (range 62–92%) indicating that organic Hg is the main form of Hg found in the hair of inhabitants; however, the percentage of MeHg is not significantly different, with a similar mean value of 80% for the highest two consumptive groups.

In order to assess the relationship between the THg measured in hair and the scalar variables (e.g. age, residence location, gender and fish

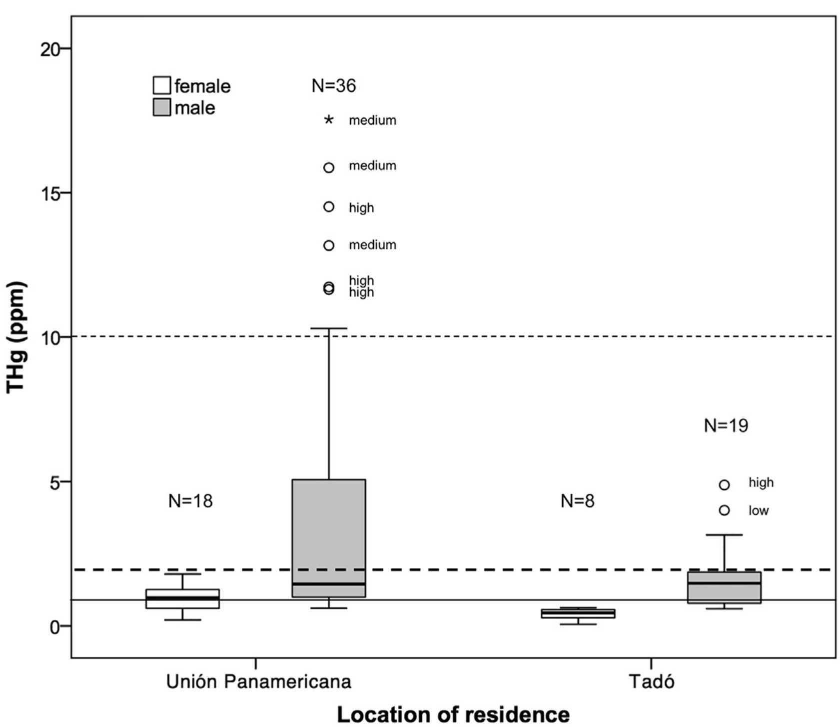

Fig. 2. Box plot of total mercury (THg) in hair in relation to location of residence, b) consumption of fish and c) fish intake categorized by gender. Outliers are represented by open circles and extremes by asterisk. Continuous line is the US EPA (2005) limit of 1 ppm, dashed thick line is the JECFA (2006) limit of 2 ppm and dashed fine line is the WHO (1990) limit of 10 ppm.

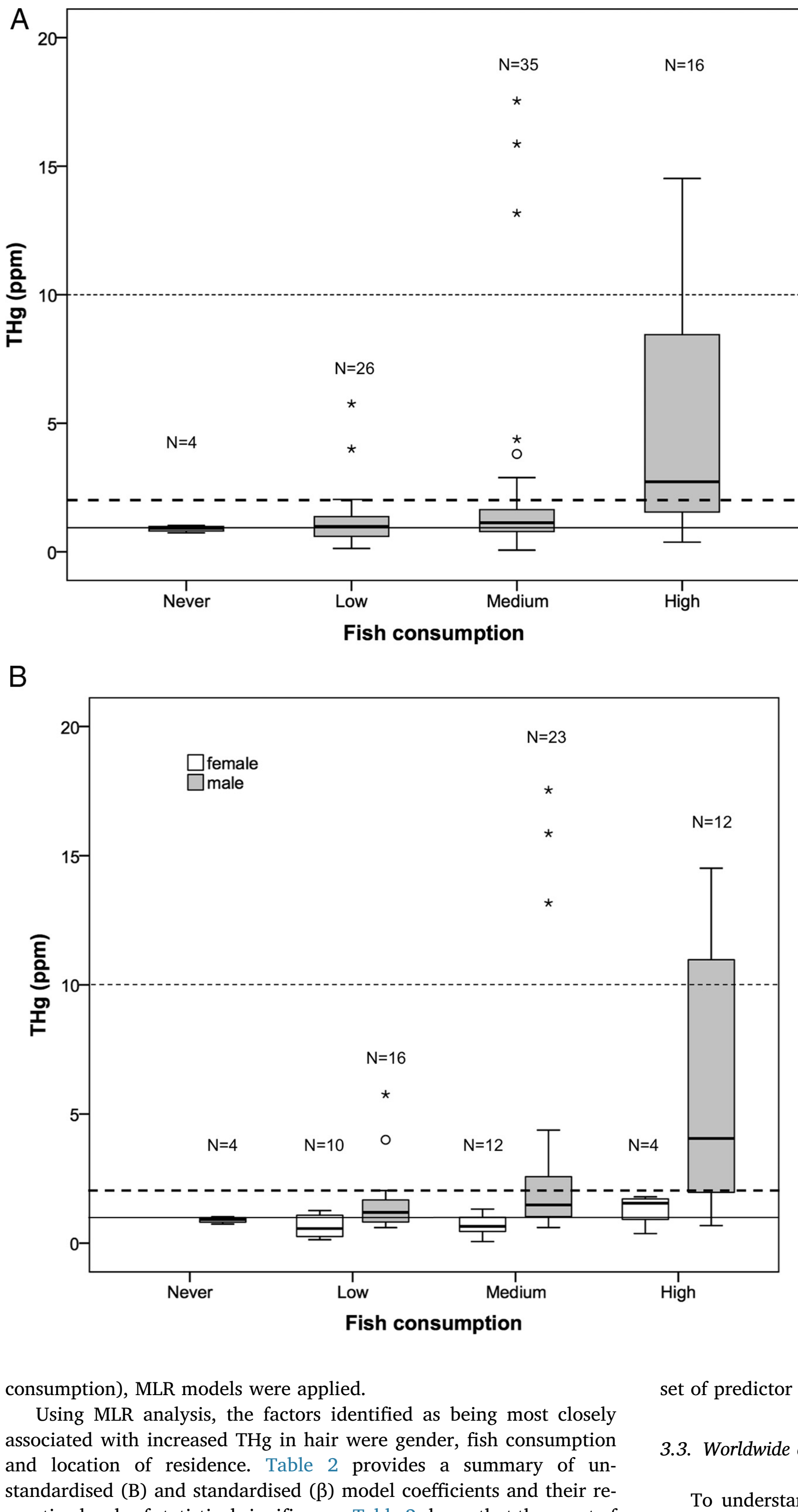

Fig. 3. Box plot of total mercury (THg) in hair in relation to consumption of fish (a) and fish intake categorized by gender (b). Fish consumption: Never, Low: 1–2 times/week, Medium: 3–4 times/week and High: 5–7 times/week. Outliers are represented by open circles and extremes by asterisk. Continuous line is the US EPA (2005) limit of 1 ppm, dashed thick line is the JECFA (2006) limit of 2 ppm and dashed fine line is the WHO (1990) limit of 10 ppm.

consumption), MLR models were applied.

Using MLR analysis, the factors identified as being most closely associated with increased THg in hair were gender, fish consumption and location of residence. Table 2 provides a summary of unstandardised (B) and standardised (β) model coefficients and their respective levels of statistical significance. Table 2 shows that three out of four of the independent variables are significantly related to THg: gender (β = 0.521; $P < 0.05$), fish intake (β = 0.332; $P < 0.05$), and residence location (β = − 0.224; $P < 0.05$). However, the relationship of age (β = 0.035; $P = 0.721$) is not significant. Hence, the output regression model uses three indicators to predict hair Hg concentrations with R equal to 0.671, by applying a stepwise method to select the best set of predictor variables for the regression equation.

3.3. *Worldwide comparison of hair mercury levels*

To understand the Hg contamination status in Chocó, concentrations of hair Hg in this study were compared with those in recent studies (2001–2017) including general population, people involved in gold-mining activities and frequent fish consumers from urban cities and mining areas (Table 3). According to Table 3, hair Hg concentration in the present study is very low (4 to 8 times) when compared to other studies in mining areas of the Colombian (Olivero-Verbel et al., 2016) and Brazilian Amazon (Harada et al., 2001; Santos et al., 2002; Barbosa

Table 2
Multiple linear regression analysis (constant (B) and slope coefficients (β) and its standard errors (SE), and *P* values) for concentrations of THg in hair.

Model	Unstandardized coefficients		Standardized coefficients	P
	B	SE	β	
(Constant)	−0.770	0.203		0.000
Gender	0.507	0.082	0.521	0.000
Fish consumption	0.185	0.048	0.332	0.000
Location of residence	−0.216	0.082	−0.224	0.011

Dependent variable: log (THg).

et al., 2001), and French Guiana (Fréry et al., 2001), where fish consumption is their major source of protein. Indonesian gold miners who eat fish daily (Sherman et al., 2015) and a fishing community in northwestern Colombia (Marrugo-Negrete et al., 2013), had mean hair Hg concentrations near three times greater than participants in Chocó, whereas the range is similar. Mean values in high fish eating populations with intense small scale gold-mining activities such as Bolivian Amazonian (Barbieri et al., 2009) and the Philippines (Drasch et al., 2001) are close to two times higher than participants in Chocó, as well as gold miners in Pará State in Brazil (Castilhos et al., 2015), although the latter do not consume fish very often compared to the Amazonian riparian populations. Recent studies in the Madre de Dios region of the Peruvian Amazon (Ashe, 2012) and San Martin de Loba (Colombia) (Olivero-Verbel et al., 2015) mining areas have reported mean values very similar to those found in the Chocó population. Several studies from the USA (McDowell et al., 2004), Italy (Díez et al., 2008), and China (Gao et al., 2007) have reported Hg level in the general population through consumption of fish, although reported values were lower than in our study.

4. Discussion

Governmental agencies throughout the world have developed regulatory guidelines aimed at limiting environmental Hg exposure. In 1990, based on neurotoxicity data from Japan and Iraq, the WHO (WHO, 1990) stated that the no observed adverse effect level (NOAEL) for Hg in adults was 50 ppm dry wt. of hair. Later on, Hg-related neuropsychological dysfunctions were revealed in children even with Hg levels below 10 ppm dry wt. in maternal hair in the Tapajos River basin, Brazil and in the Faroe Islands, Denmark (Grandjean et al., 1997, 1999) and the upper limit of a normal hair Hg level was reported by Harada et al. (1998) to be 10 ppm dry wt.. In 2001, the U.S. Environmental Protection Agency (EPA) adopted a revised reference dose (RfD) related to a maternal hair Hg concentration of 1.0 ppm (US EPA, 2005). Lately, the Joint Food and Agriculture Organization of the United Nations (FAO) and the WHO Expert Committee on Food Additives (JECFA) based its evaluation on studies in the Seychelles and Faroe Islands to establish a reference concentration. Exposure associated with maternal Hg hair concentration of 15.3 ppm was identified as the NOAEL for the Seychelles study and a benchmark lower confidence limit (BMDL) of 12 ppm Hg in maternal hair was determined from the Faroese data. The Committee used 14 ppm of maternal hair-Hg as the average from the two studies. Therefore, a provisional tolerable daily intake (PTDI) of 0.23 μg kg^{-1} day^{-1} was considered sufficient to protect the developing foetus, the most sensitive subgroup of the population (JEFCA, 2006), whereas the Committee confirmed that the earlier value of 0.47 μg kg^{-1} day^{-1} is suitable to protect adults against the neurotoxic potential of MeHg. This JECFA PTDI corresponds to 2.2 ppm of THg in the hair. We found that THg in hair of 60% of the studied population exceeded the 1.0 ppm U.S. EPA recommended limit. Moreover, 25% of the volunteers surpassed the level of 2 ppm, while 9% and 4% exceeded the reference limits of 10 ppm and 14 ppm, respectively. The average value of Hg in hair found for the whole group (2.48 ppm) also exceeded both the EPA and JECFA limits. Values above 10 ppm provide important information with regards to risks associate with activities related to ASGM in Tadó and Unión Panamericana, due to the adverse health effects that might result when THg concentration in hair exceed this tolerance limit. Of the 20 subjects that exceeded the WHO limit of 2 ppm, only 1 subject (i.e. a male from Tadó, 7 years old, identified as "low" in Fig. 2) belongs to the non-adult group. This fact might be explained because the non-adult group generally has a low fish consumption, with 80% of subjects rarely (1–2 times per week) or never eating fish.

In our study, the content of Hg in hair increased with age, with a significant correlation ($r = 0.220$, $P = 0.048$, $N = 81$). Similar findings are reported in Poland (Michalak et al., 2014), Korea (Kim et al., 2012) and in Terceira Island (Azores, Portugal) (Vieira et al., 2013), with values increasing from the youngest to the oldest age group. Moreover, Wennberg et al. (2006) reported that the increase of Hg in erythrocytes with increasing age is probably because young subjects have a lower fish intake than older subjects.

Using the MLR described above, we found that gender, fish consumption, and residence location (arranged in decreasing significance) were all significant predictors of the hair Hg levels. Age had no significant relationship to the Hg levels found in hair samples.

It is well known that Hg exposure due to fish consumption is the

Table 3
Chronologically organized summary of studies (2001–2017) on THg (ppm) in human hair collected at various worldwide locations.

Location	Mean THg	Range	Fish intake	Remarks	Reference
Mindanao, Philippines	4.14	0.03–37.8	High	Workers and local inhabitants in Diwalwal	Drasch et al., 2001
Maroni River, French Guiana	11.4	1.9–27.2	High	Native amerindians, Wayana community	Fréry et al., 2001
Tapajos River, Brazil	20.8	5.1–42.2	High	Fishing villages, far away from gold mines	Harada et al., 2001
Negro River, Brazil	21.4	1.7–59.0	High	Six agricultural and fishing communities	Barbosa et al., 2001
State of Pará, Brazil	16.0	4.50–90.4	High	Munduruku Indians, Sai Cinza community	Santos et al., 2002
USA	0.47	0.35–0.58	Low-medium	NHANES study, 16–49 yr old women	McDowell et al., 2004
Zhoushan, China	1.25	0.93–1.69	Medium	General population, coastal city	Gao et al., 2007
Naples, Italy	0.64	0.22–3.40	Medium	General population, coastal city	Díez et al., 2008
Beni River, Bolivia	3.76	0.42–15.65	High	High fish consumers in gold mining region	Barbieri et al., 2009
Madre de Dios, Perú	2.67	0.36–20.26	Low	Inhabitants in six mining zones	Ashe, 2012
Sinú River, Colombia	6.95	0.40–24.56	High	Residents of the Urrá dam near mining areas	Marrugo-Negrete et al., 2013
South Bolivar, Colombia	2.12	0.12–34.39	High	San Martin de Loba mining district	Olivero-Verbel et al., 2015
Sulawesi Province, Indonesia	8.66	4.3–20.6	High	Gold miners, high fish consumers	Sherman et al., 2015
State of Pará, Brazil	4.58	0.63–9.74	Low	Gold miners, no high fish consumers	Castilhos et al., 2015
Caqueta River, Colombia	17.29	1.2–47.0	High	Indigenous living in river artisanal mining	Olivero-Verbel et al., 2016
Chocó, Colombia	2.48	0.06–17.54	Low-medium	All participants	This study
	0.77	0.06–1.80		Female	
	3.29	0.60–17.54		Male	

main factor that contributes to body burden Hg levels, and that fish intake is considered as the most effective predictor of Hg in hair, especially in subjects with no occupational exposure (Díez, 2009; Díez et al., 2011). However, our study found that fish consumption was the second most important risk factor (β = 0.332) with respect to Hg exposure. The strongest predictor of THg levels found in hair samples was gender (β = 0.521). We found that males had higher Hg levels than females for all the consumption categories (Fig. 3b). Indeed, since there is no statistical difference between gender and frequency of fish consumption, a bigger serving size per meal consumed by men might help to explain this finding.

Location of residence was significantly ($P < 0.05$) related to the THg levels measured in hair, being the third significant predictor in the model (β = − 0.224). Mercury levels in hair of the population living in Unión Panamericana were found to be significantly higher than for the population living in Tadó (Fig. 2). This was unexpected, as both localities are close to each other, and Hg exposure within the two environments do not seem to be markedly different. According to our questionnaires, consumption rates and type of fish consumed in both villages were similar; therefore significant differences in hair THg content between locations are probably due to variation in the fish Hg burden at specific freshwater bodies where fish are caught. Indeed, the people from Union Panamericana catch fish from the Quito River, a major tributary of Atrato River, whereas San Juan River is the main source of fish for Tadó residents, but currently information about Hg concentrations in fish is lacking. In addition, several studies (Chen et al., 2005; Ward et al., 2010) have shown that even across sites where Hg inputs are similar, concentrations in fish can differ up to 10-fold. Hence, understanding the behaviour of Hg methylation and bioaccumulation in fish is difficult as it depends on several environmental factors such as organic matter type, pH, dissolved oxygen, presence of sulfate, type of bacteria, etc., in addition to the unpredictable nature of gold mining activities. Despite the uncertainties related to the transformation of metallic Hg into MeHg in ASGM areas, a simplified sequence of reactions was described by Veiga and Baker (2004). In this sequence, metallic Hg released into the environment through amalgamation tailings and by amalgam burning, oxidizes and reacts with organic acids (e.g. fulvic, humic) to form soluble Hg (II)- organic complexes before it becomes available for methylation by bacteria. Transformation of soluble organic complexes into MeHg by biotic or abiotic definitely increases bioavailability/bioaccumulation of this pollutant in fish (Meech et al., 1998). Consequently, hair can be used as a proxy for the Hg-MeHg transformation, bioaccumulation and ultimately incorporation into humans through fish consumption.

Our results show that the mean percentage of MeHg in hair samples (%MeHg) is close to 80%, which corresponds closely with several previous studies (Montuori et al., 2006), including those in Minamata (Harada et al., 1998) and Amazonia (Barbosa et al., 2001; Faial et al., 2015). No significant differences were obtained when subjects from the medium and high categories were compared by %MeHg. Although it was found that participants consuming fish 5–7 times per week had almost 2-fold higher hair THg concentration of 3.90 ppm compared to 2.70 ppm among those 3–4 times per week fish consumers (Table 1).

Most of traditional communities near mining activities (Table 3) show hair THg levels higher than in our study. Accordingly, we may suggest that the relatively low incorporation of MeHg into hair is likely due to low rates of oxidation, complexation and methylation of metallic mercury released (Hg vapour plus Hg associated with tailings) by artisanal miners into the environment of the mining district of San Juan, and/or low rate of carnivorous fish consumption by our participants.

5. Conclusions

THg concentrations were measured in human hair samples from two municipalities located in one of the largest artisanal gold mining areas in Colombia. Men had significantly higher hair THg levels than women and concentrations were significantly higher in Unión Panamericana. Mean THg concentrations in the population were well above the 1.0 ppm threshold level of safety defined by the U.S. EPA (2005). Our study indicates that 60% of the sampled volunteers exceed this recommended threshold value, which increased to 80% for those who consumed between 5 and 7 fishmeals per week. Indeed, mean value in these frequent fish consumers was close to five times greater relative to non-fish consumers.

Hair mercury levels were not as high as expected in comparison with other communities with traditional lifestyles near mining areas. Based on our results using hair as a proxy, environmental transformation rates of metallic Hg into MeHg were low. Despite the relatively low levels of MeHg measured in hair samples from exposed populations in our two study sites, continued monitoring of the environmental Hg loading from these activities is necessary. Constant Hg loading into local environments may affect future rates of transformation of Hg into more bioavailable forms thus accumulating in fish species that will subsequently be consumed by local populations.

According to our model, fish consumption, gender and location of residence were significantly related to THg levels found in hair; however further work needs to be conducted to better understand these relationships. Hence, greater number of hair samples and measurements of Hg, linked to specific environmental samples such as air, fish, and urine need to be taken in order to identify the dominant chemical forms of Hg and their sources. Additional data will support proposing alternatives that would help government entities to reduce environmental and human Hg contamination in this area.

Acknowledgements

We appreciate the anonymous reviewers and Editors for their valuable comments and suggestions to improve the quality of the manuscript. A special thanks to Dr. Gordon Price for his help in polishing the English language. The authors wish to thank the University of Cordoba, Montería-Colombia. Water, Applied and Environmental Chemistry Group, Laboratory of Toxicology and Environmental Management, University of Cordoba, Montería-Colombia.

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