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Determination of methylmercury and inorganic mercury in human hair samples of individuals from Colombian gold mining regions by double spiking isotope dilution and GC-ICP-MS

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ABSTRACT

With the aim to distinguish between routes of exposition to mercury (Hg) in artisanal and small-scale gold mining (ASGM) communities and to distinguish between Hg contamination sources, Hg species composition should be performed in human biomarkers. In this work, Hg species-specific determination were determined in human hair samples (N = 96), mostly non-directly occupied in ASGM tasks, from the six most relevant gold mining Colombian regions. Therefore, MeHg, Hg(II) and THg concentrations were simultaneously determined by double spiking species-specific isotope dilution mass spectrometry (IDMS) and GC-ICP-MS. Only 16.67% of participants were involved at some point in AGSM works and fish consumption ranged from 3 to 7 times/week, which is between medium and high intake levels. The median concentration of THg obtained from all samples is higher than the reference dose weekly acceptable of MeHg intake established by the EPA (1 ppm), whereas a 25% were more than 4 times higher than the WHO level (2.2 μg Hg g^{-1}). Median THg value of individuals consuming fish 5–7 times per week was significantly higher ($p < 0.05$) than those of the other consuming groups (12.5 μg Hg g^{-1}). Most of the samples presented a % of MeHg relative to THg higher than 80%. The average % of Hg(II)/THg was 11% and only 10 individuals presented a Hg(II) content over 30%. No significant differences ($p > 0.05$) were found when the amount of Hg(II) was compared between people involved in AGSM task and people not involved. Interestingly, significant differences among the evaluated groups where found when the percentage of the Hg (II)/THg ratio of these groups were compared. In fact, people involved in AGSM tasks showed 1.7 times higher Hg(II)/THg vs. inhabitants uninvolved. This suggest that Hg(II) determination by IDMS-GC-ICP-MS could be a good proxy for evaluating Hg(II) adsorption by direct exposure to mercury vapors onto hair.

1. Introduction

Mercury (Hg) is one of the most toxic metals which can be released to the environment by both natural and anthropogenic sources, the latter being the main source of emissions (Selin, 2009). In the 19th century, and intimately related to the industrialization (Esbrí et al., 2015), Hg emissions started to increase, reaching Hg atmospheric concentrations four times higher than previous natural levels (Outridge et al., 2018). Emissions associated with artisanal and small-scale gold mining (ASGM) account for almost 38% of the total Hg release to the biosphere (UN-Environment, 2018).

In the course of ASGM activities, an amalgam is formed by mixing Hg and gold. Then, the amalgam is heated to extract the trapped gold, releasing Hg vapors into the air and hence, exposing miners and inhabitants of neighboring areas (Telmer and Veiga, 2009; UNEP, 2013). Once Hg reaches aquatic systems, a small fraction is converted by bacteria to methylmercury (MeHg) at the water-sediment interface (Marrugo-Negrete et al., 2015). Then, MeHg is able to enter into the food chain (Outridge et al., 2018), biomagnifying and bioaccumulating (Fuentes-Gandara et al., 2018), thus, consumption of contaminated fish

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or seafood also compromises human health (Calao-Ramos et al., 2021).

Many countries from South America, Asia and Africa are involved in ASGM (Strode et al., 2009). Colombia stands out for having the largest Hg pollution rates per capita due to the high employment in gold mining tasks among rural population (Cordy et al., 2011). In addition, biomass burning and deforestation are relevant factors affecting this environmental problem. Forests act as metal storage tanks and when they are burned, Hg and other pollutants return to circulation. This is especially important in Amazonian regions, since in the last years, indiscriminate biomass burning is on the agenda (Crespo-Lopez et al., 2021). Therefore, riparian Colombian communities are exposed to Hg either directly from burning fumes or through dietary habits (Barbosa et al., 1995).

With the aim of knowing the effects of Hg in ASGM communities of Colombia, their species can be determined in several biomarkers (Poulin and Gibb, 2008). Hair is preferred over blood and urine due to the easier handling and collection which is important for monitoring (Calao-Ramos et al., 2021; Crespo-Lopez et al., 2021; Díez et al., 2011). Traditionally, total mercury (THg) analysis in hair has been used to evaluate MeHg exposition as ingested MeHg due to fish consumption is excreted in hair (Salazar-Camacho et al., 2017). However, gaseous Hg (0) can also be directly absorbed onto hair during exposition to polluted air (Queipo Abad et al., 2016) converting to Hg(II) strongly bound to hair constituents. Therefore, Hg species-specific determination may distinguish between different contamination sources in exposed individuals (Laffont et al., 2013).

Several procedures have been developed to determine Hg species concentration (Bermejo-Barrera et al., 1999; Feng et al., 1996; Kehrig et al., 1997; Liang et al., 1994; Morton et al., 2002; Wu et al., 2012). Some of these methods only allow the determination of one Hg species at a time. For example, acid digestion step prior to the aqueous-phase ethylation and in the gas chromatography coupled to cold-vapour atomic fluorescence spectrometry (GC-CVAFS) GC-CVAFS interface set-up (Montuori et al., 2004, 2006). In such cases, a second analysis is required to determine THg concentration, for example by sample catalytic combustion, preconcentration by gold amalgamation, thermal desorption, and atomic absorption spectrometry (AAS) (Díez et al., 2007).

When more than one Hg species is determined simultaneously, most methods do not consider possible alkylation and dealkylation processes during sample preparation steps (Monperrus et al., 2008). To do so, the application of multiple spiking species-specific isotope dilution mass spectrometry is required (IDMS) (Rodríguez-González et al., 2005). The combination of multiple spiking with gas chromatography (GC) hyphenated to inductively coupled plasma-mass spectrometry (ICP-MS) for Hg species composition, allows accurate and precise determinations while correcting for interconversion reactions (Queipo Abad et al., 2017).

In this work, MeHg, Hg(II) and THg concentrations were simultaneously determined by double spiking IDMS and GC-ICP-MS in human hair samples of individuals living in ASGM communities. Our three main objectives are: i) calculate the Hg species composition in hair in relation to THg for people involved and uninvolved in ASGM tasks, ii) compare hair Hg concentrations to guidelines for fish consumption, and match with bibliographic information from Colombian gold mining sites; and iii) validate if Hg species determination with this methodology is a good proxy to distinguish in human hair the MeHg coming from fish consumption and the Hg(II) absorbed into hair by direct exposure to Hg vapors during burning amalgam.

2. Materials and methods

2.1. Study area and sample collection

The study was conducted in several mining areas from six different departments of Colombia: five Andean regions (Nariño, Chocó, Antioquia, Bolívar and Sucre) and one Amazonian region (Vaupés). Dietary habits and gold mining strategies were different among regions. The diet of the population from the Amazonian region of Vaupés and the Andean region of Chocó is traditionally based on fish consumption, while the population from the two Andean regions of Antioquia and Nariño are not heavy fish consumers. ASGM is especially present in Chocó and Antioquia, where more Hg is demanded, because of the quartz mineralization of the gold, compared to the Hg demand of alluvial gold deposits (Cremers et al., 2013; Gutiérrez-Mosquera et al., 2018). The recruitment strategy was designed to include environmentally exposed residents, mostly not involved in occupational gold-mining activities. All the participants understood the purpose of the study and agreed to get involved signing an informed consent form after explaining the objectives and scope of the study. After permission, hair samples of 96 subjects were collected from the occipital area with stainless steel scissors. Then, the hair samples were stored and properly identified. Data from all participants related to their weight, height, age, gender, fish consuming habits and employment were also collected. The questionnaire included specific questions about their frequency of fish intake: less than 1 times/week, 1–2 times/week, 3–4 times/week, and 5–7 times/week.

2.2. Reagents and materials

Human hair Reference Material IAEA-086 was obtained from the International Atomic Energy Agency (IAEA, Vienna, Austria). The isotopically enriched standards were purchased from ISC-Science (Oviedo, Spain). ^{199}Hg-enriched Hg(II) and ^{201}Hg-enriched MeHg were characterized in terms of isotopic composition and concentration, as described previously (Queipo Abad et al., 2017). Hg(II) working solutions were prepared daily in 2% sub-boiled HCl (Sigma-Aldrich, St. Louis, MO, USA) in Milli-Q water ($\geq$18 MΩ cm). MeHg working solutions were diluted in a 3:1 mixture of acetic acid (Merck, Darmstadt, Germany) and methanol (Sigma-Aldrich) and stored in dark conditions at −18 °C. 25% tetramethylammonium hydroxide (TMAH) (Sigma-Aldrich) was used for the digestion of the samples. A pH 4 buffer was prepared with sodium acetate (Sigma-Aldrich) and acetic acid (Merck). Hexane (Sigma-Aldrich) was used to extract the mercury derivatized compounds with a 2% (w/v) solution of sodium tetra-n-ethylborate (LGC-Standards, Wesel, Germany) in Milli-Q water. Homemade columns packed with Florisil® (Sigma-Aldrich) were used to clean-up the organic phase.

2.3. Instrumentation

The separation of the Hg species was carried out with a gas chromatograph Agilent 7890 A (Agilent Technologies, Tokyo, Japan) fitted with a split/splitless injector and a DB-5MS capillary column from Agilent J&W Scientific (cross-linked 5% diphenyl, 95% dimethylsiloxane, 30 m × 0.53 mm i. d. × 1.0 μm). A homemade transfer line heated at 270 °C was used to couple the GC to an Inductively Coupled Plasma Mass Spectrometer Agilent 7900ce. Weighting of samples and standards was performed in an analytical balance Mettler Toledo MS Semi-micro MA 205DU (Zurich, Switzerland). Sample digestions were performed using a focused microwave Explorer Hybrid from CEM Corporation (Matthews, NC, USA). The adjustment of the pH was done with a Basic 20 CRISON pH-meter (Alella, Barcelona, Spain). The preconcentration was performed with a Mini-Vap Evaporator (Supelco, Bellefonte PA). More detailed instrumental parameters can be found in Table S1.

2.4. Sample preparation

The sample preparation procedure can be divided into three steps (spiking, digestion, and derivatization) (Laffont et al., 2013). The detailed description of the sample preparation procedure for hair analysis can be found elsewhere (Queipo Abad et al., 2017). In brief, an amount of 0.1 g of hair was weighted in 10 mL digestion vessel and gravimetrically controlled amounts of the labelled compounds were added to obtain an endogenous/labelled compound amount ratio between 0.1 and 10. The digestion of the sample was done in a CEM focused microwave unit at a fixed power of 75 W during 4.5 min, after the addition of 3 mL of 25% TMAH and a magnetic stir bar to the vial. The digested extract was adjusted to pH 4 with HCl in 4 mL of acetate buffer. Sample derivatization was carried out by manual shaking for 5 min after adding 0.4 mL of 2% w/v sodium tetra-n-ethylborate in Milli-Q water and 2 mL of hexane. The organic phase was cleaned up with homemade Florisil® columns and stored at −18 °C until analysis.

2.5. GC-ICP-MS measurements and data treatment

Hg species-specific isotope abundances were calculated for MeHg and Hg (II) as the ratio of the peak areas measured for each m/z (198, 199, 200, 201 and 202) by the sum of all peak areas. Then, mass bias was corrected as described elsewhere (Rodríguez-González et al., 2007) and the quantification of Hg (II) and MeHg was carried out by double spiking IDMS as described previously (Castillo et al., 2010). More details on the instrumental parameters are given in Table S1. For statistical analyses, IBS SPSS Statistics was used. Non-parametric tests were applied, as Hg concentrations did not follow a normal distribution. Differences between groups were tested using Kruscal-Wallis. Statistical significance was set at $p < 0.05$. The median and the interquartile range (IQR, 25th percentile and 75th percentile) were used to explain the results.

3. Results

3.1. Quality control of the measurements

Quality control of the measurements was carried out by analyzing, for each measurement session, the certified human hair reference material IAEA-086. The average results from all measurement sessions are shown in Table S2. As it can be observed, the experimental values obtained for THg and MeHg agreed well with the reference values. Also, although the IAEA-086 material is not certified for Hg(II), the experimental values were in good agreement with values obtained in previous publications (Laffont et al., 2013; Queipo Abad et al., 2017). Detection and quantification limits (LOD and LOQ, respectively) calculated from six procedural blanks are shown in Table S3. LOD and LOQ values were significantly lower than the values reported in all the hair samples analyzed in this work.

The interconversion factors determined for the reference material were statistically similar than those obtained for the hair samples as shown in Fig. S1. MeHg demethylation factor (F2) was the most relevant factor in agreement with previous results (Queipo Abad et al., 2017; Suárez-Criado et al., 2022). For most real samples, F2 (%), was lower than 5 (IQR values between 1.7% and 3.1%), except for one particular sample in which a value of 29.2% was reached. Hg(II) methylation factor (F1) was negligible for most of the samples. These interconversion reactions were considered for the calculation of the Hg species specific concentrations obtained by double spiking IDMS.

3.2. Sociodemographic study

Most of the participants (N = 96) in the study were women (77.08%, N = 74). The mean age was 36.92 years. Only 12.50% of the surveyed individuals were children ranging from 6 to 17 years. Most of the individuals (79%) had low educational levels, as 73 adults had grades below high school.

Fish intake and AGSM related tasks were considered important variables. This study was focused on general population, mostly non-involved in mining tasks. Only 16.67% of participants were involved at some point in AGSM works or in Hg involving activities. Fish consumption was classified as stated elsewhere (Calao-Ramos et al., 2021) and described in Table 1. In general, consumption of fish ranged from 3 to 7 times/week, which is between medium and high intake levels.

3.3. Methylmercury in the hair samples

MeHg concentrations in the hair samples are summarized in Fig. 1 and Table S4 According to MeHg median values, departments followed the order: Vaupés > Bolívar > Antioquia > Sucre > Chocó > Nariño. Vaupés was the region with the highest median MeHg content in hair (13.75 μg Hg g^{-1}, IQR 9.84–26.29). MeHg median value in Vaupés was statistically different from the other departments ($p < 0.05$) and no statistical difference was found among the rest of Colombian regions.

There were statistically significant differences according to gender ($p < 0.05$). Males had a median value of 8.8 μg Hg g^{-1} (IQR 0.78–16.26) and a maximum value of 45.90 μg Hg g^{-1}. On the other hand, females had a median value of 1.05 μg g^{-1} (IQR 0.54–2.74) and a maximum value of 70.36 μg Hg g^{-1}. The woman with the highest MeHg level reported a high fish consumption (7 times/week) and was not involved in AGSM tasks. In agreement with previous studies carried out in the Amazon (Crespo-Lopez et al., 2021), most of the samples presented a % of MeHg relative to THg higher than 80% as shown in Fig. S2. Statistical analyses showed that there were significant differences ($p < 0.05$) for MeHg/THg (%) when workers in ASGM were compared with people not involved in mining tasks, even if Vaupés subjects were (Fig. S3A) or were not considered (Fig. S3B).

3.4. Inorganic mercury in the hair samples

Hg(II) concentrations in the samples are also summarized in Fig. 1 and Table S4. A much lower median value than that of MeHg was obtained (0.14 μg Hg g^{-1}). Vaupés was also the region with the highest median Hg(II) value (0.86 μg Hg g^{-1}), being again statistically different from the other departments. Antioquia and Bolívar had the same median value of 0.11 μg Hg g^{-1} (IQR 0.06–0.43 and 0.05–0.11, respectively). The order of the departments, according to median values for Hg(II) was Vaupés > Antioquia = Bolívar > Nariño > Sucre > Chocó.

According to gender, women and men were statistically different ($p < 0.05$). A 4-times greater median value (0.44 μg Hg g^{-1}) was obtained for males than for females (0.11 μg Hg g^{-1}) (IQR 0.12–0.93 and 0.07–0.41, respectively). The maximum value for males was 42.14 μg Hg g^{-1} and for females 33.62 μg Hg g^{-1}.

Among all the participants, only one individual from Chocó had a

Table 1
Descriptive variables of Colombian individuals (n = 96) distributed by departments.

	All Departments (n = 96)	Chocó (n = 20)	Sucre (n = 5)	Nariño (n = 22)	Bolívar (n =12)	Antioquia (n = 6)	Vaupés (n = 31)
Gender, female (%)	77.08	75.00	60.00	90.91	83.33	100.00	64.52
Mean Age (years)	36.92	43.00	22.40	44.05	22.75	32.33	36.65
Fish consumption (%)							
<1 times/week	6.25	30.00	–	–	8.33	–	–
1–2 times/week	20.83	15.00	40.00	59.09	–	33.33	–
3–4 times/week	36.46	35.00	20.00	36.36	91.67	66.67	12.90
5–7 times/week	36.46	20.00	40.00	4.55	8.33	–	87.10
AGSM or Hg involving tasks (%)	16.67	15.00	–	50.00	–	33.33	–

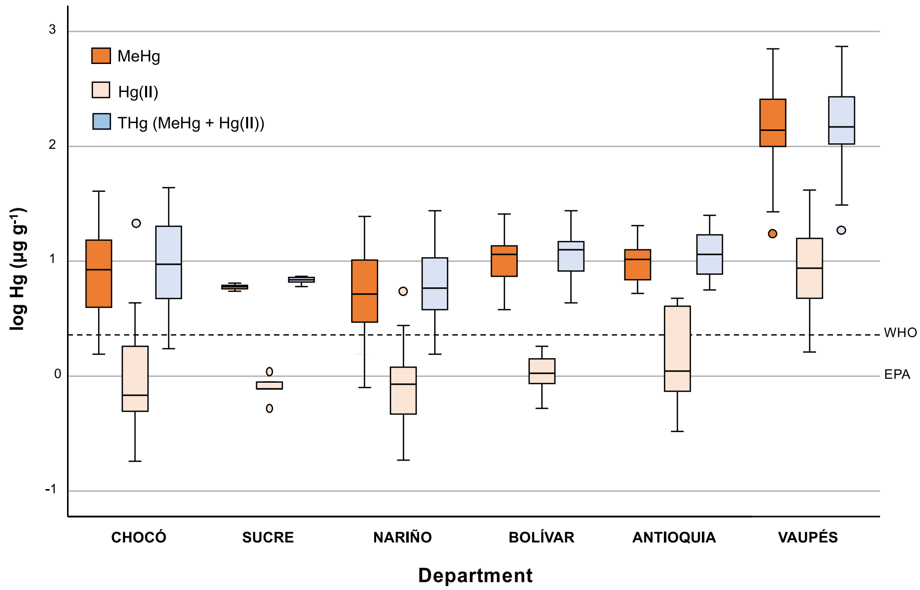

Fig. 1. MeHg, Hg(II) and THg (MeHg + Hg(II)) concentrations (μg Hg g^{-1}) obtained in the hair samples of the different Colombian departments. Dashed line represents the WHO (JECFA, 2006) limit of 2.2 μg Hg g^{-1}, and continuous line is USEPA (2005) limit of 1.0 μg Hg g^{-1}.

higher concentration level of Hg(II) than MeHg (2.11 and 1.05 μg Hg g^{-1}, respectively). This male individual reported a medium fish consumption level (3–4 times/week) and had been using Hg in his current employment for 24 months, but he did not amalgamate either at home or at work.

In all the subjects the average value of Hg(II) relative to THg was 11% and only 10 individuals had a Hg(II) content over 30%. No significant differences ($p > 0.05$) were found when the amount of Hg(II) was compared between people involved in AGSM task and people not involved (Fig. S4). Interestingly, significant differences among the evaluated groups ($p < 0.05$) where found when the percentage of Hg (II)/THg of the groups were compared (Fig. 2). In fact, people involved in AGSM tasks showed 1.7 times higher Hg(II)/THg (%) vs. people not involved, when Vaupés individuals were included ($p = 0.020$) (Fig. 2A) or were not ($p = 0.025$) (Fig. 2B).

3.5. Total mercury in the hair samples

The references doses (RfD) of weekly acceptable MeHg intake established by the EPA (USEPA, 2005) and WHO (JECFA, 2006) are equivalent to 1 μg Hg g^{-1} and 2.2 μg Hg g^{-1} of THg in hair, respectively.

In our study, THg concentrations were obtained from the sum of MeHg and Hg(II) concentrations by ID-GC-ICP-MS. THg results are summarized in Fig. 1 and Table S4. Median THg values were under the RfD WHO value for all the departments, excepting Vaupés, with levels 7 times higher (14.66 μg Hg g^{-1}, IQR 10.07–27.80). This is in agreement with previous reports (Calao-Ramos et al., 2021), that also obtained the highest THg concentration values for the Vaupés region in comparison to the other Colombian departments. Considering the EPA value, median concentration of THg obtained from all departments is higher than the weekly acceptable MeHg intake. According to THg median values, departments followed the same order as that for MeHg, excepting Chocó region with a median value higher than Sucre.

In all departments there was at least one individual above the WHO weekly acceptable MeHg intake. The THg concentration values of 25% of the samples were more than 4 times higher than the WHO level. In Vaupés, IQR values were between 4 and 12 times higher. The female individual with the highest THg concentration in hair (73.72 μg Hg g^{-1}) was the same woman that also had the highest MeHg concentration. No differences were observed among regions excluding Vaupés, which was statistically different from all departments ($p < 0.05$). THg

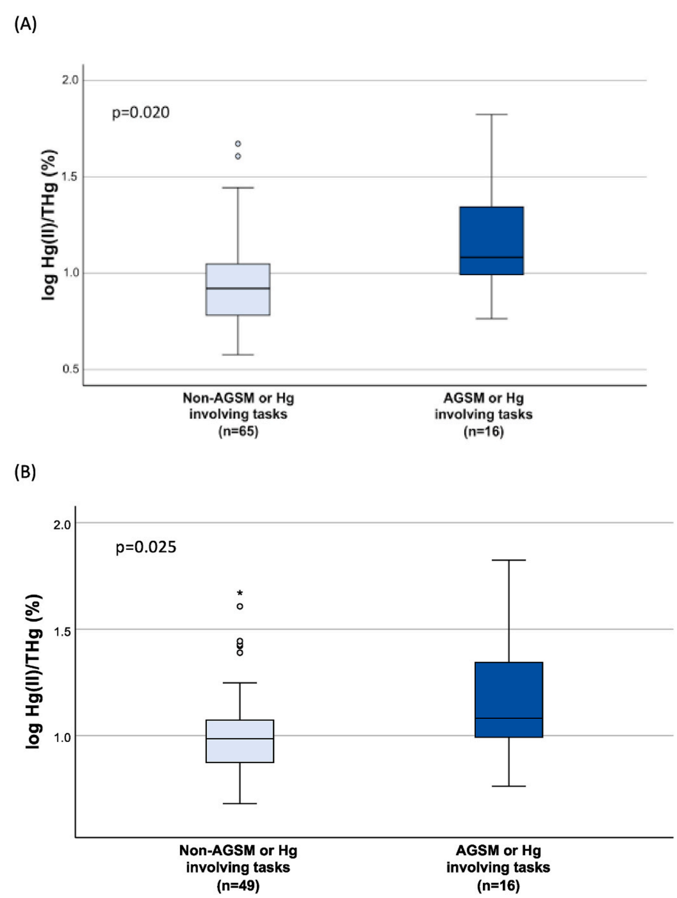

Fig. 2. Ratio of Hg(II)/THg (%) in hair of the Colombian individuals in relation to Hg involving tasks including Vaupés (A), not including Vaupés (B).

concentrations were higher in males with a median value of 11.49 µg Hg g^{-1}, than in females, with a median value of 1.21 µg Hg g^{-1}.

4. Discussion

4.1. Consumption of contaminated fish

In this study hair was used as biomarker to study human exposure to mercury species in different Colombian regions. MeHg content in hair is usually associated with dietary habits. Thus, we studied the relationship between MeHg concentration in hair and the fish consumption per week. Table 1 shows that Vaupés is the region in which more than 85% of individuals reported a high level of consumption (5–7 times per week). This could mainly explain the high MeHg levels in hair samples from Vaupés (up to 70.36 µg Hg g^{-1}). In addition, Vaupés is part of the Amazonian region, where the increased deforestation and biomass burning lead to an increase of Hg levels and, consequently, MeHg content in fishes in the Amazon is also expected to be higher than those of the Andean regions (Crespo-Lopez et al., 2021).

Fig. 3 shows that were no differences between individuals with a frequency of fish consumption less than 1, 1–2 and 3–4 times per week. However, the median of those individuals consuming the highest frequency of fish (5–7 times per week) was significantly ($p < 0.05$) higher (12.5 µg Hg g^{-1}) than the rest of consuming groups. These results agree with studies (Xie et al., 2021; Shao et al., 2013) indicating that fish consumption is an important factor for the hair MeHg accumulation. Likewise, this can be explained by the origin of most the individuals of this group (i.e. Vaupés), similar to the previous results reported (Calao-Ramos et al., 2021), that found the second highest MeHg concentration in hair in Vaupés in comparison to seven Colombian departments (e.g. Antioquia, Bolívar, Cauca, Córdoba, Caldas, Guainía and Putumayo).

Our data showed that most of the samples which present a %MeHg relative to THg higher than 95% are associated with high THg concentrations (Fig. S2). This would indicate high level of consumption of contaminated fish by these individuals. Our results show that when MeHg concentration is high, Hg(II) concentration is also high, despite of the fact that its percentage content is below 5%. Most of the individuals with the lowest %Hg(II) are originally from Vaupés as they are not involved in AGSM tasks. This Hg(II) could come from a demethylation pathway in the organism and would be incorporated in hair, distinguishing from the Hg(II) directly deposited/adsorbed from Hg vapors (Koenigsmark et al., 2021). In order to prove this, further studies on isotope fractionation of mercury species in hair should be carried out.

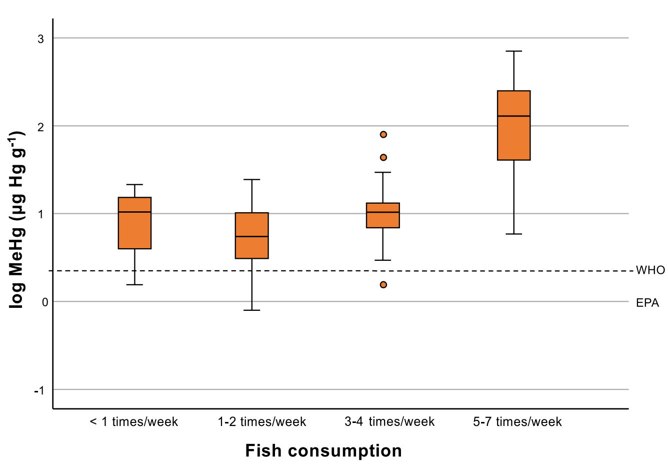

Fig. 3. MeHg concentration (log MeHg, µg Hg g^{-1}) in hair of the Colombian samples for each group of fish consumption (times/week). Dashed line represents the WHO (JECFA, 2006) limit of 2.2 µg Hg g^{-1}, and continuous line is USEPA (2005) limit of 1.0 µg Hg g^{-1}.

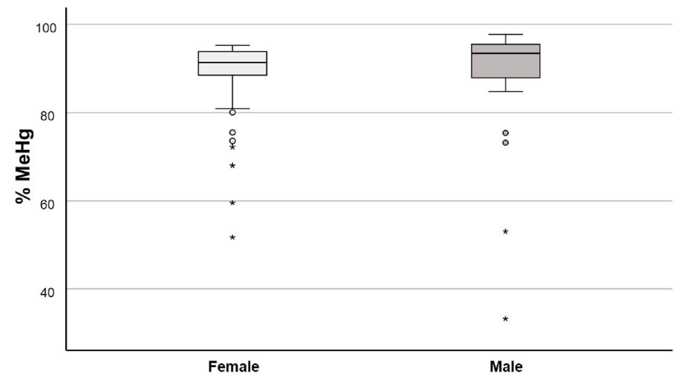

Fig. 4. Percentage of MeHg relative to THg classified by gender.

Fig. 4 shows that no statistical differences ($p > 0.05$) between males and females were found when comparing the %MeHg relative to THg despite MeHg concentrations are higher in males. This could be explained by the fact that males ingest a higher quantity of fish in the same number of meals than females (Díez et al., 2008).

4.2. Exposure to Hg vapors

Direct exposure to mercury vapors leads to Hg(II) adsorption onto hair. From the 96 individuals analyzed in this work, only 16, mostly from the region of Nariño, declared to be directly exposed to Hg vapors through burning amalgam either at work or at home.

In Fig. S4, we compare the Hg(II) concentrations in hair of the individuals in relation to Hg involving tasks, including (Fig. S4A) and excluding Vaupés department (Fig. S4B) due to the statistical differences with the other department values. No differences between the two groups were found. Nevertheless, median values of people uninvolved in Hg activities are slightly lower than the median values of the other group (0.08 µg Hg g^{-1} and 0.09 µg Hg g^{-1}, respectively). It is likely that, although most of the individuals in the study are not voluntary exposed to mercury burning vapors, they could have been indirectly exposed, due to the location of their homes near the sites where amalgams are burned such as processing centres (*entables*), or even in the backyards of houses at the communities.

4.3. Comparison with other colombian studies

Most of the studies of Hg in hair samples carried out in Colombian population have been focused on THg and only a few present MeHg values. In those studies, Hg(II) values were calculated from the difference of THg and Hg(II). Table 2 shows the summary of previous works reporting MeHg and THg in hair from individuals of different Colombian regions mainly mining areas. The values reported by previous studies for the Chocó region are a little heterogeneous (Gutiérrez-Mosquera et al., 2018; Palacios-Torres et al., 2018; Salazar-Camacho et al., 2017). The mean value obtained in this study is between the value obtained in 2018 by Palacios-Torres et al. (2018) obtained for the Paimado region and the mean value obtained in 2017 by Salazar-Camacho et al. (2017). The mean MeHg value reported by Salazar-Camacho et al. (2017) is about 1 µg Hg g^{-1} above the value reported in this study.

The values obtained in Córdoba department (Calao-Ramos et al., 2021; Gracia et al., 2010, 2016; Marrugo-Negrete et al., 2013) could be compared with those obtained from Antioquia, Sucre (Argumedo et al., 2013; Olivero-Verbel et al., 2016) and Bolívar (Carranza-Lopez et al., 2019; Olivero-Verbel et al., 2011; Olivero et al., 1995) regions, as these four regions are adjacent, and some of their territories conform the Mojana region (Diaz et al., 2020) (Fig. S5). Mean and median THg values of these departments are below 5 µg Hg g^{-1}, excepting the values of a study focused on a population living near a hydroelectric tropical dam

Table 2
Summary of THg and MeHg concentration (μg Hg g^{-1}) obtained in several studies from different Colombian regions. [a]Mean ± SD; [b]Median (range).

Department	THg ± SD (Max-Min)	MeHg ± SD (Max-Min)	Remarks	Reference
Chocó	2.48 ± 3.69[a] (n = 81)	2.70 ± 3.64[a] (n = 81)	Mining area	Salazar-Camacho et al. (2017)
Chocó	Men 15.98[b] (n = 63) Women 8.55[b] (n = 63)	–	Mining area	Gutiérrez-Mosquera et al. (2018)
Chocó	Quibdo 6.72 ± 0.89[a] (n = 248) Paimado 0.87 ± 0.08[a] (n = 112) Atrato River Basin 4.90 ± 0.63[a] (n = 360)	–	Mining area	Palacios-Torres et al. (2018)
Chocó	**0.93 ± 1.08[a] (n = 20)** **0.95 (4.32–0.17)[b]**	**0.78 ± 0.93[a] (n = 20)** **0.84 (4.06–0.15)[b]**	**Mining area**	**This study**
Córdoba	2.18 ± 1.77[a] (n = 112)	–	Mining area	Gracia et al. (2010)
Córdoba	6.95 ± 5.57[a] (n = 76)	–	Population living near a hydroelectric tropical dam	Marrugo-Negrete et al. (2013)
Córdoba	2.46 ± 1.77[a] (n = 175)	–	Fish consume	Gracia et al. (2016)
Córdoba	2.57[b] (n = 20)	1.30[b] (n = 20)	Miners	Calao-Ramos et al. (2021)
Antioquia	4.37[b] (n = 28)	1.18[b] (n = 28)	Miners	Calao-Ramos et al. (2021)
Antioquia	**1.16 ± 0.71[a] (n = 6)** **1.15 (2.54–0.56)[b]**	**1.00 ± 0.54[a] (n = 6)** **1.04 (2.05–0.52)[b]**	**Mining area**	**This study**
Sucre	4.91 ± 0.55[a] (n = 94)	–	Mining area	Olivero et al. (1995)
Sucre	Men 0.65 ± 0.32[a] Women 0.32 ± 0.07[a] (n = 20)	Men 0.52 ± 0.25[a] Women 0.27 ± 0.06[a] (n = 20)	Contaminated rice	Argumedo et al. (2013)
Sucre	**0.66 ± 0.22[a] (n = 5)** **0.67 (0.99–0.39)[b]**	**0.57 ± 0.16[a] (n = 5)** **0.59 (0.74–0.35)[b]**	**Mining area**	**This study**
Bolívar	2.84 ± 3.37[a] (n = 219)	–	Fishers, miners and others	Olivero et al. (1995)
Bolívar	1.56 ± 0.06[a] (n = 1328)	–	Mining area	Olivero-Verbel et al. (2011)
Bolívar	3.07 ± 0.14[a] 2.02[b] (n = 522)	–	Mining area	Carranza-;López et al. (2019)
Bolívar	1.43 ± 0.07[a] 1.23[b] (n = 194)	–	Teenagers	Manjarres-Suarez and Olivero-Verbel (2020)
Bolívar	0.90[b] (n = 27)	1.05[b] (n = 27)	Miners	Calao-Ramos et al. (2021)
Bolívar	**1.17 ± 0.68[a] (n = 12)** **1.27 (2.72–0.43)[b]**	**1.06 ± 0.65[a] (n = 12)** **1.15 (2.58–0.38)[b]**	**Mining area**	**This study**
Mojana (Sucre, Bolívar, Córdoba, Antioquia)	2.3[b] (n = 269)	–	Pregnant women and girls	Mireya Diaz et al. (2020)
Cauca	0.81[b] (n = 45)	0.47[b] (n = 45)	Miners	Calao-Ramos et al. (2021)
Putumayo	1.36[b] (n = 32)	2.01[b] (n = 32)	Miners	Calao-Ramos et al. (2021)
Vaupés	6.06[b] (n = 27)	3.87[b] (n = 27)	Miners	Calao-Ramos et al. (2021)
Vaupés	**14.92 ± 16.88[a] (n = 31)** **14.66 (73.72–1.88)[b]**	**14.02 ± 15.93[a] (n = 31)** **13.75 (70.36–1.72)[b]**	**Mining area**	**This study**
Amazonas	17.3 ± 0.6[a] (n = 200)	–	Mining area	Olivero-Verbel et al. (2016)
Amazonas	23.0 ± 1.2[a] (n = 110)	–	Mining area	Valdelamar-Villegas and Olivero-Verbel (2020)

(Marrugo-Negrete et al., 2013). In Bolívar region there were THg mean values registered from 1995, which are above mean values obtained in this study. The rest of the values listed in Table 2 for Bolívar region are also above the values reported in this study, except the one reported by Calao-Ramos et al. (2021), who also determined MeHg values. In fact, the MeHg median value obtained in this work is similar to that obtained by Calao-Ramos et al. (2021). MeHg values reported here from Sucre are similar to the values reported in 2001 for men in a study focused on contaminated rice consumers (Argumedo et al., 2013). MeHg values for Antioquia are also very similar to the ones obtained by Calao-Ramos et al. (2021).

We have not found any previous study reporting MeHg or THg values in populations from Nariño. However, there are some previous studies of Cauca and Putumayo departments, which are adjacent to Nariño (Calao-Ramos et al., 2021). The reported values from Cauca (Calao-Ramos et al., 2021) for MeHg and THg are similar to those obtained here.

The mean THg value of Vaupés region obtained in our work are very similar to the mean values obtained in other Amazonian departments (Olivero-Verbel et al., 2016), and much lower than values obtained in the Yaigojé Apaporis National Natural Park, in the Colombian Amazon (Valdelamar-Villegas and Olivero-Verbel, 2020). The difference in concentration of the values of the Amazonian regions with the other Colombian regions stands out. The previously reported median MeHg value for Vaupés region was 3.5 times lower than the value obtained in this study (Calao-Ramos et al., 2021).

The other studies (Calao-Ramos et al., 2021; Salazar-Camacho et al., 2017) that also determined MeHg values found a correlation with THg values and confirm dietary habits as the main exposition source. We could not find any study discussing Hg(II) sources in hair. Two potential sources may explain the presence of Hg(II) in hair: demethylation of MeHg obtained through the diet or direct adsorption of gaseous mercury from the atmosphere. Mercury isotope fractionation studies could provide insights into this question and should be carried out on real hair samples.

5. Conclusions

In this study, MeHg and Hg(II) were measured in hair samples of 96 individuals from six different Colombian regions. Samples were analyzed by ID-GC-ICP-MS, enabling accurate determinations due to the correction of species interconversion during sample preparation. In agreement with previous works (Calao-Ramos et al., 2021; Olivero-Verbel et al., 2016; Valdelamar-Villegas and Olivero-Verbel, 2020), the highest concentration values for mercury species were obtained for the Amazonian department of Vaupés, where highly amounts of contaminated fish are consumed. The MeHg and Hg(II) values obtained in the rest of departments were significantly lower than those obtained in Vaupés, but not statistically different between them. Men presented higher mercury species concentrations than women, but the same species percentages according to THg. This is probably due to the higher amount of fish consumed by men compared to women in the same number of meals. As expected, individuals consuming the highest frequency of fish (5–7 times per week) had significantly higher values than those of the other consuming groups. The median level of Hg(II) of persons involved in AGSM tasks was higher, however not significant ($p > 0.05$) than the rest of the individuals participating in this study. Nevertheless, significant differences among persons involved and uninvolved in ASGM tasks were found when the percentage of the Hg (II)/THg ratio of these groups were matched (x 1.7-fold). The results reported here contribute to broaden the information of Colombian populations affected by AGSM, and suggest that Hg(II) determination by IDMS-GC-ICP-MS could be a good proxy to unravel Hg(II) adsorption by direct exposure to mercury vapors onto hair, if any demethylation pathway could be ruled out by further experiments using isotopic techniques.

Credit author statement

Laura Suárez-Criado: Writing – original draft, Investigation, Methodology; **Pablo Rodríguez-González**: Supervision, Resources, Writing – review & editing; **José Marrugo-Negrete**: Conceptualization, Supervision, Project administration, Funding acquisition; **J. Ignacio García Alonso**: Supervision, Resources; **Sergi Díez:**Conceptualization, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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