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

Carlos Salazar-Camacho[b], Manuel Salas-Moreno[b], Siday Marrugo-Madrid[a], José Marrugo-Negrete[a,*], Sergi Díez[c,*]

[a] University of Córdoba, Faculty of Basic Sciences, Department of Chemistry, Water, Applied and Environmental Chemistry Group, Laboratory of Toxicology and Environmental Management, Montería, Colombia

[b] Faculty of Natural Sciences, Department of Biology, Universidad Tecnológica del Chocó, A.A. 292 Quibdó, Colombia

[c] Environmental Chemistry Department, Institute of Environmental Assessment and Water Research, IDÆA-CSIC, E-08034 Barcelona, Spain

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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

* Corresponding authors.
E-mail addresses: jlmarrugon@hotmail.com (J. Marrugo-Negrete), sergi.diez@idaea.csic.es (S. Díez).

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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