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Assessment of mercury exposure among small-scale gold miners using mercury stable isotopes

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ABSTRACT

Total mercury (Hg) concentrations in hair and urine are often used as biomarkers of exposure to fish-derived methylmercury (MeHg) and gaseous elemental Hg, respectively. We used Hg stable isotopes to assess the validity of these biomarkers among small-scale gold mining populations in Ghana and Indonesia. Urine from Ghanaian miners displayed similar Δ^{199}Hg values to Hg derived from ore deposits (mean urine Δ^{199}Hg=0.01‰, n=6). This suggests that urine total Hg concentrations accurately reflect exposure to inorganic Hg among this population. Hair samples from Ghanaian miners displayed low positive Δ^{199}Hg values (0.23–0.55‰, n=6) and low percentages of total Hg as MeHg (7.6–29%, n=7). These data suggest that the majority of the Hg in these miners' hair samples is exogenously adsorbed inorganic Hg and not fish-derived MeHg. Hair samples from Indonesian gold miners who eat fish daily displayed a wider range of positive Δ^{199}Hg values (0.21–1.32‰, n=5) and percentages of total Hg as MeHg (32–72%, n=4). This suggests that total Hg in the hair samples from Indonesian gold miners is likely a mixture of ingested fish MeHg and exogenously adsorbed inorganic Hg. Based on data from both populations, we suggest that total Hg concentrations in hair samples from small-scale gold miners likely overestimate exposure to MeHg from fish consumption.

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1. Introduction

Humans today are primarily exposed to methylmercury (MeHg) through fish consumption and gaseous elemental mercury (GEM) through inhalation of GEM released from dental fillings and during small-scale gold mining activities. Methylmercury can cause severe central nervous system damage and developmental delays (Clarkson, 2002; Clarkson and Magos, 2006; Grandjean et al., 1999), while exposure to high levels of GEM can cause tremors, neurological disorders, and kidney damage (Böse-O'Reilly et al., 2000; Veiga et al., 2005). To assess the health effects and risks of exposure to these two forms of mercury (Hg), epidemiological studies often use conveniently measured biomarkers as a proxy for Hg concentrations in vital internal organs. Hair total Hg concentrations are often used as a proxy for MeHg exposure from fish consumption (Goodrich et al., 2012; Paruchuri et al., 2010). Methylmercury is concentrated in human hair and, among populations that consume fish, the majority of the Hg in hair is MeHg (>80%; Berglund et al., 2005; McDowell et al., 2004). Similarly, because the majority of inhaled GEM is rapidly oxidized in the bloodstream and excreted in urine (Clarkson et al., 2007; Suzuki et al., 1992), total Hg concentrations in urine are commonly used as a measure of GEM exposure (Berglund et al., 2005; McDowell et al., 2004; Paruchuri et al., 2010). However, in populations that eat large quantities of fish or are occupationally exposed to high levels of GEM, total Hg concentrations in human hair and urine may not accurately reflect exposure to MeHg and/or GEM (Abe et al., 1995; Laffont et al., 2011; Li et al., 2008a, 2008b; Ohno et al., 2007; Sherman et al., 2013; Suzuki et al., 1992; Wilhelm et al.,

Abbreviations: ; MeHg, Methylmercury; GEM, gaseous elemental mercury; Hg, mercury; ASGM, artisanal and small-scale gold mining; Au, gold; MDF, mass-dependent fractionation; MIF, mass-independent fractionation; IPEN, International Persistent Organic Pollutants Elimination Network; MC-ICP-MS, multi-collector inductively-coupled plasma mass spectrometry

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1996).

Globally, one of the largest sources of anthropogenic Hg emissions (410–1040 metric tons annually; United Nations Environment Programme, 2013) is artisanal and small-scale gold mining (ASGM). Although at least 10–15 million people in over 70 countries are engaged in ASGM (Jennings, 1999; Swain et al., 2007; Veiga et al., 2005), these operations are very difficult to regulate because they are often located in impoverished rural areas (Hilson and Pardie, 2006; Jennings, 1999). Most small-scale gold miners lack awareness of Hg toxicity and use Hg to amalgamate gold (Au) because it has been effective and affordable and appropriate alternatives have not been widely established (Styles et al., 2010; Telmer and Veiga, 2009). Because Hg–Au amalgams are burned to separate the Au, miners and surrounding communities are exposed to high concentrations of GEM (Veiga et al., 2005). ASGM also releases Hg to local waterways (United Nations Environment Programme, 2013), which can be biologically methylated and bioaccumulated in aquatic ecosystems (Donkor et al., 2006). This can result in elevated MeHg exposure due to consumption of local fish (Barbosa et al., 2001; Lebel et al., 1998).

Recent studies have used Hg stable isotope ratios both to distinguish between human exposure to MeHg and GEM and to re-evaluate the use of total Hg concentrations in hair and urine as exposure biomarkers (Laffont et al., 2009, 2011; Sherman et al., 2013). The seven stable isotopes of Hg (196–204 amu) can undergo mass-dependent fractionation (MDF, Eq. (1)) during biogeochemical reactions including methylation (Rodríguez-González et al., 2009) and demethylation (Bergquist and Blum, 2007; Kritee et al., 2009).

$$\delta^{xxx}\mathrm{Hg}(‰) = \left(\left[\left({}^{xxx}\mathrm{Hg}/{}^{198}\mathrm{Hg}\right)_{sample}/\left({}^{xxx}\mathrm{Hg}/{}^{198}\mathrm{Hg}\right)_{\mathrm{SRM\ 3133}}\right]-1\right) \times 1000 \quad (1)$$

In Eq. (1), ^{xxx}Hg is an isotope of Hg and SRM 3133 is a National Institute of Standards and Technology Standard Reference Material (Blum and Bergquist, 2007). Mercury isotopes can also undergo mass-independent fractionation (MIF, Eq. (2)), which is reported as the deviation of a measured isotope ratio from the ratio theoretically predicted to result from MDF.

$$\Delta^{xxx}\mathrm{Hg} = \delta^{xxx}\mathrm{Hg} - (\delta^{202}\mathrm{Hg} \times \beta) \quad (2)$$

In Eq. (2), β is equal to 0.252 for ^{199}Hg and 0.752 for ^{201}Hg for kinetic reactions (Blum and Bergquist, 2007). The greatest magnitude of MIF of Hg isotopes occurs during photochemical reactions (Bergquist and Blum, 2007; Buchachenko, 2001). Because only the odd-mass-number isotopes have unpaired nuclear spin and nuclear magnetic moments, the odd- and even-mass-number isotopes recombine at different rates, resulting in an over-abundance of the odd- or even-mass-number isotopes in the reaction products.

Large positive MIF of Hg isotopes has been widely observed in fish muscle tissue (Bergquist and Blum, 2007; Perrot et al., 2012; Senn et al., 2010; Sherman and Blum, 2013). However, biotic processes have not been shown to produce MIF of Hg isotopes (Kritee et al., 2007, 2009; Kwon et al., 2012; Rodríguez-González et al., 2009) and abiotic reactions in the absence of light produce only limited MIF ($< \sim 0.3‰$; Estrade et al., 2009; Ghosh et al., 2013; Zheng and Hintelmann, 2010). It is hypothesized, therefore, that photochemical demethylation of MeHg in aquatic systems causes the preferential loss of the even-mass-number isotopes of Hg, resulting in an excess of the odd-mass-number isotopes of Hg in the remaining aqueous MeHg (Bergquist and Blum, 2007). As a result, the MeHg that subsequently enters the food web and is bioaccumulated displays positive Δ^{199}Hg values (Bergquist and Blum, 2007; Perrot et al., 2012; Senn et al., 2010; Sherman and Blum, 2013). These positive Δ^{199}Hg values are preserved through the food web to higher trophic level consumers including humans (Laffont et al., 2011; Li et al., 2014; Sherman et al., 2013). In contrast, the Hg in geologic ore deposits that is mined for use in industrial processes and ASGM does not display significant MIF of Hg isotopes because it has not undergone photochemical cycling (Cooke et al., 2013; Foucher et al., 2009; Hintelmann and Lu, 2003; Laffont et al., 2011; Smith et al., 2008; Stetson et al., 2009; Yin et al., 2013).

These differences in MIF can be used to distinguish between human exposure to fish-derived MeHg and ore-derived inorganic Hg (Laffont et al., 2009, 2011; Li et al., 2014; Sherman et al., 2013). Sherman et al. (2013) measured Hg isotope ratios in hair samples from a cohort of U.S. dentists who ate primarily open-ocean fish (e.g., tuna). Mercury in hair samples from these individuals displayed similar positive Δ^{199}Hg values as those measured in open-ocean fish (Sherman et al., 2013). This suggests that in this population, hair total Hg concentrations are a good measure of exposure to fish-derived MeHg. In contrast, among Bolivian ASGM communities, Laffont et al. (2011) found that a significant amount of inorganic Hg was exogenously adsorbed to the hair and not derived from fish MeHg.

Sherman et al. (2013) also measured Hg isotope ratios in urine samples from the same U.S. dentists from whom hair was analyzed, and concluded that Hg in the urine was a mixture of inhaled GEM derived from their dental fillings ($\Delta^{199}\mathrm{Hg} = 0‰$) and demethylated MeHg derived from consumed fish ($\Delta^{199}\mathrm{Hg} \gg 0‰$). This suggests that among people who eat large amounts of fish, total Hg concentrations in urine may overestimate exposure to GEM. However, urine total Hg concentrations may be an accurate reflection of exposure to inhaled GEM among small-scale gold miners who experience elevated GEM exposure. We conducted the study reported here to further assess the accuracy of urine and hair total Hg concentrations as biomarkers for inorganic and MeHg exposure among individuals in ASGM communities.

2. Methods

2.1. Sample collection: Ghana

Gold mining using Hg amalgamation has been conducted in Ghana since the 1800s (Bawa, 2010). Amalgams are usually burned in the open-air of household yards using small kerosene torches, releasing large amounts of GEM to the local environment (Paruchuri et al., 2010; Styles et al., 2010; Veiga et al., 2005). As part of a larger study to investigate the health impacts of ASGM, hair, urine and soil samples were collected from the mining community of Kejetia in the Upper East region of Ghana during two sampling campaigns (May–June 2010 and May–July 2011). Households ($n=54$) were selected for study participation using convenient (Paruchuri et al., 2010) and random sampling methods in 2010 and 2011, respectively. Adults in each selected household ($n=118$) were verbally surveyed regarding demographic characteristics, occupational histories, health, and diets. Members of this community typically eat only small amounts of dried fish or fish paste as a condiment or as seasoning in soup. It was not possible, therefore, to accurately determine the types or quantities of fish that each individual consumed. Spot urine samples ($\sim$20–50 mL) were collected into Hg-free containers and stored at room temperature until they could be frozen. Hair samples were collected close to the scalp from the occipital region and wrapped in paper (Goodrich et al., 2012). Soil samples were collected from an outdoor common area ("yard") identified by the head of each selected household. In each yard, surface soils were collected using acid-cleaned plastic spoons and mixed together from the four corners

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