Environmental Research 150 (2016) 592–599

Contents lists available at ScienceDirect

Environmental Research

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

Assessment of mercury exposure in human populations: A status report from Augusta Bay (southern Italy)

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ARTICLE INFO

Article history:
Received 9 July 2015
Received in revised form
8 September 2015
Accepted 12 January 2016
Available online 19 January 2016

Keywords:
Mercury
Toxicity
Human biomonitoring

ABSTRACT

Here we investigate mercury concentrations in the blood (HgB), urine (HgU) and human hair (HgH) of 224 individuals from a coastal area (Eastern Sicily, SE Italy) strongly affected by Hg contamination from one of the largest chlor-alkali plants in Europe. The factors affecting the distribution of Hg and the extent of the exposure of individuals have been explored with a multidisciplinary approach. Multiple regression analyses, together with evidence of high levels of HgB (exceeding the HBMI recommended levels in 50% of cases) and HgH (exceeding the EPA reference dose in 70% of cases), primarily suggest that the consumption of local fish is the main source of Hg for humans. no. significant exposure to inorganic mercury was identified. Toxicokinetic calculations produced a provisional tolerable weekly intake (PTWI) level that, in most cases, exceeds international recommendations, particularly for residents in the studied area.

1. Introduction

Due to its high versatility, mercury (Hg) is used intensively in a number of human activities such as industry, pharmacology, gold mining and agriculture. Among the anthropogenic contributions, chlor-alkali plants contribute up to 15% of total European Hg anthropogenic emissions (Pacyna et al., 2001). Unfortunately, the use of Hg is often connected to straight environmental damage that could be possibly associated with episodes of human intoxication (De Flora et al., 1994; Sanfeliu et al., 2003; Baird and Cann 2004). Organometallic methylmercury (MHg), which is primarily ingested through a seafood diet, is the most dangerous Hg form and, due to its high solubility in lipids, can have adverse effects on the liver, reproductive organs (JOINT FAO/WHO, 2003), and central and peripheral nervous systems (Sanfeliu et al., 2003; Pinheiro et al., 2006, 2007; Crespo-Lopez et al., 2007). Furthermore, the capacity of MHg to cross the placental barrier represents a dangerous risk for proper fetal development (Guzzi, La Porta, 2008). On the other hand, exposure to metallic mercury (Hg°) and inorganic mercury (IHg), which mainly occurs in occupational environments or by releases from amalgam fillings (WHO, 2003), is usually associated with brain and kidney diseases (WHO, 1991; Clarkson and Magos, 2006). Over the past century, increasing awareness of the risks to human health associated with environmental Hg exposure (Guzzi and La Porta, 2008) was the stimulus behind intensive and specific human biomonitoring programs aimed at assessing levels of Hg exposure and environmental risks for groups of individuals living in close proximity to highly contaminated sites (Angerer et al., 2007). Once ingested, MHg is rapidly absorbed into the red blood cells, bound to hemoglobin and distributed to the tissues and brain, where it is slowly converted to IHg, probably at a rate of about 1% of the body burden per day (Clarkson and Magos, 2006; Guzzi and La Porta, 2008). As a consequence, Hg concentrations in blood (HgB) usually increase with the frequency of fish consumption, and are widely used as a tracer exposure to MHg (Wilhelm et al., 2004). Together with HgB, investigations of mercury in human hair (HgH) can also reflect MHg exposure (Airey, 1983; Matsubara and Machida, 1985; Shao et al., 2013). However, due to the high stability of the Hg incorporated in scalp hair (with a nearly stable growth rate of 1 mm/month; Phelps et al., 1980; WHO, 1990), it is generally adopted as a specific tracer in the assessment of Hg exposure on a time-scale ranging from weeks to months (JECFA, 2003). Finally, Hg in urine (HgU) is used extensively as a biological marker to assess chronic exposure to inorganic Hg, mainly in the form of Hg°, in humans (WHO, 2003; Barregard et al., 2006). This is because, once inhaled, the Hg° vapor is absorbed by the lungs and eliminated through urine and fecal excretions (Guzzi and La Porta, 2008). The petrochemical district of Priolo (SE Italy), which is delimited by the municipalities of Augusta, Melilli and Priolo, is a highly polluted area affected by the

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http://dx.doi.org/10.1016/j.envres.2016.01.016
0013-9351/

uncontrolled discharge of chemical pollutants from industry (Ausili et al., 2008). In particular, since the early 1960s, Augusta has hosted one of the largest chlor-alkali plant in Europe (Le Donne and Ciafani, 2008) which has discharged huge amounts of Hg into the environment. Although discharge activities were definitively stopped in 2005 (Colombo et al., 2005), the Hg contamination from the chlor-alkali plant is by far the most important environmental issue. Indeed recent investigations have denounced a severe state of degradation in the Augusta's sediment (up to 788 mg kg^{-1}) (ICRAM, 2008; Bellucci et al., 2012; Sprovieri et al., 2011; Orecchio and Polizzotto, 2013) and evasional fluxes into atmosphere (9.7 ± 0.1 g d^{-1}; Bagnato et al., 2013). Ecotoxicological investigations in the area have revealed crucial DNA damage in mussels and red mullet (Ausili et al., 2008; ICRAM, 2008) and genotoxic harm in *Coris julis* (Tomasello et al., 2012). Recently, Bonsignore et al. (2013) have reported high levels of Hg in different species of fish collected from both inside and outside Augusta Bay (up to 2.7 and 9.7 μg g^{-1} in muscles and liver respectively) and the relative values of target hazard quotient (THQ) and estimated weekly intake (EWI) have advised that the consumption of fish from this area could represent a serious risk to the health of local human populations. Moreover, using Hg isotopic signatures from sediment, fish and human hair, Bonsignore et al. (2015) traced the sources and processes that transfer this contaminant from the sediment to the human population in the Augusta environment. Furthermore, significant human health concerns, including an alarming increase in spontaneous abortions, neonatal malformations and mortality rate have been denounced in this area, especially in Augusta (Madeddu et al., 2001, 2003; Bianchi et al., 2004).

The objective of this study is to assess and quantify the human exposure to Hg in the Augusta area and the key factors that influence the distribution and extent of the contamination. The Hg content in blood, urine and hair were discussed with regard to the frequency of local fish consumption, gender, age, body mass index (BMI) and education level. A toxicokinetic model was used in order to determine the effective dietary MHg intake. Moreover the estimated dietary intake previously reported for fish collected in the area (Bonsignore et al., 2013) was used to predict the expected Hg concentration in blood in individuals with exclusive local fish-based diet.

2. Materials and methods

2.1. Sample design

Randomly selected individuals living in the Augusta, Melilli and Priolo municipalities (Fig. 1) were contacted by phone and asked to participate in the biomonitoring study. A sample (~1% of the total population for each town), stratified according to the age and gender of the participants, was used to represent the entire municipality (Table 1). At the time of recruitment, 400 participants filled an extensive questionnaire to help provide a quick assessment of demographic information, health status, BMI, the frequency of seafood consumption and education level (see the details reported in the questionnaire, Supplementary material). Obesity, loss of weight (> 10 kg during the last year), cancer, and housing (for more than 10 years) in the study area were adopted as exclusion criteria for the biological sampling to prevent bias in the analysis. The frequency of fish consumption was evaluated by distinguishing between fish and shellfish origins (local vs. non-local markets). Among individuals who provided the consent for sample taking, a total of 224 individuals in the age classes 20–24, 25–29, 30–34, 35–39 and 40–44 were selected for the biological sampling (Table 1).

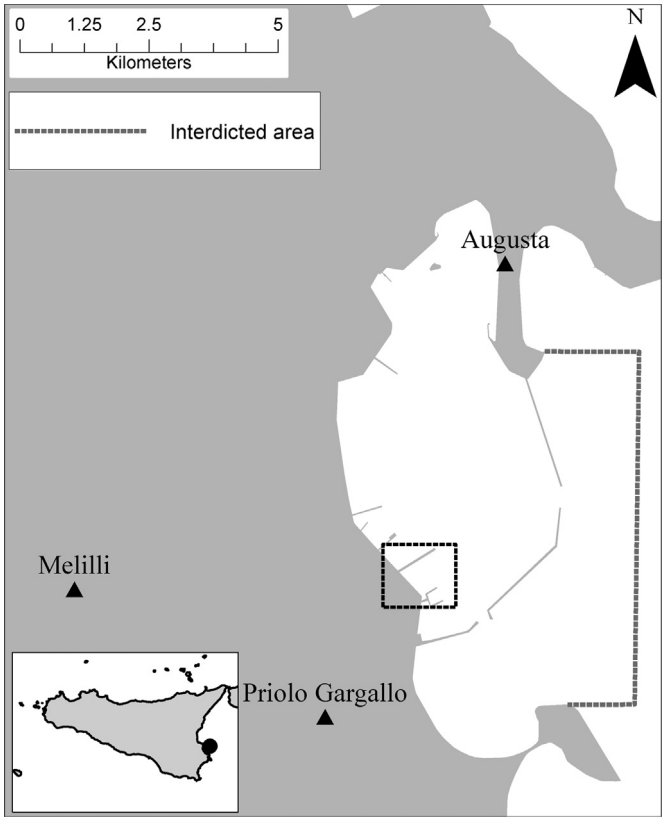

Fig. 1. Study area showing the municipalities of Augusta, Melilli and Priolo. The black dashed square indicates the chlor-alkali plant's location. The area's fishing ban is also reported with the gray dashed line.

2.2. Mercury measurements

Collection of biological samples was performed by the paramedical staff of the Public Hygiene Service (ASP N°8) of Augusta during the period within October 2012 and April 2013. Blood samples were collected in tubes containing lithium heparinate, while the first morning urine samples were deep frozen (−20 °C) until the analyses. Finally, using stainless steel scissors, a ~1 g hair sample was taken from the nape of the neck, close to the occipital region of the scalp, and kept in a clean polyethylene bag until analyses. The total Hg in the untreated blood, human hair and urine was measured by the Laboratory of Public Health of Syracuse (ASP N°8) by a Direct Mercury Analyzer (DMA80 atomic absorption spectrophotometer, Milestone, Wesleyan University, Middletown, CT, USA) according to the US EPA 7473 method (US EPA 2007).

The limit of detection of the method (LOD), estimated as three times standard deviations of the blank samples, was 0.020 μg/L blood, 0.015 μg/L urine and 0.003 μg/g hair, respectively. Accuracy was checked by running replicates of the reference materials (RM) NCS ZC 81002b (1.06 ± 0.28 μg/g), Seronorm™ Trace Elements Urine L-2 (39.8 ± 0.8 μg/L) and Seronorm™ Trace Elements Whole Blood L-2 (15.2 ± 0.8 μg/L) and L-3 (31.4 ± 1.7 μg/L). Bench quality control material was measured at the start of each analytical run (set of 20 samples) for quality assurance and control.

The measured values were, on average, within ±5% of the recommended values. In order to check the reproducibility of the analysis, about 20% of the samples were analyzed in triplicate. The coefficient of variation was between 2.4% and 3.2%.