Oral bioaccessibility and human exposure to anthropogenic and geogenic mercury in urban, industrial and mining areas

CrossMark

S.M. Rodrigues [a,*], C. Coelho [a], N. Cruz [a], R.J.R. Monteiro [a], B. Henriques [a], A.C. Duarte [a], P.F.A.M. Römkens [b], E. Pereira [a]

[a] Centre for Environmental and Marine Studies (CESAM)/Department of Chemistry, Universidade de Aveiro, 3810-193 Aveiro, Portugal
[b] Alterra – Wageningen University and Research Center, PO Box 47, Wageningen, 6700 AA, The Netherlands

HIGHLIGHTS

- There is little information about the bioaccessibility of mercury (Hg) in soils.
- This study focused on links between Hg bioaccessibility and Hg fractionation in soils.
- Hg extracted by gastric fluid was up to 1.8% of Hg total and lung fluid extractable Hg was up to 12% of Hg total.
- Ingestion or inhalation of Hg from soil particles may be responsible to up to 8% of adult Hg intake.
- Further validation of bioaccessibility tests by Hg soil speciation analysis is advised.

ARTICLE INFO

ABSTRACT

The objective of this study was to characterize the link between bioaccessibility and fractionation of mercury (Hg) in soils and to provide insight into human exposure to Hg due to inhalation of airborne soil particles and hand-to-mouth ingestion of Hg-bearing soil. Mercury in soils from mining, urban and industrial areas was fractionated in organometallic forms; mobile; semi-mobile; and non-mobile forms as well as HCl-extractable Hg. The *in vitro* bioaccessibility of Hg was obtained by extracting soils with (1) a simulated human gastric fluid (pH 1.5), and (2) a simulated human lung fluid (pH 7.4). Total soil Hg concentrations ranged from 0.72 to 1.8 mg kg^{-1} (urban areas), 0.28 to 94 mg kg^{-1} (industrial area) and 0.92 to 37 mg kg^{-1} (mining areas). Both organometallic Hg as well as 0.1 M HCl extractable Hg were lower (<0.5% of total Hg) than Hg extracted by gastric fluid (up to 1.8% of total Hg) and lung fluid (up to 12% of total Hg). In addition, Hg extracted by lung fluid was significantly higher in urban and industrial soils (average 5.0–6.6% of total Hg) compared to mining soils. Such differences were related to levels of mobile Hg species in urban and industrial soils compared to mining soils. These results strengthen the need to measure site-specific Hg fractionation when determining Hg bioaccessibility. Results also show that ingestion and/or inhalation of Hg from soil particles can contribute up to 8% of adult total Hg intake when compared to total Hg intake via consumption of contaminated fish and animal products from contaminated areas.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Mercury (Hg) is a toxic and non-essential element that bioaccumulates in aquatic and terrestrial food chains. The degree to which Hg bioaccumulates strongly relates to the chemical form that occurs in the environment including elemental Hg (Hg^0), inorganic Hg (monovalent mercurous compounds and divalent mercuric compounds) and organometallic Hg (primarily compounds such as methylmercury (MeHg)) (Gibicar et al., 2009; Syversen and Kaur, 2012).

Mercury in terrestrial systems can be of natural and anthropogenic sources. Volcanic eruptions and geothermal power are common natural sources of Hg while anthropogenic sources include fossil fuel combustion, mining activities, cement production, oil refining and production of caustic soda in chlor-alkali plants using Hg cells, the latter representing around 17% of total anthropogenic Hg emissions (Pacyna et al., 2001, 2009; Gibicar et al., 2009). In urban areas, coal combustion, waste incineration and Hg release from commercial products (including fluorescent lamps, thermometers, thermostats, electrical switches, pressure sensing devices, and blood pressure reading devices) also contribute to the Hg load to soils (Ajmone-Marsan and Biasioli, 2010). In addition to this, Hg was used for many years as dental amalgams, seed treatments, preservatives in vaccines and other consumer applications

* Corresponding author at: Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal. Tel.: +351 234370721; fax: +351 234370084.
E-mail address: smorais@ua.pt (S.M. Rodrigues).

leading to the environmental widespread of this element (Syversen and Kaur, 2012). Hence, even though worldwide regulations have imposed severe controls on Hg point source emissions, all humans are exposed to some form of Hg in their everyday life either by inhalation, ingestion or dermal contact (Syversen and Kaur, 2012). An assessment of the toxicity of Hg resulting from exposure to Hg from these sources, however, is still rather complex due to differences in toxicity and geochemical behavior of various Hg species present in the environment (Syversen and Kaur, 2012).

Due to two major human disasters of massive MeHg poisoning in the late 1940s and 1970s and considering its very high toxicity even at low intake rates, human exposure studies to Hg contamination have focused mostly on this form of the contaminant (Syversen and Kaur, 2012). Intake via food is considered the primary source of MeHg for humans. Fish and fish products are the main source responsible for human exposure to MeHg because all forms of Hg can be converted to MeHg in aquatic systems which subsequently bioaccumulates and biomagnifies in aquatic food chains (Gibicar et al., 2009). In terrestrial systems, rice consumption has also been identified as a major pathway for human exposure to MeHg, particularly in Hg contaminated areas in China. It has been shown that flooded soil conditions favor the methylation of Hg to MeHg, which is mobile in the soil–plant system and which can accumulate at high levels in the grain of paddy rice (Peng et al., 2012; Rothenberg et al., 2012).

Considering that Hg is now a widespread global pollutant and that MeHg is generally a minor fraction of this element in contaminated terrestrial systems (Barnett and Turner, 2001), potential hazards associated with the presence of all forms of Hg in soils should be quantified. Humans can be exposed to soil-borne contaminants through ingestion, inhalation and dermal contact. For long-term and low level exposure, potential risks associated with diffuse contamination of soils and ingestion/inhalation of contaminated soils should also be taken into account. Total Hg (including both inorganic and organometallic forms of Hg) in soils can be of concern for animal and human health at a number of contaminated sites, including the vicinity of several chlor-alkali plants and mining sites (Biester et al., 2002; Millán et al., 2006; García-Sánchez et al., 2009; Reis et al., 2009). A recent study in Portugal also reported that consumption of animal offal (e.g. bovine liver) significantly contributes to human exposure to total Hg (Rodrigues et al., 2012a). In urban environments inhalation of soil particles and direct ingestion of soil by children during hand-to-mouth activities are major pathways for human exposure to Hg and other soil contaminants (Rodrigues et al., 2006a, 2013; Zagury et al., 2009). At contaminated industrial sites, the inhalation of contaminated soil and dust particles during industrial processes can also be a relevant pathway of exposure, particularly for on-site workers. Finally, a recent report by the SCU (2013) emphasized that agricultural practices release soil particles into the air that can be inhaled by workers and others nearby thus forming a relevant source of exposure to metals in soils, especially for those exposed during long periods of time.

The health risks associated with human exposure to a specific contaminant are controlled by the relative oral availability which is the fraction of the ingested contaminant that reaches the systemic circulation (Zagury et al., 2009). Different Hg species exhibit different volatility, solubility and availability and thereby variable toxicity (Guney et al., 2013). MeHg is considered the most toxic form of Hg due to its strong affinity to the human brain and subsequent irreversible effects on the central nervous system even at low exposure rates (Hedegaard and Sloth, 2011) and also because MeHg is practically 100% absorbed by the human body following inhalation, dermal contact or oral exposure (Syversen and Kaur, 2012). Although the availability of elemental Hg to be absorbed in the gastro-intestinal tract is often low ($<0.1\%$), it can easily enter the blood through the inhalation pathway (Guney et al., 2013). Inorganic Hg preferentially accumulates in kidneys of living organisms (followed by accumulation in the liver) and is absorbed in lungs after inhalation of aerosols that contain Hg (Counter and Buchanan, 2004). The absorption of inorganic Hg in the gastro-

intestinal tract following oral exposure depends on the speciation of inorganic Hg, and is related to the water solubility of mercuric salts; i.e. high for mercuric chloride and low for mercuric sulfide) (Paustenbach et al., 1997; Counter and Buchanan, 2004).

To mimic the dissolution of Hg in the human gastro-intestinal tract (commonly referred to as "bioaccessibility") *in vitro* extraction methods have been developed and applied to soil and dust samples (Paustenbach et al., 1997; Zagury et al., 2009; Gray et al., 2010; Hu et al., 2011). Such tests include soil extractions using simulated human body fluids to determine the fraction of Hg potentially available for absorption and are considered a conservative assessment of the relative oral availability (Intawongse and Dean, 2006; Gray et al., 2010). Ideally, *in vitro* studies should be validated through *in vivo* tests using an adequate animal model. In the absence of comparable *in vivo* Hg oral availability studies, bioaccessibility tests have been partially validated by studying pure Hg compounds or analyzing the Hg binding forms in soils and used as surrogates for risk assessment purposes (Davis et al., 1997; Schoof and Nielsen, 1997; Barnett and Turner, 2001; Zagury et al., 2009).

To conduct comprehensive and effective risk assessments it is necessary to better understand the relative importance of the various human exposure pathways to Hg. It is equally important to obtain insight in differences in the geochemical behavior of the different forms of Hg when comparing soils from urban, mining or industrially contaminated areas and associated differences in resulting exposure to soil Hg. Finally, it is crucial to better understand how the geochemistry of Hg in soils will affect its bioaccessibility, namely the Hg absorption in the gastro-intestinal tract following soil ingestion or its absorption in the lungs following inhalation of soil particles.

In this study we evaluated the bioaccessibility of Hg in urban, industrial and mining soil samples from Portugal. Soils were extracted using a) a simulated human gastric fluid, and, b) a simulated human lung fluid. A selective extraction was also performed to determine the Hg present in organometallic forms. Furthermore, the presence of mobile, semi-mobile, and non-mobile Hg forms as well as Hg available forms was analyzed and human exposure to Hg was estimated. The main objective was to characterize the link between bioaccessibility and Hg fractionation in soils from different land uses and to provide insight into human exposure to Hg due to inhalation of airborne soil particles, hand-to-mouth ingestion of Hg-bearing soil and ingestion of contaminated animal products.

2. Materials and methods

2.1. Collection and pre-treatment of soil and plant samples

To obtain a wide range in total Hg levels, samples from 3 typical forms of land use have been included:

- Urban area: 10 sampling sites are located in the "Grande Porto" urban area (NW Portugal). In this area major sources of metal contamination include chemical and agro-food industry, intensive road traffic, the presence of an airport and an oil refinery (Cruz et al., 2014). No potential direct source of soil Hg contamination is known in this area.
- Industrial area: 10 sampling sites are located in the vicinity of the Estarreja Chemical Complex (NW Portugal). Agricultural fields in this area are under the influence of industrial activity from a chlor-alkali plant and are crossed by open streams that, in the past, transported liquid effluents from the Chemical Complex to a nearby lagoon. Although the chlor-alkali plant completely stopped using Hg cathodes in 2002, the surrounding soils are still highly contaminated by Hg (Rodrigues et al., 2006a, 2006b, 2010, 2012a, 2012b; Reis et al., 2009, 2010; Henriques et al., 2013). Soils for this study were collected in the immediate vicinity of a former effluent stream ("Vala de S. Filipe") that is known to be highly contaminated by Hg (Henriques et al., 2013), as well as away from the former effluent stream in order to sample soils with variable Hg levels.