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The bioaccessibility of soil-based mercury as determined by physiological based extraction tests and human biomonitoring in children

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HIGHLIGHTS

- Elevated levels of inorganic mercury in soil were measured in a smelter community.
- In-vitro tests showed a mean bioaccessibility of 3.0% for mercury in soil.
- Biomonitoring in children found low urinary inorganic mercury levels.
- Soil-based mercury levels did not appear to influence exposure levels in children.
- In vitro bioaccessibility tests reduce uncertainty in exposure and risk estimates.

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ABSTRACT

Environmental contaminants associated with soil particles are generally less bioavailable than contaminants associated with other exposure media where chemicals are often found in more soluble forms. In vitro methods, such as Physiological Based Extraction Tests (PBET), can provide estimates of bioaccessibility for soil-based contaminants. The results of these tests can be used to predict exposure to contaminants from soil ingestion pathways within human health risk assessment (HHRA). In the current investigation, an HHRA was conducted to examine the risks associated with elevated concentrations of mercury in soils in the northern Canadian smelter community of Flin Flon, Manitoba. A PBET was completed for residential soils and indicated mean bioaccessibilities of 1.2% and 3.0% for total mercury using gastric phase and gastric+intestinal phase methodologies, respectively. However, as many regulators only allow for the consideration of in vitro results for lead and arsenic in the HHRA process, in vitro bioaccessibility results for mercury were not utilized in the current HHRA. Based on the need to assume 100% bioaccessibility for inorganic mercury in soil, results from the HHRA indicated the need for further assessment of exposure and risk. A biomonitoring study was undertaken for children between 2 and 15 years of age in the community to examine urinary inorganic mercury concentrations. Overall, 375 children provided valid urine samples for analysis. Approximately 50% of urine samples had concentrations of urinary inorganic mercury below the limit of detection (0.1 μg/L), with an average creatinine adjusted concentration of 0.11 μg/g. Despite high variability in mercury soil concentrations within sub-communities, soil concentrations did not appear to influence urinary mercury concentrations. The results of the current investigation indicate that mercury bioaccessibility in residential soils in the Flin Flon area was likely limited and that HHRA estimates would have been better approximated through inclusion of the in vitro study results.

1. Introduction

Mercury is a naturally occurring element present in the Earth's crust but is also released into the environment through mining and smelting, combustion of fossil fuels and other industrial activities (ATSDR, 1999; US EPA, 2007). Exposure to mercury is well known to be associated with both specific and general toxicity responses in humans (ATSDR, 1999; Counter and Buchanan, 2004). In children, this is of particular

Abbreviations: EDI, estimated daily intake; EPC, exposure point concentrations; HHRA, Human health risk assessment; HQ, hazard quotient; IVG, in vitro gastrointestinal; PBET, physiological based extraction test; PTC, provisional trigger concentration; STD, standard deviation; TDI, tolerable daily intake; UCLM, upper confidence limit on the mean

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concern as this subpopulation is more vulnerable to mercury toxicity that can lead to neuro-, nephro- and immunotoxicity (Counter and Buchanan, 2004; Bose-O'Reilly et al., 2010). In addition, children can be exposed to mercury via contaminated soils through deliberate and involuntary mechanisms such as hand-to-mouth activities and play (US EPA, 2002; Ljung et al., 2007; Guney et al., 2013).

In mercury contaminated soils, inorganic mercury species generally represent approximately 98–99.9% of the total mercury content (Davis et al., 1997). The bioaccessibility of soil-bound inorganic mercury has been shown to be significantly reduced when compared to more soluble forms (Barnett et al., 1995; Barnett and Turner, 2001; Zagury et al., 2009; Guney et al., 2013). The term "bioaccessibility" refers to the fraction of the contaminant that is released from soil within gastrointestinal fluids and is available for absorption (Ruby, 2004). When contaminants are bound in soil they are typically less bioaccessible than those associated with other exposure media (e.g. water) due to the sequestration of both inorganic and organic constituents (NRC, 2003; Ruby, 2004).

Toxicity reference values used within human health risk assessments (HHRAs) are often based on animal models due to a lack of adequate or reliable human exposure data. Inorganic mercury toxicity values are based on responses to mercuric chloride ($HgCl_2$), a highly bioaccessible species that can be administered through diet or drinking water (ATSDR, 1999; Health Canada, 2009). Mercuric chloride has been shown to be up to 60-fold more bioaccessible than cinnabar (HgS) that is typically a major component of soil-based mercury (Sin et al., 1983; Schoof and Nielsen, 1997). Failure to adjust for the relative difference of bioaccessibility can produce a significant overestimation of risk and may result in costly and disruptive follow-up investigations or remediation procedures that would otherwise be unnecessary (Canady et al., 1997; Schoof and Nielsen, 1997; Schoof, 2004).

In vitro methods can provide measures of bioaccessibility of a given soil-based contaminant. For instance, physiological based extraction tests (PBET) have been established to mimic the human gastrointestinal system to estimate bioaccessibility (Ruby et al., 1993). The PBET uses pH levels similar to those found in the stomach (Phase 1) and the small intestine (Phase 2) to simulate the conditions during digestion (Ruby, 2004). For some contaminants such as arsenic and lead, in vivo models have been used to validate the results of the PBET and to adjust the bioaccessibility results of a PBET to provide an estimate of relative bioavailability (Ruby et al., 1996; Kelly et al., 2002; Rodriguez et al., 1999; Schroder et al., 2004). The bioavailability represents the fraction of the contaminant that is absorbed by the receptor and enters systemic circulation (Ruby, 2004). These adjustments have not been developed for PBET results for mercury. As a result, a default of 100% relative bioavailability is typically used in risk assessment for inorganic mercury in ingested soils despite common acceptance that this represents an overly conservative assumption (Canady et al., 1997). A number of investigations have characterized the bioaccessibility of soil-based mercury through in vitro analysis (Barnett and Turner, 2001; Bloom et al., 2003; Welfringer and Zagury, 2009; Koch et al., 2013).

The city of Flin Flon, MB (55°N, 102°W), located in west-central Manitoba, Canada, sharing the Saskatchewan provincial border with the city of Creighton, SK, has been the site of a base metal mining and smelting complex for over 80 years. A number of different metals have been emitted at the smelter, including copper, lead, zinc, and cadmium, in addition to by-products such as gold, silver, and selenium (Henderson et al., 1998; Manitoba Conservation, 2007). In 2007, Manitoba Conservation conducted a surface soil investigation to determine the concentration and distribution of metals in the Flin Flon area. Several metals, including mercury, were found to be higher than what has been recommended by the Canadian Council of Ministers of the Environment (CCME) as soil quality guidelines for human health (CCME, 1999; Manitoba Conservation, 2007).

Prompted by the release of the Manitoba Conservation report, an HHRA was initiated to estimate the exposure and risk levels associated with mercury and other contaminants in environmental media. The location of different communities within the Flin Flon area relative to the smelting complex may have a significant influence on the level of particulates in ambient air and the amount that was available for deposition to residential areas. To address differences in exposures among residents of the Flin Flon area, the HHRA included an estimate of exposure and risks for four separate communities (West Flin Flon, East Flin Flon, Creighton and Channing) (Fig. 1) which had a wide range of inorganic mercury levels in soil. As part of the HHRA, additional soil sampling from residential properties was completed.

Here we present the PBET results for mercury in residential soils collected from the Flin Flon area to investigate the bioavailability of mercury. Regulators required the HHRA to assume a 100% relative bioavailability. A biomonitoring study was conducted within the community to measure urinary inorganic mercury concentrations in children less than 15 years of age as a more refined method for assessing potential health risks. The results of this biomonitoring study are considered herein in the interpretation of soil related mercury exposure in the Flin Flon area and in assessing the validity of utilizing PBET results for mercury in HHRA in general.

Inorganic mercury in soil is expected to have a considerably lower bioaccessibility than soluble salts such as mercuric chloride ($HgCl_2$) that are typically used in tests to derive toxicity reference values (Schoof and Nielsen, 1997; Paustenbach et al., 1997). Most soils generally consist of mercury compounds that have low levels of solubility, such as mercuric sulfide or cinnabar. Animal models have shown that the relative bioavailability of mercuric sulfide can be approximately 1–4% that of mercuric chloride (Paustenbach et al., 1997). Our research hypothesis was that failing to adjust for differences in the bioavailability of inorganic mercury in soil relative to the bioavailability of mercuric chloride in animal-based experimental studies will result in an overestimation of health hazards.

2. Methods

2.1. Residential soil sampling

Soil core samples were collected from homes located in Creighton, SK, East Flin Flon, MB, West Flin Flon, MB and Channing, MB (n = 29, 63, 76, 10 respectively). Homes were selected on a volunteer basis. A minimum of ten 1.5 cm inner diameter core samples were taken in an "X" pattern using a stainless steel probe from the lawn of each home. A soil particle size fraction of <250 μm from each soil sample was submitted for chemical analysis for total mercury concentration using the Mercury (Hot Block) in Soil method as outlined by the US EPA (2001). Only surface soil samples collected at the 0–2.5 cm or 0–5 cm profile were considered as a possible source of incidental ingestion and direct dermal contact.

2.2. Physiological based extraction test

Bioaccessibility studies utilizing the PBET method were conducted to estimate the bioaccessibility of contaminants present in soil collected from the Flin Flon area. A total of 50 soil samples collected from residential properties across each of the four communities were selected for testing (Creighton, West Flin Flon, East Flin Flon and Channing; n = 10, 20, 10 and 10, respectively). Soil samples were selected to provide a wide range of mercury concentrations (0.31 to 971 mg/kg) to allow for an analysis of the relationship between concentration and bioaccessibility. Testing was conducted by the Environmental Services Group (ESG) of the Royal Military College of Canada (RMC) and the Analytical Services Unit (ASU) of Queen's University.

Test conditions, such as soil particle size and dilution ratio, were examined in a pilot study prior to the finalization of the study protocol. The results of this pilot study supported the use of an extraction fluid volume to soil mass ratio of 100:1 and the <250 μm fraction of soils.