Environ Geochem Health
DOI 10.1007/s10653-014-9644-1

ORIGINAL PAPER

Speciation and bioaccessibility of mercury in adobe bricks and dirt floors in Huancavelica, Peru

Nicole Hagan · Nicholas Robins ·
Ruben Dario Espinoza Gonzales ·
Heileen Hsu-Kim

Received: 23 February 2014 / Accepted: 12 August 2014

Abstract Huancavelica, Peru, a historic cinnabar refining site, is one of the most mercury (Hg)-contaminated urban areas in the world. Exposure is amplified because residents build their adobe brick homes from contaminated soil. The objectives of this study were to compare two Hg-leaching procedures, and their application as risk-assessment screening tools in Hg-contaminated adobe brick homes in Huancavelica. The purpose was to evaluate potential health implications, particularly for children, after ingestion of Hg-contaminated particles. Hg was measured in adobe brick and dirt floor samples from 60 households by total Hg extraction, simulated gastric fluid (GF) extraction, and sequential selective extraction (SSE), which provides more detailed data but is resource-intensive. Most of the Hg present in samples was relatively insoluble, although in some households soluble Hg species were present at concentrations that may be of concern after ingestion. A strong correlation was identified between results from simulated GF extraction of adobe bricks and dirt floors and the more soluble fractions of Hg from SSE. Simulated GF extraction data were combined with ingestion and body mass characteristics for small children to compare potential risk of ingestion of Hg-contaminated soil with current health standards. Simulated GF extraction can be used as a risk assessment screening tool for effective allocation of time and resources to households that have measurable concentrations of bioaccessible Hg. Combining simulated GF extraction data with health standards enables intervention strategies targeted at households with the greatest potential health threat from ingestion of Hg-contaminated particles.

Keywords Adobe · Bioaccessibility · Ingestion · Mercury · Peru · Soil · Speciation

Introduction

Mercury (Hg) is emitted from natural and anthropogenic sources and is present in all compartments of the

---

Disclaimer The work reported in this document was funded in part by the US Environmental Protection Agency. It has been subjected to review by the National Center for Environmental Assessment and approved for publication. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the US Environmental Protection Agency.

N. Hagan (✉)
Department of Environmental Sciences and Engineering,
The University of North Carolina at Chapel Hill, CB
#7431, Chapel Hill, NC 27599-7431, USA
e-mail: nicoleahagan@gmail.com

N. Robins
Department of History, North Carolina State University,
Raleigh, NC, USA

R. D. E. Gonzales
Environmental Health Council, Huancavelica, Peru

H. Hsu-Kim
Department of Civil and Environmental Engineering,
Duke University, Durham, NC, USA

environment. Hg is transformed and transported in air, deposited on to the earth's surface, and can be stored in or emitted by soil, sediment, and water, continuously being cycled in the environment and being oxidized and reduced to different species. Once deposited from the atmosphere, Hg compounds in soil can undergo in-situ reactions resulting in the formation of elemental Hg and organomercury compounds (US EPA 1997). Although all species of Hg are toxic, some are less mobile and bioaccessible than others (Gochfield 2003; Gray et al. 2010; Revis et al. 1990). Bioaccessibility refers to the fraction of total Hg that is desorbed from contaminated particles and dissolved in the gastrointestinal tract (Zagury et al. 2009).

In Huancavelica, Peru, a previous study measured levels of total Hg in residential samples and identified the primary indoor sources of Hg exposure in adobe brick homes (Hagan et al. 2013). On the basis of the results of that study, inadvertent ingestion of Hg-contaminated soil particles by children was identified as an exposure pathway of interest. Health standards are available for ingestion of Hg-contaminated soil and are often cited in the literature when evaluating total Hg measurements (Hagan et al. 2011; Li et al. 2013; Li 2013; Robins et al. 2012). Health standards such as those listed in Table 1 issued by the UK Environment Agency (EA), the Agency for Toxic Substances and Disease Registry (ATSDR), the US Environmental Protection Agency (US EPA), and the Joint FAO/WHO Committee on Food Additives (JECFA) are all based on mercuric chloride, which is up to 100 % soluble after ingestion (ATSDR 1999; Environment Agency 2009; JECFA 2010; US EPA 1995). Because total Hg measurements do not distinguish between soluble and insoluble forms of Hg, comparisons between total Hg measurements and existing health standards may overestimate potential risks from exposure. Site-specific additional chemical analysis (e.g., sequential selective extraction or simple bioaccessibility extraction tests) can be used to further classify the species of Hg present in soils and to provide more detailed information for evaluating potential risks from ingestion.

The objectives of this study were to compare two Hg-leaching procedures, to use these as risk-assessment tools for screening Hg-contaminated adobe brick and dirt floor samples from adobe brick homes in Huancavelica, Peru, and to evaluate Hg bioaccessibility after ingestion of Hg-contaminated particles. The purpose of the study was to evaluate the potential health implications of ingestion, particularly for children, on the basis of the solubility of Hg present in adobe bricks and dirt floors, to support effective development, implementation, and evaluation of future strategies for intervention, mitigation, and remediation in the community.

Study area

Huancavelica, located in the Andean region of Peru, was the primary source of Hg used in amalgamation-based silver refining in South America for over 350 years. Beginning in 1563, Spanish colonists used the cinnabar ore in the Santa Barbara Hill outside of the city to produce liquid Hg in Huancavelica, which was then shipped to Andean silver-refining centers. As a result of the cinnabar refining process, the local community was extensively contaminated as a result of routine release of Hg vapor and liquid, a legacy that still haunts the residents of Huancavelica decades after refining ceased in the 1970s (Robins 2011; Robins and Hagan 2012; Robins et al. 2012).

More than 80 % of homes in Huancavelica are built from adobe bricks (Mendoza 2012). Participants in the

Table 1 Current health standards for oral exposure to inorganic Hg

Agency	Description	Value of standard (μg Hg/kg BW/day)	Ref.
EA	Mean daily intake (MDI): 70-kg adult	0.014	Environment Agency (2009)
	Mean daily intake (MDI): 20-kg child	0.037	
ATSDR	Minimum risk level (MRL)	2	ATSDR (1999)
EPA	Reference dose (RfD)	0.3	US EPA (1995)
JECFA	Provisional tolerable weekly intake (PTWI)	0.57[a]	JECFA (2010)

[a] Adjusted from units of μg Hg/kg BW/week to μg Hg/kg BW/day

study reported that they made adobe bricks from materials present on their property rather than purchasing manufactured adobe bricks or materials from somewhere other than their property. A previous study revealed elevated levels of total Hg in adobe bricks and dirt floors collected in Huancavelica, with concentrations ranging up 1,070 and 926 μg/g, respectively (Hagan et al. 2013). Because the walls and floors of adobe brick homes are usually uncovered and unsealed, residents are exposed to particle-bound Hg and vapor from these surfaces and to Hg-contaminated soils (Robins et al. 2012).

Materials and methods

Sample collection

Triplicate samples of adobe bricks and dirt floors were collected from 60 residences in Huancavelica in August 2010, as described by Hagan et al. (2013). In brief, adobe brick and dirt floor samples were collected in each home from the room residents identified as being where they spent the most time. Samples were collected from three locations within the room by scraping approximately 20 g material from the surface of either the walls or the floors to a depth of approximately 2.5 cm. A previous study found no statistically significant differences between Hg concentrations in the triplicate samples collected from each household, suggesting a composite sample for adobe bricks and dirt floors could be used for each household (Hagan et al. 2013). Composite samples for this study were obtained by weighing and combining approximately 1 g of each triplicate sample and removing any particles, rocks, debris, etc., greater than 3 mm at the widest diameter. Composite samples were created, so one adobe brick and one dirt floor sample was obtained for each of the 60 residences.

Analytical methods

Households were assigned to batches by computer-generated randomization. Total Hg extraction, sequential selective extraction (SSE), and simulated gastric fluid (GF) extraction were performed on composite adobe brick and dirt floor samples from each household. All solutions were prepared by use of reagent-grade chemicals and all procedures were performed using ultra-clean sample handling to avoid low-level Hg contamination.

Total Hg was extracted from adobe brick and dirt floor samples by digesting samples in 4:1 $HCl:HNO_3$ at 85 °C for 5 h. After digestion, samples were diluted to a final volume of 40 mL with deionized (DI) water and oxidized by use of 1 % bromine monochloride.

SSE was performed by the method developed by Bloom et al. (2003) and verified by use of complementary spectroscopic methods (Kim et al. 2003). The SSE method utilizes five extractant solutions that separate Hg compounds on the basis of chemical behavior. The five Hg fractions included in the SSE procedure, in sequential order, are: deionized water (F1), 0.2 M acetic acid, adjusted to pH 2 by addition of HCl (F2), 1 M KOH (F3), 12 M HNO_3 (F4), and aqua regia (F5). All extractions were performed on 0.2 ± 0.02 g composite sample with 20 mL extractant, a 1:100 solid:liquid ratio. In each extraction step, the solid–liquid slurry was mixed end-over-end for 18 ± 4 h. The liquid phase was then separated from the solid by centrifugation and decanted into trace-clean 40-mL glass vials. The solid pellet was rinsed with extractant fluid, suspended, and the rinsing solutions were separated and added to the initial extraction solution. All fractions were preserved for analysis with bromine monochloride.

Previous work with soil and sediment (Bloom et al. 2003; Kim et al. 2003) indicated that the SEE approach roughly partitions mercury into the major forms: water soluble (F1), human stomach acid soluble (F2), organic matter chelated Hg, Hg_2Cl_2, and methylmercury (F3), elemental Hg, Hg_2Cl_2, and strongly complexed Hg (F4), and HgS and HgSe (F5). However, we note that speciation of Hg cannot be discerned solely from SSE data and that complementary methods such as spectroscopy are needed.

Simulated GF extraction (pH 1.5) was performed by use of a simple bioaccessibility extraction test (SBET) that has often been used for trace metals other than Hg, but has increasingly been used to simulate Hg bioaccessibility (Schaider et al. 2007). However, this method has not been validated in vivo for Hg uptake in the same way it has for other metals, for example lead. In-vivo absorption of metals typically occurs in the epithelium of the small intestine which has circumneutral pH; however, rates of absorption can be limited by dissolution of particulate metals in the acidic gastric fluids. Therefore, the SBET was performed with a simulated gastric fluid comprising 0.4 M glycine and adjusted to pH 1.5 by addition of concentrated HCl. A 1:100 solid:liquid mass ratio was used (as for SSE). The liquid–solid slurry was mixed for 1 h at 37 °C and separated by centrifugation before decanting the liquid phase into trace clean 40 mL glass vials and oxidation with bromine monochloride.

All samples were analyzed for Hg by direct thermal desorption by use of an RA-915+ Lumex mercury vapor analyzer equipped with an RP-M324 attachment (Ohio Lumex, Twinsburg, OH, USA). For total Hg, SSE, and simulated GF extraction of adobe bricks and dirt floors, aliquots up to 100 μL of each sample were analyzed for total Hg by use of EPA Method 30B (US EPA 2008a). Instrument calibration was performed by use of mercuric chloride standards (SCP Science, Champlain, NY, USA, and Inorganic Ventures, Christiansburg, VA, USA). Method blanks ($n = 11$) were all below the limit of detection of the instrument (~1 ng Hg). An NIST-certified SRM (2709 San Joaquin soil) was digested with each batch of samples. Two SRM recoveries fell outside of the acceptable range of the certified value (1.4 ± 0.08 μg/g). The other four SRM recoveries were 90 ± 10 % of the certified value.

Statistical methods

Mass-based Hg concentrations for total Hg, SSE, and GF extraction were tested for normality and found to be non-normally distributed; mass-based data were therefore log-transformed before statistical analysis. Before log-transformation, the raw data were adjusted for values below calibration range and below the limit of detection of the instrument. Measurements below the lowest calibration point but with area counts greater than 200 were adjusted by use of a response factor (US EPA 2008a). For SSE, samples for which recovery was <60 % or >140 % of the total Hg extracted were excluded. In the reporting of summary statistics, only, measurements below the LOD of ~1 ng Hg (equivalent to an area count of 200) were set to 0.00125 μg/g Hg (0.5LOD mass adjusted to 0.2 g sample); all other analyses were performed without substitution. Method duplicates that met inclusion criteria were included in the analysis. Statistical analysis was performed by use of SAS 9.2 software (SAS Institute, Cary, NC, USA).

Results

Recovery of Hg by SSE and GF extraction

Summary statistics for extractable Hg in each fraction of the SSE are shown in Table 2. Percentage Hg recovered in each fraction is consistent with results from other studies that have performed SSE on refining-related soil contamination, with lower amounts recovered in F1, F2, and F3, and most of the Hg present in fractions F4 and F5 (Hagan et al. 2011; Male et al. 2013; Zagury et al. 2009).

Percentage bioaccessible Hg in simulated GF extraction of adobe bricks and dirt floors is also shown in Table 2. The percentage of bioaccessible Hg in adobe brick samples ranged from below the limit of detection to 7.4 % of total Hg. The percentage of bioaccessible Hg in dirt floor samples ranged from below the limit of detection to 6.8 %.

Comparisons of methods of extraction

Pearson correlation coefficients were calculated for extractable Hg measured by use of SSE and simulated GF extraction; the results are listed in Table 3. For these calculations, the log-transformed mass of extractable Hg obtained by use of simulated GF extraction was compared with amounts of Hg in individual and combined fractions from the sequential selective extraction procedure that would represent the more soluble forms of Hg after ingestion (F1, deionized water; F2, acetic acid–HCl; and F3, 1 M KOH).

The mass of extractable Hg in the individual SSE fractions was significantly correlated with the mass obtained in simulated GF extractions. Although statistically significant, the simulated GF extractions were not as strongly correlated with the F2 fraction as expected, given the similarity of the fluids in the F2 fraction and the simulated GF extraction. Both F2 and GF reagents contained approximately 0.01–0.3 M dissolved chloride (from the HCl), so Cl^- was the dominant ligand for Hg^{2+} in both solutions. The mass of extractable Hg obtained by use of simulated GF extraction was strongly correlated with the F3 fraction for adobe bricks, also unexpected, given the very different chemical compositions of the F3 and simulated GF extraction fluids. When the mass of extractable Hg in the F1, F2, and F3 fractions was summed and compared with that from simulated GF extractions, the

Table 2 Extractable Hg in adobe bricks and dirt floors from residences in Huancavelica, Peru, expressed on a mass basis (μg/g) and as a percentage of total Hg (%)

		Fraction 1 (F1): deionized water	Fraction 2 (F2): 0.2 M acetic acid (pH 2)	Fraction 3 (F3): 1 M KOH	Fraction 4 (F4): 12 M HNO_3	Fraction 5 (F5):aqua regia ($HCl + HNO_3$)	Simulated GF
Adobe bricks							
n		61	61	61	61	61	61
Mean ± 1 sd	μg/g	1.9 ± 4.5	1.0 ± 2.7	4.2 ± 6.6	17 ± 17	150 ± 210	1.6 ± 2.7
	%	0.73 ± 1.7	0.30 ± 0.77	1.7 ± 2.1	13 ± 10	69 ± 17	0.81 ± 1.4
Min, max	μg/g	0.0013, 20	0.0013, 17	0.0013, 25	0.0013, 80	2.9, 1,100	0.0013, 11
	%	0.00013, 8.8	0.00013, 3.8	0.00052, 9.2	0.0067, 45	33, 120	0.00013, 7.4
Dirt floors							
n		49	49	49	49	49	49
Mean ± 1 sd	μg/g	1.8 ± 3.9	1.2 ± 3.3	5.0 ± 9.6	20 ± 19	120 ± 190	1.9 ± 3.7
	%	0.57 ± 1.0	0.73 ± 2.1	3.2 ± 4.4	16 ± 9.6	76 ± 25	0.89 ± 1.5
Min, max	μg/g	0.0013, 17	0.0013, 17	0.0013, 49	0.0013, 67	2.1, 1100	0.0013, 20
	%	0.00058, 4.2	0.00023, 12	0.00058, 21	0.016, 41	37, 130	0.00023, 6.8

Table 3 Pearson correlation coefficients, *p* values, and sample sizes for log-transformed mass of extractable Hg in adobe bricks and dirt floors

	F1	F2	F3	F1 + F2 + F3
Simulated GF adobe bricks	0.546	0.559	0.782	0.780
	<0.001*	<0.001*	<0.001*	<0.001*
	47	44	49	
Simulated GF dirt floors	0.738	0.478	0.565	0.728
	<0.001*	0.005*	<0.001*	<0.001*
	35	33	40	40

* Statistically significant at $\alpha = 0.05$

bioaccessible fractions were strongly correlated for both adobe brick and dirt floor samples.

Comparison of adobe brick and dirt floor samples

The relationship between the sum of the most soluble fractions of Hg from SSE (F1, F2, and F3) of adobe bricks and dirt floors was investigated for the 38 residences for which paired SSE data were available for both sample types. A moderate correlation was observed between the F1 + F2 + F3 fractions of the adobe bricks and dirt floors ($r = 0.437$, $p = 0.006$). The relationship between simulated GF extractable Hg in adobe bricks and dirt floors was investigated for the 32 households for which paired simulated GF extraction data were available for both sample types. The Pearson correlation coefficient, *r*, was 0.866 ($p < 0.0001$), suggesting a very strong, statistically significant, correlation between GF-extractable Hg concentrations in adobe bricks and dirt floors. These results are consistent with those from a previous study in which total Hg concentrations in adobe bricks and dirt floors were found to be statistically correlated within a residence (Hagan et al. 2013).

Discussion

Comparison of extraction methods

The Bloom et al. (2003) SSE method is capable of providing qualitative information about the solubility of the Hg present in contaminated soil, including the more soluble forms of Hg, on the basis of its chemical behavior. However, this procedure is very time and resource-intensive. If the first three fractions were

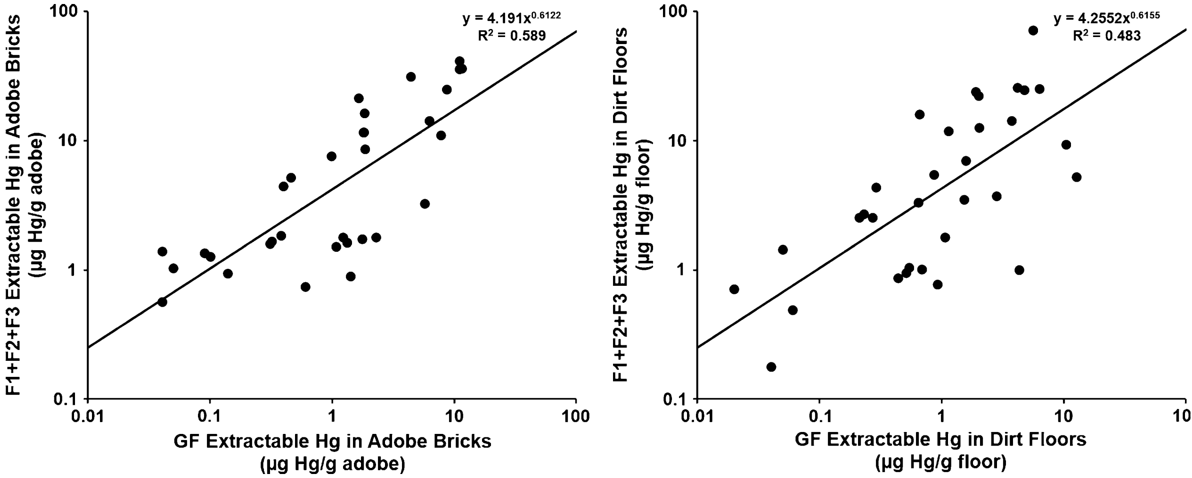

Fig. 1 Least-squares regression for mass of F1 + F2 + F3 extractable Hg (µg/g) versus simulated GF extractable Hg (µg/g)

used as a proxy for bioaccessibility after ingestion, the SSE method would require approximately three days of tumbling and three different extraction fluids to measure the different fractions. In comparison, the simulated GF extraction requires only 1 h and one extraction fluid to measure the more bioaccessible forms of Hg after ingestion. The strong correlation between F1 + F2 + F3 and simulated GF extraction (Table 3) suggests that simulated GF extraction could be used for initial screening of the bioaccessibility of Hg at contaminated sites, followed by the Bloom et al. (2003) sequential selective extraction procedure as warranted by simulated GF extraction results, if necessary for more detailed information.

To further investigate the relationship between F1 + F2 + F3 and simulated GF extraction, a least-squares regression was fitted for households for which complementary SSE and simulated GF extraction data were available ($n = 32$), and power regression was applied to the data, as shown in Fig. 1. The regressions for adobe bricks and dirt floors suggest a moderate relationship between F1 + F2 + F3 extractable Hg and simulated GF extractable Hg (adobe: $r^2 = 0.589$, floors: $r^2 = 0.483$). The average ratio of F1 + F2 + F3 extractable Hg to simulated GF extractable Hg is 6.9 for adobe bricks and 7.9 for dirt floors. This suggests that although the correlation between the two types of sample is very strong, the mass of Hg recovered in simulated GF extraction is proportional to the mass of Hg recovered in the more bioaccessible fractions of the SSE and the method has the potential to serve as a screening tool for additional analysis.

For Huancavelica, use of simulated GF extraction as a preliminary measure of bioaccessible Hg would enable time and resources for more detailed analysis, and for intervention, mitigation, or remediation strategies, to be allocated first to households for which the health implications of ingestion of soil containing more soluble Hg are greatest.

Relationship between sample types

In this study, total Hg, SSE, and simulated GF extraction were performed on adobe brick and dirt floor samples from all participants' residences ($n = 60$). To perform the extractions, samples were collected in the field and transported to a laboratory in the US, so significant cost, time, and resources were required to obtain additional information. Details regarding speciation and bioaccessibility of Hg are helpful in prioritizing households for future phases of research; identifying a sampling procedure that minimizes cost, time, and resources would be useful for providing this information. Because of the strong correlation between Hg in adobe bricks and dirt floors in a previous study (Hagan et al. 2013) and in this study, it was expected that this relationship would also exist for Hg concentrations from simulated GF extraction.

The relationship between Hg concentrations from simulated GF extraction of adobe bricks and dirt floors was further investigated by performing a least-squares regression for households for which complementary simulated GF extraction data were available for both

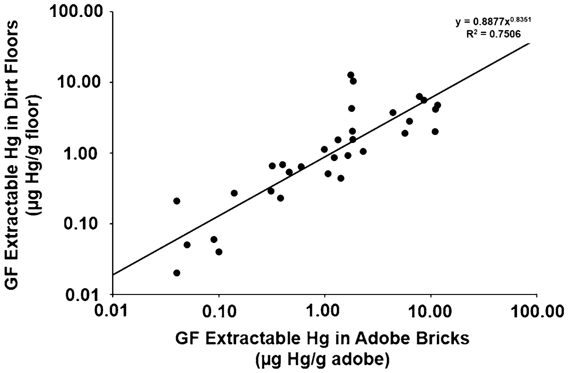

Fig. 2 Least-squares regression for mass of Hg (μg/g) from simulated GF extraction of adobe bricks and dirt floors

sample types ($n = 32$). As shown in Fig. 2, the power regression reveals a strong relationship between sample types ($r^2 = 0.75$) and the average ratio of Hg concentrations from simulated GF extraction of these types of sample is 1.4. This finding suggests that, in future research efforts, it may be possible to use either an adobe brick or dirt floor sample to develop a scheme for prioritization of intervention, mitigation, and remediation strategies among the households. Using either an adobe brick or a dirt floor sample, rather than both, would save time and resources while providing similar information with regard to residential Hg contamination and potential exposure.

Implications for risks from soil ingestion

The EPA Child-Specific Exposure Factor Handbook assumes a one-year old child has a median body weight of 11 kg and ingests 100 mg dirt and dust per day as a result of hand-to-mouth activity (US EPA 2008b). Although these values are descriptive of children in the US, application to children in other parts of the world may result in underestimation of the risk from ingestion of contaminated soil. In Huancavelica, children are often smaller; average body weight of one-year olds is 9 kg (Ecos E, Hagan N, Robins N; personal communication). For the purpose of this discussion, we chose to use a body weight of 10 kg for a one-year-old toddler. In addition, the amount ingested assumed in the Child-Specific Exposure Factor Handbook is not representative of ingestion of soil and dust in a home with unsealed dirt walls and floors, as in Huancavelica. Such ingestion data for exposure within adobe brick homes are not currently available in the published literature; it is not unreasonable to double or triple US-based median ingestion for such a very dusty environment.

Table 4 Level of soil contamination (LSC) that may result in the health standard being exceeded by a 10 kg child ingesting different amounts

Agency	Health standard (μg Hg/kg BW/day)	Amount ingestion (g soil/day)	LSC (μg Hg/g soil)
EA	0.037	0.1	0.37
		0.2	0.19
		0.3	0.12
ATSDR	2	0.1	20
		0.2	10
		0.3	6.7
EPA	0.3	0.1	3
		0.2	1.5
		0.3	1
JECFA	0.57	0.1	5.7
		0.2	2.9
		0.3	1.9

To identify households at greatest potential risk from ingestion of Hg-contaminated soil in relation to health standards, a 10 kg body weight and different amounts ingested were used in Eq 1 to calculate a level of soil contamination (LSC). The LSC is the concentration of Hg in adobe bricks or dirt floors that may result in a child with the given characteristics exceeding the health standard.

$$\mathrm{LSC} = \frac{\mathrm{BM} \times \mathrm{BW}}{\mathrm{IR} \times \mathrm{AF}} \tag{1}$$

where LSC is the level of soil contamination (μg Hg/g soil) that may result in the health-standard value being exceeded, BM = health standard (μg Hg/kg BW/day), BW = body weight (kg), IR = amount ingested (g soil/day), AF = adjustment factor of 10 to adjust for the proportionality of the Hg concentrations in the F1 + F2 + F3 and simulated GF extractions.

As shown in Table 4, the LSC varies substantially between health standards, with the ATSDR MRL of 2 μg Hg/kg BW/day (ATSDR 1999) yielding the highest LSCs and the Environment Agency MDI of 0.037 μg Hg/kg BW/day (Environment Agency 2009) producing the lowest LSCs.

In previous studies, total Hg concentrations were compared with the EPA reference dose (RfD); the

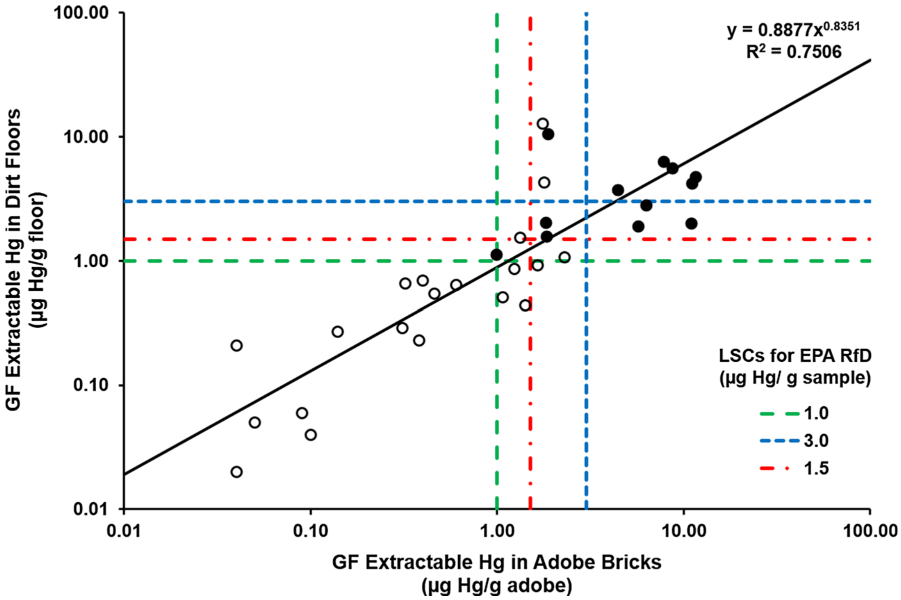

Fig. 3 Least-squares regression for mass of Hg (µg/g) from simulated GF extraction of adobe bricks and dirt floors with level of soil contamination (LSCs) for the EPA reference dose (RfD)

results suggested the potential public health problem from Hg exposure in Huancavelica was widespread (Hagan et al. 2013; Robins et al. 2012), with up to 75 % of the 60 households exceeding the RfD. However, by comparing the simulated GF extraction data with the LSCs calculated for the EPA RfD, the number of households identified as being at potential risk from ingestion is substantially reduced.

For example, comparison of the simulated GF extraction data with the LSCs calculated for the EPA RfD (after application of adjustment factor of 10), as shown in Fig. 3, identifies households with GF extractable Hg in adobe bricks and floor dust above the LSC (upper right quadrant). These households would have a higher priority for additional analysis and mitigation than those households with GF extractable Hg in adobe bricks and floor dust below the LSC. Assuming a worst case scenario of 0.3 g per day soil ingested (LSC for EPA RfD, large dashed (green) line in Fig. 3), the simulated GF extraction data indicate that 15 of the sample households would exceed the LSC. Similar analysis comparing F1 + F2 + F3 extractable Hg in adobe bricks and dirt floors with the LSCs for the EPA RfD was done to ensure the simulated GF extractions identified the same households exceeding the LSCs as did SSE. The solid black data points in Fig. 3 represent the 12 households that would also exceed the LSC when using the SSE procedure.

Although traditional application of health standards is intended to be protective by assuming a worst-case scenario, time and resources should be allocated to those households with the greatest potential risk from ingestion of Hg-contaminated soil. By use of a minimum of calculations and utilizing more detailed information from additional Hg analysis, households exceeding the LSCs have been identified and can be prioritized for future intervention, mitigation, and remediation strategies, particularly for those households with small children.

Conclusions

The purpose of this study was to characterize the species of Hg present in adobe brick and dirt floor samples and to evaluate the bioaccessibility of Hg in simulated gastric fluid. Results of this study suggest, as is typical for soils, most of the Hg in adobe bricks and dirt floors was bound with sulfur and relatively insoluble in weakly acidic and strongly basic solutions. However, for some households soluble Hg species were present in the more mobile F1, F2, and F3 fractions of SSE. The percentage of the total Hg extracted by simulated GF extraction of adobe bricks and dirt floors was up to 7.4 and 6.8 %, respectively. Although the bioaccessible Hg is only a small fraction of the total Hg present in a sample, there is still potential for concern after ingestion.

The results of this study demonstrate a strong correlation between the sum of the more soluble fractions of the SSE method (F1 + F2 + F3) and simulated GF extractions for both sample types. This is an important finding, in that simulated GF extractions have the potential to be used as a screening tool for most effective allocation of time and resources by performing SSE on samples that have measurable concentrations of bioaccessible Hg.

By combining information related to body weight and amounts ingested by children and health standards for oral exposure to Hg, it was possible to calculate levels of soil contamination (LSC) resulting in different exposure. These calculations revealed that Hg concentrations obtained by use of simulated GF extraction of adobe brick and dirt floor samples from some households exceed health standards for soluble Hg, although the magnitude of the potential public health impact is much lower than when total Hg is compared. Combining simulated GF extraction data within the home with LSCs will enable more targeted intervention, mitigation, and remediation strategies for households with the greatest potential health implications from ingestion of contaminated particles.

Acknowledgments This work was supported in part by a Duke Global Health Institute pilot grant. Nicole Hagan would like to acknowledge support from an Oak Ridge Institute Science and Education fellowship at the US EPA National Center for Environmental Assessment, Office of Research and Development and from the EPA/UNC Toxicology Training Agreement CR-83515201-0, with the Curriculum in Toxicology, University of North Carolina at Chapel Hill. Special thanks to the residents of Huancavelica who participated in the study, to research collaborators Enrique Ecos, Susan Halabi, Dan Richter, and John Vandenberg for support, to Jeff Ryan, Peter Kariher, and Eric Morris for experimental and analytical assistance, to David Svendsgaard for statistical guidance, and to David Leith and Joe Pedit for review of the manuscript. The authors would also like to thank Paul Heine and Barbara MacGregor, USDA-recognized Soil-Containment Officers, for coordinating soil import and containment.

References

ATSDR (Agency for Toxic Substances and Disease Registry). (1999). T*oxicological profile for mercury*. Atlanta, GA: US Department of Health and Human Services, Public Health Service. Available: http://www.atsdr.cdc.gov/toxprofiles/tp.asp?id=115&tid=24. Accessed 10 January 2011.

Bloom, N. S., Preus, E., Katon, J., & Hiltner, M. (2003). Selective extractions to assess the biogeochemically relevant fractionation of inorganic mercury in sediments and soils. *Analytica Chimica Acta, 479*, 233–248.

Environment Agency (2009). *Contaminants in soil: updated collation of toxicological data and intake values for humans, mercury*. Bristol: Environment Agency. http://a0768b4a8a31e106d8b0-50dc802554eb38a24458b98ff72d550b.r19.cf3.rackcdn.com/scho0309bpqn-e–e.pdf. Accessed 15 July 2013.

Gochfield, M. (2003). Cases of mercury exposure, bioavailability, and absorption. *Ecotoxicology and Environmental Safety, 56*, 174–179.

Gray, J. E., Plumlee, G. S., Morman, S. A., Higueras, P. L., Crock, J. G., Lowers, H. A., et al. (2010). In vitro studies evaluating leaching of mercury from mine waste calcine using simulated human body fluids. *Environmental Science and Technology, 44*, 4782–4788.

Hagan, N., Robins, N., Hsu-Kim, H., Halabi, S., Espinoza Gonzales, R. D., Richter, D., et al. (2013). Residential mercury contamination in adobe brick homes in Huancavelica. *Peru. PLoS One, 8*, e75719.

Hagan, N., Robins, N., Hsu-Kim, H., Halabi, S., Morris, M., Woodall, G., et al. (2011). Estimating historical atmospheric mercury concentrations from silver mining and their legacies in present-day surface soil in Potosí, Bolivia. *Atmospheric Environment, 45*, 7619–7629.

JECFA. (Joint FAO/WHO Expert Committee on Food Additives). (2010). Summary and conclusions. In: *Joint FAO/WHO expert committee on food additives seventy-second meeting*, 16–25 February 2010, Rome, Italy. Available: http://www.who.int/foodsafety/chem/summary72_rev.pdf. Accessed 12 September 2013.

Kim, C. S., Bloom, N. S., Ryutba, J. J., & Brown, G. E. (2003). Mercury speciation by X-ray absorption fine structure spectroscopy and sequential chemical extractions: a comparison of speciation methods. *Environmental Science and Technology, 37*, 5102–5108.

Li, Y. (2013). Environmental contamination and risk assessment of mercury from a historic mercury mine located in southwestern China. *Environmental Geochemistry and Health, 35*, 27–36.

Li, P., Feng, X., Qiu, G., Zhang, J., Meng, B., & Wang, J. (2013). Mercury speciation and mobility in mine wastes from mercury mines in China. *Environmental Science and Pollution Research, 20*, 8374–8381.

Male, Y. T., Reichelt-Brushett, A. J., Pocock, M., & Nanlohy, A. (2013). Recent mercury contamination from artisanal gold mining on Buru Island, Indonesia—potential future risks to environmental health and food safety. *Marine Pollution Bulletin, 77*, 428–433.

Mendoza, J. (2012). *86.5% de casas en Huancavelica son de adobe y tapia* [in Spanish]. Correo (Huancavelica, Peru) 14 November. http://diariocorreo.pe/ultimas/noticias/2271103/edicion+huancavelica/86-5-de-casas-de-huancavelica-son-de-adobe-y. Accessed 25 February 2013.

Revis, N. W., Osborne, T. R., Holdsworth, G., & Hadden, C. (1990). Mercury in soil: A method for assessing acceptable limits. *Archives of Environmental Contamination and Toxicology, 19*, 221–226.

Robins, N. A. (2011). *Mercury, mining, and empire, the human and ecological costs of colonial silver mining in the Andes*. Indiana: Indiana University Press.

Robins, N. A., & Hagan, N. A. (2012). Mercury production and use in colonial Andean silver production: emissions and health implications. *Environmental Health Perspectives, 120*, 627–631.

Robins, N. A., Hagan, N., Halabi, S., Hsu-Kim, H., Espinoza Gonzales, R. D., Morris, M., et al. (2012). Estimations of historical atmospheric mercury concentrations from mercury refining and present-day soil concentrations of total mercury in Huancavelica, Peru. *Science of the Total Environment, 426*, 146–154.

Schaider, L. A., Senn, D. B., Brabander, D. J., McCarthy, K. D., & Shine, J. P. (2007). Characterization of zinc, lead, and cadmium in mine waste: Implications for transport, exposure, and bioavailability. *Environmental Science and Technology, 41*, 4164–4171.

US EPA (US Environmental Protection Agency). (1995). *Mercuric chloride*. http://www.epa.gov/iris/subst/0692.htm. Accessed 15 January 2011.

US EPA (United States Environmental Protection Agency). (1997). *Mercury study report to congress*. Washington, DC: US EPA. Available: http://www.epa.gov/hg/report.htm. Accessed 9 September 2013.

US EPA (US Environmental Protection Agency). (2008a). *Method 30B—determination of total vapor phase mercury emissions from coal-fired combustion sources using carbon sorbent traps*. http://www.epa.gov/ttn/emc/methods/method30B.html. Accessed April 2012.

US EPA (US Environmental Protection Agency). (2008b). *Child-specific exposures factor handbook (Final Report)*. http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=199243. Accessed 15 January 2011.

Zagury, G. J., Bedeaux, C., & Welfringer, B. (2009). Influence of mercury speciation and fractionation on bioaccessibility in soils. *Archives of Environmental Contamination and Toxicology, 56*, 371–379.