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Residential metal contamination and potential health risks of exposure in adobe brick houses in Potosí, Bolivia

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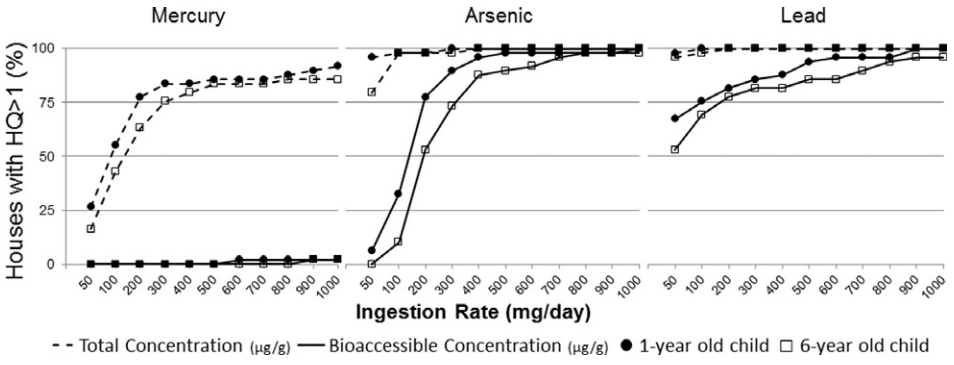
HIGHLIGHTS

- Potosí, Bolivia has been a center of silver mining activity since the 16th century.
- Measured total trace elements in residential samples from Potosí were elevated.
- A simulated gastric fluid extraction was used to measure bioaccessibility.
- Hg, As, and Pb in adobe particles may represent a health risk for children.
- Adobe brick houses are a potential source of exposure to metals/metalloids.

GRAPHICAL ABSTRACT



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ABSTRACT

Potosí, Bolivia, is the site of centuries of historic and present-day mining of the Cerro Rico, a mountain known for its rich polymetallic deposits, and was the site of large-scale Colonial era silver refining operations. In this study, the concentrations of several metal and metalloid elements were quantified in adobe brick, dirt floor, and surface dust samples from 49 houses in Potosí. Median concentrations of total mercury (Hg), lead (Pb), and arsenic (As) were significantly greater than concentrations measured in Sucre, Bolivia, a non-mining town, and exceeded US-based soil screening levels. Adobe brick samples were further analyzed for bioaccessible concentrations of trace elements using a simulated gastric fluid (GF) extraction. Median GF extractable concentrations of Hg, As, and Pb were 0.085, 13.9, and 32.2% of the total element concentration, respectively. Total and GF extractable concentrations of Hg, As, and Pb were used to estimate exposure and potential health risks to children following incidental ingestion of adobe brick particles. Risks were assessed using a range of potential ingestion rates (50–1000 mg/day). Overall, the results of the risk assessment show that the majority of households sampled contained concentrations of bioaccessible Pb and As, but not Hg, that represent a potential health risk. Even at the lowest ingestion rate considered, the majority of households exceeded the risk threshold for Pb, indicating that the concentrations of this metal are of particular concern. To our knowledge, this is the first study to quantify key trace elements in

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building materials in adobe brick houses and the results indicate that these houses are a potential source of exposure to metals and metalloids in South American mining communities. Additional studies are needed to fully characterize personal exposure and to understand potential adverse health outcomes within the community.

1. Introduction

The arrival of Spanish colonists in South America in the 16th century marked the beginning of a long period of mining for the rich polymetallic deposits within the region (Garcia-Guinea and Harffy, 1998). In the city of Potosí, Bolivia, Spanish colonists established intensive mining operations at the Cerro Rico, one of the world's largest silver deposits, in 1545. By the early 1570s, mercury amalgamation was adopted for silver refining, resulting in the release of mercury and other toxic compounds into the surrounding air and watershed of the city (Robins, 2011). Between 1564 and 1800, it is estimated that 39,000 metric tons of mercury vapor were released from the silver refining operations in Potosí (Robins and Hagan, 2012). As the production of silver began to decline in the late 1800s, mining for other metals, primarily tin, lead, and zinc, increased, and these operations continue today, with an estimated 20,000 miners working old mine tailings or new mine shafts at Cerro Rico (Strosnider et al., 2011).

Several studies have investigated the ecological and environmental effects of mining operations on communities downstream of Potosí in the Pilcomayo River Basin (Miller et al., 2004; Strosnider et al., 2011). Within the city of Potosí, research has focused primarily on mercury contamination from the historical amalgamation-based refining operations, which ceased in the early 1900s (Miller et al., 2004). Previously reported present-day measurements of average total mercury in ambient surface soils across Potosí ranged from 0.105 to 155 μg/g (Hagan et al., 2011). The authors of this study reported that these concentrations were approximately 20 to 30,000 times greater than concentrations in surface soil collected from Sucre, a non-mining town in Bolivia. Additionally, the range of concentrations reported in Potosí exceeded the U.S. EPA soil screening level for the protection of human health (23 μg/g) (Hagan et al., 2011; U.S. EPA, 2002). Hagan et al. (2011) found that total mercury concentrations in ambient soils increased with proximity to the former site of the *ribera*, the canal that ran through the center of Potosí and supported the amalgamation activities. Another study reported that while present-day ambient mercury vapor concentrations along the *ribera* in Potosí were low, excavation of topsoil near former mill sites caused the release of elemental mercury vapor in concentrations over 3000 ng/m^3, which is an order of magnitude greater than the U.S. EPA reference concentration for the inhalation of elemental mercury (300 ng/m^3) (Higueras et al., 2012; U.S. EPA, 1995a). While there have been a number of studies related to mercury, studies of other mining-related pollutants (e.g., lead, arsenic, zinc) in Potosí are lacking.

The residents of Potosí may be chronically exposed to toxic, mining-related metals from a number of sources, including contaminated soil. Particles of this contaminated soil, as well as mining waste piles or mining-related emissions, may be directly ingested or inhaled, or may deposit and accumulate as indoor or outdoor dust (Schaider et al., 2007). Exposure may be greater to the residents of Potosí as a result of airborne particulates generated from active mining activities and compounded by living in adobe brick homes constructed with historically contaminated soil. Previous studies in Huancavelica, a historic cinnabar mining town in Peru, have shown that the adobe brick walls and dirt floors in adobe brick houses contain concentrations of mercury that are among the highest in the world (Hagan et al., 2013). As in Potosí, the building materials in Huancavelica were sourced from the immediate vicinity in which the house was built and reflect legacy contamination resulting from centuries of mining and refining operations. Additionally, a study in Oruro, Bolivia suggested that uncovered, earthen building materials contribute to levels of indoor house dust, which are already high due to the dry and dusty outdoor environment (Fontúrbel et al., 2011).

Exposure to contaminated building materials is of particular concern for children, who are not only more sensitive to the adverse effects of mercury and other metals/metalloids, but also have increased exposures due to frequent hand to mouth activity, increased time spent playing on dirt or dusty floors, and other behaviors (Hubal et al., 2000). Studies in Oruro, Bolivia found that children living in a mining district had significantly higher exposure to elements such as lead and arsenic than children living in a peripheral district where mining and metallurgical activities were not occurring (Barbieri et al., 2011; Fontúrbel et al., 2011). Additionally, concentrations of trace elements in hair and indoor dust samples were more strongly correlated in the mining district than the peripheral district (Barbieri et al., 2014). The majority of households in Oruro had characteristics that may have increased indoor dust levels and exposure, such as walls without a coating or the presence of miners who carried work equipment and clothing into the house (Fontúrbel et al., 2011).

The objectives of this study were to: quantify total and bioaccessible concentrations of trace elements, particularly metals, in adobe brick houses; compare metal and metalloid elements in residential samples from Potosí with Sucre, a non-mining reference site in Bolivia; and estimate potential health risks for children following exposure to these elements. To our knowledge, this is the first study to report the concentrations of several trace elements, including mercury, lead, arsenic, zinc, and copper, in residential samples from Potosí and the first study to compare the total and operationally-defined bioaccessible concentrations of these elements in adobe bricks.

2. Methods

2.1. Sample collection

Samples of interior adobe brick, dirt floor, and surface dust were collected from 49 residences across Potosí in June 2011. Household locations, shown in Fig. 1, were selected based on the results of previous ambient soil sampling, estimates of historical mercury emissions, and modeled historic mercury air concentrations (Hagan et al., 2011). Adult residents or homeowners were recruited from public meetings or interactions prior to the sampling event and were asked to provide written consent, as outlined in the human subjects research protocol approved by the Duke University Institutional Review Board (IRB).

All samples in each household were collected in triplicate from the room that the residents indicated they spent most of their time, when possible. In 16 of the 49 households, samples were taken from multiple rooms. Surface dust was obtained by wiping a 100 cm^2 area with a smear tab (Whatman Low Ash Grade 50 Filter Paper, Fisher Scientific) moistened with water. Surfaces were typically a hard, flat surface such as a dresser or kitchen table. Adobe brick samples were collected by scraping approximately 20 g of surface material to a depth of approximately 2 cm from interior adobe walls of the room(s).

Dirt floor samples were collected by removing approximately 20 g of surface material (approximately top 3 cm) from the dirt floor or patio at three different locations. Indoor earthen (dirt) floor samples were collected in the ten households that did not have sealed or covered floors. For the 32 households that had sealed indoor floors, dirt floor samples were collected from the outdoor patio area immediately outside the home. Seven homes with sealed floors either did not have dirt patios or had sealed patios outside of their home; therefore, dirt floor samples were not collected from these households.

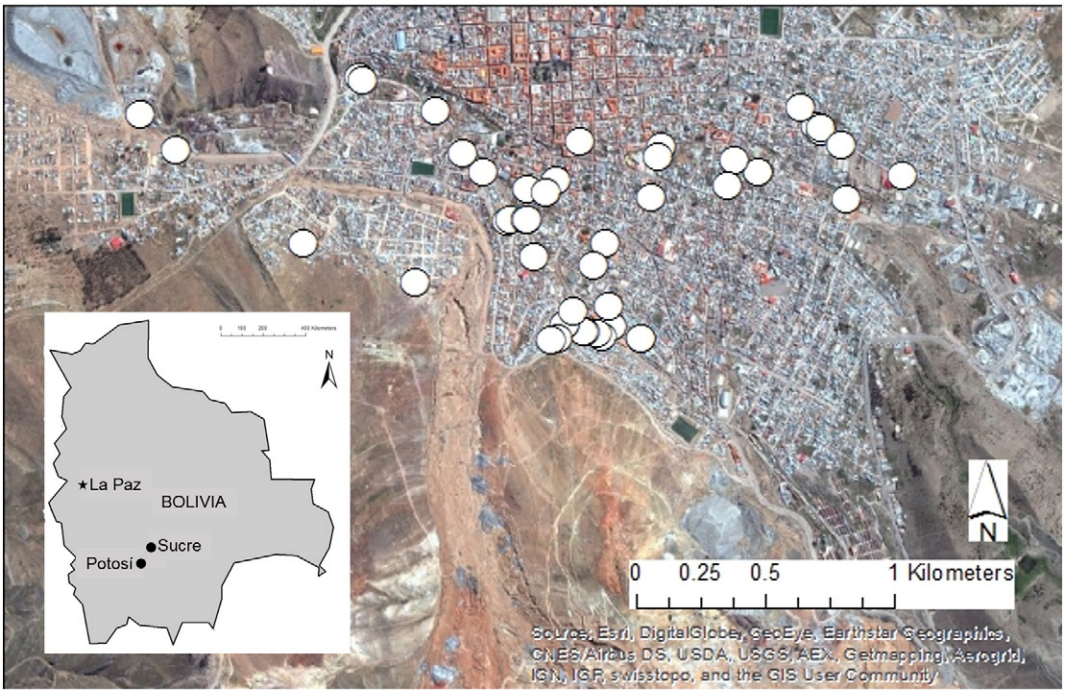

Fig. 1. Locations of households sampled in Potosi ($n = 49$) and map of Bolivia. Household samples ($n = 5$) were also collected in Sucre, a community with no known history of mining activities. La Paz shown for reference only. Created using ArcMap v10.2 (ESRI, 2014).

In Sucre, a non-mining town located approximately 80 km northwest of Potosí, triplicate samples of dirt floors ($n = 4$ households) and adobe bricks ($n = 5$ households) were collected using the same methods used to collect samples in Potosí.

All samples were stored in individual zip-top plastic bags and transported to the laboratory at Duke University. Upon arrival at the lab, the samples were stored at 4 °C until the time of analysis.

2.2. Sample analyses

Adobe brick, dirt floor, and surface dust samples were extracted for major and trace element content by acid hot block digestion in 4:1 hydrochloric acid (HCl):nitric acid (HNO_3) at 85–90 °C for 6 h. Approximately 0.2–0.5 g of the adobe brick and dirt floor samples were digested, while the entire surface dust sample (dust + wipe) was digested. Following acid digestion, the samples were diluted in filtered water (Milli-Q Millipore, 18 MΩ-cm). Approximately half of the acidified digestate was dispensed into pre-cleaned glass vials (BrooksRand) and preserved with 1% bromine monochloride (BrCl) for total mercury analysis. The remaining sample was reserved for analysis of major and trace elements. For every 30 samples digested, a soil standard reference material (SRM; NIST San Joaquin soil 2709 and 2709a) and a method blank were digested in parallel for quality assurance/quality control.

A simplified bioaccessibility extraction test (SBET) in simulated gastric fluid (GF) was performed on adobe brick samples to estimate the amount of trace element that would be available for absorption by the body following ingestion. The method used in this study was adapted from a protocol developed and validated for the analysis of lead (U.S. EPA, 2007), but has also been used for other elements, including zinc, cadmium, and mercury (Schaider et al., 2007; Hagan et al., 2014). These studies have also demonstrated that this method provides site-specific information that improves the accuracy of exposure and risk calculations, while being less resource and time intensive than other methods. The simulated GF extraction was only performed on one of the triplicate adobe brick samples collected from each household. The sample selected for the GF extraction was the one representing the median total Pb concentration for the household.

The simulated GF contained 0.4 M glycine dissolved in Milli-Q water adjusted to pH 1.5 using trace metal-grade HCl. Samples of 0.2–0.5 g adobe brick were extracted in this solution at a 1:100 solid:liquid ratio for 1 h at 37 °C (±2 °C). The slurry was mixed end-over-end by hand every 10 min during the simulated GF digestion. Following the 1 h extraction time, the liquid was filtered with a 0.45 μm cellulose acetate syringe filter. An aliquot of approximately 5–7 mL was reserved for major and trace element analysis. The remaining sample was preserved for mercury analysis with the addition of 1% BrCl. For every 10 samples in the GF extractions, a method blank, SRM (NIST 2709a), and replicate sample were extracted using the same method.

All samples were analyzed for mercury using cold vapor atomic fluorescence spectroscopy (CVAFS; Brooks Rand T-MERX, EPA Method 1630E). Instrument calibrations were performed with a mercuric nitrate stock solution. Reagent blanks, matrix spikes on blanks, and SRMs were included in order to monitor and evaluate analytical performance.

Major and trace elements were quantified by inductively coupled plasma mass spectrometry (ICP-MS; Agilent Technologies 7700×). Prior to analysis, samples were diluted by 20- to 100-fold with a 2% HNO_3 and 0.5% HCl mixture (Optima-grade acids, VWR). Instrument calibrations were performed with multi-element and major cation element stock solutions. The calibrations were verified before and during the sample run with SRMs (NIST 1643e and High Purity Standards CRM-TMDW-A).

All samples were analyzed for a suite of 21 major and trace elements. Only 14 of these elements had SRM recoveries (for the heated HCl:HNO_3 acid digestion procedure) within the acceptable range for quantitative or semi-quantitative analysis (67–118%). These elements and their percent recoveries were: zinc (Zn, 118%), mercury (Hg, 117%), arsenic (As, 105%), manganese (Mn, 105%), nickel (Ni, 102%), copper (Cu, 102%), cobalt (Co, 99%), magnesium (Mg, 97%), iron (Fe, 96%), vanadium (V, 93%), silver (Ag, 92%), calcium (Ca, 89%), chromium (Cr, 79%), and lead (Pb, 67%). From this point on, all elements are referred to by their element symbol (i.e., Hg). Percent recoveries for all 21 elements analyzed are presented in Table S1 of the Supplementary Material. No adjustments for percent recovery were made.

All analytical results were adjusted for blank concentrations (i.e. acidified Milli-Q water) when blank results were <10 times smaller than sample results. In cases where results were below the limit of detection (LOD), this value was replaced with the detection limit divided by the square root of two.

Total element concentrations in surface wipes were converted from units of μg/wipe to μg/cm^2 by multiplying by a factor of 0.01 (1 wipe = 100 cm^2). The GF extractable fraction (%) was calculated by dividing the GF extractable concentration (μg/g) by the total element concentration (as determined by HCl:HNO_3 digestion) of the same individual triplicate sample and multiplying this value by 100.

2.3. Statistical and data analysis

Total element concentrations (Mg, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ag, Hg, Pb) for all triplicate samples within a household were averaged for each sample type (adobe brick, dirt floor, and surface dust). For all elements and sample types, the resulting concentration data were not normally distributed. Major earth elements (Mg, Ca, and Fe) were not included in the statistical analysis.

Results of a Wilcoxon rank sum test showed that there were no statistically significant differences between total element concentrations in dirt floor samples collected inside ($n = 10$) and outside ($n = 32$) houses in Potosí; therefore, analytical results from indoor and outdoor samples were both used in all statistical analyses and are collectively referred to as dirt floor samples.

Our hypothesis was that the total concentrations of each of the 11 trace elements (Ag, As, Co, Cu, Cr, Hg, Mn, Ni, Pb, V, Zn) were greater in dirt floor and adobe brick samples from Potosí than samples from Sucre households. The Wilcoxon rank-sum test was used to compare element concentrations in adobe bricks and dirt floors from Potosí samples with the reference site, Sucre. No correction for multiple testing was performed. The Wilcoxon rank sum, rather than the *t*-test, was performed on untransformed data due to the limited number of samples collected from the Sucre site and to avoid any distribution misspecification of the concentration levels. In addition, the Spearman rank correlation coefficients (rho) were calculated to estimate the correlations between total trace element concentrations in adobe brick, dirt floor, and surface dust samples.

When applicable, trace element concentrations were also compared against generic, U.S.-based soil screening levels (shown in Table 1 and Supplementary Material: Table S2), which are risk-based concentrations developed to protect human health from ingestion exposures to chemicals in residential scenarios (U.S. EPA, 2002). Soil screening levels from California were used when Federal reference values were not available (Cal EPA, 2005). While these screening levels were developed to assist in the evaluation of contaminated soils at sites on the National Priorities List (NPL) in the United States, they provide a useful screening level tool to prioritize metal and metalloid elements quantified in this study for further evaluation, given that site-specific screening levels were not available for Potosi or Bolivia. Major metal elements (Ca, Mg, Fe), which do not have soil screening values and are generally not associated with adverse health effects at naturally occurring levels, were excluded from this analysis.

All statistical analyses were completed using R 3.10 (R Core Team, 2014). Unless noted, all tests were run at the 5% significance level. For boxplots shown in figures, the boxes represent the first quartile, median, and third quartile; whiskers represent minimum and maximum values; and the squares represent arithmetic means.

Table 1
U.S.-based soil screening levels for selected elements.

Element	Soil screening level[a] (μg/g)
Arsenic (As)[b]	0.4
Mercury (Hg)	23.0
Silver (Ag)	390.0
Lead (Pb)[c]	400.0
Copper (Cu)[d]	3000.0
Zinc (Zn)	23,000.0

[a] Federal U.S. value based on ingestion (U.S. EPA, 2002) unless otherwise noted.
[b] U.S. EPA (2002); based on cancer risk to 1 in 1 million.
[c] U.S. EPA (1994).
[d] Cal EPA (2005); based on total exposure.

3. Results and discussion

3.1. Total element concentrations in adobe bricks, dirt floors, and surface dust

The total concentrations of elements, such as Hg, As, Pb, Ag, Cu, and Zn, in adobe brick, dirt floor, and dust samples varied considerably, and sometimes by orders of magnitude between households. Summary statistics (median, mean, standard error, range) for total element concentrations in adobe brick, dirt floor, and surface dust samples from Potosí and Sucre are presented in Tables S3 and S4 of the Supplementary Material.

3.1.1. Adobe brick

Median total concentrations of Hg, As, Pb, Ag, Cu, and Zn measured in adobe bricks from Potosí were significantly higher ($p < 0.001$) than concentrations reported in adobe bricks from Sucre (Fig. 2). In particular, the concentrations of total Hg and Ag in adobe bricks from Potosí were three orders of magnitude greater than in adobe bricks from Sucre. These results confirm our hypothesis that concentrations of these elements were significantly elevated in samples from Potosí compared to Sucre and highlights the legacy of historical mining and amalgamation-based refining operations in the city of Potosí. On the other hand, there were no statistically significant differences in median concentrations of total Co, Cr, V, and Mn between adobe bricks in Potosí and Sucre ($p > 0.05$) and the median concentration of total Ni was significantly higher in adobe bricks from Sucre than adobe bricks from Potosí ($p = 0.028$) (Supplementary Material: Fig. S1).

Other sources of metals, such as consumer waste products or non-mining industries could have contributed to the elevated metals in Potosí; however, we are not aware of specific examples, other than the multi-century mining legacy. Natural geological variations could

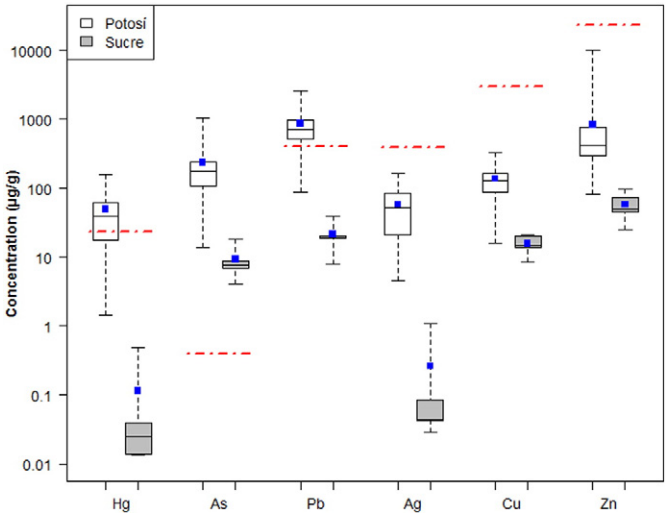

Fig. 2. Comparison of total element concentrations (μg/g) in adobe bricks from Potosí ($n = 49$) with concentrations in adobe bricks from Sucre ($n = 5$) and U.S.-based soil screening reference levels (dashed horizontal lines, corresponding to values shown in Table 1).

also contribute to the variations between Potosí and Sucre. Nevertheless, with the orders of magnitude differences in concentrations, especially for Hg and Ag, we believe the mining legacy is a major contribution to soil composition in Potosí.

As shown in Fig. 2, median household concentrations of total Hg, As, and Pb in adobe samples also exceeded U.S.-based soil screening reference values, which suggests that these elements may pose a risk to human health. Although median concentrations of total Ag, Cu, and Zn were statistically greater in samples from Potosí relative to Sucre, all sample concentrations of these elements were well below the U.S.-based soil screening levels. These results are unsurprising, given that Ag, Cu, and Zn have relatively low toxicity in comparison to Hg, As, and Pb, the latter of which are known to induce a variety of adverse health outcomes in humans even at low doses (U.S. EPA, 1993, 1995b, 2004).

The highest concentrations of Ni, V, Cr, and Co found in adobe bricks in Potosí (13.8, 61.2, 20.0, and 10.3 μg/g, respectively) were at least one order of magnitude below applicable U.S.-based soil screening levels (Supplementary Material: Fig. S1, Table S2). Although there was no published health screening value for Mn, a screening value of 10,900 mg/kg for ingestion exposure was calculated using equation 3-2 from the Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites (default inputs used; U.S. EPA, 2002). The highest concentration of Mn reported in adobe bricks from Potosí was below this screening value (Supplementary Material: Fig. S1).

3.1.2. Dirt floor

The comparison of total metal/metalloid concentrations in dirt floor samples from Potosí ($n = 42$) and Sucre ($n = 4$) yielded similar results to those reported for adobe bricks. Results from the dirt floor samples are shown in greater detail in Figs. S2 and S3 of the Supplementary Material. The median concentrations of total Hg ($p < 0.001$), As ($p < 0.001$), Ag ($p < 0.001$), Cu ($p < 0.001$), Zn ($p < 0.001$), and Pb ($p = 0.037$) were significantly higher in dirt floor samples from Potosí than dirt floor samples from Sucre. Additionally, the median concentration of Ni was significantly higher in dirt floor samples from Sucre than dirt floor samples from Potosí ($p = 0.008$), but there were no significant differences between median concentrations of Co, Cr, V, or Mn.

Median concentrations of As and Pb in dirt floor samples from Potosí exceeded the U.S. based soil screening values. Although the median concentration of Hg (17.5 μg/g) in dirt floors from Potosí was below the U.S. based soil screening value (23 μg/g), the mean concentration (26.6 μg/g) exceeded this value. As with adobe brick samples, the highest concentrations of the other elements (Co, Ni, Cr, V, and Mn) reported in dirt floor samples from Potosí were below applicable soil screening levels.

3.1.3. Surface dust in Potosí residences

Surface dust samples were not collected from Sucre, therefore, levels in Potosí could not be compared against those found at a reference site. Additionally, there are no human health reference values for surface dust loadings for metals, with the exception of Pb. The U.S. EPA has set two Pb surface dust hazard standards: 40 μg/ft^2 (0.043 μg/cm^2) for floors and 250 μg/ft^2 (0.270 μg/cm^2) for interior window sills (U.S. EPA, 2001). In Potosí, the median Pb loading (0.022 μg/cm^2) in surface dust was below both of these standards. A total of 11 households had surface dust Pb levels that exceeded the U.S. standard for floors, while no households exceeded the standard for interior window sills. It should be noted that the majority of surface dust samples collected in Potosí were taken from elevated surfaces, such as tables, and not from floor areas.

It is also of interest that the element with the highest median surface dust loading, besides Ca and Fe, was Zn (0.100 μg/cm^2). The median Zn surface dust loading was greater than that for Mg (0.091 μg/cm^2), which is a major earth element and was one of the predominant elements in the adobe and floor samples.

3.2. Correlations between adobe bricks, dirt floors, and dust

The Spearman correlation coefficients (rho) between total element concentrations in household adobe bricks, dirt floors, and surface dust samples are shown in Table 2. Moderate, positive correlations ($0.5 < \text{rho} < 0.75$) were observed between adobe brick and dirt floor samples for total Hg (rho = 0.617), As (rho = 0.572), and Ag (rho = 0.528) concentrations. This is expected, as adobe bricks were commonly built from soil located at the site of the household. Additionally, this suggests that concentrations of these elements in adobe brick and dirt floors within a household share a common source. In particular, the moderate correlations observed for Hg and Ag highlight the legacy of silver refining through the mercury amalgamation process used in the city of Potosí. On the other hand, weak correlations ($\text{rho} < 0.5$) were observed between adobe brick and dirt floor samples for the following elements: Cu (rho = 0.460), Zn (rho = 0.113), and Pb (rho = 0.264). It is unclear why moderate or strong correlation was not observed for all elements. A plausible explanation may be that there are multiple sources of trace element contamination, changes in the type of mining that altered the distribution of metals release in the city, or weathering processes occurring outdoors, as the majority of dirt floor samples were collected from outside the house.

Correlations between total element concentrations in adobe bricks and surface dust were weak to moderate for all elements (Table 2). The highest correlation coefficient was observed for Hg (rho = 0.453). There was also a moderate, positive correlation between total Hg concentrations in dirt floor samples and surface dust (rho = 0.636); however, correlations between concentrations in dirt floors and surface dust were weak for all other elements. The moderate correlations observed between total Hg concentrations in surface dust and concentrations in adobe bricks or dirt floors suggests that particles of adobe bricks or dirt floors may contribute to surface dust loading of Hg.

With the exception of total Hg, the lack of correlations between the concentrations in surface dust and adobe bricks or dirt floors may indicate that adobe bricks or dirt floors are not the primary or only source of indoor surface dust loading. It is likely that surface dust loading is a combination of particles from indoor sources, such as re-entrained particles from adobe bricks or dirt floors, as well as infiltration of particles from external sources. Adobe brick houses are generally not well sealed to the external environment, and other housing factors, such as open windows and cracks in the walls, have been shown to influence the prevalence of outdoor particles entering the indoor environment (Adamkiewicz et al., 2011; Jacobs et al., 2007; Matte and Jacobs, 2000). For example, the recent use of leaded gasoline in motor vehicles might more directly affect Pb surface dust loading, but not adobe brick or dirt floor concentrations, which are more likely from historical mining sources; however, lead isotope analysis would be required to confirm this explanation. Additional factors, such as having a resident who is a miner and carries work equipment into the house, may also contribute to indoor surface dust (Fontúrbel et al., 2011). However, it is difficult to interpret correlations between surface dust loading and concentrations of elements in adobe bricks or dirt floors, as they are measured in different units (μg/g versus μg/cm^2) and the amount of dust on furniture surfaces varied between households.

Table 2
Spearman rank correlation coefficients (rho) for total concentrations of select elements in adobe bricks, dirt floors, and surface dust.

Element	Bricks — floors	Bricks — dust	Floors — dust
n	42	48	41
Hg	0.617	0.453	0.636
Cu	0.460	0.161	0.046
Zn	0.113	0.079	0.050
As	0.572	0.298	0.308
Ag	0.528	0.170	0.300
Pb	0.264	0.082	0.098

3.3. Gastric fluid (GF) extractable elements in adobe bricks

Based on the limited surface dust samples available for analysis and the fact that the majority of houses had sealed floors, subsequent analyses for bioaccessibility and health risks focused on the adobe brick samples. Results from the GF extraction are only presented for Hg, As, and Pb, as these elements had reported median concentrations that exceeded the U.S.-based soil screening values shown in Table 1. Median (range) concentrations (μg/g) of GF extractable Hg, As, and Pb were 0.085 (0.006–5.462), 25.6 (3.3–85.9), and 224.7 (6.8–868.8), respectively (Fig. 3, left panel). There were positive correlations between total and GF extractable concentrations for Hg, As, and Pb, which indicates that households with higher total element concentrations also had higher GF extractable concentrations (data not shown).

The median GF extractable Hg fraction was 0.085%, and ranged from 0.020% to 9.69% of the total Hg concentration (Fig. 3, right panel). The relatively low percentage of the total Hg present in the GF extractable fraction suggests that the majority of the Hg in adobe bricks is likely present in insoluble mineral forms, such as mercury sulfide (HgS). These results are consistent with a previous study that characterized the species of Hg in ambient soil samples from Potosí using sequential selective extraction and found that the majority of Hg was present in insoluble mineral phases, such as metacinnabar (Hagan et al., 2011). It is likely that the metallic Hg emissions from the historical silver refining operations accumulated in the local terrain, but over time, weathering and other transformations (e.g. microbial, photochemical) converted the Hg to mineral phases with low bioaccessibility. Other studies that have used the same method as the present study reported low percentages of GF extractable Hg in adobe bricks from a former cinnabar mining town in Peru (0.00013% to 7.4%) and mining soils from the South of Portugal (0.10% to 1.2%) (Hagan et al., 2014; Rodrigues et al., 2014). However, there is evidence that the GF extraction may underestimate Hg concentrations compared to other methods, such as the more time consuming and resource intensive sequential selective extraction procedure (Hagan et al., 2014).

For As, the median GF extractable fraction was 13.9% of the total As concentration and ranged from 4.89% to 38.1% (Fig. 3, right panel). These percentages are greater than those reported for Hg, but are still a small fraction of the total As found in the samples, indicating that the majority of As is present in forms that are not soluble in the simulated GF, such as mineral oxides, sulfide minerals, or sulfosalts. Various studies have suggested that As bioaccessibility is controlled by the presence of Fe oxide minerals that strongly sorb As oxyanions, particularly at weakly acidic pH conditions (Juhasz et al., 2007; Yang et al., 2002). There was a moderate, negative correlation between total Fe concentrations in adobe bricks and As bioaccessibility (%) (rho = −0.643, $n = 49$). This relationship suggests that the low As bioaccessibility may be explained by higher amounts of Fe oxide that sorb As and prevent release of dissolved As in the low pH of the simulated GF.

The median GF extractable fraction of Pb was 32.2%, with a range from 1.12% to 92.8% of the total concentration (Fig. 3, right panel). GF extractable Pb concentrations from the method used in the present study are well reported in literature and vary widely depending on the type of soil analyzed (U.S. EPA, 2007). A previous study showed that galena (PbS), a type of Pb sulfide, exhibits limited bioaccessibility in a simulated GF extraction (0–3%), while the carbonate-bearing mineral cerrusite ($PbCO_3$) exhibits very high bioaccessibility (97%) (Schaider et al., 2007). The wide range of results reported in this study suggests that the dominant species of Pb present in adobe bricks may vary between households and may have different origins and extents of weathering. Households with lower percentages may reflect naturally-occurring Pb mineral deposits in the area, while households with higher percentages may reflect contamination from mining or smelting activities or deposition from other sources, such as leaded gasoline or paint.

3.4. Health risk assessment

3.4.1. Risk assessment model

Total and GF extractable Hg, As, and Pb concentrations were used to estimate exposure and potential health effects for 1 and 6 year old children. These age groups were selected because children are especially vulnerable to the potentially toxic effects of these elements, as they have an increased body burden due to their small size and increased exposures from inherent behaviors, such as hand to mouth contact and proximity to the ground (Hubal et al., 2000). Risks were not calculated for other elements, as they were below the U.S. soil screening levels.

To assess potential health risks following incidental ingestion of combined soil-dust particles, exposure was estimated by calculating an average daily intake (ADI) for a 1-year old child and a 6-year old child using Eq. (1) (U.S. EPA, 2014):

$$\mathrm{ADI} = \frac{\mathrm{C} \times (\mathrm{IR} \times \mathrm{Y}) \times \mathrm{EF} \times \mathrm{ET} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}}. \quad (1)$$

Equation variables and input values were derived according to the U.S. EPA Child-Specific Exposure Factors Handbook (U.S. EPA, 2008) for both exposure scenarios and are shown in Table 3. Exposure factors were chosen in accordance with U.S. EPA guidelines and in order to produce a conservative estimate that is protective of health. Both total

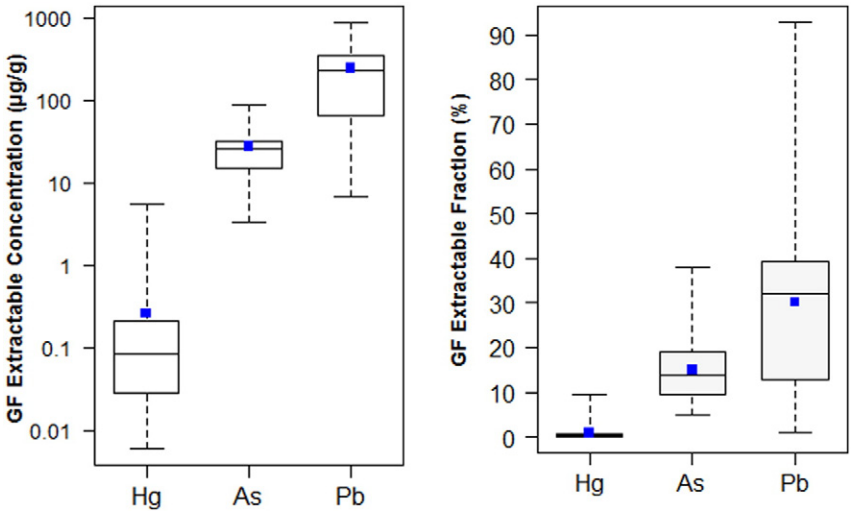

Fig. 3. Gastric fluid extractable elements in adobe bricks from Potosí expressed on a mass basis (μg/g) (left) and as a percentage of the total element concentration (%) (right) ($n = 49$).

Table 3
Input values for exposure factors used to calculate average daily intake (ADI) for a 1 and 6 year old child.

Exposure factor	1 year old	6 year old
ADI = potential sub-chronic average daily intake (μg element/kg body weight-day)	Equation output	
C = element concentration in adobe bricks (μg/g)	Household specific	
IR = average daily intake rate of combined soil and dust (mg/day)	Range between 50 and 1000	
Y = conversion factor (mg to g)	0.001	
EF = exposure frequency (days/year)	365	365
ET = exposure time (unitless)	1	1
ED = exposure duration (year)	1	5
BW = body weight (kg)	10	16.2
AT = averaging time (days)	365	1825

and GF extractable element concentrations in adobe brick were input into the equation. While adobe brick particles may not be the primary exposure media, these concentrations were used due to a lack of mass-based measurements in surface dust and because the majority of houses had sealed floors. An exposure time (ET) of 1 (unitless) was used with the assumption that outdoor environments would also contain the same elements, therefore exposure time does not just occur while inside the home. For the 6-year old child, an exposure duration (ED) and averaging time (AT) of 5 years (1825 days) was used based on assumption that children cease frequent hand to mouth or crawling activities after 5 years of age (U.S. EPA, 2014). Inhalation and dermal absorption were not considered in this analysis.

The exposure estimates used here were calculated using input data based on the characteristics of children in North America, and therefore do not necessarily reflect the exposure patterns for children in Potosí. However, U.S. EPA exposure factors have been used in site-specific risk assessments in Peru (Hagan et al., 2014) and Mexico (Carrizales et al., 2006). In the absence of site-specific exposure factors, these values are a suitable surrogate to represent children in Potosí. It is likely that body weights would be lower in Potosí and incidental ingestion would be increased given the exposed, earthen building materials present within many houses. Studies have reported mean body weights of 1 year old children in Bolivia between 8.31 kg and 9.59 kg, depending on growth rate (Ruiz-Castell et al., 2013). The body weight for a 1-year old child was adjusted from the U.S. recommended value of 11.4 kg to 10 kg to account for this difference.

One uncertainty in the exposure estimates relates to the ingestion rate (IR) for children. The EPA Child-Specific Exposure Factors Handbook (U.S. EPA, 2008) assumes a 1-year old child ingests 100 mg of dirt and dust per day from hand to mouth activity. However, in dustier environments, such as tribal or subsistence communities, ingestion rates up to 400 mg/day have been identified as an upper bound estimate for children (CTUIR, 2011). In studies in arid regions and ubiquitously dusty environments, like that in Potosí where children are exposed to more dust indoors and outdoors than U.S. children, the uncertainty in ingestion rates is even greater. In the study in Huancavelica, Hagan et al. (2014) found that potential risks varied depending on the ingestion rate that was used. In an attempt to address the uncertainties associated with ingestion rates, the exposure estimates in this study were calculated for a range of ingestion rates, from 50 mg/day to 1000 mg/day. A conversion factor of 0.001 (variable Y) was used to convert the ingestion rate from units of mg/day to g/day.

The exposure estimate (ADI) from Eq. (1) was used to estimate non-carcinogenic risk in terms of a Hazard Quotient (HQ) (U.S. EPA, 1989) using Eq. (2);

$$HQ = \frac{ADI}{RfD} \quad (2)$$

where RfD is the element-specific oral reference dose from Table 4. A hazard quotient greater than or equal to 1 represents a potential health risk, whereas a hazard quotient <1 indicates there is no appreciable health risk. While Hg, As, and Pb are associated with a variety of health endpoints, the oral RfD is developed in order to capture the most sensitive endpoint (critical effect). The oral reference doses for Hg and As are peer-reviewed values from the U.S. EPA IRIS (Integrated Risk Information System) database (U.S. EPA, 1993, 1995b).

The U.S. EPA does not have an RfD for chronic exposure to Pb, as this is considered to be a toxicant with no safe threshold, especially for children (U.S. EPA, 2004). The Joint FAO/WHO Committee on Food Additives (JECFA) had previously issued a provisional tolerable weekly intake (PTWI) value of 25 μg/kg-day; however this value was withdrawn as it was found to be associated with a decrease of 3 or more IQ points in children, which is considered unacceptable when viewed at the population level (JECFA, 2011). As the JECFA also considers Pb to be a no-threshold toxicant now, no new PTWI was proposed. For our analysis, a reference level of 0.6 μg/kg-day was used, based on an analysis of epidemiological data which estimated that chronic dietary exposure to 0.6 μg/kg-day corresponded to a decrease of 1 IQ point in children (JECFA, 2011). The selection of a level estimated to correspond to a 1 point IQ loss is consistent with the decision to set U.S. National Ambient Air Quality Standards that prevent air-related IQ loss of <2 points (40 C.F.R., pp. 67000, November 12, 2008).

3.4.2. Potential health risks

Fig. 4 shows the percentage of households with reported total and GF extractable concentrations of Hg, As, or Pb that exceeded a health benchmark according to the risk assessment model used in this study. For all three elements, the percentage of sampled households that exceeded a HQ of 1 is greater for a 1 year old child (closed circles) than a 6 year old (open squares). As expected, when using the GF extractable concentrations, rather than the total element concentrations, the risk estimates decreased substantially for all elements. This decrease in risk reflects the lower fraction of the total element concentration that is extractable in simulated GF, as discussed in Section 3.3.

Using the Child-Specific Exposure Factors Handbook recommended ingestion rate of 100 mg/day for a 1 year old and a 6 year old, 55 and 43% of households, respectively, have adobe bricks with total Hg concentrations that would exceed an HQ of 1 and therefore represent a potential health risk (Fig. 4, Panel A). However, as the ingestion rate increases the percentage of households exceeding a HQ of 1 for total Hg concentrations begins to plateau toward 100%. Increasing the ingestion rate above 300 mg/day for a 1 year old and 400 mg/day for a 6 year old makes little difference in the risk estimates, with nearly all homes having total Hg concentrations exceeding the health benchmark.

In contrast, the percentage of households with concentrations of GF extractable Hg that represent a potential health risk is consistently low for both 1 and 6 year old children (<2% of households), which reflects the low oral bioaccessibility of the Hg present in the adobe bricks. Additionally, it should be noted that the reference dose used to estimate risk is based on mercuric chloride ($HgCl_2$), which is the most soluble form of inorganic mercury. Because the percentage of GF extractable Hg is so low (median: 0.085%, Fig. 3), comparing total Hg measurements against this reference value substantially overestimates the potential health risks. Overall, these results indicate that Hg concentrations in adobe bricks likely do not represent a significant health risk to children following incidental ingestion, due to the low bioaccessibility of Hg present in the adobe bricks.

The results for total As show that even at the lowest ingestion rate (50 mg/day), over 80% of households have concentrations of total As that represent a potential health risk (Fig. 4, Panel B). As with total Hg, the percentage of households reaches a plateau, indicating that an ingestion rate above 100 mg/day does not substantially change the percentage of households with total As concentrations that represent a potential health risk, for both 1 and 6 year old children. Under the Child-Specific Exposure Factors Handbook recommended ingestion rate of 100 mg/day, only 33% and 10% of households, respectively,

Table 4
Toxicological characteristics and regulatory screening values for elements of potential concern. RfD is the oral ingestion reference dose and the critical effect is the effect used to derive this reference dose.

	RfD (μg/kg-day)	Critical effect	Other health endpoints	Citation
Hg	0.3[a]	Autoimmune	Neurological, kidney, developmental, gastrointestinal	U.S. EPA (1995b)
As	0.3[b]	Hyperpigmentation, keratosis, possible vascular complications	Neurological, developmental, liver, respiratory, hypertension	U.S. EPA (1993)
Pb	0.6	Decrease of 1 IQ point	Neurological, kidney, developmental, hypertension, coronary heart disease	JECFA (2011)

[a] Based on mercuric chloride ($HgCl_2$).
[b] Based on inorganic arsenic.

have concentrations of GF extractable As that represent a potential health risk (U.S. EPA, 2008). However, at ingestion rates above this, the majority of households have GF extractable concentrations that indicate a potential health risk and the percentage of households begins to plateau so that increasing the ingestion rate above 400 mg/day results in only a small increase in the percentage of sampled households that exceed a HQ of 1. Overall these results suggest that As concentrations in adobe bricks may represent a potential health risk, depending on the amount ingested. When GF extractable As is considered, an ingestion rate at or above 200 mg/day will represent a potential health risk to the majority of the community, based on the households sampled.

Unlike Hg and As, the majority of households have both total and GF extractable Pb concentrations that represent a potential health risk to both 1 and 6 year old children, even at the lowest ingestion rate used in the risk assessment model (Fig. 4, Panel C). Using the Child-Specific Exposure Factors Handbook recommended ingestion rate of 100 mg/day for a 1 year old and a 6 year old, 76% and 69% of households, respectively, contain concentrations of GF extractable Pb that may cause adverse health effects following incidental ingestion. These figures steadily increase toward 100% as the ingestion rate increases. While the exact number of children living in Potosí is not known, assuming that a child is present in each house would suggest that children in approximately three out of every four households may be exposed to GF extractable levels of Pb that correspond to a decrease in at least 1 IQ point (JECFA, 2011). This estimate includes only concentrations measured in indoor adobe brick samples, but it is likely that children are exposed to other Pb sources from air, water, outdoor soil and dust, and diet.

Although the present study did not estimate exposure and potential health effects in adults, it is worth noting that a study by Farag et al. (2015) found that non-smoking women living in mining towns 30 to 40 km south of the city of Potosí had blood Pb levels that were 3-fold higher than non-smoking women living in non-mining villages in Bolivia and 20-fold higher than the U.S. average. While Farag et al. (2015) did not examine the relationship between blood Pb levels and housing characteristics, the majority of individuals surveyed indicated that they lived in households with earthen floors. It is unclear if these households were built of adobe bricks as well.

3.4.3. Uncertainties and limitations

There are limitations and uncertainties in all stages of a risk assessment. Within this assessment and overall study, recovery rates for total aluminum, titanium, cadmium, and several other elements in the samples were not suitable for quantitative analysis; therefore, we were unable to assess potential health risks of these elements. Additionally, there were consistently low recoveries for total Pb during the HCl/HNO_3 digestion procedure for the soil SRM; so the values reported for the brick, dust, and floor samples could be an underestimation of Pb concentrations. The simulated GF extraction is one of the simpler protocols used to estimate bioaccessibility, and cannot fully simulate the complex pharmacokinetic processes following ingestion, although gastric fluid has been shown to be the rate-limiting step in trace element absorption (U.S. EPA, 2007). It should also be noted that the measurements in this study do not refer to internal bioavailability, which is the ability of an element to be absorbed and reach the target organ where it would exert a toxic effect (Caussy et al., 2003).

This study focused only on bioaccessibility from ingestion of contaminated adobe brick particles, and did not explore potential exposures through dermal or inhalation routes, or other ingestion exposures such as diet. Ingestion is thought to be the most important route of exposure for children, although these other routes may contribute to the overall exposures and potentially pose additional health risks. In the absence of total and GF extractable element concentrations in surface dust, concentrations in adobe bricks were used as a surrogate to estimate exposure from incidental ingestion of contaminated particles from within a household. Given the difference in units between element concentrations in adobe bricks (μg/g) and surface dust ($\mu g/cm^2$), it is unclear if the concentrations of elements in adobe bricks directly correspond to concentrations of elements in surface dust, the latter of which is likely the most relevant source of exposure within a household.

The estimation of potential health effects in children following ingestion exposure is also limited by uncertainties, including the lack of data on the age-specific body weights of children in Potosí, ingestion rates of children in Potosí, or Bolivia, and mining towns in general, and the impact of ubiquitous exposure to elements, as well as the use of U.S.-specific variables and health benchmarks in estimating risk for non-U.S. populations. It should also be acknowledged that the exposure estimation in this study provides an incomplete picture and probably an underestimate of daily exposures to Hg, As, Pb and other metals; however, highly conservative health reference values are used to mitigate this underestimation and provide a conservative estimation of potential health risks. Other sources that may contribute considerably to element exposure include water and food consumption. There was also no estimate of cumulative health effects from co-exposures to multiple trace elements. Hg, As, and Pb all affect similar toxicological endpoints (Table 4), including the neurological system, which is particularly sensitive in developing children.

Despite these limitations, the risk assessment presented here provides a useful approach to compare houses within this area and to identify priority areas for additional research in the community.

4. Conclusions

To our knowledge, this is the first study to investigate a wide selection of metal and metalloid elements in adobe brick houses in South America. The results from this study confirm our hypothesis that concentrations of total Hg, As, Pb, Ag, Cu and Zn were significantly higher in adobe bricks and dirt floors in Potosí than in Sucre. Furthermore, in Potosí, adobe bricks contain Hg, As, and Pb at concentrations that exceeded health benchmarks. Risk estimates incorporating information on bioaccessibility indicated the majority of households have Pb concentrations in adobe bricks that may pose a potential health risk to 1- and 6-year old children following incidental exposure through ingestion of adobe brick particles. Under situations where ingestion rates were >150 to 200 mg-day, this statement also holds true for

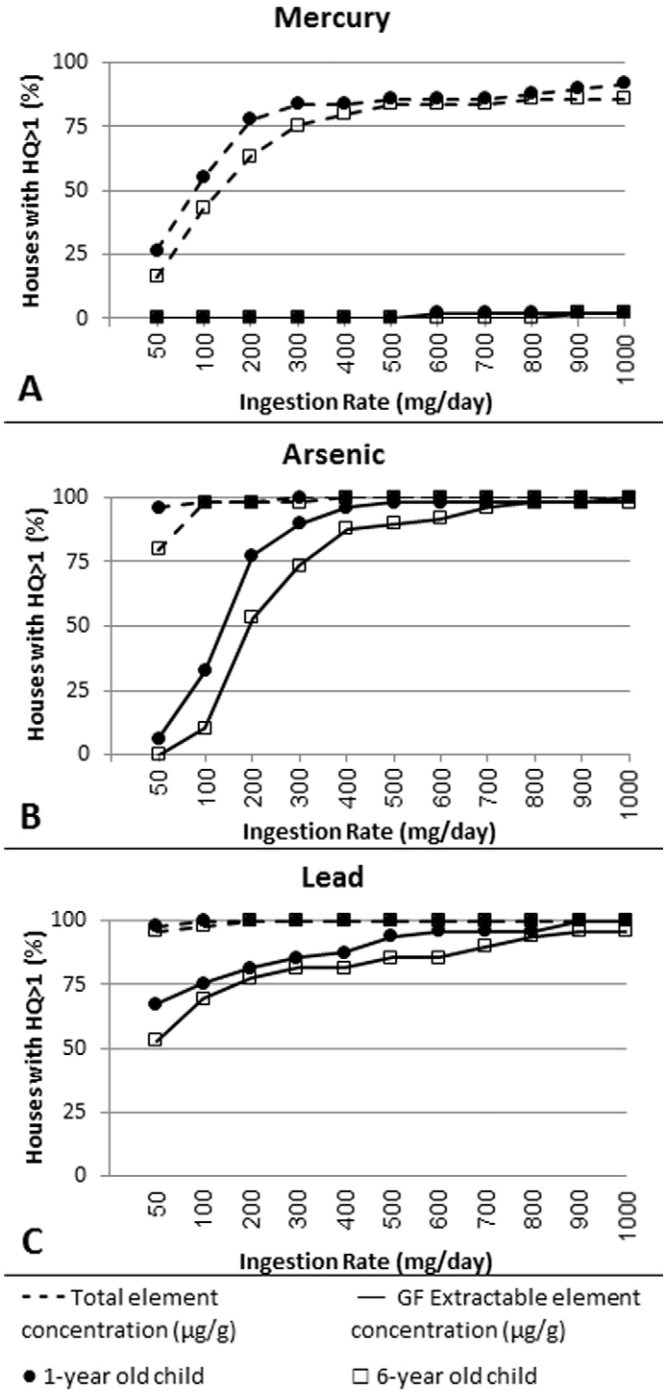

Fig. 4. Percentage of households with potential risk (Hazard Quotient HQ ≥ 1) for a 1 and 6 year old children according to estimates using total or gastric fluid (GF) extractable element concentrations in adobe brick samples from Potosí. Mercury (A), arsenic (B), and lead (C).

bioaccessible As concentrations. Despite the legacy of Hg pollution in Potosí, concentrations of Hg in adobe brick houses do not appear to represent a potential health risk, as Hg is present in mostly insoluble forms. Additional environmental sampling, biomonitoring, and personal questionnaires are needed to fully understand exposure sources and adverse health effects within the community of Potosí, particularly as they relate to Pb exposure. Broadly, these results show that adobe houses are an important source of exposure to potentially toxic trace elements in South American mining communities and should be considered when assessing health risks or outcomes in these communities.

Disclaimer

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.03.152.

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