Environ Geochem Health
DOI 10.1007/s10653-011-9444-9

ORIGINAL PAPER

Arsenic bioaccessibility in a gold mining area: a health risk assessment for children

Fábio Benedito Ono · Luiz Roberto Guimarães Guilherme · Evanise Silva Penido · Geila Santos Carvalho · Beverley Hale · Regla Toujaguez · Jochen Bundschuh

Received: 24 June 2011 / Accepted: 2 December 2011

Abstract High concentrations of total arsenic (As) have been measured in soils of gold mining areas of Brazil. However, bioaccessibility tests have not yet been conducted on those materials, which is essential for better health risk estimates. This study aimed at evaluating As bioaccessibility in samples from a gold mining area located in Brazil and assessing children's exposure to As-contaminated materials. Samples were collected from different materials (a control and four As-contaminated soils/sediments) found in a gold mine area located in Paracatu (MG), Brazil. Total and bioaccessible As concentrations were determined for all samples. The control soil presented the lowest As concentrations, while all other materials contained high total As concentrations (up to 2,666 mg kg^{-1}) and low bioaccessible As percentage (<4.2%), indicating a low risk from exposure of resident children next to this area. The calculated dose of exposure indicated that, except for the pond tailings, in all other areas, the exposure route considering soil ingestion contributed at most to 9.7% of the maximum As allowed ingestion per day (0.3 μg kg^{-1} BW day^{-1}).

Keywords Trace elements · In vitro tests · Human health · Anthropogenic impacts · Environmental contamination

Introduction

Arsenic (As) is ranked number one in the list of priority pollutants harmful to human health by ATSDR (2007), because certain compounds are toxic and carcinogenic. Elevated As concentrations have been found in the environment (Girouard and Zagury 2009; Nathanail et al. 2005; Palumbo-Roe et al. 2005, 2007; Pouschat and Zagury 2006; Rieuwerts et al. 2006; Sarkar et al. 2007), which may pose a threat to human health. This is especially true for tailings around gold mining areas (Borba et al. 2003; Bossy et al. 2010; Chung et al. 2005; Juhasz et al. 2007), with the highest concentration of total As reaching 31% (Meunier et al. 2010).

Soil guideline values for human health and ecological risk assessment are not yet well established for As, with suggested values ranging according to the country (CCME 1997; DEFRA and EA 2002). In

F. B. Ono (✉) · L. R. G. Guilherme · E. S. Penido · G. S. Carvalho · R. Toujaguez
Department of Soil Science, Federal University of Lavras, CP 3037, Campus UFLA, Lavras, MG 37200-000, Brazil
e-mail: onofabiob@gmail.com

B. Hale
School of Environmental Sciences, University of Guelph, Guelph, ON N1G 2W1, Canada

J. Bundschuh
Faculty of Engineering and Surveying, University of Southern Queensland, Toowoomba, QLD 4350, Australia

Published online: 18 December 2011

Brazil, a soil guideline value of 15 mg As kg^{-1} soil has been established as a screening level based on ecological risk assessment, with intervention values set as 35 mg As kg^{-1} soil for agricultural, 55 mg As kg^{-1} soil for residential, and 150 mg As kg^{-1} soil for industrial areas, which were all derived from human health risk assessments, considering 100% bioaccessibility (CONAMA 2009).

Mining and smelting of metals generate large quantities of tailings and their inappropriate handling can contaminate the region and lead to the uptake of arsenicals into the food chain through uptake by plants. More directly in these contaminated areas, residential children may unwittingly or deliberately ingest soil, which is considered the main route of exposure in As-contaminated soils (Hemond and Solo-Gabriele 2004; Kwon et al. 2004; Rodriguez et al. 1999). In fact, studies have shown that incidental ingestion of As-contaminated soil is a major concern (Ljung et al. 2006) and that exposure to As by dermal absorption, and inhalation is considered negligible compared to ingestion (De Miguel et al. 2007; Kwon et al. 2004).

The As high toxicity for mammals has raised a growing concern about environmental contamination with this element. In an assessment of human health risk from ingestion of As-contaminated soils, in vivo tests using animals (e.g., swine, rats, monkeys, rabbits) have been used in order to estimate the As amount arriving in the circulatory system from the gastrointestinal tract (bioavailability) (Koch et al. 2007; Ruby et al. 1996, 1999).

Bioaccessibility tests (in vitro), which measure the fraction of a contaminant that is soluble and potentially available to be absorbed, are fast, simple and low cost tools for estimating exposure compared with in vivo tests (Koch et al. 2007; Oomen et al. 2002; Paustenbach 2000; Ruby et al. 1996, 1999). Such tests have been used for assessing As bioavailability in gold mining areas worldwide (Chung et al. 2005; Juhasz et al. 2007; Meunier et al. 2010).

In soils, substrates and tailings from gold mining areas of Brazil, high levels of total As have been measured, e.g., up to 46,493 mg As kg^{-1} (Andrade et al. 2008; Borba et al. 2000, 2003; Deschamps et al. 2002; Matschullat et al. 2000); however, bioaccessibility tests for this element have not yet been carried out for these areas. In general, such mining areas are quite densely populated regions, with cities located very close to the mines.

Given the above, studies on As bioaccessibility in soils and sediments of areas impacted by mining activities, seeking to obtain relevant information for human risk assessments, are of great importance. Such studies are scarce in Brazil and may give an indication of the risk from exposure of residents near these areas, helping also to guide public policies.

This study was conducted with the objectives of (i) evaluating As bioaccessibility in stratified samples from a gold mining area and (ii) assessing children exposure to As-contaminated materials.

Experimental section

Description of the studied site and sampling procedure

The samples of soil, substrates and tailings were collected in December 2008, at the facilities of a gold mine located in the Northwest of Minas Gerais State, Brazil.

The collection areas were as follows: (i) a Private Natural Reserve (PNR), which is an area of native vegetation (Cerrado) located inside the mine area, covering a total of 73.44 hectares; (ii) B1 = a mined oxidized soil layer, collected at a site located in one end of the mining area having many residences in its vicinity; (iii) Exp. B1 = B1 material that had been revegetated for the previous 6 years; (iv) undisturbed material, a non-commercially mined ore body, because of its low gold content; and, (v) pond tailing samples, obtained from the retention dam used to collect the waste materials from gold smelting. Five composite samples of each material ($\sim$300 g) were collected manually in each area, at two depths (0–2 and 2–10 cm), using a straight blade. Pond tailings were removed at two points in the retention dam, with two significant portions of the material collected at one site and additional three samples collected at another site, comprising five sub-samples without distinct strata.

The samples were transported to the Department of Soil Science (DCS) at Federal University of Lavras (UFLA), Brazil, air-dried and then passed through a 2-mm diameter sieve. All analytical procedures were performed at the DCS/UFLA.

Arsenic determinations

Total arsenic

The As total content was obtained by acid digestion of the soil sample, using USEPA Method 3051 A (USEPA 1998a) in a MARS-5® microwave oven. For this, 1 g of solid material (<150 μm fraction) with 10 mL of concentrated HNO_3 was added in a Teflon bottle. After digestion, the extract was filtered through Whatman No. 40 filter paper and brought to a volume of 20 mL with ultra pure water. The filtered extracts were preserved under refrigeration (4°C) until analysis by either graphite furnace atomic absorption spectroscopy (GFAAS) or flame atomic absorption spectroscopy (FAAS) using a Perkin Elmer AAnalyst 800 equipment.

Bioaccessible arsenic

Arsenic bioaccessibility in the samples was determined using the In Vitro Gastrointestinal (IVG) protocol proposed by Rodriguez et al. (1999), which consists of two sequential phases (gastric and intestinal), with a modification to the original method, i.e. removal of the bubbling of argon gas to simulate mixing. Such modification did not affect the results as proved by data obtained for our standard reference materials, which were similar to those found elsewhere (Girouard and Zagury 2009; Koch et al. 2005, 2007; Pouschat and Zagury 2006).

The gastric phase consisted of a mixture of 1 g of air-dried, 2-mm diameter sieve solid material, disaggregated and sieved (<150 μm fraction, which is the same particle size used for total As analysis) with 150 mL of a gastric solution consisting of 1% pepsin (Sigma–Aldrich, St. Louis, MO, Cat No P7000) in 0.15 mol L^{-1} NaCl (pa, Merck, Darmstadt, Germany). The gastric solution was acidified before adding the solids with concentrated HCl (37%, Merck, Darmstadt, Germany) to reach pH = 1.80 ± 0.05. The flasks (Erlenmeyer flasks) containing the gastric solution and the solid material were placed in a water bath (Dubnoff type with adjustable digital temperature and agitation) at 37 ± 0.5°C and left under constant horizontal agitation (100 ± 2 rpm), for 1 h.

The intestinal medium consisted of adjusting the gastric solution pH with $NaHCO_3$ (pa, Merck, Darmstadt, Germany) to 5.5 ± 0.1 followed by adding 0.525 g of a porcine bile extract (Sigma Aldrich, St. Louis, MO, Cat No B8631) and 0.053 g of pancreatin (Sigma–Aldrich, Cat No P1500). The container with the mixture was also left under horizontal shaking (100 ± 2 rpm) for 1 h at 37 ± 0.5°C.

At the end of each phase (gastric and intestinal), 10 mL were collected and centrifuged at 10,000 rpm for 15 min, the supernatant was filtered through a 0.45 μm polyethersulfone membrane (nylon) into 15-mL polypropylene centrifuge tubes. The filtered extracts were preserved under refrigeration (4°C) until analysis by GFAAS.

Percent bioaccessible As was calculated using the following equation:

$$\text{Bioaccessible As}\,(\%) = \frac{\text{In vitro As}}{\text{Total As}} \times 100 \qquad (A.1)$$

Quality assurance and quality control

Ultra pure water with a resistivity of 18.2 MΩ-cm (Milli-Q water system) was used to prepare all solutions. All glass bottles, jars and materials used in the research were washed with a solution of 10% HNO_3 for 24 h and then rinsed three times with distilled water before use.

All samples were digested and analyzed in triplicate, with the exception of the total As content in certified NIST materials (duplicate). A blank sample was conducted in parallel for quality control purposes in each battery of sample digestion. Arsenic concentrations in blank samples were always lower than the detection limit calculated for the method, using graphite furnace (4 μg As L^{-1}).

Certified reference materials (NIST 2710 and NIST 2709) were used to evaluate the reproducibility and the accuracy/precision of the tested analytical procedures as well as for comparison purposes with other published results. Both reference materials were analyzed by the USEPA 3051A method and only the NIST 2710 was evaluated by the IVG protocol. The NIST 2710 has been used in other studies of As bioaccessibility (Girouard and Zagury 2009; Koch et al. 2005, 2007; Pouschat and Zagury 2006), which was not the case for the NIST 2709.

Exposure assessment

To estimate, in a preliminary way, the non-cancer risk for children, the most likely category of population

exposed in areas with As-contaminated materials and considering the involuntary ingestion of soil as a major route of exposure to As, we calculated the exposure dose by the following equation, as suggested by Pouschat and Zagury (2006):

$$\mathrm{CDI} = \frac{\mathrm{EPC} \times \mathrm{SIR} \times \mathrm{EF} \times \mathrm{B} \times \mathrm{CF}}{\mathrm{BW}} \quad \text{(B.1)}$$

where CDI = chemical daily intake = ingested As (μg kg^{-1} body weight day^{-1}); EPC = exposure point concentration = total As in soil (mg kg^{-1}); SIR = soil ingestion rate for a child (100 mg day^{-1}); EF = exposure frequency (0.5 = 182 days $year^{-1}$), B = bioaccessibility (%); BW = body weight (15.4 kg for a 0- to 6-year-old child); and CF = unit conversion factor (10^{-3}).

The mean soil ingestion rate of 100 mg day^{-1} for a child is in accordance with USEPA (2002) and Dube et al. (2004), the frequency of exposure is in agreement with Hemond and Solo-Gabriele (2004) and the value of body mass in children aged 0–6 years was estimated from data available on a Consumer Expenditure Survey 2002–2003 (Brazilian Institute of Geography and Statistics—IBGE 2006), calculated by Guilherme and Marchi (2007).

The average daily intake (CDI) of a contaminant identified via a route indicates the amount of the chemical ingested per kilogram of body weight per day and that effectively enters systemic circulation. The criterion of toxicity for substances that could potentially cause non-carcinogenic effects is based on reference doses (RfDs) or on an oral minimal risk level (MRL) for chronic intake (e.g., 0.3 μg As kg^{-1} body weight day^{-1}), these being the threshold level above which toxic effects may occur (ATSDR 2009). The ratio of the average daily intake and RfD provides the risk quotient (RQ), which tells how the route of exposure in question (i.e., ingestion of soil) contributes to the maximum allowed entry of the contaminant. The sum of all potential RQs (i.e., via inhalation, skin absorption, ingestion, water, food, etc.) generates the hazard index (HI). If the calculated HI is less than 1, it can be concluded that adverse non-cancer outcomes of exposure to contaminants are negligible.

To estimate the non-cancer risk, evaluation of dose–response was obtained using the RfD derived from the IRIS database (USEPA 1998b). The chronic oral RfDs are specifically developed to be protective for long-term exposure to a compound (Guilherme and Marchi 2007).

Results and discussion

Quality assurance and quality control

The accuracy and precision in determining total As were verified using the certified reference materials NIST 2710 and 2709. The average recovery rates obtained in the study were 89.9 ± 0.8 (NIST 2710) and 90.4 ± 2.0% (NIST 2709), with relative standard deviations (RSDs) of 0.9 and 2.2%, respectively.

Bioaccessibility values obtained for the reference material NIST 2710 were 28.4 ± 2.1% (gastric phase) and 27.4 ± 1.6% (gastrointestinal). These values were close to those reported by Pouschat and Zagury (2006): 27.6 ± 0.4 gastric and 25.2 ± 0.3% gastrointestinal; and for Girouard and Zagury (2009): 25.7 ± 4.7 gastric and 23.4 ± 3% gastrointestinal, both using the IVG method. The results are also similar to those determined by Koch et al. (2005): 28 ± 17% gastric; and Koch et al. (2007): 36% gastric. Thus, one can say that the reproducibility and the accuracy/precision of the IVG protocol were satisfactory, thus this technique could be applied to the samples of this study.

Total arsenic

Samples from the studied areas showed a great variability in the average levels of total As, ranging from 25 (PNR, 0–2 cm) to 1,891 mg kg^{-1} (tailings) (Table 1). A great variability was also found among the samples ($n = 5$) collected in the same area and depth, with the undisturbed material (2–10 cm) showing the lowest RSD (8%) and the waste, the largest (41%) (Table 1). Such heterogeneity in trace elements concentration in samples of the same area and among areas is common in mining areas due to the constant movement and excavation of materials to be mined.

In pond tailing samples ($n = 5$), total As concentrations varied from 1,065 to 2,666 mg kg^{-1} (Table 1). It is worth noting that these samples were collected at the same retention pond, but at two distinct sites. The mean concentrations ± standard deviation of these different sites were 1,080 ± 21 ($n = 2$) and

Table 1 Total arsenic content in samples from the mining area and in certified reference materials

Material[b]	Total As (mg kg^{-1})[a]	
	0–2 cm[c]	2–10 cm
PNR	25 ± 7	35 ± 9
Exp. B1	298 ± 68	381 ± 67
B1	281 ± 102	550 ± 108
Undisturbed material	393 ± 77	426 ± 34
Pond tailings	1,891 ± 773	
NIST 2710	563 ± 5	
NIST 2709	16 ± 0.4	

[a] Mean ± standard deviation ($n = 5$, except NIST $n = 3$)

[b] Particle size <150 μm except for the certified reference material (<74 μm)

[c] 0–2 cm, except for pond tailings and NIST

2,431 ± 318 mg kg^{-1} ($n = 3$), demonstrating how As content varies among materials collected at different points in the same retention pond.

The average As levels were higher at the 2–10 cm depth (about 41, 28, 96, and 8%) compared with the depth of 0–2 cm, for PNR, Exp B1, B1, and undisturbed material areas, respectively (Table 1). The B1 material had the highest difference regarding As values with depth stratification, ranging from 281 ± 102 (0–2 cm) to 550 ± 108 mg kg^{-1} (2–10 cm).

For a risk assessment considering involuntary ingestion of soil by children as the major route of exposure, the most important layer of soil to be considered in this assessment is the most superficial one (top surface layer). In areas with very high levels of trace elements, few plant species survive and hence the top layer remains mostly uncovered by vegetation. Thus, the top layer of these areas can be eroded by wind and water (rain and surface run off) and the material transported to urban areas, rivers, farmland, etc. However, for risk assessment purposes, not only the most superficial layer, but also the layer underneath has to be characterized, since once the first few centimeters are washed or eroded away, the layer underneath will become the top layer.

Bioaccessible arsenic

Bioaccessible As in stratified samples of Exp B1, B1, and undisturbed material areas was very low (Table 2). The lowest values were found in the PNR (<DL), which was expected since this is a native area (control area). The highest values found in these samples were always lower than 10 mg kg^{-1}, which are smaller than those reported by Juhasz et al. (2007) and Meunier et al. (2010) in gold mining sites located in Nova Scotia, Canada, and Victoria, Australia. The highest average content of bioaccessible As (68.6 gastric and 79.0 mg kg^{-1} gastrointestinal) were found in the pond tailings (Table 2). However, such values are still smaller than most of those observed by Juhasz et al. (2007) and Meunier et al. (2010).

Similar to that observed for total As contents (Table 1), one could see also a considerable variability (large error bars) in the levels of bioaccessible As in samples from each area, as well as the different

Table 2 Bioaccessible arsenic in samples from the mining area and in a certified reference material

Material[b]	Bioaccessible As (mg kg^{-1})[a]		Bioaccessible As (mg kg^{-1})[a]	
	(0–2 cm)[c]		(2–10 cm)	
	Gastric	Gastrointestinal	Gastric	Gastrointestinal
PNR	<DL	<DL	<DL	<DL
Exp. B1	5.4 ± 0.9	5.2 ± 0.9	7.7 ± 1.5	7.0 ± 1.0
B1	6.9 ± 0.7	7.6 ± 0.5	7.7 ± 0.9	7.7 ± 0.8
Undisturbed material	3.4 ± 1.7	4.8 ± 2.2	5.2 ± 2.1	5.9 ± 2.2
Pond tailings	68.6 ± 37	79 ± 43		
NIST 2710	159.8 ± 12	154.2 ± 8.7		

<DL = below the detection limit

[a] Mean ± standard deviation ($n = 5$, except NIST $n = 3$)

[b] Particle size <150 μm except for the certified reference material (<74 μm)

[c] 0–2 cm, except for pond tailings and NIST 2710

Table 3 Average As bioaccessibility in samples of the mining area and in a certified reference material

Material[b]	Bioaccessible As (%)[a] (0–2 cm)[d]		Bioaccessible As (%)[a] (2–10 cm)	
	Gastric	Gastrointestinal	Gastric	Gastrointestinal
PNR	<DL	<DL	<DL	<DL
Exp. B1	1.8 ± 0.3	1.8 ± 0.3	2.0 ± 0.4	1.9 ± 0.3
B1	2.5 ± 0.2	2.7 ± 0.2	1.4 ± 0.2	1.4 ± 0.1
Undisturbed material	0.9 ± 0.4	1.2 ± 0.6	1.2 ± 0.5	1.4 ± 0.5
Mean[c]	1.7	1.9	1.5	1.6
Pond tailings	3.6 ± 1.9	4.2 ± 2.3		
NIST 2710	28.4 ± 2.1	27.4 ± 1.6		

<DL = below the detection limit

[a] Mean ± standard deviation ($n = 5$, except NIST $n = 3$)

[b] Particle size <150 μm except for the certified reference material (<74 μm)

[c] Exp. B1, B1, and undisturbed material

[d] 0–2 cm, except for pond tailings and NIST 2710

sampling depth, with a larger RSDs for the pond tailings material (RSDs = 53.5% gastric and 54.5% gastrointestinal) (Table 2).

The average values of bioaccessible As (gastric and gastrointestinal) for samples collected at the depth of 2–10 cm were always higher than those of the 0–2 cm depth (Table 2), showing a similar behavior of that found for total As in the same samples.

Bioaccessibility of arsenic

The average bioaccessibility (%) for each area and depth was calculated as the ratio between the average content of bioaccessible As and the total As (Table 3). The average bioaccessibility (%) in all samples was very low, the lowest value being the one for the PNR (<DL) and the highest for the pond tailings (3.6% gastric and 4.2% gastrointestinal).

Taking into consideration the total number of samples in the study ($n = 45$), one could easily estimate a worst-case scenario figure for As bioaccessibility (%) (maximum = 5.4%) in all samples of the mining area, since the bioaccessibility values were all low and close to each other. This value could then be used for risk assessment purposes in the case of new samples when only the total As content is available.

However, one should keep in mind that materials with different mineralogies and sorbing capacities will present varying percentages of bioaccessibility. Pouschat and Zagury (2006), Sarkar et al. (2007), and Girouard and Zagury (2009) used the IVG protocol in soils with high As contents and found the following ranges (minimum and maximum) of bioaccessible As (%) in the gastrointestinal phase: 25 ± 2.7 to 66 ± 2.3, 3 to 90, and 17 ± 0.4 to 46.9 ± 1.1, respectively.

To the best of the authors' knowledge, no previous research on As bioaccessibility has been held in gold mining areas in Brazil, so that data from this study could be compared. However, data from research in gold mining sites worldwide (Australia, England, and Korea) have shown average values of bioaccessible As higher than those found in this study (Chung et al. 2005; Juhasz et al. 2007; Meunier et al. 2010), which is most likely to be related to the above-mentioned differences in mineralogy and sorbing capacity of the soils/sediments being evaluated. For the study by Juhasz et al. (2007), bioaccessible As ranged from 5 to 36%. Meunier et al. (2010) reported bioaccessible As in gold mining sites ranging from very low (i.e., 0.1%) to very high percentages (i.e., 49%). In our study, As bioaccessibility ranged from <DL to 4.2%.

Dose exposure estimate

The calculation of the exposure dose (CDI) (Table 4) was carried out one sample of each area and depth, being selected the worst-case scenario, i.e. the sample with the highest content of bioaccessible As, based on its total As content and the As bioaccessibility (%).

Table 4 Estimated daily intake of As by children exposed to the materials in the mine area

Sample[a]	EPC	B	CDI	RQ
Exp. B1[b]	335	2.0	0.022	0.073
Exp. B1[c]	358	2.3	0.027	0.090
B1[b]	262	3.1	0.026	0.087
B1[c]	664	1.3	0.028	0.093
Undisturbed material[b]	527	1.6	0.027	0.090
Undisturbed material[c]	372	2.4	0.029	0.097
Pond tailings	2,666	4.4	0.381	1.270

EPC exposure point concentration = total arsenic in soil (mg kg^{-1}), *B* bioaccessibility (%), *CDI* ingested arsenic (μg kg^{-1} BW day^{-1}), *RQ* risk quotient

[a] Sample with the highest content of bioaccessible As in each area

[b,c] Collected at the depths of 0–2 and 2–10 cm, respectively

Data from Table 4 indicate that children exposed to the hypothetical worst scenario could ingest from 0.022 (Exp. B1, 0–2 cm) to 0.381 μg As kg^{-1} BW day^{-1} (tailings). It was observed that all samples had low CDI, except for the pond tailings material that was greater than the RfD of 0.3 μg kg^{-1} BW day^{-1}. These results are similar to those of Pouschat and Zagury (2006) who found for the As daily intake values between 0.05 and 0.32 μg kg^{-1} BW day^{-1} (average of 0.18 μg kg^{-1} BW day^{-1}) for soils contaminated by CCA-treated wood structures.

A study by Rieuwerts et al. (2006), estimating the exposure through ingestion of garden soils ($n = 20$; ingestion rate of 100 mg soil day^{-1}) and considering a bioaccessibility of 44% (the highest value found) and a body mass of 16.15 kg (children), obtained intake values between 0.06 and 1.28 μg kg^{-1} BW day^{-1}.

The daily As ingestion estimated for the stratified samples were similar, on average: 0.025 μg kg^{-1} BW day^{-1} (RQ = 0.083) for 0–2 cm and 0.028 μg kg^{-1} BW day^{-1} (RQ = 0.093) for 2–10 cm (Table 4). This indicates that approximately 8–9% of As intake in this scenario depends on the route of soil ingestion. Other routes of entry may be through inhalation, dermal contact, etc.

The most contaminated material in the mining area was the mining tailings, which had its estimated RQ greater than 1.0 (Table 4). This value (RQ = 1.27) indicates that under this risk scenario, the permitted maximum intake of As (0.3 μg kg^{-1} BW day^{-1}) has been exceeded by 27%, considering only ingestion of pond tailings materials.

In calculating the daily As dose that can be ingested by a child, considering an intake of 100 mg soil day^{-1} and a exposure frequency of 0.5 as well as the low As bioaccessibility, it is clear that, except for the pond tailing materials, all other materials from the mining area contribute no more than 9.7% for the maximum allowed As daily intake (0.3 μg kg^{-1} BW day^{-1}) (Table 4).

Thus, it is evident that setting limits for maximum allowed As values in soils and sediments considering only the total As concentration may overestimate the RQ or the hazard index on a risk assessment and generate additional costs in remediation strategies of certain areas. Elevated levels of a contaminant in a medium are not sufficient to diagnose the real risk, if their bioavailability is low. Therefore, bioaccessible values instead of total values should be used in risk assessments for soil ingestion, the main route of exposure for children.

It is worth to note that the values of the dose intake were calculated on a hypothetical scenario of maximum risk (worst-case scenario). Currently, the population has no free access to the mining area in question, which is fenced and guarded by security staff. Thus, there is no health risk, due to the absence of exposure.

Correlation between the arsenic levels

Pearson correlation analysis showed no significant relationship between the contents of total and bioaccessible As. Other authors found the same trend (Girouard and Zagury 2009; Pouschat and Zagury 2006), whereas the opposite was found by Juhasz et al. (2007), Sarkar et al. (2007) and Meunier et al. (2010).

Significant correlation ($p < 0.001$) was observed between the two phases (gastric and gastrointestinal)

of bioaccessible As, considering the stratified samples (Exp. B1, B1, and undisturbed material) in the study data set ($n = 30$, $r = 0.91$). Sarkar et al. (2007) reported the same trend, i.e. the existence of significant correlation ($r = 0.95$, $p < 0.001$) between the two phases, indicating that both extracted As similarly from soils.

It is observed that the gastric phase behaves very similar to the gastrointestinal phase in terms of As extraction. Thus, for cost and time to complete the second phase, in samples from the mining area, there is the possibility of performing only the first phase in order to determine bioaccessible As to be used in risk assessment estimates. Even though this might be true for As in the tested materials, it is not the case of As in mine tailings from Nova Scotia, Canada (Meunier et al. 2010) and other trace elements (e.g., Pb), as it has been observed elsewhere (Lu et al. 2011).

Conclusions

Total As concentrations were high in mining area, however, the bioaccessible As was low (<4.2%), indicating a low risk from exposure of children residents next to this area.

The calculated dose of exposure indicated that, except for the pond tailings, in all other areas, the exposure route considering soil ingestion contributed at most to 9.7% of the maximum As allowed ingestion per day (0.3 μg kg^{-1} BW day^{-1}).

Acknowledgments The authors acknowledge The National Council for Scientific and Technological Development (CNPq Grant 577513/2008-7); The Research Foundation of the State of Minas Gerais (FAPEMIG Grants CAG PPM 187-09 & CAG APQ 118-09); and The Kinross Canada-Brazil Network for Advanced Education and Research in Land Resource Management for their financial support.

References

Agency for Toxic Substances and Disease Registry (ATSDR). (2007). *Cercla priority list of hazardous substances, 2007*. Accessed June 25, 2010 from http://atsdr.cdc.gov/cercla/07list.html.

Agency for Toxic Substances and Disease Registry (ATSDR). (2009). *Minimal Risk Levels (MRLs)*. Accessed September 25, 2010 from http://www.atsdr.cdc.gov/mrls/mrls_list.html.

Andrade, R. P., Santana-Filho, S., Mello, J. W. V., Figueiredo, B. R., & Dussin, T. M. (2008). Arsenic mobilization from sulfidic materials from gold mines in Minas Gerais state. *Química Nova, 31*(5), 1127–1130.

Borba, R. P., Figueiredo, B. R., & Matschullat, J. (2003). Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from iron quadrangle, Brazil. *Environmental Geology, 44*(1), 39–52.

Borba, R. P., Figueiredo, B. R., Rawlins, B., & Matschullat, J. (2000). Arsenic in water and sediment in the iron quadrangle, state of Minas Gerais, Brazil. *Revista Brasileira de Geociência, 30*(3), 558–561.

Bossy, A., Grosbois, C., Beauchemin, S., Courtin-Nomade, A., Hendershot, W., & Bril, H. (2010). Alteration of As-bearing phases in a small watershed located on a high grade arsenic-geochemical anomaly (French Massif Central). *Applied Geochemistry, 25*(12), 1889–1901.

Canadian Council of Ministers of the Environment (CCME). (1997). *Canadian soil quality guidelines for the protection of environmental and human health: arsenic (inorganic) fact sheet*. CCME (pp. 1–7).

Chung, E., Lee, J. S., Chon, H. T., & Sager, M. (2005). Environmental contamination and bioaccessibility of arsenic and metals around the Dongjeong Au-Ag-Cu mine, Korea. *Geochemistry: Exploration, Environment, Analysis, 5*(1), 69–74.

Conama, Resolução No420/2009. (2009). *Valores orientadores de qualidade do solo quanto à presença de substâncias químicas, Conselho Nacional de Meio Ambiente, 2009*. Accessed September 2, 2011 from http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=620.

De Miguel, E., Iribarren, I., Chacon, E., Ordonez, A., & Charlesworth, S. (2007). Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). *Chemosphere, 66*, 505–513.

Department for Environment, Food and Rural Affairs and the Environment Agency (DEFRA and EA). (2002). *Soil guideline values for arsenic contamination*. Bristol: Environment Agency.

Deschamps, E., Ciminelli, V. S. T., Lange, F. T., Matschullat, J., Raue, B., & Schmidt, H. (2002). Soil and sediment geochemistry of the iron quadrangle, Brazil. *Journal of Soils and Sediments, 2*(4), 216–222.

Dube, E. M., Petito Boyce, C., Beck, B. D., Lewandowski, T., & Schettler, S. (2004). Assessment of potential human health risks from arsenic in CCA-treated wood. *Human and Ecological Risk Assessment, 10*(6), 1019–1067.

Girouard, E., & Zagury, G. J. (2009). Arsenic bioaccessibility in CCA-contaminated soils: Influence of soil properties, arsenic fractionation and particle-size fraction. *Science of the Total Environment, 407*(8), 2576–2585.

Guilherme, L. R. G., & Marchi, G. (2007). *Metais em Fertilizantes Inorgânicos: avaliação de risco à saúde após a aplicação*. São Paulo: Associação Nacional para Difusão de Adubos.

Hemond, H. F., & Solo-Gabriele, H. M. (2004). Children's exposure to arsenic from CCA-treated wooden decks and playground structures. *Risk Analysis, 24*(1), 51–64.

Juhasz, A. L., Smith, E., Weber, J., Rees, M., Rofe, A., Kuhcel, T., et al. (2007). In vitro assessment of arsenic bioaccessibility in

contaminated (anthropogenic and geogenic) soils. *Chemosphere, 69*(1), 69–78.

Koch, I., Duso, A., Haug, C., Miskelly, C., Sommerville, M., Smith, P., et al. (2005). Distinguishing between naturally and anthropogenically elevated arsenic at an abandoned Artic military site. *Environmental Forensics, 6*(4), 335–344.

Koch, I., Sylvester, S., Lai, V. W. M., Owen, A., Reimer, K. J., & Cullen, W. R. (2007). Bioaccessibility and excretion of arsenic in Niu Huang Jie Du Pian pills. *Toxicology and Applied Pharmacology, 222*(3), 357–364.

Kwon, E., Zhang, H. Q., Wang, Z. W., Jhangri, G. S., Lu, X. F., Fok, N., et al. (2004). Arsenic on the hands of children after playing in playgrounds. *Environmental Health Perspectives, 112*(14), 1375–1380.

Ljung, K., Selinus, O., Otabbong, E., & Berglund, M. (2006). Metal and arsenic distribution in soil particle sizes relevant to soil ingestion by children. *Applied Geochemistry, 21*, 1613–1624.

Lu, Y., Yin, W., Zhang, G., Huang, L., & Zhao, Y. (2011). Assessment of bioaccessibility and exposure risk of arsenic and lead in urban soils of Guangzhou City, China. *Environmental Geochemistry and Health, 33*(2), 93–102.

Matschullat, J., Borba, R. P., Deschamps, E., Figueiredo, B. R., Gabrio, T., & Schwenk, M. (2000). Human and environmental contamination in the iron quadrangle, Brazil. *Applied Geochemistry, 15*, 181–190.

Meunier, L., Walker, S. R., Wragg, J., Parsons, M. B., Koch, I., Jamieson, H. E., et al. (2010). Effects of soil composition and mineralogy on the bioaccessibility of arsenic from tailings and soil in gold mine districts of Nova Scotia. *Environmental Science and Technology, 44*(7), 2667–2674.

Nathanail, C. P., McCaffrey, C., & Haynes, D. (2005). Assessing exposure to pedogenic arsenic contamination at a dwelling in Northamptonshire, UK: A case study. *Soil Use and Management, 21*, 508–517.

Oomen, A. G., Hack, A., Minekus, M., Zeijdner, E., Cornelis, S. C., Schoeters, G., et al. (2002). Comparison of five in vitro digestion models to study the bioaccessibility of soil contaminants. *Environmental Science and Technology, 36*(15), 3326–3334.

Palumbo-Roe, B., Cave, M. R., Klinck, B. A., Wragg, J., Taylor, H., O'Donnell, K. E., et al. (2005). Bioaccessibility of arsenic in soils developed over Jurassic ironstones in eastern England. *Environmental Geochemistry and Health, 27*(2), 121–130.

Palumbo-Roe, B., Klinck, B., & Cave, M. (2007). Arsenic speciation and mobility in mine wastes from a copper–arsenic mine in Devon, UK: An SEM, XAS, sequential chemical extraction study. *Trace Metals and other Contaminants in the Environment, 9*(6), 431–460.

Paustenbach, D. J. (2000). The practice of exposure assessment: A state-of-the-art review. *Journal of Toxicology and Environmental Health Part B, 3*(3), 179–291.

Pouschat, P., & Zagury, G. J. (2006). In vitro gastrointestinal bioavailability of arsenic in soils collected near CCA—treated utility poles. *Environmental Science and Technology, 40*(13), 4317–4323.

Rieuwerts, J. S., Searle, P., & Buck, R. (2006). Bioaccessible arsenic in the home environment in southwest England. *Science of the Total Environment, 371*, 89–98.

Rodriguez, R. R., Basta, N. T., Casteel, S. W., & Pace, L. W. (1999). An in vitro gastrointestinal method to estimate bioavailable arsenic in contaminated soils and solid media. *Environmental Science and Technology, 33*(4), 642–649.

Ruby, M. V., Davis, A., Schoof, R., Eberle, S., & Sellstone, C. M. (1996). Estimation of lead and arsenic bioavailability using a physiologically based extraction test. *Science of the Total Environment, 30*(2), 422–430.

Ruby, M. V., Schoof, R., Brattin, W., Goldade, M., Post, G., Harnois, M., et al. (1999). Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environmental Science and Technology, 33*(21), 3697–3705.

Sarkar, D., Makris, K. C., Parra-Noonan, M. T., & Datta, R. (2007). Effect of soil properties on arsenic fractionation and bioaccessibility in cattle and sheep dipping vat sites. *Environment International, 33*(2), 164–169.

U.S. Environmental Protection Agency. (1998). *Test methods for evaluation solid waste physical and chemical methods: Microwave assisted acid digest of sediments, sludges, soils and oils, SW-846*. Washington, DC: U.S. Government Printing Office.

U.S. EPA (1998b) *Integrated risk information system: Arsenic, inorganic*; CASRN 7440-38-2; Environmental Protection Agency; U.S. Government Printing Office: Washington, DC.

U.S. Environmental Protection Agency. Child-specific exposure factors handbook. (2002). EPA/600/P-00/002B; Office of Research and Development; U.S. Government Printing Office: Washington, DC; Accessed June 25, 2010 from http://www.epa.gov/ncea.