Science of the Total Environment 673 (2019) 36–43

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Health risk apportionment of arsenic from multiple exposure pathways in Paracatu, a gold mining town in Brazil

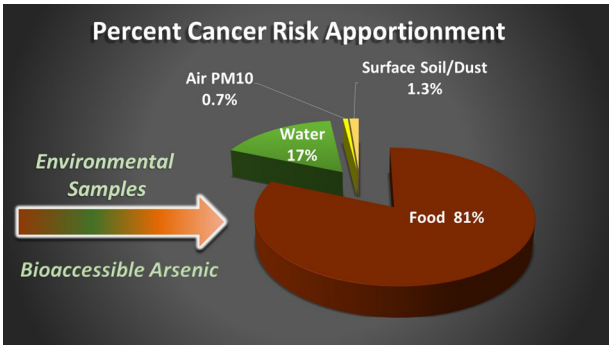
Jack C. Ng [a,c,*], Virginia Ciminelli [b,c], Massimo Gasparon [c,d,e], Claudia Caldeira [b,c]

[a] The University of Queensland, Queensland Alliance for Environmental Health Sciences (QAEHS), Brisbane, QLD 4102, Australia
[b] Department of Metallurgical and Materials Engineering, Universidade Federal de Minas Gerais, Brazil
[c] National Institute of Science and Technology on Minerals Resources, Water and Biodiversity, INCT-Acqua, Brazil
[d] The University of Queensland, School of Earth and Environmental Sciences, Brisbane, QLD 4072, Australia
[e] EIT RawMaterials GmbH, Berlin 10789, Germany

HIGHLIGHTS

- Arsenic (As) emission of a gold mine over 300 years has led to community concern.
- First comprehensive health risk assessment of As from multiple exposure pathways.
- Rice and bean are the major dietary As contributors to the risk apportionment.
- Geogenic exposure is much lower than that of dietary sources.
- Combined health risk of all pathways in Paracatu is within the acceptable range.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 December 2018
Received in revised form 26 March 2019
Accepted 3 April 2019
Available online 05 April 2019

Keywords:
Risk assessment
Bioaccessibility
Arsenic speciation
Arsenic monitoring
Air-particulate arsenic

ABSTRACT

This study assessed various exposure pathways of arsenic and their health risk apportionment to the residents of Paracatu, a gold mining town in Brazil. We measured arsenic concentrations in 50 groundwater and surface town water samples from nearby residences, 38 surface soil dust from residential/commercial dwellings and roadside of Paracatu, and 600 airborne dust samples including PM_{10} and total suspended particulates (TSP), in additional to a previous reported food survey containing 90 samples from 15 major food categories. For the surface soil dust, bioaccessibility of arsenic as a surrogate of bioavailability was determined using an in vitro physiologically based extraction test (PBET). Rice and bean were found to contain the highest levels of arsenic in which the arsenic speciation was measured whereas the percentages of inorganic arsenic of other food items were taken from the literature for the risk apportionment calculation. The results show that the contribution of inhaled arsenic is ≤3% of the total daily intake, even assuming 100% BAC. The average bioaccessibility of arsenic in the surface soil dust was $3.4 \pm 2.0\%$ ($n = 17$) with a bioaccessible concentration of 4.1 ± 3.7 mg/kg. Food was the main contributor of the daily total intake of arsenic with rice and beans being the most significant ones. The total arsenic intake (ingestion + inhalation) is about 10% of the JECFA $BMDL_{0.5}$ of 3 μg/kg b.w. per day, and the combined risk based on the cancer slope calculation is similar to the arsenic intake from the consumption of 2 L of water containing 10 μg/L of arsenic, a maximum concentration recommended by WHO. The holistic approach by

* Corresponding author at: Queensland Alliance for Environmental Health Sciences, the University of Queensland, PACE Building, 20 Cornwall Street, Woolloongabba, Brisbane, QLD 4102, Australia.
E-mail address: j.ng@uq.edu.au (J.C. Ng).

https://doi.org/10.1016/j.scitotenv.2019.04.048

addressing multiple pathways of exposure is considered a useful tool for health risk assessment throughout the life of mine including mine closure, and can be applied at legacy sites.

1. Introduction

Arsenic is widespread in the environment. Natural sources of arsenic contamination may have come from volcanic emission, soil erosion, dissolution of As-bearing minerals into ground water and bush fires whereas anthropogenic sources may include pesticides, fertilizers, animal feed, chemicals used for timber preservation, burning of fossil fuels, mining and smelting of non-ferrous metals (IPCS, 2001). Gold mining activities have been ongoing in Paracatu in Minas Gerais, Brazil for >300 years. Release of arsenic into the environment that is associated with mining and extracting gold from the gold-bearing ore is of a health concern of the local population. Arsenic is a well-known human carcinogen in addition to its wide spectrum of non-carcinogenic effects (IARC, 2004). For arsenic health risk assessment, the increased cancer risk is generally the focal endpoint. For long-term exposure, arsenic is related to increased risks of cancers in the skin, lung, bladder and kidney; and the more recent development of a benchmark dose of chronic arsenic cancer risk is actually based on the lung cancer epidemiological data of Taiwan (JECFA, 2011).

Minas Gerais is a mineral rich state of Brazil where Paracatu is a relatively small size town with a population of about 90,000 and is in close proximity of a large gold production mine currently operated by Kinross Brasil Mineração (KBM). Over the last three centuries, this mine and its surrounding areas have been actively mined by various small to large miners with varying industrial practices although operational standards and environmental emission control have improved significantly over time.

It may be difficult to exactly pinpoint which sources (natural v anthropogenic, historical v recent times) contribute to the total environmental arsenic load, and the relative contribution from each source in the greater Paracatu Township. From an environmental and human health risk perspective, however, it would be unhelpful to try and exactly define these processes and sources before it can be demonstrated that the risk level is not acceptable. From an ethical and scientific point of view, it would also be inappropriate to assume that certain processes and sources are the main contributors to the total contaminant load. Therefore, the primary goal of this study was to consider various exposure pathways including both inhalation and ingestion routes and assess their respective potential health risks in order to identify the most significant contributor(s) so that a more effective intervention strategy can be developed for the protection of the environment and public health.

In this study, we assessed the environmental concentrations of arsenic in the drinking water, surface soil/dust, airborne particles (air PM_{10} and TSP), and food to get an insight of the combined daily intake of arsenic and its resultant risk. Bioaccessibility, an estimation of the bioavailable fraction of the arsenic in soil and food, was also determined in order to provide a more refined risk estimate (Ng et al., 2015). A holistic environmental apportionment study of this type may provide a benchmark in terms of exposure and related risk characterization for the current operation phase or for implementing intervention and/or future mine closure phase when this mine is deemed to be exhausted.

2. Material and methods

2.1. Study site

Paracatu, with a population of approximately 90,000 (IBGE, 2015), is a mining town located in the western part of the State of Minas Gerais in Brazil where there is one of the largest gold mine (Fig. 1) currently operated by KBM with annual tonnage of raw ore of about 60 M tons. Fig. 2 shows the sampling locations of surface soil dust and water in close proximity of the mine and the greater Paracatu Township.

Prevalent wind direction of Paracatu between Nov 2012 and Nov 2018 is typically to the NE (34.7%), E (21.1%), and less frequently to the ESE (12.8%), SW (9%), W (4.5%), NW (6.2%), N (6.8%), respectively, (Windfinder, 2018) suggesting relatively lower amount of airborne fugitive dust that might have contributed to the arsenic-load of the residential surface soil/dust deposited on the Paracatu township which is south of the mine site compared to other regions surround the mine site.

2.2. Reagents and instrument

All reagents were of analytical grade and prepared using ultrapure concentrated HNO3 (Merck KGaA, Darmstadt, Germany) and Milli-Q water (18 MΩ·cm Milli-Q water purification system, Millipore Corporation, Bedford, USA). All lab-ware were thoroughly cleaned by soaking at 60 °C in 1% HCl + 3% HNO3 distilled high-purity acids for at least 48 h, then rinsed several times and soaked in Milli-Q water for at least 48 h at 60 °C, rinsed again and dried under HEPA drying-hood before use (Ciminelli et al., 2017). Certified Reference Materials (CRM) were purchased from Graham B Jackson (Aust) Pty Ltd. (a division of Certified Reference Materials Trust, Victoria, Australia). The CRMs included Water TM24.3, Sediment BCSS-1, Montana I Soil SRM NIST 2710a, Tomato Leaves NCS-ZC-85006, Parsnip Root Powder CS-PR-2, Peach Leaves 1547, Dog Fish Muscle DORM-3, and Bovine Liver 1577b analyzed in the same manner as the environmental samples (Section 2.3) with an optimum sample weight of 0.25 to 0.5 g. Representative procedure blanks and spike recovery samples were also included in each batch run of every 10 samples. These QC standards allow for the evaluation of instrument performance and assay precision. Arsenic concentrations were measured using the ICP-MS (Agilent 7500cs, Agilent Technology, Tokyo, Japan) or ICP-OES (Optima 8300, Perkin Elmer Inc. Boston, USA) following acid digestion based on USEPA (2007a) or AS4479.2 (Standard Australia, 1997). Arsenic speciation in rice and bean was determined using HPLC-HG-AFS (Millennium Excalibur system, PSAnalytical, Kent, England) (Ciminelli et al., 2017) which is based on Farias et al. (2015).

2.3. Environmental survey

Fifty-two water samples were collected directly from the wells (bore-water), domestic reservoirs or taps of nearby residences, and the reservoirs at the town water supply authority COPASA including some duplicate and triplicate samples were collected at the same premises using a 1 L polyethylene beaker rinsed three times with the water sample before collection. A subsample was filtered using a 0.45 μm cellulose membrane (Millex HA MCE, Millipore Australia, Victoria, Australia), and 490 mL of the filtered water was preserved with the addition of 10 mL of 30% ultrapure HNO_3 (Merck KGaA, Darmstadt, Germany). The filtered and acidified water samples were stored in a cool box for transportation to the laboratory then kept in a fridge at +4 °C until analysis by ICP-MS.

Thirty-eight surface soil/dust samples were collected from the top 1 cm of the surface with a stainless-steel spade or brush and stored in plastic zip-lock plastic bags at ambient temperature until ICP-MS analysis following microwave digestion (USEPA, 2007a). Each soil/dust

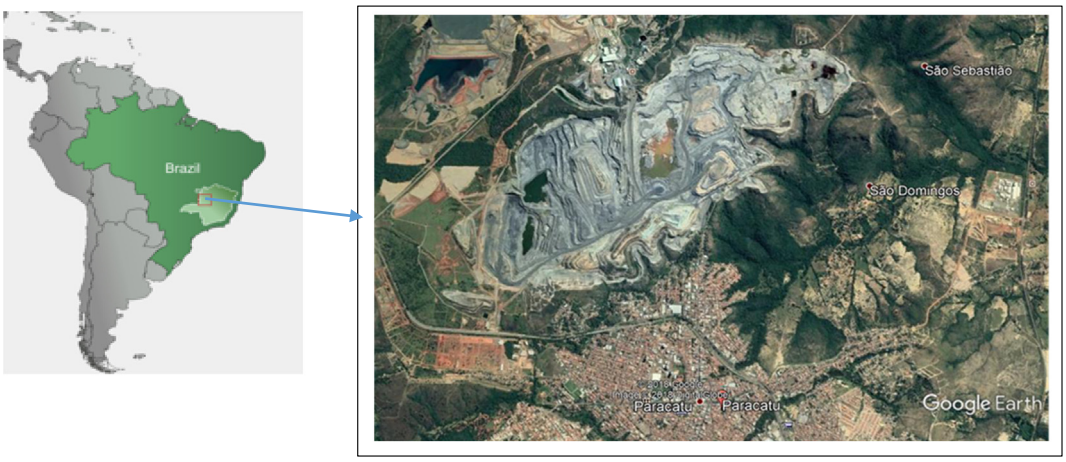


Fig. 1. Map of Brazil showing the geographical location of Paracatu in the Minas Gerais State of Brazil and the gold mine site north of the town.

sample was dried in a laboratory oven at 40 °C until complete dryness to remove moisture then sieved mechanically to obtain the ≤250 μm particle size fraction for total elemental analyses, and bioaccessibility assessment. All samples were analyzed in duplicate unless otherwise specified. Fig. 2 depicts the locations of surface soil/dust and water surveys.

Low-volume active air sampler (AAS) (*E*-BAM, Met One Instruments, Grants Pass, OR, USA) were deployed for air fine dust sample collection and arsenic concentration measurement. The locations of the air monitoring stations are shown in Fig. 3. The E-BAM is a portable, real-time beta gauge that is comparable to U.S. EPA methods for PM 2.5 and PM 10 particulate measurements. More detailed sampling and measurement procedures are provided in the Supplementary Materials.

2.4. Food survey

Ninety food samples of fifteen representative food categories were purchased from local markets including egg ($n = 5$), chicken (5), beef (5), fish (2), potato (3), carrot (4), tomato (4), garlic (4), cabbage (4), lettuce (4), milk (3), coffee (7), beans (18), rice (16) and pasta (6).

Fig. 2. Map showing the sampling locations from residential areas in Paracatu (Red Circle = surface soil/dust; White Square = follow up additional surface soil/dust; Blue Triangle = water). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Locations of air PM_{10} sampling stations.

Sample preparation and total arsenic concentration measurement by ICP-MS including quality control/quality assurance certified reference standards were as previously described (Ciminelli et al., 2017). Arsenic speciation was conducted only in rice and bean based on an extraction method by Huang et al. (2010) following by HPLC-HG-AFS measurement (Farias et al., 2015). Several certified reference materials for total arsenic and arsenic speciation were included as part of the quality control/quality assurance measures (Table 1).

2.5. Bioaccessibility test

Soil and surface dust samples were mechanically sieved to ≤250 μm size for the bioaccessibility measurement based on the physiologically based extraction test (PBET) (Ruby et al., 1996).

For the PBET method, the soil/dust sample (≤250 μm fraction) was extracted using a synthetic gastrointestinal fluid in a solid: liquid ratio of 1:100 at pH 1.5, 2.5, 4.0 and 7.0 over a number of hours simulating the GI tract pH conditions representing fasting, semi-fed, and fully-fed stomach (stomach phase I – pH 1.5, 2.5 and 4.0), and the small intestine (phase 2 pH 7.0) respectively, at 37 °C over a period of 4 h. Each sample was assessed across all pH values and three different time intervals to derive a set for 12 extracts. Arsenic was measured in the 0.22 μm (Millipore Corporation, Bedford, MA, USA) filtrate of the supernatant after centrifugation at 10000*g* for 15 min in an IEC MicroMax Centrifuge (IEC, MA, USA) of the GI simulation extracts. The amount found in each extract was then compared to the actual amount (calculated from the initial total elemental concentration of the ≤250 μm soil/dust particles) put in the G.I. digestion tube to derive the BAC value. The overall BAC is the average of 12 measurements from each of the duplicates to represent the various physiological states of a human during his/her active period of a day (Diacomanolis et al., 2016).

Table 1
Results of certified reference materials representing the average of duplicates unless otherwise specified.

SRM	Certified (mg/kg)	Measured (mg/kg)
TM-24.3 (Lake Ontario water)	5.21 ± 0.53 μg/L	5.11 ± 0.50* μg/L ($n = 3$)
SLRS-5 (River water)	0.413 ± 0.039 μg/L	0.460 μg/L
NCS-ZC-85006 (Tomato leaves)	1.05 ± 0.13	0.94
CS-PR-2 (Parsnip root powder)	0.03 ± 0.02	0.03
DORM-3 (Dog fish muscle)	6.88 ± 0.03	6.23
NIST 1577b (Bovine liver)	0.05	0.042
NIST 1568b (Rice flour) iAs	0.092 ± 0.010	0.104 ± 0.007 ($n = 3$)
NIST 1568b (Rice flour) As_{total}	0.285 ± 0.014	0.278
BCSS-1 (Sediment)	11.9 ± 1.4	11.88

Where * indicate mean of data from two laboratories at the University of Queensland; iAs = inorganic arsenic, As_{total} = total arsenic.

3. Results and discussion

3.1. Quality of results

Results of certified reference materials were within the range of their respective certified concentrations (Table 1). Arsenic concentrations reported in this study were those without further adjustment for the recovery.

3.2. Drinking water surveys

Total arsenic concentrations of the drinking water samples collected are shown in Table 2. The detection limit is 0.04 μg/L. All mean values

Table 2
Arsenic concentrations (μg/L) of drinking water samples collected in Paracatu Township.

Water source	No. of samples	Arsenic (μg/L)
COPASA (central water supply)	5	0.21 ± 0.01
Drinking water	25	0.74 ± 1.62
Drinking water and bore water	52	3.90 ± 3.12

were higher than the median concentration (data not shown). For the exposure and risk characterization, only the mean values were used in the calculation.

3.3. Soil/dust surveys

Three surface soil/dust surveys were conducted (Table 3). For the first survey (dry season), we had access to seven nearby properties in close proximity of the mine site, the number of sites increased by three in the second survey when we repeated the sampling on the same seven previously surveyed properties plus three additional properties, and the third survey (before the wet seasons) included 21 sites that extended the distances further away from the sites. There were no statistical differences in the mean arsenic concentrations amongst the samples of the three surveys. For the PBET bioaccessibility assessment (Ruby et al., 1996), the solubilized arsenic in the synthetic gastrointestinal fluid is the bioaccessible fraction that is considered potentially available for absorption by humans upon ingestion. The ≤250 μm fraction is regarded as the particle size that is likely to stick to hands and hence could result in exposure via hand-to-mouth activities (Duggan et al., 1985; Drahota et al., 2018). Methods simulating the gastrointestinal absorption have been widely adopted as a surrogate for the prediction of bioavailability of arsenic and metals for the risk assessment of contaminated sites (Ruby et al., 1996; Basta et al., 2007; Bruce et al., 2007; Juhasz et al., 2007; Denys et al., 2012; Xia et al., 2016; Tang et al., 2018). The application of BAC for tier-two risk assessment has been adopted by regulatory agencies such as in USA and Australia. BAC of lead was validated against in-vivo models and accepted by USEPA (2007b) and similarly for arsenic (USEPA, 2017). The acceptance of the same was recommended as part of the National Environmental Protection Measures (NEPM) review (Ng et al., 2009) and subsequently adopted by the National Environmental Protection Council (NEPC) in Australia (NEPC, 2013). BAC data can support and inform a more refined tier-two health risk assessment of site contamination.

BAC was determined in samples collected in the first two surveys with a respective of 3.7 ± 2 (1.8–7.5) and 3.2 ± 2 (1.1–6.7) % BAC representing a bioaccessible arsenic concentration of 5.8 mg/kg and 3.0 mg/kg in the surface soil/dust tested. The overall average bioaccessible arsenic concentration in the surface soil/dust was found to be 4.1 ± 3.7 mg/kg ($n = 17$) calculated from an average BAC of 3.4 ± 2%, and was used in the risk apportionment calculation.

Table 3
Total arsenic concentrations (mg/kg) and bioaccessibility (%) in the ≤250 μm fraction of surface soil/dust samples collected in Paracatu Township.

I.D.	As (mg/kg)	BAC (%)	BAC*As (mg/kg)
Survey 1 (May 2011)			
Mean ± SD ($n = 7$)	201 ± 155	3.7 ± 2	5.8 ± 4.8
Median	186	3.2	5.4
Range	6–461	1.8–7.5	0.5–14.8
Survey 2 (Nov 2011)			
Mean ± SD ($n = 10$)	153 ± 177	3.2 ± 2	3.0 ± 2.3
Median	83	2.3	2.4
Range	13–568	1.1–6.7	0.3–8.0
Combining surveys 1 and 2			
Mean ± SD ($n = 17$)	173 ± 165	3.4 ± 2.0	4.1 ± 3.7
Median	136	2.9	3.4
Range	6–568	1.1–7.5	0.3–14.8
Survey 3 (September 2012)			
Mean ± SD ($n = 21$)	153 ± 114		
Median	134		
Range	20–403		
Combining three surveys			
Mean ± SD ($n = 38$)	162 ± 138		
Median	135		
Range	6–568		
NEPM HIL-A*	100		
Brazil (Minas Gerais)**	55		

Where * is NEPM = National Environmental Protection Measures Health Investigation Level (NEPC, 2013); ** Residential Investigation Value in Brazil - Normative Deliberation COPAM n° 166, June 29, 2011 (Anonymous, 2011).

3.4. Arsenic in airborne particles

Arsenic concentrations were measured in air PM_{10} samplers collected in 2011–2013 (Fig. 3) as part of a larger air quality monitoring program that also included total suspended particles and $PM_{2.5}$ (data not shown but noting that the arsenic concentration in $PM_{2.5}$ is lower than that of PM_{10}) to provide data for the human health risk from inhalation. The number of monitoring stations when included the TSP and $PM_{2.5}$ stations (not shown) in addition to the PM_{10} stations exceeds EU guidelines of one station per 100,000 inhabitants, and the use of mean values measured in PM_{10} over an extended period of time (one year or longer) is consistent with EU guidelines (Anonymous, 2005). Arsenic concentrations of the air PM_{10} from the four monitoring stations are provided in Table 4 and the arsenic intake from PM_{10} based on inhalation rate are low compared to that of the surface soil/dust and its relative risk is considered less important in terms of risk apportionment as discussed later.

The PM_{10} arsenic concentrations shows that they were typically within the EU target value of 6 ng As/m^3 of air. The mean arsenic concentrations were mostly in the range of 3–5 ng/m^3 with the exception of 10.8 ng/m^3 was observed in a very short period between 1/4/2012

Table 4
Air quality data for arsenic (ng As/m^3) in PM_{10} samples.

	PM_{10} (ng As/m^3)			PM_{10} (ng As/m^3)	
São Domingos			União		
Period 1	1/06/2012 to 31/5/2013		Period 1	1/06/2012 to 31/5/2013	
	Mean	4.9		Mean	5.3
	Median	4.0		Median	4.9
	No. (days)	318		No. (days)	314
Period 2	1/08/2012 to 31/7/2013		Period 2	1/08/2012 to 31/7/2013	
	Mean	4.4		Mean	4.4
	Median	3.8		Median	3.2
	No. (days)	322		No. (days)	318
Period 3	1/10/2012 to 23/9/2013		Period 3	1/10/2012 to 26/9/2013	
	Mean	4.1		Mean	3.8
	Median	3.8		Median	2.9
	No. (days)	317		No. (days)	316
Lagoa			Ulhoa		
Period 1	1/06/2012 to 31/5/2013		Period 1	1/06/2012 to 31/5/2013	
	Mean	3.1		Mean	4.9
	Median	2.9		Median	4.1
	No. (days)	150		No. (days)	334
Period 2	1/08/2012 to 31/7/2013		Period 2	1/08/2012 to 31/7/2013	
	Mean	3.1		Mean	4.2
	Median	2.9		Median	3.9
	No. (days)	193		No. (days)	342
Period 3	1/10/2012 to 23/9/2013		Period 3	1/10/2012 to 23/9/2013	
	Mean	3.3		Mean	4.2
	Median	3.2		Median	4.1
	No. (days)	235		No. (days)	338
São Domingos			União		
Period 1	17/12/2011–31/3/2012		Period 1	17/12/2011 to 31/3/2012	
	Mean	2.3		Mean	3.6
	Median	1.6		Median	1.7
	No. (days)	87		No. (days)	18
Period 2	1/04/2012 to 22/5/2012		Period 2	1/04/2012 to 22/5/2012	
	Mean	4.4		Mean	0.1
	Median	4.6		Median	0.1
	No. (days)	47		No. (days)	62
Lagoa			Ulhoa		
Period 1	17/12/2011 to 31/3/2012		Period 1	17/12/2011 to 31/3/2012	
	Mean	3.6		Mean	3.3
	Median	4.0		Median	0.8
	No. (days)	87		No. (days)	90
Period 2	1/04/2012 to 24/5/2012		Period 2	1/04/2012 to 24/5/2012	
	Mean	4.7		Mean	10.8
	Median	5.1		Median	12.0
	No. (days)	52		No. (days)	13

and 24/5/2012 at Ulhoa where spikes were observed during the bush fire season and are considered as outliners. The continuous, low-volume PM_{10} data for the period from December 2011 to September 2013 at the four sampling sites (Table 4) were used for exposure assessment, consistent with European Union guidelines (Anonymous, 2005). According to USEPA (2013), an arsenic concentration in air of 5.7 ng/m^3 can be ascribed to a 1:100,000 target risk, corresponding to the "tolerable" risk defined in CONAMA 420 (Anonymous, 2009). For a conservative approach for risk assessment where no data exist for arsenic bioaccessibility in atmospheric dust, the maximum mean annual value measured in the four PM_{10} stations (5.3 ng As/m^3 of air, and assuming that 100% of this As is bioaccessible) was used to assess As intake from inhalation in this study. A more detailed characterization of fine particles and their inhalation bioaccessibility assessment using a simulated lung fluid assay will be discussed elsewhere (Morais et al., this issue).

3.5. Arsenic in food

We have previously reported the arsenic concentrations in 15 categories of food items commonly consumed by the local Brazilian population (Ciminelli et al., 2017) and the results are summarized in Table 5. Arsenic speciation in 13 out of 16 rice samples showed the inorganic arsenic (iAs) represented by the sum of $As^{III} + As^{V}$) was 48 ± 21% (102 μg/kg) of the total As 212 ± 184 μg/kg (Ciminelli et al., 2017) and the iAs is in the same order to that of global survey (139 μg/kg) reported by WHO (2012), and is below the WHO recommended standard of 200 μg/kg of iAs in rice (WHO, 2012). The rice total As is also below the Brazil national standard of 300 μg/kg (ANVISA, 2013), and within the range of 2–1830 μg/kg reported by JECFA (2011). The beans were found to contain 100% iAs. Total arsenic concentrations of all other food groups were also below the maximum concentrations of available national standards.

3.6. Risk apportionment - intake of arsenic from water

For the risk apportionment calculation, the exposure factors including body weight, water consumption, incidental soil ingestion and dust inhalation rate of adults and children are those in accordance with the national guidelines (Ministério da Saúde, 2010); these include adult/child: body weight (70/16 kg), daily drinking water volume (2/1 L), daily soil/dust ingestion (50/100 mg), and daily inhalation volume of air (22/15 m^3).

The mean concentration of arsenic in all drinking water and bore water samples collected from nearby residential area of Paracatu was 1.34 ± 3.12 μg/L ($n = 52$), whereas other domestic drinking water averaged 0.74 ± 1.62 μg/L ($n = 25$) and is considered as good quality because it is below the current WHO maximum recommended concentration of 10 μg/L and the Brazilian national drinking water standard. Further, the COPASA reservoir water is of very high quality (0.21 ± 0.01 μg/L ($n = 5$). For risk assessment, we assumed the nearby residents are more likely to drink the water containing 1.34 μg/L as one possible scenario; whereas for a wider community the residents maybe drinking the COPASA water containing 0.21 μg/L as a second scenario. The third scenario maybe the average concentration of 0.76 μg/L derived from the average of the mean values of three water sources.

Table 5
Arsenic concentration (μg/kg) in surveyed food items in fresh weight unless specified.

Food item	Total As: mean ± SD (n) (μg/kg)	iAs%	Brazil As standards[b] (μg/kg)
Beans[a]	50 ± 5 (18)	100	100
Beef	21 ± 7 (5)	50	500
Cabbage	6 ± 2 (4)	50	300
Carrot	7 ± 1 (4)	50	200
Chicken breast	21 ± 15 (5)	50	500
Coffee[a]	49 ± 60 (7)	50	200
Egg	13 ± 2 (5)	50	300
Fish	233 ± 261 (2)	10	1000
Garlic	13 ± 5 (4)	50	200
Lettuce	17 ± 11 (4)	50	300
Milk	3 ± 1 (3)	50	50
Pasta[a]	45 ± 2 (6)	50	N/A
Potato	9 ± 1 (3)	50	200
Rice[a]	212 ± 184 (16)	48	300
Tomato	5 ± 2 (4)	50	100

Where [a] indicates dried weight as purchased; iAs % is percent of inorganic arsenic (taken from Ciminelli et al., 2017); [b] Brazil food standards for total arsenic in food (ANVISA, 2013).

3.7. Intake of arsenic from food

The percentages of inorganic arsenic in various tested food items were taken from the literature as previously reported (Ciminelli et al., 2017). In line with the current literature, we assumed 10% iAs in fish and 50% iAs in the other food samples, except for rice and beans where we used our own speciation data.

It is noted that rice and beans are the staple of a typical Brazilian diet and that they are the major contributors to the total dietary arsenic intake and that the consumption of fish in a typical Brazilian diet is relatively low (IBGE, 2008). Various ingestion scenarios based on consumption patterns in Brazil (IBGE, 2008) were reported by Ciminelli et al. (2017) in which the daily arsenic intakes from the fifteen food groups were calculated to be 0.179, 0.188, 0.142 and 0.255 μg/kg b.w./d for the populations of Brazil, Southeast Brazil, Total Southeast Brazil and Rural Southeast Brazil, respectively. For the risk assessment in this study, we have taken the average daily food intake of arsenic of 0.188 μg/kg b.w./d as a reasonable approximate value for the local Paracatu population as we previously discussed (Ciminelli et al., 2017). We would then assume that a child consumes half the amount of the food per body basis (0.094 μg/kg b.w./d) as the adult for the risk apportionment calculation, which would be a very conservative estimate because the body weight was assumed 16 kg over the lifetime risk assessment. It is included here for illustration purpose compared to the lifetime risk of an adult. The daily intakes of As would be 0.038, 0.006, and 0.022 μg/kg b.w./d, and 0.084, 0.013, and 0.048 μg/kg b.w./d, for adults and children, respectively. The daily consumption of water, and the body weights of adults, and children are set at 2 L and 1 L, and 70 kg, and 16 kg, respectively, for adults and children.

3.8. Intake of arsenic from ingestion and inhalation of geogenic material

Exposure to arsenic can come from incidental ingestion of small particles (≤250 μm fraction) of surface soil/dust via hand-to-mouth activities, and children are likely to have a higher exposure rate compared to adults. After adjusting for BAC, the bioaccessible concentrations of As in the surface soil/dust was 4.1 ± 3.7 mg/kg ($n = 17$) with an average BAC of 3.4 ± 2.0%. The BAC (3.4%) of surface soil/dust (0 to −2 cm) is similar to our previous report on surface but deeper mineralized and non-mineralized soil (0 to −20 cm) ranged 0.86–5.0% BAC in Paracatu region (Ciminelli et al., 2018). These authors observed a clear correlation between As and Fe in Paracatu soil and that arsenic was found trapped in the orientated aggregates of crystalline iron (hydr)oxides nanoparticles, which explains the low As BAC (Ciminelli et al., 2018). It has also been reported that mineral composition and the forms of arsenic that govern the solubility of arsenic such as ferric arsenate and arsenic sulfides in mine waste materials are well correlated to the bioaccessibility of arsenic (Diacomanolis et al., 2016). In that paper, the authors reported an R^2 of 0.756 between the predicted BAC values using XANES spectroscopy speciation data and actual measured BAC data. In this current study and using the average bioaccessible As of 4.1 mg/kg, an adult with a body weight of 70 kg who ingests 50 mg of soil/dust per day would give a daily exposure rate of 0.003 μg/kg/d;

whereas a child with a body weight of 16 kg who ingests 100 mg of soil/dust per day would give a daily exposure rate of 0.026 μg/kg/d.

For the inhalation route, taking the average As concentration in the inhalable fine dust (PM_{10}) as 5.3 ng/m^3 and assuming the BAC is 100%, then the daily intake rates of As by an adult and child would be 0.0017 μg/kg/d and 0.0050 μg/kg/d, respectively. Although air arsenic standard is not available in Brazil this level (5.3 ng/m^3) is within the target concentration of air arsenic (6.0 ng/m^3) in Europe.

3.9. Health risk characterization of total exposure

Taking the various exposure pathways discussed above we have derived the risk apportionment as shown in Table 6.

Results indicate that the combined food and water represent 81.5% and 45% of the total daily arsenic intake by adults and children, respectively. Whereas the ingestion and inhalation intakes of As are relatively low. It is worthy of notice that the inhalation route is <3% of the total daily exposure of As even assuming 100% BAC. This finding supports the conclusion that geogenic exposure is minor contributor relatively to all possible exposure sources in this township. The low BAC of As in the surface dust is probably due to the arsenic is in an insoluble form of nanostructured iron (hydr)oxides as found in the local geogenic materials (Ciminelli et al., 2018).

Total dietary iAs from food is estimated to be 0.188 and 0.094 μg/kg b.w./d ingested by adults and children, respectively. The total dietary iAs is about 40 fold higher than that of the combined ingestion and inhalation routes from the geogenic sources by adults (0.0047 μg/kg b.w./d) and 3 fold higher in children (0.031 μg/kg b.w./d). This means that the major contributor to arsenic intake is the dietary source but geogenic sources are minor when one considers the bioaccessibility.

For the combined geogenic ingestion and inhalation exposure, the intake is 638 and 97 times lower than the JECFA $BMDL_{0.5}$ of 3 μg/kg b.w./d for adults and children (JECFA, 2011), respectively. The total daily intake is 13 and 14.4 times lower than the $BMDL_{0.5}$ for adults and children, respectively, indicating that the total exposure is low. It is noted that the BMDL approach as used by JECFA/WHO does not assume a linear dose response relationship.

The USEPA opts for a more conservative approach by using a linear dose relationship for setting the arsenic Cancer Slope Factors (CSF) for oral ingestion and inhalation respectively (ATSDR, 2007). Its CSF for the oral route is set at 1.5 per mg/kg b.w.-d; and CSF for inhalation is 4.3 × 10–3 per μg As/m^3. If these slope factors are used then the predicted cancer risks for all the different exposure pathways are those shown in Table 6.

To put the interpretation of predicted cancer risk in perspective, it may be a pragmatic approach to compare the study data with a hypothetic situation. In that, the data are compared to the WHO recommended drinking water standard and also the Brazilian standard of 10 μg/L for arsenic (Table 6). This standard is generally accepted as a safe level for life-time exposure without appreciable risk. Yet, the cancer slope factor gives a predicted cancer risk of over 4.3 in 10,000 for adults and 9.4 in 10,000 children. This cancer risk calculated from drinking water containing 10 μg As/L is similar but slightly higher compared to the sum of predicted risk of 3.5 and 3.4 in 10,000 of adults and children, respectively, for the Paracatu population from all exposure pathways in the current study as shown in Table 6. This scenario (WHO 10 μg/L vs sum of risks in Paracatu) can be considered similar magnitude of risks despite the slightly lower risk in adults, and 3 fold lower in children of the Paracatu population.

Regardless whether the data are compared to the WHO $BMDL_{0.5}$ value or the predicted cancer risk derived from the cancer slope factors, the current study confirms that food and water arsenic intakes and their respective associated risks are the major sources of exposure and that geological sources are the minor contributors. Our study design and results have demonstrated that it is imperative to consider all exposure scenarios/pathways when conducting health risk assessment of metals/metalloids whether it is during mining operation or the mine closure phase. The data here inform a more strategic intervention objective over the life of mine for the protection of the environment and the population health.

Table 6
Risk apportionment of exposure pathways to arsenic from ingestion of food, water and soil, and inhalation of air.

Pathway	iAs Intake (μg/kg b.w./day)		Predicted cancer risk		Percent of total intake	
	Adult	Child	Adult	Child	Adult	Child
Ingestion of surface soil (4.1 mg/kg)	0.003	0.026	$4.5E^{-06}$	$3.9E^{-05}$	1.3	12.4
Inhalation of dust (5.3 ng/m^3)	0.0017	0.0050	$7.3E^{-06}$	$2.2E^{-05}$	0.7	2.4
Food	0.188	0.094*	$2.8E^{-04}$	$1.4E^{-04}$	81.5	45.0
Water-S1 (1.34 μg/L)	0.038	0.084	$5.7E^{-05}$	$1.3E^{-04}$	16.5	40.2
Water-S2 (0.21 μg/L)	0.006	0.013	$9.0E^{-06}$	$2.0E^{-05}$	NC	NC
Water-S3 (0.76 μg/L)	0.022	0.048	$3.3E^{-05}$	$7.2E^{-05}$	NC	NC
Total exposure (Ingestion + Inhalation + Food + Water-1)	0.2307	0.209	$3.5E^{-04}$	$3.3E^{-04}$	100	100
Water (10 μg/L) – WHO $BMDL_{0.5}$	0.2857 3	0.625 3	$4.3E^{-04}$	$9.4E^{-04}$		
CSF Oral	1.5 per mg/kg b.w./day					
CSF Inhalation	4.3×10^{-3} per μg/m^3					

Where * assumes a child will consume half the amount of food as the adult per body weight basis; NC = not calculated for these two scenarios are included for illustration purpose, where the probable exposure to As in water for the local population is assumed to be at 1.34 μg/L. Water-S1, S2, & S3 represent drinking water scenarios 1, 2, & 3, respectively.

4. Conclusion

Arsenic concentrations in the water, surface soil/dust, airborne particles, and most commonly consumed food groups, which encompass both ingestion, and inhalation exposure pathways for the health risk apportionment. The survey data indicate that the water quality in terms of arsenic concentration is good in Paracatu with an average concentration almost 10 times lower than the WHO recommended maximum guideline of 10 μg/L. The bioaccessibility of As in the surface soil/dust is very low resulting in an averaged bioaccessible concentration of As being 4.1 mg/kg. The low BAC is probably due to arsenic being tightly bound in its mineral forms that in turn affords relatively lower risk. Food contributes up to 81.5% of the total arsenic intake for adults and 45% for children. Rice and beans are the major contributors of the As intake from food. The sum of predicted cancer risks from all exposure pathways (geogenic, food and water) in Paracatu township is in a similar order of magnitude of the risk from drinking the WHO recommended safe level of water containing 10 μg/L of arsenic for adults, and the corresponding risk for children is 3 fold lower, hence the overall health risk is considered low. The approaches utilized in this study is appropriate for health risk assessment of mines during operation and mine closure phases and can inform intervention strategy over the life of mine.

Acknowledgements

The authors are grateful to the Brazilian government agencies – CNPq (*Conselho Nacional de Desenvolvimento Científico e Tecnológico*), FAPEMIG (*Fundação de Amparo a Pesquisa do Estado de Minas Gerais*) and CAPES (*Coordenação de Aperfeiçoamento de Pessoal de Nível Superior*), and to Kinross Brasil Mineração (KBM) for financial, and logistic and field support by its staff; the PVE fellowship from the Science Without Borders program to M. Gasparon; sample collection and preparation by Dr. Adelia Oliveira, Dr. Graziele Duarte, Dr. Gabriela Silva and Thiago Pascholin; for the assistance of André Luiz Martins Costa and Rossana Ciminelli with the IBGE; and the ICP-MS analysis by Dr. Lixia

Qi at QAEHS. QAEHS is a partnership between the University of Queensland and Queensland Health.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.04.048.

References

Anonymous, 2005. Directive 2004/07/EC of the European parliament and of the council. Off. J. Eur. Union (L 23/3 of 26.1.2005).

Anonymous, 2009. Resolução N° 420, de Dezembro de 2009. CONSELHO NACIONAL DO MEIO AMBIENTE (CONAMA). Resolução n° 420, de 28 de dezembro de 2009 - Dispõe sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas e estabelece diretrizes para o gerenciamento ambiental de áreas contaminadas por essas substâncias em decorrência de atividades antrópicas.

Anonymous, 2011. Deliberação Normativa N° 166, de 29 de Junho de 2011. Conselho Estadual de Política Ambiental. Altera o Anexo I da Deliberação Normativa COPAM/CERH no. 02, de 06 setembro de 2010, estabelecendo os valores de referência de qualidade dos solos. Diário Executivo de Minas Gerais, Belo Horizonte, 27 de Julho de 2011.

ANVISA (National Agency for Sanitary Surveillance), 2013. Resolution no. 42 from august 29th, 2013, technical regulation MERCOSUL for the maximum levels of inorganic contaminants in food (in Portuguese). Di_ario Oficial da Uni~ao no. 168, sexta-feira, 30 de agosto de 2013, Brasilia, Brazil.

ATSDR (Agency for Toxic Substances and Disease Registry), 2007. Public Health Statement for Arsenic, Toxic Substances Portal. Arsenic U. S. Department of Health and Human Services, Public Health Service, Atlanta, GA http://www.atsdr.cdc.gov/phs/phs.asp?id=18&tid=3, Accessed date: 14 November 2015.

Basta, N.T., Foster, J.N., Dayton, E.A., Rodriguez, R.R., Casteel, S.W., 2007. The effect of dosing vehicle on arsenic bioaccessibility in smelter-contaminated soils. J. Environ. Sci. Health A 42 (9), 1275–1281. https://doi.org/10.1080/10934520701434927.

Bruce, S., Noller, B.N., Matanitobua, V., Ng, J.C., 2007. In-vitro physiologically-based extraction test (PBET) and bioaccessibility of arsenic and lead from various mine waste materials. J. Toxicol. Environ. Health, Part A 70, 1700–1711.

Ciminelli, V.S.T., Gasparon, M., Ng, J.C., Silva, G.C., Caldeira, C.L., 2017. Dietary arsenic exposure in Brazil: the contribution of rice and beans. Chemosphere 168, 996–1003.

Ciminelli, V.S.T., Antônio, D.C., Caldeira, C.L., Freitasa, E.T.F., Delbema, I.T., Fernandes, M.M., Gasparon, M., Ng, J.C., 2018. Low arsenic bioaccessibility by fixation in nanostructured iron (hydr)oxides: quantitative identification of As-bearing phases. J. Hazard. Mater. 353, 261–270.

Denys, S., Caboche, J., Tack, K., Rychen, G., Wragg, J., Cave, M., Jondreville, C., Feidt, C., 2012. In vivo validation of the unified BARGE method to assess the bioaccessibility of arsenic, antimony, cadmium, and lead in soils. Environ. Sci. Technol. 46, 6252–6260. https://doi.org/10.1021/es3006942.

Diacomanolis, D., Noller, B.N., Taga, R., Harris, H.H., Aitken, J.B., Ng, J.C., 2016. Relationship of arsenic speciation and bioavailability in mine wastes for human health risk assessment. Environ. Chem. 13, 641–655. https://doi.org/10.1071/EN14152.

Drahota, P., Raus, K., Rychlíková, E., Rohovec, J., 2018. Bioaccessibility of As, Cu, Pb, and Zn in mine waste, urban soil, and road dust in the historical mining village of Kank, Czech Republic. Environ. Geochem. Health 40, 1495–1512.

Duggan, M.J., Inskip, M.J., Rundle, S.A., Moorcroft, J.S., 1985. Lead in playground dust and on the hands of school children. Sci. Total Environ. 44, 65–79.

Farias, S.S., Londonio, A., Quintero, C., Befani, R., Soro, M., Smichowski, P., 2015. On-line speciation and quantification of four arsenical species in Rice samples collected in Argentina using a HPLC-HG-AFS coupling. Microchem. J. 120, 34–39.

Huang, J.H., Ilgen, G., Fecher, P., 2010. Quantitative chemical extraction for arsenic speciation in rice grains. J. Anal. At. Spectrom. 25, 800–802.

IARC, 2004. IARC Monograph 84: Some Drinking Water Disinfectants and Contaminants Including Arsenic. International Agency for Research on Cancer. World Health Organization, Geneva, Switzerland.

IBGE (Brazilian Institute of Geography and Estatistics), 2008. Dietary consumption pattern of Brazilian population (in Portuguese). http://www.ibge.gov.br/home/estatistica/populacao/condicaodevida/pof/2008_2009_analise_consumo/, Accessed date: 15 May 2015.

IBGE (Brazilian Institute of Geography and Estatistics), 2015. Population estimation (in Portuguese) https://ww2.ibge.gov.br/home/estatistica/populacao/estimativa2015/estimativa_tcu.shtm, Accessed date: 1 December 2018.

IPCS, 2001. Arsenic and arsenic compounds. Environmental Health Criteria 224, 2nd ed. International Programme on Chemical Safety, World Health Organization, Geneva, pp. 1–521.

JECFA, 2011. Evaluation of certain contaminants in food. The Seventy-second Report of Joint FAO/WHO Expert Committee on Food Additives. WHO, pp. 1–115.

Juhasz, A.L., Smith, E., Weber, J., Rees, M., Rofe, A., Kuchel, T., Sansom, L., Naidu, R., 2007. In vitro assessment of arsenic bioaccessibility in contaminated (anthropogenic and geogenic) soils. Chemosphere 69, 69–78.

Ministério da Saúde, 2010. Diretrizes para elaboração de estudo de avaliação de risco à saúde humana por exposição a contaminantes químicos (Brasília).

Morais, M.D.A., Gasparon, M., Delbem, I.D., Caldeira, C.L., Freitas, E.T.F., Ng, J.C., Ciminelli, V.S.T., 2019. Gastric/Lung Bioaccessibility and Identification of As–Bearing Phases and Sources in Fine Surface Dust in a Gold Mining District (this issue).

NEPC, 2013. Amendment of the National Protection (Assessment of Site Contamination) Amendment Measure 2013. National Environmental Protection Council, Canberra, Australia https://www.legislation.gov.au/Details/F2013L00768, Accessed date: 17 August 2018.

Ng, J.C., Juhasz, A.L., Smith, E., Naidu, R., 2009. Contaminant Bioavailability and Bioaccessibility: Part 2. Guidance for Industry. CRC CARE Technical Report 14. CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia 978-1-921431-17-3, pp. 1–11.

Ng, J.C., Juhasz, A., Smith, E., Naidu, R., 2015. Assessing the bioavailability and bioaccessibility of metals and metalloids. Environ. Sci. Pollut. Res. 22, 8802–8825. https://doi.org/10.1007/s11356-013-1820-9.

Ruby, M., Davis, A., School, R., Eberle, S., Sellstone, C., 1996. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. Environ. Sci. Technol. 30, 422–430.

Standards Australia, 1997. AS4479.2 – Analysis of Soils, Part 2: Extraction of Heavy Metals and Metalloids from Soil by Aqua Regia – Hotplate Digestion Method (Australia).

Tang, W., Xia, Q., Shan, B., Ng, J.C., 2018. Relationship of bioaccessibility and fractionation of cadmium in long-term spiked soils for health risk assessment based on four in vitro gastrointestinal simulation models. Sci. Total Environ. 631-632, 1582–1589.

USEPA, 2007a. Microwave Assisted Acid Digestion of Sediment, Sludges, Soils, and Oils. in: Agency, USEPA 3051A/3051–3030. USEPA (3051–3030).

USEPA, 2007b. Estimation of Relative Bioavailability of Lead in Soil and Soil-like Materials Using In Vivo and In Vitro Methods. USEPA OSWER 9285.7-77. Office of Solid Waste and Emergency Response U.S. Environmental Protection Agency, Washington, DC, p. 20460.

USEPA, 2017. Standard Operating Procedure for an In Vitro Bioaccessibility Assay for Lead and Arsenic in Soil. OLEM 9200.2–164. U.S. Environmental Protection Agency, Washington, DC, p. 20460.

USEPA United States Environmental Protection Agency, 2013. Regional Screening Level (RSL) Resident Air Table.

WHO, 2012. Joint WHO/FAO Food Standards Programme Codex Committee on Contaminants in Foods Sixth Session Maastricht, 2012. The Netherlands, 26–30 March 2012, Proposed Draft Maximum Levels for Arsenic in Rice.

Windfinder, 2018. https://www.windfinder.com/windstatistics/paracatu, Accessed date: 27 December 2018.

Xia, Q., Peng, C., Lamb, D., Mallavarapu, M., Naidu, R., Ng, J.C., 2016. Bioaccessibility of arsenic and cadmium assessed for in vitro bioaccessibility in spiked soils and their interaction during the unified BARGE method (UBM) extraction. Chemosphere 147, 444–450.