INCT-Acqua - KBM research project

ARSENIC EXPOSURE ASSESSMENT FOR THE POPULATION OF PARACATU, MINAS GERAIS, BRAZIL.

Prepared for

KBM

Prepared by

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Virginia S. T. Ciminelli is a Professor of the Department of Metallurgical and Materials Engineering at the *Universidade Federal de Minas Gerais* (UFMG) and Coordinator of the National Institute of Science and Technology on Mineral Resources, Water and Biodiversity, INCT-Acqua. Member of the Brazilian Academy of Sciences, Member of the National Academy of Engineering, Brazil and Foreign Member of the US National Academy of Engineering; admitted to the National Order of Scientific Merit, and Level 1A Researcher of the National Council for the Scientific and Technological Development- CNPq. She leads partnerships with several institutions in Brazil and abroad. Since the late nineties she has been working with speciation and stability of arsenic in environmental samples. Her publications on the topic are characterized by the use of molecular and experimental modeling enabling the identification of the molecular structure of arsenic complexation in mineral samples containing iron and aluminum (hydr) oxides, mining tailings, in vegetables and avicultural waste. Her early works researched the fundamentals for the selection of oxisol with high capacity to fixate arsenic. Her most recent work provided the explanation of the long-term fixation mechanism in these oxisols. She was an invited keynote speaker in the event Arsenic 2014 with the lecture: *Arsenic in Mining: Sources and Stability*. Recipient of several awards and prizes, such as the Mercosur Award of Science and Technology, Integration Category *(The Arsenic Issue in Mercosur)*, in 2011, for her work at the IBEROARSEN network with Latin America and Iberia Peninsula researchers.

GLOSSARY

ABNT	Associação Brasileira de Normas Técnicas (Brazilian Association of Technical Standards)
Bioaccessibility	Bioaccessibility (BAC) refers to the fraction of a compound that is soluble in the gastrointestinal tract and is therefore available for absorption – which is specifically referred to when *in-vitro* assessment models are used
Bioavailability	Bioavailability (BA) is the amount of a contaminant that is absorbed into the body following skin contact, ingestion, or inhalation. BA is usually measured using an animal model (*in-vivo)*
BMD	Benchmark Dose
CONAMA	Conselho Nacional do Meio Ambiente (The National Council for Environment)
Dermal	Of or relating to the skin or dermis
Exposure	Contact of a chemical, physical, or biological agent with the outer boundary of an organism (inhalation, ingestion or dermal contact)
FAO	Food and Agriculture Organization of the United Nations
FEAM	Fundação Estadual do Meio Ambiente (State Foundation for the Environment)
Guideline Values	Values such as concentrations in soil, which are derived after appropriate allocation of Tolerable Intake (TI) among the possible different media of exposure
Hazard	The capacity of an agent to produce a particular type of adverse health or environmental effect
Health Risk Assessment	The process of estimating the potential impact of a chemical, biological, physical or social agent on a specific human population system under a specific set of conditions and timeframe
IARC	International Agency for Research on Cancer
IBGE	Instituto Brasileiro de Geografia e Estatística (Brazilian Institute of Geography and Statistics)
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
INCT-Acqua	National Institute of Science and Technology on Mineral Resources, Water and Biodiversity
In-vitro	Test-tube test
In-vivo	Whole organism (animal) test

IPCS	International Program on Chemical Safety
JECFA	FAO/WHO joint expert committee on food additives
μg/kg bw d	Micrograms per kilogram of body weight per day
NBR	Norma Técnica Brasileira (Brazilian Technical Standard)
NEPC	Australian National Environmental Protection Council
NEPM	Australian National Environmental Protection Measure
n	number of samples
ng/m^3	Nanograms per cubic meter of air
NHMRC	Australian National Health and Medical Research Council
PBET	Physiologically based extraction test; an *in-vitro* test for the measurement of bioaccessibility
PM_{10}	Atmospheric particulate matter with aerodynamic diameter smaller than 10 μm
$PM_{2.5}$	Atmospheric particulate matter with aerodynamic diameter smaller than 2.5 μm
Risk	The probability that, in a certain timeframe, an adverse outcome will occur in a person, group of people exposed to a hazardous agent
SBRC	Solubility Bioaccessibility Research Consortium
SENAI/FIEMG	National Service of Industrial Training/ State of Minas Gerais Federation of Industries
Soil	The part of the earth's surface consisting of humus and disintegrated rock that is located above the high water mark of an adjacent river or stream
TSP	Total Suspended Particles – atmospheric particulate of any aerodynamic diameter
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

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OVERVIEW

Since 2009, a series of research studies has been carried out by a multidisciplinary team from the National Institute of Science and Technology on Minerals Resources, Water and Biodiversity (INCT-Acqua) in Paracatu, Minas Gerais. The Institute was established by a program created by the Brazilian Ministry of Science, Technology and Innovation with the aim of supporting the development of institutes at the forefront of scientific and technological knowledge in strategic areas for the sustainable development of the country. With a multidisciplinary team from Brazil and abroad, INCT-Acqua offers a systemic and integrated approach to problems arising from the interface of mineral and metallurgical activities with water quality, soil, air and aquatic biodiversity.

The project in Paracatu is led by Professors Virginia Ciminelli, an environmental hydrometallurgist from the Department of Metallurgical and Materials Engineering of the Universidade Federal de Minas Gerais – UFMG, Massimo Gasparon, a geochemist from the School of Earth Sciences of The University of Queensland (Australia) and Professor Jack Ng, a certified toxicologist from the National Research Centre for Environmental Toxicology of The University of Queensland. The project scope is the “Assessment of Arsenic Exposure to the Population of Paracatu, Minas Gerais, Brazil”. The project is funded by Kinross and its major purpose is to provide Kinross Brasil Mineração (KBM) with the scientific data related to the potential availability and mobility of arsenic in Paracatu both from background and anthropogenic origin. Collectively, this team has extensive experience in arsenic research and is able to provide an objective and scientifically based exposure assessment of arsenic in Paracatu.

The approach to the assessment is based on the determination of the population exposure considering the main exposure routes such as ingested arsenic (As) (water + foods + ground dust/soil) and inhaled arsenic (airborne dust). The measured arsenic exposure is compared to the $BMDL_{0.5}$ (Benchmark Dose Lower Limit) set by the World Health Organization (WHO) and Food and Agriculture Organization (FAO) Joint Expert Committee in Food Additives (JECFA, 2011). The study includes the calculation of the relative contribution of various exposure pathways to the total daily arsenic intake. The $BMDL_{0.5}$ refers to the quantity of ingested inorganic arsenic which would imply an increase of 0.5% in the frequency of lung cancer in a population by exposure to all pathways: *"Based on data from an epidemiology study conducted on a highly-exposed population, the inorganic arsenic lower limit on the benchmark dose for a 0.5% increased incidence of lung cancer was calculated to be 3 μg/kg bw per day (range: 2–7 μg/kg bw per day) using a range of assumptions to estimate total dietary exposure of the study population to inorganic arsenic from drinking water and food."(JECFA, 2011)"*

The main conclusions are summarized below:

(i) The average As concentrations in samples of surface and community wells drinking water are 7 times lower than of the Brazilian standard and the WHO recommended value of 10 μg/L. The mean value of the As concentration in the drinking water samples (0.74 μg/L, n=25) and in the water supplied by the private and public equity water supply company COPASA (0.21 μg/L), which is consumed by the majority of the population of Paracatu, was below 1 μg/L. Arsenic concentrations in almost all the samples were lower than 1.0 μg/L, with most values lower than 0.3 μg/L. These results indicate that the exposure from water consumption represents a low risk to human health in Paracatu. The low concentrations of arsenic in water are confirmed by another work commissioned by Paracatu City Council and coordinated by the Centre of Mineral Technology - CETEM (CETEM, 2013). This study concluded, that "Most of As contents in water for human consumption in Paracatu are below the detection limit - LD (<0.5 μg/L) of the analytical technique". And further, "Under current conditions, the Paracatu population is not exposed to As contents by consumption of the supply water representing risk to human health".

(ii) PM10 and PM2.5 (that is, suspended particulates with size below 10 and 2.5 micrometers, respectively) dust samples were analyzed, each representing a composite of continuous low-flow samples collected over a period of between 72 and 96 hours. The average arsenic value measured in PM_{10} in each of these four stations is below the target values of 6 ng/m^3 (average over one year), set by the European Union (Anonymous, 2005a) and within an excess lifetime risk of 1:100,000. The contribution of inhaled arsenic derived from PM_{10} to total intake is up to 4.1% in children and 0.8% in adults, under the conservative assumptions of BAC = 100%. Therefore the contribution of atmospheric dust to the total exposure can be considered of minor importance.

(iii) The arsenic concentrations in soil samples in the mineralized area are higher than the investigation values (VI) of 55 mg/kg (ppm) for soil samples in residential areas defined by CONAMA 420 (Anonymous, 2009a). These results were obtained through a study conducted by the group leading the "*Solos de Minas*" survey . (http://www.feam.br/noticias/1/949-mapas-de-solo-do-estado-de-minas-gerais) to establish soil quality reference values across the state. The measured arsenic concentrations reflect the well-known arsenic anomalies in gold mining regions, common in Minas Gerais and in many mineral-rich areas of the world. However, the bioaccessible arsenic fraction – soluble fraction which would be actually available to be absorbed by the human body or, in other words, actually released into the stomach – is lower than 3%. Thus the concentrations of bioaccessible arsenic are lower than the investigation value (VI) set by CONAMA 420 and therefore, as ruled by the same Resolution, "do not represent potential direct or indirect risks to human health considering a standardized exposure scenario ".

The low arsenic bioaccessibility measured in our work in soils from this region is in agreement with another study by a group from the University of Lavras (Ono et al., 2012)

Such low bioaccessibility is explained in a recent publication by our team (Freitas et al., 2015) through a mechanism whereby arsenic is adsorbed in Al-Fe (hydr)oxides nanoparticles–in a process which ultimately produces Al-hematite nanocrystals which are more stable in the soil than the original As-bearing minerals (e.g. arsenopyrite). Such highly stable arsenic form is reflected in its extremely low bioaccessibility measured in samples of geogenic materials of both natural (e.g. soil, sediments and fallout dust) and anthropogenic origin. Subsequent research carried out by the group also showed that the fixation process is very fast (days to weeks) and that arsenic is not extracted using relatively aggressive chemical media and therefore is expected to remain stable under mild conditions prevailing in the environment.

(iv) Food arsenic is a significant contributor to the total daily intake, which places the Paracatu population within the standard of other cities in Brazil, Europe and the United States: “Compared to dietary exposure, non-dietary exposure to arsenic is likely to be of minor importance to the general population in the European Union” (Anonymous, 2009b). The US Agency of Toxic Substances and Disease Registry – ATSDR (2007) also stated that: “The general population may be exposed to arsenic in air, drinking water, and food. Of these, food is usually the largest source of arsenic.” (*http://www.atsdr.cdc.gov/toxguides/toxguide-2.pdf, accessed on May 5, 2015*). Rice is known to be the major source of dietary arsenic in populations that consume rice as a staple food. Rice plants are a natural arsenic accumulator, as they are capable of taking up arsenic from the contact with water containing traces of the element and this occurs as a result of the form of production in flooded field. Rice has consistently showed higher levels of inorganic As than other foods (Lynch, 2014). In 2014 WHO established As values of 0.20 mg/kg for white rice and 0.40 mg/kg for whole rice as safe. According to our work, the brands of rice more commonly purchased by the population in the Paracatu region have an average of 0.194 mg/kg of total arsenic.

(v) The total intake (herein considered ingestion + inhalation) of arsenic from all exposure sources is below 10% of the $BMDL_{0.5}$ of 3 µg/kg b.w. day and therefore the overall risk to the local population is low.

In conclusion, based upon the data obtained so far we can affirm that the risk of arsenic exposure to human health in Paracatu, Minas Gerais, is low. For instance, for a person weighing 70 kg, the arsenic intake due to consumption of 2 liters of water containing 10 micrograms per liter of arsenic (a guideline set by WHO and by Brazilian legislation) would be 0.28 µg/kg b.w. day. This is the same order of magnitude as the total intake calculated in our studies. The low risk is corroborated by the work conducted by CETEM under City Council commission.

ARSENIC CONCENTRATIONS IN WATER, SOIL, SURFACE DUST, AIR PARTICULATES AND FOOD

Arsenic in Water

Water samples were collected between May 2011 and September 2012 by the INCT-Acqua team with the assistance of KBM personnel. Sampling locations are shown in Figure 1.

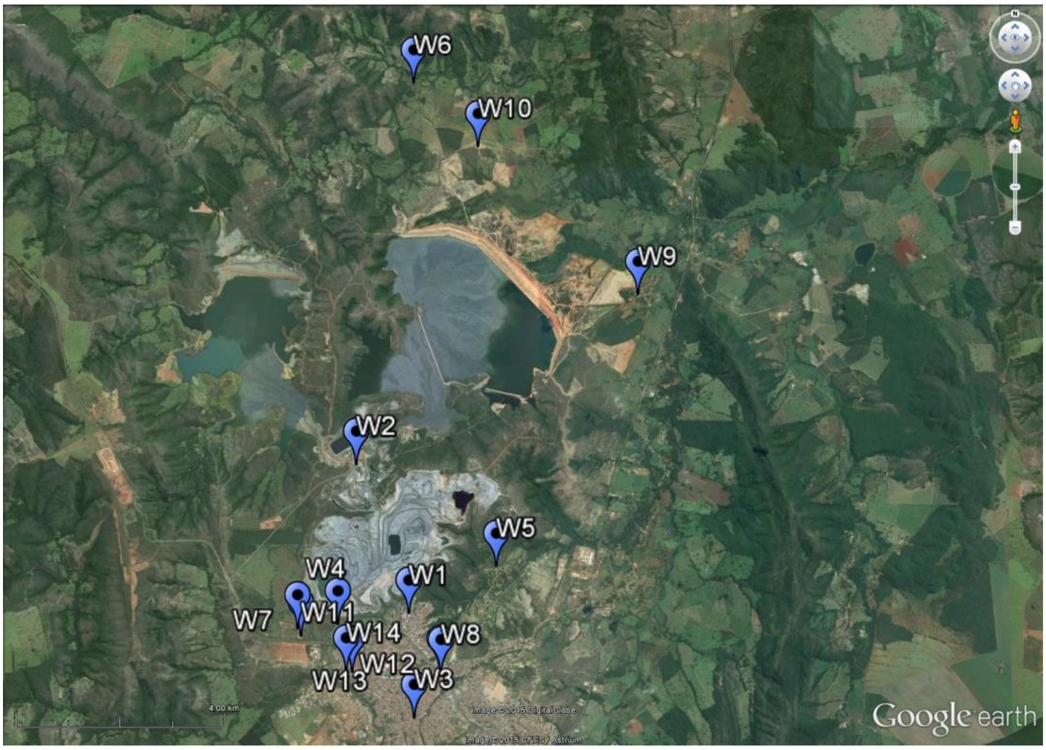

Figure 1. Water sampling locations. Background map from Google Earth™.

The drinking water samples were collected directly from the wells reservoirs or taps in the surveyed sites following the preservation and sampling procedures described in NBR 9898 (1987) and NBR 9897 (1987).

All water samples tested (a total of 57 analyses from 10 sites) had arsenic concentration significantly below the national drinking water guideline value of 10 µg/L, except for one site (also considered in the calculations). Three different scenarios were contemplated for arsenic exposure from drinking water:

1) consumption of municipal water (public and private equity water company, COPASA) with mean As content of 0.21 μg/L (5 analyses);
2) consumption of both municipal and non-municipal water (pumped from bores and subjected to some level of filtration/treatment before consumption) with mean As content of 0.74 μg/L (25 analyses);
3) consumption of both municipal and non-municipal drinking water (as in point 2) above) as well as bore water (sampled directly from the well) with mean As content of 1.34 μg/L (52 analyses).

The mean As concentrations for the three scenarios are listed in Table I.

Table I

Arsenic concentrations in water for the three scenarios

	Number of analyses	Mean μg/L	Standard deviation
COPASA reservoir water	5	0.21	0.01
All drinking water	25	0.74	1.62
All drinking and bore water	52	1.34	3.12

Arsenic concentrations in almost all the samples of drinking water were lower than 1.0 μg/L, with most values lower than 0.3 μg/L. The only exception was one site situated within the city of Paracatu and outside the area of influence of the Morro do Ouro mine. The average As concentration in all the three scenarios are significantly lower than the 10 μg/L values established by the WHO and Brazilian legislation. The results demonstrate a low As exposure from water ingestion (independent of its source, COPASA municipal water or local groundwater drawn from house bores) for the general population.

The low concentrations of arsenic in water are confirmed by another work commissioned by Paracatu City Council and conducted by the Centre of Mineral Technology - CETEM and collaborators (2013). This study concluded, that “Most of As contents in water for human consumption in Paracatu are below the detection limit - LD (<0.5 µg/L) of the analytical technique (original in Portuguese “A maioria dos teores de As em águas de consumo humano em Paracatu estão abaixo do LD ⩽ 0,5 µg/L; nestes casos usa-se a metade do LD = 0,25 µg/L”).

Arsenic in Soil and Surface Dust Samples

Soil samples were provided through a survey undertaken by the group responsible for the State Program *Solos de Minas,* coordinated by the state of Minas Gerais Environmental Agency. A sampling network capable to identify the areas of influence of the gold mineralization and the areas to represent the background of the region was established (Figure 2). Four (4) geological units and eleven (11) classes of soils occurring on Santa Rita and Rico Creek watersheds were considered. Forty-nine samples in duplicate were collected from June to July 2014, at depths of 0-20 cm, according to procedures described in EMBRAPA/UFRRJ/UFV/IBGE(2013) and FEAM/UFV/UFLA/UFOP/CETEC (2013 a,b). One set of the samples was sent to INCT-Acqua for determination of bioacessibility. The other set of samples was analysed for a number of parameters of relevance in soil classification by the SENAI/FIEMG group, and results are reported elsewhere (SENAI/FIEMG, 2014). The analyses of trace elements (Anonymous, 2010, 2011) were carried out in the Centre of Technology and Innovation SENAI FIEMG - CITSF / IEF Campus, using the partial dissolution method described by the USEPA SW-846 Method 3051A (US EPA, 2007). A detailed description of the experimental procedures is provided in the report (SENAI/FIEMG, 2014). Bioaccessibility was determined according to the Solubility/Bioavailability Research Consortium *in vitro* assay method (Kelley et al., 2002) on a subset of 7 non-mineralized and 7 mineralized samples selected based on the data reported in (SENAI/FIEMG, 2014). This simplified version of the PBET (Physiologically-based extraction test) procedure is designed to simulate the worst-case scenario at acidic pH (pH=1.5) in the stomach phase. Prior to the bioaccessibility tests the samples were dried under 40°C, disaggregated and then sieved at ≤250 µm.

The locations of the samples selected for BAC testing are shown in Figure 3. Two of the mineralized samples were collected along the Rico Creek downstream of the city.

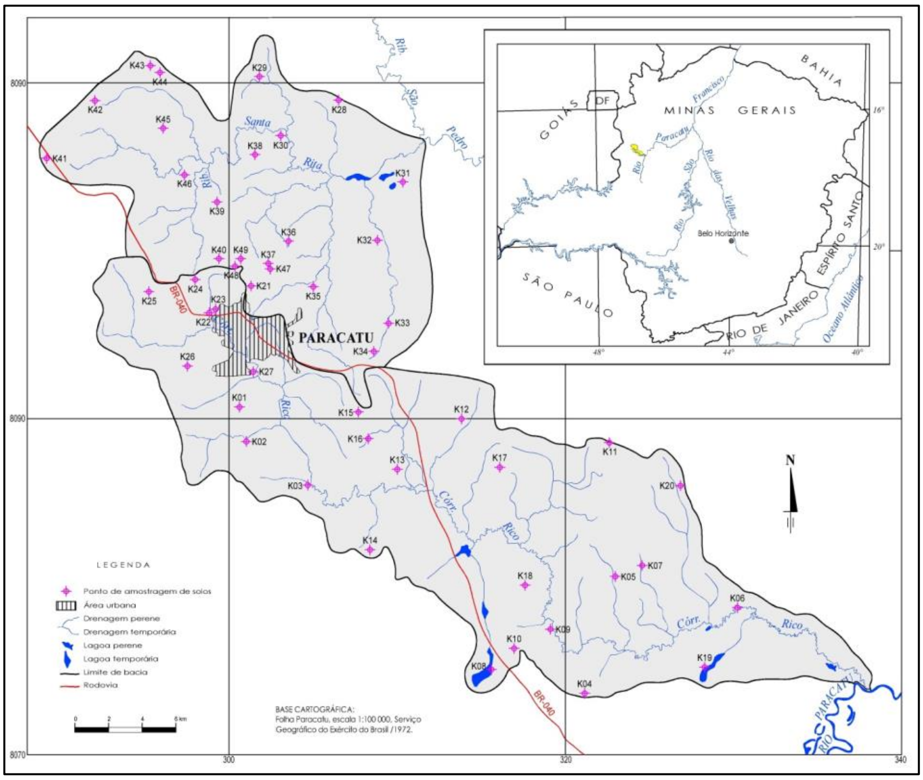

Figure 2. Sampling points for soil analysis in Santa Rita and Rico Creek watersheds (SENAI/FIEMG, 2014).

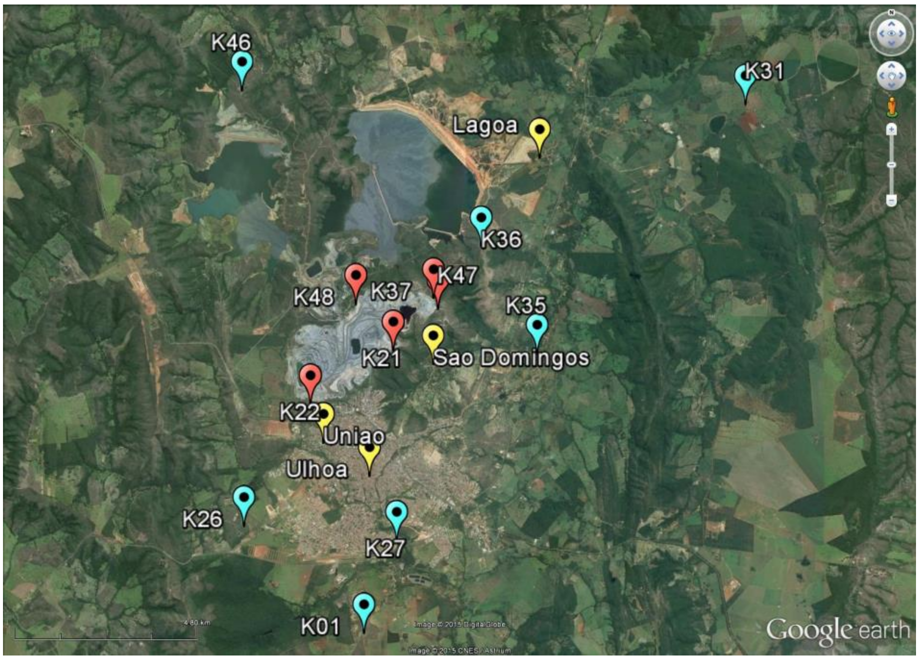

Figure 3. Location of air sampling stations (yellow symbols) and soil samples used for BAC tests (red symbols – mineralized soils; turquoise symbols – non-mineralized soils). Note that samples K03 and K06 (Rico Creek) are located to the S and SE of Paracatu outside the field of the figure. Background map from Google Earth™.

Soil samples obtained from the SENAI/FIEMG work, as described previously, were used for the calculation of As exposure from soil ingestion. Fourteen samples out of 49 samples were selected for the BAC measurements. Samples were divided into two groups:

1) soils from naturally mineralized areas with As concentration above 300 mg/kg;
2) soils from non-mineralized areas with As concentration below 55 mg/kg.

In order to assess the worst case scenario, the selection of samples was intentionally biased to high arsenic content, according to the data available from SENAI/FIEMG report (2014), which determined arsenic background of 259mg/kg in the mineralized area.

The results of mean As concentration, % bioaccessibility and As bioaccessible are shown in Tables II and III.

Table II

Arsenic bioaccessible in non-mineralized soil samples, fraction ≤250 µm.

NON-MINERALIZED SAMPLES (n=7)	
Mean As BAC (%)	2.7 ± 1.9
Mean As (mg/kg)	22 ± 13
Mean bioacessible As (mg/kg)	0.4 ± 0.2

Table III

Arsenic bioaccessible in selected, high Arsenic content, mineralized soil samples, fraction ≤250 µm.

MINERALIZED SAMPLES (n=7)	
Mean As BAC (%)	1.6 ± 1.1

Mean As (mg/kg)	450* ± 137
Mean bioaccessible As (mg/kg)	8.1 ± 8.1

*Obs.: Arsenic content higher than the background value of 259mg/kg, as determined by others (SENAI/FIEMG, 2014)

Arsenic concentration in soil samples in the mineralized area (Paracatu Formation) were found to be higher than the investigation values for soil samples set in CONAMA 420 (Anonymous, 2009a). Further “detailed investigation and risk assessment according to technical standards or procedures in place” was carried out according to Article 23 of CONAMA 420 and these investigations revealed that bioaccessible (BAC) arsenic levels, which represent the “free” or “mobile” fraction of arsenic according to accepted international protocols, are lower than the value of investigation (VI) for residential areas (55 mg/kg), and therefore do not pose “potential direct or indirect risks to human health, considering a scenario of standardized exposure”. Mineralized soil is less bioaccessible (1.6% BAC) compared with non-mineralized soil (2.7% BAC).

Based on bioacessibility measurements, mean bioaccessible As content of 0.4 and 8.1 mg/kg for the non-mineralized and mineralized soils, respectively, were established. Note that only the ≤250 μm particle size fraction was used to measure bioaccessibility, following the procedure described in Kelley et al. (2002). These values were used as two different scenarios for As exposure from soil ingestion. It should be noted that the northern side of the Paracatu urban area is partly located on mineralized lithologies, while the southern side is located on non-mineralized lithologies. Considering the significant landscape disturbance associated with urban areas, generally speaking the urban Paracatu soils can be expected to be a mixture of the two endmembers. This assumption is corroborated by the data shown below.

Surface dust samples were collected by team members from the University of Queensland (UQ) and Universidade Federal de Minas Gerais (UFMG) from 7 sites in Paracatu township residential area in close proximity to KBM in May and November 2011. The dust samples were collected by sweeping the ground with a paint brush, catching the dust with a clean white sheet of paper and storing it in plastic bags at room temperature for transportation to the laboratory. The mineral phases identified in the surface dust samples were quartz, moscovite, kaolinite, clinochlore, albite, calcite, dolomite, pyrite and arsenopyrite. Some of the samples also had gibbsite. Rietveld refinement confirmed the presence of less than 1% of arsenopyrite in some samples (note that the method has a 1% detection limit). Measurements by Synchrotron light, X-Ray Absorption Near Edge Structure - XANES showed that As is present mainly as As(V) species, less toxic and mobile than As(III), and rarely as arsenopyrite in the surface dust samples

The ≤250 µm fraction of each dust sample was measured for bioaccessibility (BAC) using an *in-vitro* physiologically based extract test (PBET) method (Ruby et al., 1996). Briefly, the dust sample was leached using a synthetic gastrointestinal (GI) fluid in a solid:liquid ratio of 1:100 simulating the GI tract pH conditions representing fasting, semi-fed, and fully-fed stomach (stomach phase I – pH 1.3, 2.5 and 4.0), and the small intestine (phase 2 pH 7.0) respectively over a period of 4 hours. BAC was done in duplicate unless otherwise specified. The mean As concentrations in these samples were found 162±138 mg/kg and 135 mg/kg, respectively. The mean bioaccessible As from the two campaigns were 6.4±3 and 4.9±3 mg/kg, respectively (Table IV).

Table IV
Arsenic concentrations (mg/kg) and bioaccessibility values (%) in surface dust collected in Paracatu town, fraction ≤250 µm.

I.D.	**As (mg/kg)**	**BAC (%)**	**BAC*As (mg/kg)**
Survey 1 (May 2011)			
Mean±SD	201±155	3.7±2.0	6.4±3.0
Survey 2 (November 2011)			
Mean±SD	153±177	3.2±2.0	4.9±3.0

Arsenic in Atmospheric Particulates

A set of high-volume TSP (Total Suspended Particles) and PM_{10} (particulate matter with aerodynamic diameter smaller than 10 μm) samplers, as well as continuous low-volume TSP, PM_{10} and $PM_{2.5}$ samplers installed in Paracatu in 2011, were available to our research team for the assessment of human health risk from inhalation. The number of monitoring stations shown in Figure 3 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, 2004). The locations of the monitoring stations used to collect the PM_{10} and $PM_{2.5}$ samples are shown in Figure 3.

A summary of the results from all stations is shown in Table V. No mean arsenic value exceeded the EU target value of 6 ng of As per cubic meter of air. The continuous, low-volume PM_{10} data for the period from December 2011 to September 2013 were used for exposure assessment, consistent with European Union guidelines (Anonymous, 2005a). According to USEPA (2013b), an As 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. In line with a conservative approach for risk assessment, and considering that no data exist for bioaccessibility in atmospheric dust, the maximum mean annual value measured in the four stations (5.3 ng of As per cubic meter of air, and assuming that 100% of this As is bioaccessible) was used to assess As intake from inhalation.

Table V - Air quality data for arsenic (ng As/m^3) in PM_{10} and $PM_{2.5}$ samples

			PM_{10}
São Domingos			
Period 1	1/06/2012 to 31/5/2013		
	mean		4.9
	median		4.0
	no. (days)		318
Period 2	1/08/2012 to 31/7/2013		
	mean		4.4
	median		3.8
	no. (days)		322
Period 3	1/10/2012 to 23/9/2013		
	mean		4.1
	median		3.8
	no. (days)		317
Lagoa			
Period 1	1/06/2012 to 31/5/2013		
	mean		3.1
	median		2.9
	no. (days)		150
Period 2	1/08/2012 to 31/7/2013		
	mean		3.1
	median		2.9
	no. (days)		193
Period 3	1/10/2012 to 23/9/2013		
	mean		3.3
	median		3.2
	no. (days)		235

		PM_{10}	$PM_{2.5}$
União			
Period 1	1/06/2012 to 31/5/2013		
	mean	**5.3**	2.8
	median	4.9	2.2
	no. (days)	314	276
Period 2	1/08/2012 to 31/7/2013		
	mean	4.4	2.4
	median	3.2	1.6
	no. (days)	318	287
Period 3	1/10/2012 to 26/9/2013		
	mean	3.8	2.0
	median	2.9	1.4
	no. (days)	316	258
Ulhoa			
Period 1	1/06/2012 to 31/5/2013		
	mean	4.9	1.8
	median	4.1	1.5
	no. (days)	334	218
Period 2	1/08/2012 to 31/7/2013		
	mean	4.2	1.4
	median	3.9	1.3
	no. (days)	342	212
Period 3	1/10/2012 to 23/9/2013		
	mean	4.2	1.3
	median	4.1	1.2
	no. (days)	338	186

São Domingos			**União**			
Period 1	17/12/2011 to 31/3/2012		*Period 1*	17/12/2011 to 31/3/2012		
	mean	2.3		mean	3.6	3.5
	median	1.6		median	1.7	3.9
	no. (days)	87		no. (days)	18	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	0.1
	median	4.6		median	0.1	0.1
	no. (days)	47		no. (days)	62	63
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	0.9
	median	4.0		median	0.8	0.4
	no. (days)	87		no. (days)	90	80
Period 2	1/04/2012 to 24/5/2012		*Period 2*	1/04/2012 to 24/5/2012		
	mean	4.7		mean	10.8	2.8
	median	5.1		median	12.0	0.1
	no. (days)	52		no. (days)	13	14

Arsenic in Food

Arsenic intake from food ingestion was calculated based on the results of 90 samples of fifteen different food items commonly consumed in Brazil, and including 18 bean and 16 rice samples. It should be noted that rice and beans are main staple foods in Brazil and have a major contribution to As intake as shown in Table VI.

Relatively high total As concentrations were found in rice (mean 0.194 mg/kg) and beans (mean 0.050 mg/kg) compared to other food items. These two items alone contributed to approximately 75% of the total % As intake from food. Rice is known to be the major source of dietary arsenic in populations that consume rice as a staple food. Rice plants are a natural arsenic accumulator, as they are capable of taking up arsenic from the contact with water containing traces of the element and this occurs as a result of the form of production in flooded fields (Sohn, 2014). In 2014 a joint FAO/WHO committee (FAO/WHO, 2014) established maximum As values of 0.20 mg/kg for white rice and 0.40 mg/kg for whole rice. The results shown in Table VI indicate total As concentration below these limits.

The consumption pattern of a Brazilian diet for the population studied (IBGE, 2008/09) was used together with our own dietary elemental concentrations to calculate the daily intake per kg of body weight per day (μg/kg bw d**)** for the exposure assessment. It is important to know the inorganic arsenic (arsenic speciation) component of the total arsenic level. Although arsenic speciation was not measured for this report, assumptions were made based on literature data (JECFA, 2011) and papers on rice and beans. These publications have reported values of approximately 60% inorganic As in Brazilian rice (Batista et al., 2011) and 100% inorganic As in beans (Juhasz et al., 2008). Based on these data, total inorganic As intake (iAs) considering the diet pattern from southeast Brazil was 0.2017 iAs μg/kg bw d for adults, and half of this value (0.1009 iAs μg/kg bw d) for children. Rice and beans alone contributed to approximately 75% of the total As intake from food. The results are shown in Table VI.

Table VI

Inorganic arsenic intake from selected food items

Food item	As content (mg/kg)	As μg/kg bw d*	iAs (%)	iAs μg/kg bw d*	% As intake
Egg (n=5)	0.013	0.0022	50	0.0011	0.5
Chicken breast (grilled) (n=5)	0.021	0.0111	50	0.0081	4.0
Beef (grilled) (n=5)	0.021	0.0189	50	0.0148	7.4
Fish (fried) (n=2)	0.233	0.0766	10	0.0081	4.0
Potatoes (boiled) (n=3)	0.009	0.0019	50	0.0012	0.6
Carrot (n=4)	0.007	0.0001	50	0.0001	0.0
Tomato (n=4)	0.005	0.0005	50	0.0003	0.1
Garlic (n=4)	0.013	<0.0001	50	-	-
Cabbage (n=4)	0.006	0.0001	50	0.0001	0.0
Lettuce (n=4)	0.017	0.0010	50	0.0005	0.2
Milk (n=3)	0.003	0.0015	50	0.0008	0.4

Coffee (n=7)	0.049	0.0210	50	0.0105	5.2
Beans (n=18)	0.050	0.0307	100	0.0435	21.6
Rice (boiled) (n=16)	0.194	0.1580	60	0.1077	53.4
Pasta (cooked) (n=6)	0.045	0.0167	50	0.0049	2.4
		TOTAL		0.2017	100.0

* Daily dose rounded up to four decimal digits; dietary intake for southeast Brazil (IBGE, 2008/09)

ARSENIC EXPOSURE ASSESSMENT

The assessment of risk from As exposure was based on current Brazilian regulations and guidelines supported (ABNT NBR 16209, 2013; Ministério da Saúde, 2010; CETESB, 2007; Maximiano, 2014). The factors EF, ED, ET, EV and AT used in the ABNT NBR 16209 (2013) equations are equivalent to the factor FE (Exposure Factor) used in the Ministério da Saúde (2010) document. The product of these factors ranges from 0 (in case of non-exposure) to 1 for continuous exposure - worst case scenario. In this exposure assessment we have used the value of 1 (worst case) considering that people living in Paracatu could be continually exposed to its air, soil, water and food. Therefore calculations apply to the resident population (living in Paracatu all their life), and are consistent with ABNT NBR 16209 (2013).

Section 4.2.2.2 of the ABNT NBR 16209 (2013) lists the exposure routes that must be considered in the risk assessment and equations that must be used for intake calculations. All these have been considered. Accidental water ingestion during swimming and recreation was not included in the calculations because a) it only applies to particular individuals/family groups, not for the population as a whole, and b) it can only be calculated if data is available for the concentration of As in the specific water course, the frequency of the exposure for each individual, his/her age and body weight. All dermal As exposure is known to be negligible and was therefore not included in this report. Inhalation of vapours from soil and water applies only to volatile substances (not As) and for this reason it was also excluded from calculations. ABNT NBR 16209 (2013) prescribes that soil should be used to quantify contaminant intake by inhalation. This approach requires the input of parameters that cannot be generalized for a population (e.g., rate of particle inhalation) and a number of assumptions related to particle size distribution to simulate the fraction that reaches the bronchioles and alveoli - the fractions below 10 μm (Asgharian et al., 2001). Therefore, the PM_{10} arsenic concentrations measured in our studies were used in the calculations.

Mean values were used throughout this report to calculate As intake of exposure for the general population of Paracatu, consistent with Brazilian standards (ABNT NBR 16209, 2013) and with the European Union target values for As content in air (Anonymous, 2005a).

Table VII lists the basic exposure parameters for the risk characterization. The results from the overall assessment of arsenic exposure from geogenic material, water and food intakes are summarized in Tables VIII to XIV.

Table VII

Exposure parameters in accordance with Brazilian risk assessment guidelines (Ministério da Saúde, 2010)

Exposure parameters	Adult	Child
Body weight (kg)	70	16 (1-6 y age)
Water consumption (L/day)	2	1
Soil ingestion (mg/d)	50	100 (1-6 y age)
Air inhalation (m^3/d)	23 (male); 21 (female) 22 (mean)	15

Table VIII. Scenario 1 – risk apportionment using COPASA water and non-mineralized soil arsenic concentrations

Pathway	iAs intake (µg/kg bw d)		Predicted Cancer Risk		% of Total intake	% of Total intake
	Adult	Child	Adult	Child		
Ingestion of geogenic material (0.4 mg/kg)	0.0003	0.0025	4.3E-07	3.8E-06	0.1	2.1
Inhalation of dust (5.3 ng/m^3)	0.0017	0.0050	2.3E-05	2.3E-05	0.8	4.1
Food	0.2017	0.1009	3.0E-04	1.5E-04	96.2	83.0
Water (0.21 µg/L)	0.0060	0.0131	9.0E-06	2.0E-05	2.9	10.8
Total	*0.2097*	*0.1214*	*3.3E-04*	*2.0E-04*	*100.0*	*100.0*
$BMDL_{0.5}$	3	3				

Table IX. Scenario 2 - risk apportionment using bore and drinking water and non-mineralized soil arsenic concentrations

Pathway	iAs intake (µg/kg bw d)		Predicted Cancer Risk		% of Total intake	% of Total intake
	Adult	Child	Adult	Child		
Ingestion of geogenic material (0.4 mg/kg)	0.0003	0.0025	4.3E-07	3.8E-06	0.1	1.3
Inhalation of dust (5.3 ng/m^3)	0.0017	0.0050	2.3E-05	2.3E-05	0.7	2.6
Food	0.2017	0.1009	3.0E-04	1.5E-04	83.4	52.5
Water (1.34 µg/L)	0.0383	0.0838	5.7E-05	1.3E-04	15.8	43.6
Total	0.2419	0.1921	3.8E-04	3.0E-04	100.0	100.0
$BMDL_{0.5}$	3	3				

Table X. Scenario 3 - risk apportionment using drinking water and non-mineralized soil arsenic concentrations

Pathway	iAs intake (µg/kg bw d)		Predicted Cancer Risk		% of Total intake	% of Total intake
	Adult	Child	Adult	Child		
Ingestion of geogenic material (0.4 mg/kg)	0.0003	0.0025	4.3E-07	3.8E-06	0.1	1.6
Inhalation of dust (5.3 ng/m^3)	0.0017	0.0050	2.3E-05	2.3E-05	0.7	3.2
Food	0.2017	0.1009	3.0E-04	1.5E-04	89.7	65.2
Water (0.74 µg/L)	0.0211	0.0463	3.2E-05	6.9E-05	9.4	29.9
Total	0.2248	0.1546	3.6E-04	2.5E-04	100.0	100.0
$BMDL_{0.5}$	3	3				

Table XI. Scenario 4 - risk apportionment using COPASA water and mineralized soil arsenic concentrations

Pathway	iAs intake (µg/kg bw d)		Predicted Cancer Risk		% of Total intake	% of Total intake
	Adult	Child	Adult	Child		
Ingestion of geogenic material (8.1 mg/kg)	0.0058	0.0506	8.7E-06	7.6E-05	2.7	29.9
Inhalation of dust (5.3 ng/m^3)	0.0017	0.0050	2.3E-05	2.3E-05	0.8	2.9
Food	0.2017	0.1009	3.0E-04	1.5E-04	93.7	59.5
Water (0.21 µg/L)	0.0060	0.0131	9.0E-06	2.0E-05	2.8	7.7
Total	0.2152	0.1696	3.4E-04	2.7E-04	100.0	100.0
$BMDL_{0.5}$	3	3				

Table XII. Scenario 5 - risk apportionment using bore and drinking water and mineralized soil arsenic concentrations

Pathway	iAs intake (µg/kg bw d)		Predicted Cancer Risk		% of Total intake	% of Total intake
	Adult	Child	Adult	Child		
Ingestion of geogenic material (8.1 mg/kg)	0.0058	0.0506	8.7E-06	7.6E-05	2.3	21.1
Inhalation of dust (5.3 ng/m^3)	0.0017	0.0050	2.3E-05	2.3E-05	0.7	2.1
Food	0.2017	0.1009	3.0E-04	1.5E-04	81.5	42.0
Water (1.34 µg/L)	0.0383	0.0838	5.7E-05	1.3E-04	15.5	34.9
Total	0.2474	0.2402	3.9E-04	3.8E-04	100.0	100.0
$BMDL_{0.5}$	3	3				

Table XIII. Scenario 6 - risk apportionment using drinking water and mineralized soil arsenic concentrations

Pathway	iAs intake (µg/kg bw d)		Predicted Cancer Risk		% of Total intake	% of Total intake
	Adult	Child	Adult	Child		
Ingestion of geogenic material (8.1 mg/kg)	0.0058	0.0506	8.7E-06	7.6E-05	2.5	25.0
Inhalation of dust (5.3 ng/m^3)	0.0017	0.0050	2.3E-05	2.3E-05	0.7	2.5
Food	0.2017	0.1009	3.0E-04	1.5E-04	87.6	49.8
Water (0.74 µg/L)	0.0211	0.0463	3.2E-05	6.9E-05	9.2	22.8
Total	0.2303	0.2027	3.7E-04	3.2E-04	100.0	100.0
$BMDL_{0.5}$	3	3				

When the different exposure scenarios are considered, the maximum contribution of water to the daily total As intake is 15.8% for adults and 43.6% for children (Table IX). But notice that 43.6% corresponds to an As concentration in water 7 times lower than that recommended by WHO and established by Brazilian legislation. Our results are in agreement with the conclusion from the work commissioned by Paracatu City Council and conducted by the Centre of Mineral Technology - CETEM and collaborators (2013), which stated that under current conditions, the population of Paracatu is not exposed to levels of As in the water supply that represent a risk for human health (original in Portuguese: "*Nas atuais condições, a população de Paracatu não está exposta a teores de As via consumo de água de abastecimento que representem riscos à saúde humana*").

Soil samples from Paracatu town possibly represent a combination of fugitive dust from construction and excavation sites (including the mine site), natural geological background and baseline associated with local and regional industrial and agricultural activities. Bioaccessibility tests were selected in the present work as accepted standard practice for risk assessment in the international scientific community, and therefore qualified (based on CONAMA 420) as "*detailed investigation and risk assessment according to technical standards or procedures in place*". Therefore, in the event that bioaccessibility tests establish that the bioaccessible (hence potentially bioavailable) concentration of a given chemical is below the value of investigation (VI), it is not necessary to carry out further action (e.g. Intervention; Article 23, Part III) as Intervention has the aim to eliminate or reduce, to tolerable levels, the risks identified by the diagnosis stage. This interpretation of CONAMA 420 is consistent with the US EPA's and Australian NEPC's recognition that bioavailability (and therefore bioaccessibility) must be considered in risk assessment (US EPA 2013a; Section 5.10, page 32; see also US EPA 2012; NEPC 2013).

The equivalent bioaccessible arsenic concentrations are 8.1 mg/kg and 0.4 mg/kg in mineralized and non-mineralized soils, respectively. Based on this data the maximum contribution of soil ingestion to the daily total As intake is up to 2.7% and 29.9% in adults and children, respectively (Table XI). The predicted cancer risks are lower than 1:100,000, thus complying with CONAMA 420.

The bioacessible As concentration in the samples of surface dust collected in urban area of Paracatu (6.4±3 and 4.9±3 mg/kg) are below the value of 8.1 mg/kg used in the exposure calculations, thus confirming our conservative approach in the selection of geogenic material for exposure assessment. Although the surface soil samples cannot be used for risk assessment for Brazilian regulatory purposes, they are significant as they provide direct information on As concentrations and bioaccessibility in the outdoor urban dust, and show an even lower, more realistic level of population exposure.

The mean annual concentrations of As in PM_{10} at the three urban monitoring stations (São Domingos, Ulhôa and União) ranged from 3.8 to 5.3 ng/m^3, while the values at Lagoa station (background levels) were in the 3.1-3.3 ng/m^3 range. Considering that no data exist for bioaccessibility in atmospheric dust, the As intake from inhalation was calculated by the maximum mean annual As value measured in the four stations (5.3 ng/m^3 at União station) and assuming that 100% of this As is bioaccessible. The daily As intakes from inhalation calculated from this data are 0.0017 µg/kg bw d and 0.0050 µg/kg bw d in adults and children, respectively. These values account for a maximum of 0.8% and 4.1% of the total As intake for adults and children, respectively (Table XIII), and therefore represent a minor risk (<5%) compared to the overall risk contribution from all other exposure pathways.

The daily intake of inorganic arsenic calculated from our food surveys gave a mean of 0.2017 µg/kg bw d for adults and 0.1009 µg/kg bwd for children (assuming 50% of adult food intake for children). This values represent up to 96.2% and 83.0% of the total As intake for adults and children, respectively (Table VIII).

Risk assessment calculations were carried out according to Benchmark Dose Lower Confidence Limit (BMDL) and linear dose relationship for setting the arsenic Cancer Slope Factors (CSF). There is significant evidence from international studies confirming that the Benchmark Dose Lower Confidence Limit (BMDL) approach adopted by WHO and JECFA (JECFA, 2011) is more realistic and suitable than the US EPA approach (linear dose relationship for setting the arsenic Cancer Slope Factors (CSF) for oral ingestion and inhalation respectively; see ATSDR, 2007) for risk assessment calculations. As there are no specific Brazilian guidelines both approaches were applied.

Total exposure will comprise the total iAs (inorganic) intake calculated from all sources, including geogenic materials, water and food. The numbers range from 0.2097 to 0.2474 µg/kg bw d for adults and from 0.1214 to 0.2402 µg/kg bw d for children, depending on the scenario. Thus, even under the worst-case scenario, the total intake is below 10% of the Benchmark dose lower limit - $BMDL_{0.5}$ of 3 µg/kg bw d established by FAO/WHO (JECFA, 2011). Therefore the overall risk of arsenic exposure to the general population in Paracatu is considered low.

The total dietary As intake is about the same order of magnitude of the combined ingestion and inhalation routes from the geogenic sources, especially for adults. Food contributes up to 96.2% of the total exposure to arsenic for adults and 83.0% for children. This means that the major contributor to arsenic intake is the dietary source, and that geogenic sources are minor if one considers their bioaccessibility.

To put the interpretation of predicted cancer risk into perspective, we consider a hypothetical situation where the study data are compared to the WHO recommended drinking water standard (and also Brazilian standard) of 10 µg/L for arsenic. This standard is generally accepted as a safe level for life-time exposure without appreciable risk. This would result in an As intake of 0.2857 µg/kg bw d for adults and

0.6250 μg/kg bwd for children, with both values being significantly higher (especially for children) that the values calculated in this study. This confirms that the overall risk to the local population is low, and below or similar to the arsenic intake from daily consumption of water containing 10 μg/L of arsenic.

Regardless of 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 followed by water arsenic intake and their respective associated risks are the major sources of exposure in the population of Paracatu, and that geological sources are the minor contributors. The combined risk from all sources of exposure is low.

CONCLUSIONS

The main findings of the investigation are summarized as follows:

(i) The mean value (1.34 μg/L) of the As concentrations in the drinking waters and community bore samples is 7 times lower than the Brazilian and WHO limit of 10 μg/L. Arsenic concentrations in almost all the samples were lower than 1 μg/L.

(ii) Arsenic concentrations in soil samples in the mineralized area were found to be higher than the investigation values for soil samples set in CONAMA 420 (Anonymous, 2009a). Further “detailed investigation and risk assessment according to technical standards or procedures in place” was carried out according to Article 23 of CONAMA 420, and these investigations revealed that bioaccessible arsenic levels are lower than the value of investigation-VI, and therefore do not pose “potential direct or indirect risks to human health, considering a scenario of standardized exposure” and so, no mitigation action is required. The contribution of ingested mineralized soil to the total daily arsenic intake was up to 2.7% and 29.9% for adults and children, respectively. The ingestion of non-mineralized soil contributes up to 2.1% in children and 0.1% in adults.

(iii) PM_{10} and $PM_{2.5}$ dust samples were analyzed, each representing a composite of continuous low-flow samples collected over a period of between 72 and 96 hours. The concentration of arsenic in dust (5.3 ng/m^3) was lower than the European Union target value of 6 ng/m^3. The contribution of inhaled arsenic derived from PM_{10} fine dust to total intake is up to 4.1% in children and 0.8% in adults under the conservative assumptions of bioaccessibilty (BAC) of 100% in the calculations and therefore its contribution to the total exposure can be considered insignificant.

(iv) Food contributes up to 96.2% of the total exposure to arsenic for adults and 83.0% for children, which places Paracatu population within the standard of other cities in Brazil, Europe and United States.. Rice is the major contributor to the total daily arsenic intake but the average As concentration is within the level of 0.2 recommended by WHO. (FAO/WHO, 2014)

(v) The calculated arsenic total intakes from all the sources are up to 0.25 µg/kg bw d and therefore below 10% of the $BMDL_{0.5}$ of 3 µg/kg bw d established by FAO/WHO (2011). Therefore the overall risk of arsenic exposure to the general population in Paracatu is considered low.

(vi) Calculation for predicted cancers risks using the USEPA IRIS cancer slope factor confirms that food followed by water are the major arsenic sources, with their cancer risk being one order of magnitude higher compared with that of geogenic sources for both adults and children.

(vii) The sum of predicted cancer risks from all exposure pathways (geogenic, food and water) in the Paracatu township is similar to the risk from drinking water containing 10 µg/L of arsenic (WHO and Brazilian drinking water standard, Portaria 2914 do Ministério da Saúde de 12/12/2011). This confirms the low overall risk of arsenic exposure to the general population of Paracatu.

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