



# Lead and other trace elements in edibles and in topsoil as a pathway for human contamination in a mining area in Brazil

Talita Lammoglia<sup>1</sup>  
Bernardino Ribeiro Figueiredo<sup>1</sup>  
Alice Momoyo Sakuma<sup>2</sup>  
Márcia Liane Buzzo<sup>2</sup>  
Isaura Akemi Okada<sup>2</sup>  
Carmen Silvia Kira<sup>2</sup>

<sup>1</sup>Department of Geology and Natural Resources (DGRN)  
University of Campinas, UNICAMP, São Paulo, Brazil  
<sup>2</sup>Adolfo Lutz Institute, Health Secretary, São Paulo, Brazil

## Abstract

*During the last century several lead mines and a metal smelter have operated in the Upper Ribeira Valley, located in southeastern Brazil. After fifty years of activity, the smelter was closed down in November 1995 and soon after the last mines in operation were also closed. In 1998, a multidisciplinary research group started carrying out an ambitious investigation among the population of the Ribeira Valley to assess human exposure to lead. The highest blood-lead levels were found among residents of vicinity of the smelter, where soil and indoor-dust were highly contaminated. In the present study, lead, chromium, copper, zinc and arsenic contents of several food species that comprise part of the local population diet were investigated. Samples of greens, vegetables, corn, chicken eggs and cow milk were collected in two occasions (July 2004 and February 2005) from two different areas: the Vila Mota village, which is close to the smelter, and the Serra village, far away from the smelting plant but still in the geological and mining context. Edibles were analyzed by Atomic Absorption Spectrometry. Topsoil samples, collected from vegetable gardens, were analyzed by X-ray fluorescence spectroscopy for both grain fractions  $<177\ \mu\text{m}$  and  $<63\ \mu\text{m}$ . The results are very impressive because 100% of the greens, vegetables and eggs from the Vila Mota village yielded lead concentrations exceeding the Pb limit of  $0.5\ \text{mg.kg}^{-1}$  established by Brazilian regulations. Lead concentrations up to  $1540\ \text{mg.kg}^{-1}$  were found in soil, far exceeding the  $180\ \text{mg.kg}^{-1}$  Pb threshold, considered the intervention value for agriculture use. On the other hand, elevated concentrations of lead in edibles collected at the Serra mining district were not observed. The quality of edibles and soils were also tested for other trace elements such as Cr, Cu, Zn and As, but the results do not indicate that they are potentially hazardous to public health. However, considering the lead contamination at the Vila Mota village alone, the maximum tolerable weekly dose of lead is exceeded by about 4 times solely through local food consumption. The whole situation exposes these families to a great risk on a long term basis. Immediate environmental intervention is required in order to mitigate contamination effects and human exposure to lead.*

## Keywords

Lead, chromium, copper, zinc, arsenic, food, topsoil, Ribeira Valley, Brazil

## 1. Introduction

During the last century, several Pb-Zn-Ag ore deposits and a metal smelter belonging to the extinct Plumbum Company had operated in the

Upper Ribeira Valley, located in Southeast Brazil (Figure 1). After fifty years of activity, the smelter was closed down in November 1995 and soon after the last mines were also closed. Although the contamination of the Ribeira River had already been



detected, no information on the local population exposure to heavy metals was available. A multi-disciplinary research group formed by geologists, chemists and toxicologists started in 1998 an ambitious investigation among the population of five municipalities, in the Upper and Middle Ribeira Valley, to assess human exposure to lead and arsenic in both urban and rural areas (Paoliello et al., 2002, 2003; Cunha et al., 2005; Sakuma, 2004, Sakuma et al., 2010).

The blood-lead levels (BLL) corresponding to 472 children (7 to 14-years-old) and 523 adults (15 to 70-years-old) were determined in these previous studies. The investigation was in accordance with the regulations adopted by the Ethics Committee of the Medical Sciences Faculty at the University of Campinas. The population of Cerro Azul, a town located upstream from the mineral province and thought not to have been exposed to mining contamination, was included in the survey as a reference group. The population of two villages in Adrianópolis, located in the vicinity (radius of 1 km) of the smelter, presented the highest median BLL (11.2  $\mu\text{g}/\text{dL}$ ). This is six times higher than the reference group median (1.8  $\mu\text{g}/\text{dL}$ ). Among those families, 60% exhibited BLL exceeding 10  $\mu\text{g}/\text{dL}$  and 13% more than 20  $\mu\text{g}/\text{dL}$  (Paoliello et al., 2002, 2003; Cunha et al., 2005). It is acknowledged worldwide that lead contamination is seriously hazardous to humans because it can cause, among other adverse side effects, anemia and mental retardation (WHO, 1995; Paoliello & De Capitani, 2003).

Previous environmental studies carried out by Cunha et al. (2005) in the same area revealed very low Pb and As contents in river water, as well as in tap water. On the other hand, concentrations of up to 916  $\mu\text{g}/\text{g}$  Pb were found in topsoil from Vila Mota, as well as up to 3268  $\mu\text{g}/\text{g}$  Pb in indoor dust collected from some of the houses (Cunha et al., 2005). These results led to the conclusion that contact with topsoil and dust was the primary cause of human contamination in the locality. Additionally, Paoliello et al. (2003) found out that the families who consumed vegetables grown in their own backyards presented a mean BLL higher than that detected in the group who declared that it did not consume vegetables at all. In previous studies the mean BLL for the Serra population was found to be very low. However, the highest mean value (8.90  $\text{mg}/\text{dL}$  As) of arsenic in urine

for the whole Upper Ribeira Valley was detected in its population (Sakuma, 2004). On a long-term basis, arsenic poisoning can lead to severe health problems such as skin cancer, lung cancer, nervous system damage, and liver failure (Abernathy et al., 1997).

Despite the potential of harmful effects, heavy metals and arsenic concentrations in locally produced food, such as greens and vegetables, had not been analyzed yet. This study is an attempt to better understand the lead and other trace elements lead route to the human body in two different areas, where residents have already been under investigation due to their exposure to toxic substances. In the present work, food (e.g. vegetables and eggs) and soil samples from Vila Mota (Municipality of Adrianópolis, State of Paraná, Brazil) and Serra (Municipality of Iporanga, State of São Paulo, Brazil) neighborhoods, both with ca. 500 inhabitants, were analyzed for Pb, Cu, Zn, and As, which are all trace elements commonly found in Pb-Zn ores. Furthermore, these samples were analyzed for chromium which could potentially present in some of the mafic rocks of the region. Adrianópolis is located in the vicinity of the Plumbum smelter and Serra is close to the Furnas Mine, one of the most important lead-zinc ore producers during the last century (Fig. 1). The purpose of this work was to investigate of Pb, As, Cr, Cu and Zn levels in the local population's diet, to verify the existence of a subsequent pathway of human exposure. In addition, soil samples collected from vegetable plantations were also analyzed for these elements in order to better assess the risk to which residents are being exposed.

Despite the fact that a small amount of chromium is a nutritional necessity for humans, overdoses can cause respiratory, vascular, hematological, hepatic and gastrointestinal problems, as well as cancer (Silva, 2003a). Copper is essential for many plants and animals, but it becomes toxic for human beings if the daily ingestion exceeds 3 mg for adults and 1 mg for children. It can cause thickening of the skin that may become green in color, hepatic disturbances, and lung cancer (Pedrozo, 2003). Like chromium and copper, zinc is essential for plants and animals in small concentrations. When humans are exposed to high zinc concentrations, they can develop hematological, respiratory, gastrointestinal, neurological, and immunologic problems (Silva, 2003b).

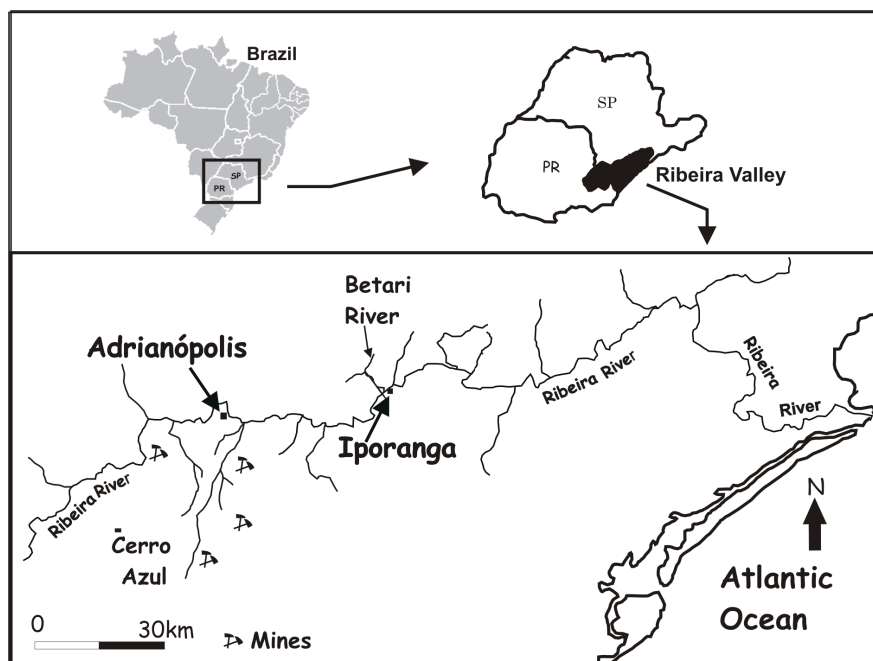


Figure 1 – Location map of the Ribeira Valley

## 2. Methodological aspects

### 2.1. Sampling and sample preparation

Edibles and soil samples were collected from the Vila Mota (Adrianópolis) and Serra (Iporanga) villages in residential backyards and vegetable plantations in the period of 2004-2005. A total of 39 samples of edibles, which included 23 leafy vegetables, 7 brassica, bulb or root vegetables, 3 sets of 5 eggs, 3 ears of corn, and 3 samples of half liter milk were collected. In addition a total of 10 samples of 1 kg of surface soil (0-20 cm depth) were collected from each one of the sites. Edibles were washed with potable water before further treatment at the laboratory Adolfo Lutz Institute in São Paulo city.

### 2.2. Analytical procedures for measuring metals and arsenic concentrations in soil

The soil samples were dried at room temperature, disaggregated, and then sieved with a Nylon DIN 4197 to separate grain-size fractions  $<177 \mu\text{m}$  and  $<63 \mu\text{m}$ . Aliquots were separated to produce 40 mm diameter pressed pellets, by mixing a 9 g sample with 1.5 g of wax powder (Hoescht, Germany) in a mixer (Spex, USA) for three minutes, and then pressing it at 119 Mpa (60 s) with a semi-automatic press (HTP40, Herzog, Germany). The moisture and loss on ignition were measured

for all samples. The concentration of metals and arsenic were determined by X-ray fluorescence spectroscopy using a Philips sequential spectrometer, model PW 2404 at University of Campinas, following procedures recommended by Potts (1992) and Enzweiler & Vendemiatto (2004).

A measure of reliability for those element concentrations was given by simultaneous analyses of international reference materials, GSS-2 (soil) and GSD-5

(sediments), acquired from IGGE in China. For GSS-2 the certified values  $\pm 1$  standard deviation (sd) are  $20 \pm 4$ ;  $47 \pm 6$ ;  $16.3 \pm 1.4$ ;  $42 \pm 5$  and  $13.7 \pm 1.8 \text{ mg.kg}^{-1}$ ; and the determined values were 23; 41; 17; 37;  $14.3 \text{ mg.kg}^{-1}$  for Pb, Cr, Cu, Zn and As, respectively. For GSD-5 the certified values  $\pm 1$  sd are  $112 \pm 13$ ;  $70 \pm 9$ ;  $137 \pm 10$ ;  $243 \pm 23$  and  $75 \pm 11 \text{ mg.kg}^{-1}$ ; and the determined values were 122; 69; 120; 228 and  $75 \text{ mg.kg}^{-1}$  for Pb, Cr, Cu, Zn and As, respectively. The results of trace-element analyses for the reference materials are within the recommended  $\pm 2$  standard deviations interval (Darnley et al., 1995). The quantification limits were:  $2 \text{ mg.kg}^{-1}$  for As and Pb,  $2.5 \text{ mg.kg}^{-1}$  for Cr, and  $1.5 \text{ mg.kg}^{-1}$  for Cu and Zn.

### 2.3. Analytical methods for detecting lead, chromium, zinc and copper in edibles

Metal concentrations were determined using the AOAC methodology (AOAC, 1995). Three portions of 25 g each were weighed and then dehydrated in an oven at  $105^\circ\text{C}$ . After that, the samples were burned using a Bunsen burner. Organic material within the samples was destroyed through the use of a muffle furnace slowly raised to  $450^\circ\text{C}$ ; the temperature inside the furnace remained constant at  $450^\circ\text{C}$  for a period of 8 hours. The samples were then removed and allowed to cool to room tem-



perature while 1mL  $\text{HNO}_3$  was cautiously added to the containers and swirled. The excess  $\text{HNO}_3$  was evaporated carefully on a warm hot plate to the point of dryness. The crucible was returned to the furnace and ash for an additional 2 hours at  $450^\circ\text{C}$ . The ash was dissolved with hydrochloric acid. Lead complexes, formed with ammonium pyrrolidinedithiocarbamate, (APDC) were extracted into isobutyl methyl ketone (MIBK) and determined by Flame Atomic Absorption Spectrometry. For lead, chromium, copper and zinc determinations the Atomic Absorption Spectrometer, model Analyst 100, Perkin Elmer was used.

In order to evaluate the accuracy and quantification limits of these experiments, 6 replicates of the following reference materials were used. For lead the certified reference material was NIST SRM 1570a – Trace Elements in Spinach Leaves with certified value of  $0.20 \text{ mg.kg}^{-1}$  and the experimental value of  $0.192 \pm 0.020 \text{ mg.kg}^{-1}$  Pb. For Chromium the reference material used was the MA-A-2 N° 963 – Fish Homogenate – IAEA, with a certified value of  $1.3 \pm 0.1 \text{ mg.kg}^{-1}$  and experimental value of  $1.3 \pm 0.2 \text{ mg.kg}^{-1}$  Cr. For copper and zinc the certified reference material was NIST 1515 – Apple Leaves. The certified value for copper is  $5.64 \pm 0.24 \text{ mg.kg}^{-1}$  whilst our measured value was  $5.81 \pm 0.43 \text{ mg.kg}^{-1}$  Cu. For zinc, the certified value is  $12.5 \pm 0.3 \text{ mg.kg}^{-1}$  and the experimental value was  $12.6 \pm 0.6 \text{ mg.kg}^{-1}$  Zn. The quantification limits were calculated according to procedures listed in EURACHEM (1998) at  $0.05 \text{ mg.kg}^{-1}$  for Pb and Zn,  $0.02 \text{ mg.kg}^{-1}$  for Cr, and  $0.10 \text{ mg.kg}^{-1}$  for Cu.

## 2.4. Analytical method for arsenic detection in edibles

The sample preparation for determining arsenic concentrations was based on Leblanc & Jackson (1973). After the edible samples were homogenized they were weighed in two 10 g portions. Six grams of cellulose and three grams of magnesium oxide were added to each portion. The samples were then dehydrated in an oven at  $105^\circ\text{C}$  and subsequently burned using a Bunsen burner. Thereafter, 3 grams of magnesium nitrate [ $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] were added to each portion. The destruction of organic material was accomplished through use of a muffle furnace at  $500^\circ\text{C}$ . Ash was then dissolved with hydrochloric acid. In order to reduce AsV to AsIII, potassium iodide and

ascorbic acid were also added (Yamamoto et al., 1985). Arsenic concentrations were determined using an AA Spectrometer Perkin Elmer, model Analyst 100, coupled with flow injection hydride generation and with a FIAS 400 system.

Similarly, in order to evaluate the accuracy and quantification limit of As, 6 replicates of the certified reference material NIST SRM 1566a – Oyster Tissue were analyzed. This reference material contains  $14.0 \pm 1.2 \text{ mg.kg}^{-1}$  As and the measured value was  $12.0 \pm 0.9 \text{ mg.kg}^{-1}$  As. The yielded quantification limit was  $0.002 \text{ mg.kg}^{-1}$ , according to calculation recommended by EURACHEM (1998).

## 3. Results and discussions

### 3.1. Lead in edibles and soil

The lead contents in edibles for the Vila Mota village (Adrianópolis) are shown in **Table 1**. 100% of the leaves, vegetables and eggs yielded lead concentrations that exceed the limits established by Health Ministry of Brazil (HMB) (Brasil, 1965; 1990; 1998a; 1998b) and CODEX values (FAO/WHO, 2006). Lead concentrations in milk and corn samples were  $0.02$  and  $0.03 \text{ mg.kg}^{-1}$ , respectively. These concentrations are below  $0.05$  and  $0.5 \text{ mg.kg}^{-1}$  Pb limits, respectively, permitted by HMB. Lead concentrations in soil varied between  $156$  and  $1935 \text{ mg.kg}^{-1}$  (grain size fraction  $<63 \mu\text{m}$ ) or from  $101$  to  $1153 \text{ mg.kg}^{-1}$  Pb (grain size fraction  $<177 \mu\text{m}$ ), which reflect, to a certain extent, the results of previous studies in the area (Cunha et al., 2005). Lead concentrations in soil were all above the reference concentration of lead in Brazilian soil, which is  $17 \text{ mg.kg}^{-1}$  (CETESB, 2005). Furthermore, most samples presented lead concentrations exceeding the intervention value for agriculture soil ( $180 \text{ mg.kg}^{-1}$  Pb as established by CETESB, 2005). Not only is the use of this soil inappropriate for agricultural purposes, but it may be detrimental to the health of local children as lead concentrations in most of samples exceed the maximum reference value established by USEPA (2005) of  $400 \text{ mg.kg}^{-1}$ .

The lead contents in soil and edibles from the Serra neighborhood (Iporanga) are also shown in Table 1. Lead concentrations exceeding regulated values were found in only 7% to 13% of the leafy vegetables. Furthermore, only 33% of the root, legume and tuber vegetables had lead concentra-

**Table 1** – Lead contents (mg.kg-1) in edibles and soil from Vila Mota and Serra

Sites	Locality	Lead in soil (mg.kg-1)		Edibles	Lead in edibles (mg.kg-1)	Standard Deviation	Maximum tolerated value according to regulations *	Maximum tolerated value according to CODEX**
		Grain size fraction < 177µm	Grain size fraction < 63 µm					
1	Vila Mota	1153	1292	Egg (Gallus spp)	0.2	0.01	0.1	
2	Vila Mota	804	944	Lettuce (Lactuta sativa)	1.17	0.03	0.5	0.3
				Carrot (Daucus carot)	0.58	0.03	0.5	0.1
				Basil (Ocimum basilicum)	30.79	3.07	0.5	0.3
				Kale (Brassica oleracea)	0.87	0.17	0.5	0.3
				Sweet Marjoram (Origanum majorana)	7.03	0.32	0.5	0.3
				Maize (Zea mays)	0.03	0.00	0.5	0.2
				Manioc (Manihot esculenta)	2.18	0.16	0.5	0.1
3	Vila Mota	1534	1935	Lettuce (Lactuta sativa)	2.96	0.13	0.5	0.3
				Manioc (Manihot esculenta)	13.38	0.88	0.5	0.1
				Radish (Raphanus sativus)	1.6	0.15	0.5	0.3
4	Vila Mota	842	1379	Kale (Brassica oleracea)	0.54	0.03	0.5	0.3
				Manioc (Manihot esculenta)	5.21	0.17	0.5	0.1
5	Vila Mota	101	156	Egg (Gallus spp)	0.18	0.00	0.1	
				Sweet Marjoram (Origanum majorana)	1.76	0.07	0.5	0.3
				Basil (Ocimum basilicum)	0.8	0.07	0.5	0.3
6	Vila Mota			Milk (Bos spp)	<0.05		0.05	
7	Vila Mota			Milk (Bos spp)	<0.05		0.05	
8	Serra	107	96	Lettuce (Lactuta sativa)	0.07	0.00	0.5	0.3
				Kale (Brassica oleracea)	0.07	0.00	0.5	0.3
				Egg (Gallus spp)	0.07	0.00	0.1	
9	Serra	65	56	Lettuce (Lactuta sativa)	0.09	0.00	0.5	0.3
				Kale (Brassica oleracea)	<0.05		0.5	0.3
				Manioc (Manihot esculenta)	0.09	0.01	0.5	0.1
				Basil (Ocimum crispum)	0.06	0.01	0.5	0.3
				Sweet Marjoram (Origanum majorana)	0.42	0.05	0.5	0.3
				Basil (Ocimum basilicum)	0.04	0.00	0.5	0.3
				Mint (Mentha arvensi)	0.11	0.04	0.5	0.3
10	Serra	157	166	Lettuce (Lactuta sativa)	0.12	0.04	0.5	0.3
				Carrot (Daucus carot)	0.19	0.01	0.5	0.1
				Kale (Brassica oleracea)	0.05	0.00	0.5	0.3
				Sweet Marjoram (Origanum majorana)	2.09	0.02	0.5	0.3
				Maize (Zea mays)	<0.05		0.5	0.2
				Elephant garlic (Allium porrum)	<0.05		0.5	0.1
11	Serra	1200	1520	Maize (Zea mays)	<0.05		0.5	0.2
12	Serra	39	43	Basil (Ocimum basilicum)	0.07	0.00	0.5	0.3
				Sweet Marjoram (Origanum majorana)	0.23	0.01	0.5	0.3
				Mint (Mentha arvensi)	0.17	0.00	0.5	0.3
				Basil (Ocimum crispum)	0.14	0.01	0.5	0.3
13	Serra			Milk (Bos spp)	<0.05		0.05	
Limit for agriculture soil		180						

\* Source: Ministry of Health, Sanitary Surveillance Secretary, Documents no. 685 of 1998.08.27, no. of 1990.03.19, and no. 55871 of 1965.03.26

\*\* Values from FAO/WHO (2006)



tions exceeding the maximum value of  $0.1 \text{ mg.kg}^{-1}$  established by CODEX (FAO/WHO, 2006). Concerning topsoil samples, all measured lead contents exceeded the reference value, but at only one site (40 m from the Betari River) was the intervention value for agriculture exceeded.

It is well known that lead, as well as chromium, zinc and copper, contents in some plant species vary consistently with metal concentrations in soil. In Figure 2 the positive correlation between lead concentrations in soil and in edibles is shown for kale (*Brassica oleracea*), manioc (*Manihot esculenta*), lettuce (*Lactuca sativa*), and Sweet Marjoram (*Origanum majorana*). Several other factors also exist that influence the bioavailability of lead and were not assessed in this study. These factors include soil pH, its cationic exchange capacity, clay and organic matter contents, local climate and the characteristics of plant species, among others (Kabata-Pendias & Pendias, 1992; Alloway, 2005).

$\text{mg.kg}^{-1}$  Cr recommended limit. Brassica, bulb, root or vegetables, corn and eggs yielded chromium concentrations below the regulated value. All soil samples presented Cr levels above the  $40 \text{ mg.kg}^{-1}$  Cr established by CETESB (2005).

In the Serra neighborhood the chromium contents of half of the greens exceeded the  $0.10 \text{ mg.kg}^{-1}$  permitted limit (Brasil, 1965). The values range from below the detection limit up to  $1.26 \text{ mg.kg}^{-1}\text{Cr}$ . Chromium concentrations in the corn samples varied from  $0.10$  to  $0.13 \text{ mg.kg}^{-1}$ , exceeding the regulated values. On the other hand, all milk, egg, roots and vegetable samples yielded chromium concentrations below the permitted limit. Additionally, Cr levels for most of the soil samples exceeded the reference value established by CETESB (2005) for agriculture use.

It is important to mention that chromium is not present in the Pb-Zn ores extracted and refined in the Ribeira Valley, but may be present in some mafic volcanic rocks outcropping in the region.

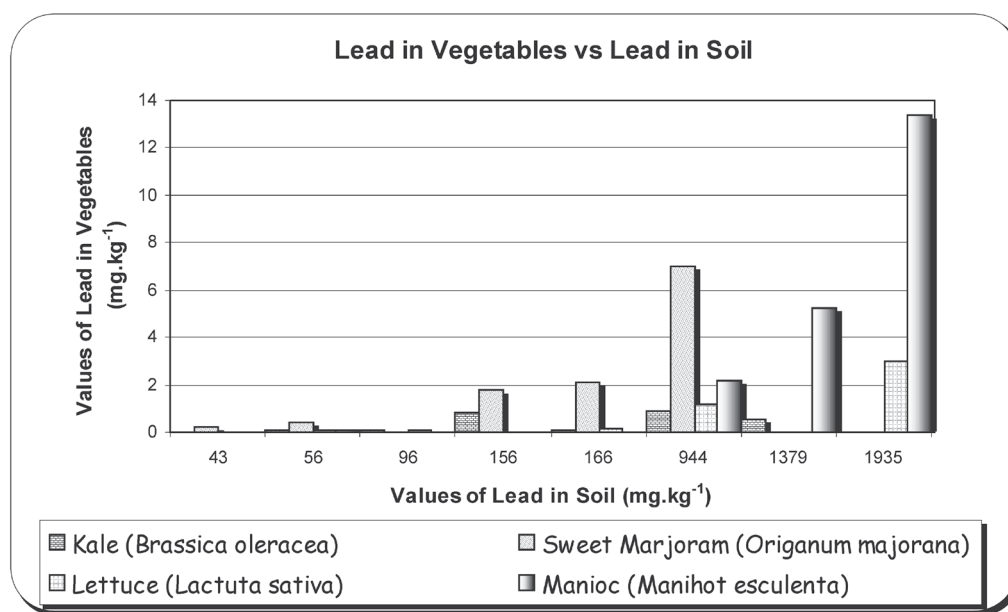


Figure 2 – Lead concentration ( $\text{mg.kg}^{-1}$ ) in edibles and soil from Vila Mota and Serra

### 3.2. Chromium in edibles and soil

At the Vila Mota village the chromium contents in greens, which can be seen in Table 2, range from below the detection value (ND) of  $0.01 \text{ mg.kg}^{-1}$  up to  $0.92 \text{ mg.kg}^{-1}\text{Cr}$ . Chromium concentrations exceeding the regulated limit of  $0.10 \text{ mg.kg}^{-1}$  (Brasil, 1965) for greens were found in 5 samples (63%). One of the milk samples exceeded the  $0.15$

Consequently, the presence of chromium in soil may be a residual affect. Thus any causal relation to local mining wastes and to the smelter emissions is unlikely to exist.

### 3.3. Copper, zinc and arsenic in edibles and soil

The results obtained for Vila Mota and Serra



**Table 2** – Chromium contents (mg.kg<sup>-1</sup>) in edibles and soil from Vila Mota and Serra

Sites	Locality	Cr in soil (mg.kg <sup>-1</sup> ) Grain size fraction <63µm	Edibles	Cr in edibles (mg.kg <sup>-1</sup> ) *	Standard Deviation
1	Vila Mota	63	Egg ( <i>Gallus spp</i> )	<0.02	
2	Vila Mota	50	Lettuce ( <i>Lactuta sativa</i> )	0.09	0.03
			Carrot ( <i>Daucus carot</i> )	<0.02	
			Basil ( <i>Ocimum basilicum</i> )	0.92	0.06
			Kale ( <i>Brassica oleracea</i> )	0.10	0.03
			Sweet Marjoram ( <i>Origanum majorana</i> )	0.22	0.01
			Maize ( <i>Zea mays</i> )	0.05	0.00
			Manioc ( <i>Manihot esculenta</i> )	0.05	0.01
3	Vila Mota	42	Lettuce ( <i>Lactuta sativa</i> )	0.03	0.00
			Manioc ( <i>Manihot esculenta</i> )	<0.02	
			Radish ( <i>Raphanus sativus</i> )	<0.02	
4	Vila Mota	43	Kale ( <i>Brassica oleracea</i> )	0.07	0.00
			Manioc ( <i>Manihot esculenta</i> )	<0.02	
5	Vila Mota	41	Egg ( <i>Gallus spp</i> )	<0.02	
			Sweet Marjoram ( <i>Origanum majorana</i> )	0.27	0.01
			Basil ( <i>Ocimum basilicum</i> )	0.19	0.01
6	Vila Mota		Milk ( <i>Bos spp</i> )	0.05	0.01
7	Vila Mota		Milk ( <i>Bos spp</i> )	0.15	0.01
8	Serra	39	Lettuce ( <i>Lactuta sativa</i> )	0.04	0.00
			Kale ( <i>Brassica oleracea</i> )	0.05	0.00
			Egg ( <i>Gallus spp</i> )	0.03	0.00
9	Serra	26	Lettuce ( <i>Lactuta sativa</i> )	0.19	0.01
			Kale ( <i>Brassica oleracea</i> )	0.05	0.00
			Manioc ( <i>Manihot esculenta</i> )	<0.02	
			Basil ( <i>Ocimum crispum</i> )	0.05	0.00
			Sweet Marjoram ( <i>Origanum majorana</i> )	0.34	0.03
			Basil ( <i>Ocimum basilicum</i> )	0.11	0.13
			Mint ( <i>Mentha arvensi</i> )	0.03	0.00
10	Serra	49	Lettuce ( <i>Lactuta sativa</i> )	0.03	0.00
			Carrot ( <i>Daucus carot</i> )	<0.02	
			Kale ( <i>Brassica oleracea</i> )	0.03	0.00
			Sweet Marjoram ( <i>Origanum majorana</i> )	1.26	0.31
			Maize ( <i>Zea mays</i> )	0.13	0.02
			Elephant garlic ( <i>Allium porrum</i> )	0.05	0.01
11	Bairro da Serra	89	Maize ( <i>Zea mays</i> )	0.11	0.01
12	Serra	79	Basil ( <i>Ocimum basilicum</i> )	0.11	0.01
			Sweet Marjoram ( <i>Origanum majorana</i> )	0.37	0.01
			Mint ( <i>Mentha arvensi</i> )	0.40	0.02
			Basil ( <i>Ocimum crispum</i> )	0.21	0.03
13	Serra		Milk ( <i>Bos spp</i> )	0.05	0.00
Limit for agriculture soil		150			

\* The maximum tolerated Cr content in food is 0.1 mg.kg<sup>-1</sup> according to HMB

show that the concentrations of copper, zinc and arsenic in edibles do not exceed the values permitted by HMB. The minimum and maximum concentrations of copper and zinc were  $<0.10 \text{ mg.kg}^{-1}$  and  $4.68 \text{ mg.kg}^{-1}$ ;  $1.96 \text{ mg.kg}^{-1}$  and  $24.03 \text{ mg.kg}^{-1}$ , respectively. All samples yielded arsenic concentrations below the quantification limit of  $0.002 \text{ mg.kg}^{-1}$ . The established copper and zinc concentration limits, for any edible, are 10 and  $50 \text{ mg.kg}^{-1}$ , respectively (Brasil, 1965; 1998a). For arsenic, the maximum established limits for egg and milk are  $1.0$  and  $0.1 \text{ mg.kg}^{-1}$ , respectively (Brasil, 1998). For other edibles the maximum is  $1.0 \text{ mg.kg}^{-1}$  As (Brasil, 1965).

The Cu, Zn and As contents in top soil are shown in Table 3. Most of the soil samples from Vila Mota yielded Cu and Zn contents above the reference level established by CETESB (2005) at  $35 \text{ mg.kg}^{-1}$  Cu and  $60 \text{ mg.kg}^{-1}$  Zn, respectively. For arsenic only one sample of topsoil showed a concentration above the reference value of  $3.5 \text{ mg.kg}^{-1}$ . Copper, zinc and arsenic concentrations in soil are not only due to the background geology, but also due to the particulate emissions released by the Plumbum Company into the atmosphere.

At Serra neighborhood, all soil samples presented Cu, Zn and As concentrations above the reference values. In the case of zinc and arsenic, the intervention values of  $450 \text{ mg.kg}^{-1}$  Zn and  $35 \text{ mg.kg}^{-1}$  As were exceeded by only one sample.

### 3.4. Dietary intake of lead and chromium

The results of this study clearly indicate that the risk of ingestion of metal contaminated food is of great concern, especially in Vila Mota and particularly when it comes to lead and chromium.

The Provisionally Tolerable Weekly Intake (PTWI) for lead is  $0.025 \text{ mg}$  per  $\text{kg}$  of body weight (FAO/WHO 2006). Thus, a person weighing  $70 \text{ kg}$  may tolerate approximately  $1.75 \text{ mg}$  Pb per week without any significant health problems. In Brazil, the average consumption of greens (any kind of herbaceous plant of which one or more of its parts is used as food in its natural manner) is around  $660 \text{ g}$  per week. Similarly, the consumption of pulse, root, legume, bulb and brassica vegetables is around  $750 \text{ g}$  per week (IBGE 1998).

At Vila Mota the average concentrations of lead in greens and in vegetables are, respectively,  $5.74 \text{ mg.kg}^{-1}$  and  $4.59 \text{ mg.kg}^{-1}$ . Hence, based on these

**Table 3** – Copper, zinc and arsenic contents ( $\text{mg.kg}^{-1}$ ) in soil from Vila Mota and Serra

Sites	Locality	Cu in soil ( $\text{mg.kg}^{-1}$ ) Grain size fraction <177 $\mu\text{m}$	Cu in soil ( $\text{mg.kg}^{-1}$ ) Grain size fraction <63 $\mu\text{m}$	Zn in soil ( $\text{mg.kg}^{-1}$ ) Grain size fraction <177 $\mu\text{m}$	Zn in soil ( $\text{mg.kg}^{-1}$ ) Grain size fraction <63 $\mu\text{m}$	As in soil ( $\text{mg.kg}^{-1}$ ) Grain size fraction <177 $\mu\text{m}$	As in soil ( $\text{mg.kg}^{-1}$ ) Grain size fraction <63 $\mu\text{m}$
1	Vila Mota	102	113	395	407	<2	<2
2	Vila Mota	78	92	170	196	<2	4.8
3	Vila Mota	109	136	148	184	10.3	10.6
4	Vila Mota	55	90	102	135	2	<2
5	Vila Mota	19	32	48	70	<2	<2
8	Serra	36	37	162	156	15	12
9	Serra	41	34	114	100	10	9
10	Serra	50	53	140	149	23	24
11	Serra	51	53	799	990	207	217
12	Serra	70	79	87	99	7.3	10
Limits for agriculture soil		200		450		35	





average values, those who live in Vila Mota are likely to intake 3.78 mg and 3.44 mg of lead per week through greens and vegetables, respectively. That leads to an estimated ingestion *per capita* of 7.22 mg Pb per week, amount that exceeds PTWI limit by 5.47 mg Pb a week. In other words, those living in Vila Mota are consuming about 4.12 times PTWI values.

Adult food-lead absorption may range from 10% to 15% (Paolliello & Capitani, 2003). Considering that 10% of the lead intake by Vila Mota residents is absorbed, we can assume that a resident that ingests about 7.22 mg of lead per week may absorb about 0.72 mg of lead.

At Serra neighborhood the average concentration of lead in greens and vegetables is 0.25 mg.kg<sup>-1</sup> and 0.11 mg.kg<sup>-1</sup>, respectively, based on the national average of food consumption (IBGE, 1998). This population may ingest 0.165 mg of lead from greens and 0.083 mg of lead through vegetables a week (i.e. 0.25 mg/week). Thus they may not reach the recommended maximum of 1.75 mg of Pb per week. Note that this limit was established for an individual who weighs 70 kg. Therefore, the health risk for those who consume greens and vegetables from their backyards at Serra can not be anticipated from the present results. These figures are also supported by previous average BLL determinations for the local population of 3.46 µg/dL for adults and 5.36 µg/dL for children (Paoliello et al., 2002; 2003) well below the 10 µg/dL suggested by the WHO (1995) as a limit for good health.

Chromium, unlike lead, is an essential nutrient for humans. The Dietary Reference Intake for adult (males and females) and children are 30, 25, and 15 µg per day, respectively (Food and Nutrition Board, 2000, Silva 2003a). For the Food and Nutrition Board Recommended Dietary Allowances (1989) that limit is 50-200 µg/day. The regulated dietary intake of chromium in the country is 35 µg for adults and 15 µg for children between 4 and 10 years old (Brasil, 2005). Based on the Cr concentration obtained in this study and taking into account that the average consumption of greens and vegetables in Brazil is 94 and 107 grams per day respectively (IBGE, 1998), it is possible to estimate one's daily chromium intake from his or her consumption of home-grown vegetables.

At Vila Mota the average chromium concentration in greens is 0.26 mg.kg<sup>-1</sup> and in vegetables is 0.02 mg.kg<sup>-1</sup>. Therefore, assuming that those who

live there consume 94 g of greens and 107 g of vegetables cultivated in their backyards, the daily Cr ingestion is 27 µg. At Serra the average chromium concentration in greens is 0.23 mg.kg<sup>-1</sup> and in vegetables is 0.06 mg.kg<sup>-1</sup>. Hence, assuming that people consume the daily average of greens and vegetables and these plants are all home-grown, they may ingest 28.3 µg Cr per day. The evaluation of these values indicates that the intake of chromium from home-grown edibles at Vila Mota and Serra is comparable to the Dietary Reference Intake and it does not reach the daily intake established by the HMB for adults. In summary, no health risk for these residents concerning chromium content in edibles was observed in this study.

## 4. Conclusions

The results obtained for Vila Mota, which is located in the vicinity of the Plumbum smelter, show considerable lead contamination in soil and home grown vegetables. Based on the average Brazilian diet, Vila Mota inhabitants are likely to be ingesting around 4 times the maximum amount of lead that a human body can tolerate. Observing the results of this work and of previous studies in Vila Mota, one can readily conclude that its population lives in an area severely contaminated by lead, representing a serious health risk. Previous epidemiological campaigns have also shown that the mean BLL value for those who consume greens and vegetables is higher than that for those who do not. The data presented in this research, together with other previously recorded BLL results, indicate that home grown greens and vegetables have been functioning as a conduit for lead contamination, from contaminated soil to the human body. Living conditions in Vila Mota are prone to become unbearable on a long-term basis. This neighborhood needs immediate environmental intervention, such as cleaning up of home interiors, the paving of roads, and replacement of soil for basic agriculture.

Concerning chromium, at Vila Mota, some edibles show concentrations exceeding the values established by HMB. However, comparing the amount of chromium in edibles and the average for a Brazilian diet, it is possible to assume that there is no serious health risk to Vila Mota residents regarding Cr intake by eating home-grown vegetables. No food contamination for copper, zinc,



and arsenic was detected in the present study and the presence of these elements may not represent a serious risk there. Even so, Vila Mota needs to be monitored for these heavy metals and arsenic as a precautionary measure.

This study revealed that there is no significant health risk posed to Serra inhabitants who consume home-grown vegetables on the basis of the average Brazilian diet. This is despite the fact that a considerable percentage of edibles showed lead values higher than the recommended national and international levels. Furthermore, some edibles and soil samples from Serra yielded chromium concentrations greater than regulated acceptable values. However, after evaluating the amount of chromium in the local food and taking the average Brazilian diet into consideration, it is possible to conclude that there is no health risk. With regards to copper, zinc, and arsenic no contaminated food was detected, despite some soil samples containing higher concentrations than those recommended.

The present data for Serra inhabitants are consistent with low mean BLL and low mean As content in urine as reported in previous studies (Paoliello et al., 2003; Cunha et al. 2005; Sakuma, 2004). In conclusion, the Serra neighborhood cannot be considered a risk area concerning consumption of home-grown vegetables. However, this area would also need to be monitored for metals and arsenic as a precautionary measure.

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