ABSTRACT  For several decades, the Ribeira Valley, Brazil, was under the influence of the full activity of Pb-Zn mines and of the Plumbum refinery. Since 1996, all the mines and the refining plant have been closed. The objective of the present study was to assess the exposure of children to lead and to verify the probable sources of human contamination. For the lead exposure study, blood samples were collected from 335 children aged 7 to 14, residing in municipalities around the mines and the refinery. To assess the probable sources of lead exposure, a parallel study of surface water, water from residential taps, stream sediments and surface soils was carried out. The results showed significant correlation between high blood lead levels and the proximity of the residential area to the lead refinery. Lead concentrations in water are consistently low. Stream sediment samples showed elevated lead concentrations, but do not constitute a risk for human exposure because the water pH conditions (pH > 7) prevent the release of lead into the water. Soil samples revealed high lead concentrations, with the highest values found in areas close to the refinery. The highly contaminated soils are considered the main source for human exposure in the Upper Ribeira Valley.

KEYWORDS  environmental geochemistry, medical geology, lead exposure, Ribeira Valley, Brazil
Introduction

The Ribeira de Iguape Valley is located in the southern region of the state of São Paulo and the eastern part of the state of Paraná, Brazil. That area has been known since the 16th century for its deposits of lead and silver, and to a lesser extent zinc. For decades Plumbum Mineração and Metalurgia Ltda. operated in the region along with several lead mines and processing plants. The mines and the processing and refining plants stopped all activities at the end of 1995. Some of the residues of the metallurgical and processing operations are stored in the open air approximately 800 m away from the Plumbum refinery, located in the rural area of Adrianópolis (Fig. 1).

Environmental studies for heavy metals in that region, aiming specifically at the assessment of the Ribeira river, have been performed before (e.g. CETESB 2000, Eysink et al. 1988, 1991; Tessler et al. 1987, Moraes 1997, Cunha and Figueiredo 1999), however, no data on human exposure have been produced so far.

High lead concentrations in the environment caused by either geological processes or anthropic activities should be carefully examined since this element is highly toxic to human beings. Children are more vulnerable to lead-related health problems than adults. Among residents in lead polluted land, children are more susceptible to absorb the metal present in soil and dust when playing outdoors and because their higher gastrointestinal absorption rates (CDC 1991, Ziegler et al. 1978, WHO 1995, ATSDR 2000).

In Brazil, there have been few studies assessing lead exposure among children. The most impressive occurred in Santo Amaro da Purificação, in the state of Bahia, where high levels of lead and toxic effects from that metal were detected among children living close to a lead refinery (Carvalho et al. 1984, 1985, 1995; Tavares et al. 1989, Silvany-Neto et al. 1989, 1996).

The present study considered that the population of the Upper Ribeira Valley has been exposed to lead poisoning for decades, both from mining activities and emission of gases and particles into the atmosphere by the Plumbum refinery. Then the possibility that environmental contamination could be affecting people, especially infants, living in the Upper Ribeira Valley was investigated in several municipalities both in urban and rural areas. The ecotoxicological study also included a group of children living in the municipality of Cerro Azul (upstream the mining area in the State of Paraná) making up the reference population for comparison purposes.

Figure 1 – Location of the study area
Materials and Methods

From June 1999 until October 2000, fieldwork was conducted in public schools in the municipalities of Adrianópolis (in the urban area and in the rural areas Vila Mota, Capelinha and Porto Novo), Ribeira (an urban area), Iporanga (in the rural area of Serra) and Cerro Azul (an urban area). Blood samples were taken from a total of 335 children from 7 to 14 years old. The municipalities of Adrianópolis, Ribeira and Iporanga were selected due to their proximity to the lead mines and the Plumbum refinery. Cerro Azul in turn was chosen because of its location upstream from the lead deposits, in a region where the population was not exposed to mining activity effects, and therefore constituting a suitable reference group for the study.

Meetings with parents and responsible guardians were held at schools. They agreed to let their children participate in the study and voluntarily signed a form authorizing the blood sampling procedures.

At the time of the collection of the blood samples, questionnaires were applied to evaluate certain critical parameters such as age, sex, period of residence in the community, distance of premises from the mining areas and/or the refinery, previous employment of parents in the mines and/or the refinery, food consumption habits and other issues.

Approximately 5 ml of blood was drawn from each subject. Vacutainer tubes equipped with blue tap (trace metal free) containing heparine were used. The samples were refrigerated at 4°C before being shipped to the toxicology laboratory, where they were kept at -20°C until the lead assays were performed. The samples were analyzed at the Adolfo Lutz Institute in São Paulo by graphite furnace atomic absorption with ZEEMAN background correction (Model SIMAA 6000, Perkin-Elmer).

From May 1998 to April 2001, twenty surface water and four stream sediments samples were collected. In this period, tap water was also sampled from 15 houses in the municipalities of Adrianópolis, Ribeira, Iporanga and Cerro Azul. The tap water samples for the municipalities of Ribeira and Iporanga was supplied by the São Paulo State Basic Sanitation Company – Sabesp. The Paraná Sanitation Company – Sanepar - was responsible for the water samples for Adrianópolis and Cerro Azul. In the communities of Vila Mota and Capelinha, most of the families use water from natural sources (springs), and at Porto Novo, people generally drink water obtained directly from the Ribeira River.

The surface water samples were sampled in different seasons. The water samples were filtered on-site through 0.45 μm filters and stored in polyethylene tubes. For the lead analysis, the samples were acidified to pH 2 with super-pure HNO₃ (1:1) and were measured by inductively coupled plasma/atomic emission spectrometry (ICP/AES) TJA, model IRIS-AP HR.

The stream sediment samples were stored in plastic bags and labeled. In the laboratory they were dried in an oven at 40°C, homogenized and subsequently sieved with nylon sieves. Granulometric fractions of less than 0.177 mm were used for the lead measurement.

In December 2000 and April 2001, 21 soil samples were collected at Vila Mota and Capelinha, including four samples from home vegetable gardens. The samples were taken at depths from 0 to 15 cm. Two samples were collected from residue piles of the metallurgical and processing operations of the Plumbum plant.
The soil samples were packed in paper bags. In the laboratory they were dried in an oven at 40°C and desegregated. After desegregation, the grains larger than 0.177 mm were discarded.

The analysis of sediments and soils was performed by inductively coupled plasma/atomic emission spectrometry (ICP/AES) TJA, model IRIS-AP HR. The samples were digested in hot aqua regia (HNO\textsubscript{3}/HCl 1:5). Accuracy was controlled by including an interlaboratory-calibrated standard sample in each sample set and sample replicates were used for quality control.

The analysis of water, sediment and soil samples was carried out at the Mineral Analysis Laboratory - LAMIN of the Geological Survey of Brazil, Rio de Janeiro.

**Results and Discussion**

**Lead levels in blood samples**

The mean lead level yielded for all blood samples was 7.40 μg dL\textsuperscript{-1}, with a range from 1.8 to 37.8 μg dL\textsuperscript{-1}. The average blood lead levels (BLL) of children from the communities studied were: 5.40 μg dL\textsuperscript{-1} for the town of Ribeira, 6.06 μg dL\textsuperscript{-1} for the urban area of Adrianópolis, 11.89 μg dL\textsuperscript{-1} for Vila Mota and Capelinha, 4.17 μg dL\textsuperscript{-1} for the community of Porto Novo, 5.36 μg dL\textsuperscript{-1} for Serra, a district of Iporanga, and 2.37 μg dL\textsuperscript{-1} for the town of Cerro Azul (Fig. 2).

The highest average was found in the children from Vila Mota and Capelinha, rural communities of the municipality of Adrianópolis, located very close to the Plumbum refinery and the Panelas de Brejafiva mine. This population also presented the highest blood lead level of the entire studied group, 37.8 μg dL\textsuperscript{-1}, which is almost four times the value of 10 μg dL\textsuperscript{-1} suggested by the Center for Disease Control & Prevention - CDC (1991) and the WHO (1995) as the limit for good health.

It can also be seen that the average value found in Cerro Azul is between 2 and 5 times less than that of the other communities studied. This value can be considered a good estimate of background for the Upper Ribeira Valley. These results indicate that the lead mining caused contamination of the population living in the entire Upper Ribeira Valley region, with the communities of Vila Mota and Capelinha being the most affected, since they live very close to the Panelas mine and the Plumbum refinery. The results of this study are similar to those obtained in studies carried out by Taskinen et al. (1981) and Murgueytio et al. (1998).

This study also shows that in all the communities studied, boys had higher blood lead levels than girls (Fig. 3). Boys are more inclined to play outdoors than girls, therefore probably being more exposed to soil and dust. This particular result confirms a world trend (WHO, 1995).

In the evaluation of the data recorded in the questionnaires, it was observed that children who are accustomed to eating vegetables and fruit grown in their home vegetable gardens presented higher BLL than those who rarely do so, which is the case of the communities of Vila Mota and Capelinha. This suggests that food may be one of the pathways of lead contamination of local children.

The children that reported that they are accustomed to playing outdoors had higher BLL values than those that said they do not. This suggests that the ingestion of soil and the inhalation of dust may have significantly contributed to the high blood lead levels of the Upper Ribeira Valley children.
The study also showed that the children whose normal diet includes fish from the Ribeira and the Betari rivers in the communities of Porto Novo and Serra presented blood lead levels of 4.17 $\mu$g dL$^{-1}$ and 5.36 $\mu$g dL$^{-1}$, respectively. These values are very low and suggest that the local fish cannot be considered as a pathway of lead contamination in the Upper Ribeira Valley region. This confirms the study carried out by Lamparelli et al. (1996) which demonstrated that there is no risk to children's health associated with the consumption of local fish.

According to the classification of the CDC (1991), which ranks children’s health risk as related to metal contamination (Table 1), Vila Mota and Capelinha are the communities in the most critical situation: 40.4% of the studied children are in Class I (values $\leq$ or $<$ 9 $\mu$g dL$^{-1}$), 37.2% in Class IIA (10-14 $\mu$g dL$^{-1}$), 9.6% in Class IIB (15-19 $\mu$g dL$^{-1}$) and 12.8% in Class III (20-44 $\mu$g dL$^{-1}$). It was found that 44 children presented blood lead levels exceeding 10 $\mu$g dL$^{-1}$ and needed regular medical monitoring, whereas 12 children with blood lead levels exceeding 20 $\mu$g dL$^{-1}$ required medical intervention.

In addition, the data shown in Figure 4 demonstrate that with the exception of Cerro Azul, all of the communities in the study had cases with blood lead levels (BLL) exceeding 10 $\mu$g dL$^{-1}$, which characterizes a long-term risk to health, according to the CDC (1991).

### Surface and residential tap water

The lead concentration of the Ribeira river water at the CETESB station of Itaóca varied from <0.02 to 0.23 mg L$^{-1}$ in the period from 1982 to 2000. In this series, it can be observed that: a) up to 1986, the concentrations of lead detected in the water were lower than 0.02 mg L$^{-1}$; b) between 1986 and 1996, lead contents of 0.04 to 0.23 mg L$^{-1}$ were detected; and c) from 1997 on, lead was no longer found at concentrations exceeding 0.03 mg L$^{-1}$, the maximum acceptable concentration limit for this element in the river water according to the National Environmental Council (CONAMA 1986).

Eysink et al. (1988) showed that the lead levels in the water of the Ribeira river sampled between the towns of Ribeira and Iporanga varied between <0.01 and 0.21 mg L$^{-1}$ in 1986, which are considerably higher than the level prescribed by CONAMA (1986).

### Table 1 – Class of child based on blood lead levels (from CDC 1991)

<table>
<thead>
<tr>
<th>Class</th>
<th>Blood lead levels (mg/dL)</th>
<th>Comments</th>
<th>Ribeira</th>
<th>Adrianópolis</th>
<th>Vila Mota and Capelinha</th>
<th>Porto Novo</th>
<th>Serra</th>
<th>Cerro Azul</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$\leq$ or $&lt;$ 9</td>
<td>A child is not considered to have lead poisoning</td>
<td>92.5%</td>
<td>86.6%</td>
<td>40.4%</td>
<td>98%</td>
<td>90.7%</td>
<td>100%</td>
</tr>
<tr>
<td>IIA</td>
<td>10-14</td>
<td>Many children or a large proportion of children with blood levels in this range should trigger community-wide childhood lead poisoning prevention activities. Children in this range may need to be screened more frequently</td>
<td>5.0%</td>
<td>10.4%</td>
<td>37.2%</td>
<td>–</td>
<td>7%</td>
<td>–</td>
</tr>
<tr>
<td>IIB</td>
<td>15-19</td>
<td>A child in Class IIB should receive nutritional and educational interventions and more frequent screening. If blood lead levels remain in this range, environmental investigation and intervention should be undertaken</td>
<td>2.5%</td>
<td>3.0%</td>
<td>9.6%</td>
<td>–</td>
<td>2.3%</td>
<td>–</td>
</tr>
<tr>
<td>III</td>
<td>20-44</td>
<td>A child in this Class should receive environmental evaluation and remediation and a medical evaluation. Such a child may need pharmacological treatment for lead poisoning</td>
<td>–</td>
<td>–</td>
<td>12.8%</td>
<td>2%</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
The results shown above reveal that between 1986 and 1996, the waters of the Ribeira river were contaminated by lead as a result of the higher waste discharge into the drainage in the period due to more intense mining activity and refinery operation in the area.

The chemical analyses of river water performed during this study confirmed that currently the lead concentrations in the Upper Ribeira Valley water have remained low (<0.005 to 0.006 mg L\(^{-1}\)) since lead ore mining and refining activities in the region were stopped.

In this study lead concentrations of water samples collected from house taps were also determined. The values obtained were very low (<0.005 to 0.008 mg L\(^{-1}\)), demonstrating that the water consumed by the local population is not contaminated by lead, regardless of the origin of the water.

The pH values obtained from the surface and house tap water samples varied between 7 and 8.7. The pH values are slightly alkaline due to the presence of carbonaceous rocks in the region, a feature that does not favor the solubility of lead compounds. Eysink et al. (1988) showed that downstream from the town of Iporanga, the pH of the Ribeira River water becomes slightly acid, around 6.5, reflecting the change in lithology in the drainage area.

**Stream sediments**

There are several research projects which present data on lead concentrations in stream sediment samples collected in the region. Morgental et al. (1975, 1978) found lead concentrations varying between 2.5 and 280 µg g\(^{-1}\) and from 1.5 to 1300 µg g\(^{-1}\), respectively, in stream sediments of the Upper Ribeira Valley, and estimated a regional background between 12 µg g\(^{-1}\) and 16 µg g\(^{-1}\) Pb.

Eysink et al. (1988) found that stream sediments in the upper Ribeira river basin contained very high lead concentrations reaching a peak of 4,000 µg g\(^{-1}\) in the Betari Creek. This suggests that the volume of material discharged in the drainage from the mines and the refinery in the past must have been considerable. Subsequently Eysink et al. (1991) presented further data on lead contents in stream sediments in the Upper Ribeira Valley in the range of 105 to 358 µg g\(^{-1}\).

CETESB (2000), based on data obtained in 1998, reported lead concentrations between 41.7 µg g\(^{-1}\) and 389.0 µg g\(^{-1}\) in stream sediments of the Ribeira River and the Betari Creek in the municipalities of Ribeira and Iporanga, respectively.

In the present study the following lead concentrations in stream sediments from the Ribeira River were obtained: 30.8 µg g\(^{-1}\) Pb in the vicinity of the Ribeira town, 34.7 µg g\(^{-1}\) Pb at the Itaóca ferry-boat cross and 175.5 µg g\(^{-1}\) Pb near to the town of Iporanga. In addition, one stream sediment sample collected from the Betari Creek in the district of Serra, near Iporanga, showed a lead content of 527.2 µg g\(^{-1}\) Pb. These results indicate that lead contents of stream sediment in the Upper Ribeira Valley continue to be very high, considerably above the regional background levels estimated by Morgental et al. (1975, 1978) as well as much higher than the limit of 40 µg g\(^{-1}\) Pb for uncontaminated sediments recommended by Prates and Anderson (1977).

The data from previous studies and the results of the present study are summarized in Figure 5. The highest lead concentration is found in stream sediments of the Betari Creek, a tributary of the Ribeira River at Iporanga that in the past might have received a large quantity of waste from the Furnas mine.
Since inorganic lead compounds have a very low solubility in surface waters with pH > 7 and since the pH is governed principally by the abundance of limestone in the region, the lead tends to be retained in the stream sediments and is therefore not bioavailable.

Soils and residue piles

Lead concentrations between 21.4 and 915.6 μg g⁻¹ were found in surface soil collected at various distances from the refinery as depicted in Table 2.

With respect to the lead concentration in soil samples, it was found that: (a) soil samples 10, 15, 16, 17, 18, 19, 20, and 21 developed from substratum of Itaoca granite (pH values between 5 and 6), and have lead concentrations close to the background estimated by Morgental et al. (1975, 1978) and Lopes Jr. and Pinto Filho (1981); (b) lead concentrations in soils are higher in areas closer to the Plumbum refining plant, developed from substratum of metacalcareous and carbonaceous schist (pH values between 6 and 8); (c) vegetable garden soils located close to the refinery (samples 1, 4, 22 and 23) also exhibit higher lead concentrations as compared with those located elsewhere.

These data strongly suggest that the lead distribution in the soils reflects the emission of particles from the Plumbum refinery, followed by deposition in areas close to this source. However, since the exposed residue piles have high lead concentrations, 0.7% and 2.6%, the hypothesis of re-suspension of the finer particles of this material by the wind and redistribution of the metal on the surrounding soil cannot be ruled out.

In Vila Mota and Capelinha there are no paved roads or streets so the contaminated soils and the soil dust can be significant sources of lead exposure in children (CDC 1991, Murgueytio et al. 1998, Berglund et al. 2000). In this study, it was found that the children in this area usually play outdoors, behavior that increases the possibility of lead absorption, principally due to the natural tendency of children to touch their mouths with their hands.

Table 2 – Lead concentration in soil and soil pH at various distances from the Plumbum refinery

<table>
<thead>
<tr>
<th>Number sample</th>
<th>Lead level (μg/g)</th>
<th>pH</th>
<th>Distance from Plumbum refinery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>174.6</td>
<td>6.6</td>
<td>5 km</td>
</tr>
<tr>
<td>2</td>
<td>432.4</td>
<td>6.6</td>
<td>2.5 km</td>
</tr>
<tr>
<td>3</td>
<td>342.8</td>
<td>7.9</td>
<td>1.2 km</td>
</tr>
<tr>
<td>4</td>
<td>63.0</td>
<td>6.2</td>
<td>1 km</td>
</tr>
<tr>
<td>5</td>
<td>671.6</td>
<td>6.7</td>
<td>1 km</td>
</tr>
<tr>
<td>6*</td>
<td>904.0</td>
<td>6.5</td>
<td>300 m</td>
</tr>
<tr>
<td>7</td>
<td>397.3</td>
<td>6.5</td>
<td>500 m</td>
</tr>
<tr>
<td>8</td>
<td>915.6</td>
<td>6.3</td>
<td>900 m</td>
</tr>
<tr>
<td>9*</td>
<td>801.6</td>
<td>5.5</td>
<td>900 m</td>
</tr>
<tr>
<td>10</td>
<td>75.7</td>
<td>5.0</td>
<td>1 km</td>
</tr>
<tr>
<td>11</td>
<td>117.4</td>
<td>6.7</td>
<td>1.4 km</td>
</tr>
<tr>
<td>12</td>
<td>244.6</td>
<td>5.9</td>
<td>1.5 km</td>
</tr>
<tr>
<td>13*</td>
<td>216.8</td>
<td>7.2</td>
<td>1.7 km</td>
</tr>
<tr>
<td>14*</td>
<td>292.6</td>
<td>6.3</td>
<td>1.8 km</td>
</tr>
<tr>
<td>15</td>
<td>37.4</td>
<td>5.9</td>
<td>2 km</td>
</tr>
<tr>
<td>16</td>
<td>51.6</td>
<td>5.6</td>
<td>3.5 km</td>
</tr>
<tr>
<td>17</td>
<td>75.8</td>
<td>5.9</td>
<td>3.6 km</td>
</tr>
<tr>
<td>18</td>
<td>57.9</td>
<td>5.8</td>
<td>4.5 km</td>
</tr>
<tr>
<td>19</td>
<td>21.4</td>
<td>5.6</td>
<td>6.5 km</td>
</tr>
<tr>
<td>20</td>
<td>37.4</td>
<td>5.8</td>
<td>6.0 km</td>
</tr>
<tr>
<td>21</td>
<td>26.0</td>
<td>5.5</td>
<td>9.5 km</td>
</tr>
</tbody>
</table>

* vegetable-garden
when playing. In addition to wind transport, soil particles can also enter the houses carried by adults on their clothes and shoes, and by domestic animals, as reported by authors (Rosen and Munter 1998).

Lead is persistent in soil because of its low solubility and may persist in the surface soils which function as a secondary contamination source (Kabata-Pendias and Pendias 1986). It can be concluded that local inhabitants are coexisting with poisoned soils at Vila Mota and Capelinha.

In Brazil, Casarini et al. (2001) suggested a standard reference value of 17 $\mu g$ g$^{-1}$ Pb for soil as well as an alert value of 100 $\mu g$ g$^{-1}$ Pb. These authors considered intervention values as following: residential (350 $\mu g$ g$^{-1}$ Pb), industrial (1200 $\mu g$ g$^{-1}$ Pb) and agricultural land use (200 $\mu g$ g$^{-1}$ Pb). These soil guidelines serve as references to evaluate the lead concentrations of soils found in this study.

It is known that the risk to human health is a function of both the frequency and duration of lead exposure and the socioeconomic conditions of the population involved. Taking these factors into consideration, the Upper Ribeira Valley is a very critical region because of both the long time of exposure, more than 50 years, and the unfavorable socioeconomic conditions of the population.

Conclusions

This study clearly demonstrates that certain areas of the Upper Ribeira Valley region show that the local population is exposed to significant lead contamination levels, particularly in the villages of Vila Mota and Capelinha in the vicinity of both the Plumbum refinery and the Panelas de Brejáviva mine. The metal contamination occurred over the 50 years in which the Plumbum refinery was in operation and emitted lead-bearing particulate matter into the atmosphere. Although the refinery plant was closed down in 1995, the metal deposited in the soil and the industrial residues stockpiled in the area continue to constitute a significant source through which local population, children in particular, are exposed to lead contamination.

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