



**Centro de Tecnologia Mineral  
Ministério da Ciência e Tecnologia  
Coordenação de Desenvolvimento Sustentável**

**ENVIRONMENTAL AND HEALTH ASSESSMENT IN TWO  
SMALL-SCALE GOLD MINING AREAS – BRAZIL  
SÃO CHICO AND CREPORIZINHO**

**FINAL REPORT**

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**RT2004-004-02 – Final Technical Report to UNIDO - RESERVED**

April 2004

**BRAZILIAN MINISTRY OF SCIENCE AND TECHNOLOGY  
CENTRE FOR MINERAL TECHNOLOGY – CETEM**

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Ref.: Report Requested by UNIDO, United Nations Industrial Development Organization,  
No. P. 2003/007 – EG/GLO/01/G34 – Removal of Barriers to the Introduction of Cleaner  
Artisanal Gold Mining and Extraction Technologies

April 2004

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## **Acknowledgements**

**Dr. Gildo de A. Sá Cavalcanti de Albuquerque** (*in memorian*)  
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## Executive Summary

The present report describes the results achieved in two small scale gold mining areas in the Brazilian Amazon - São Chico and Creporizinho - as part of the environmental and health assessment (E&HA) conducted by the Centre for Mineral Technology (CETEM) with the collaboration of the Evandro Chagas Institute (IEC), under the general coordination of the United Nations Industrial Development Organization (UNIDO). The E&HA is a part of the GEF/UNIDP/UNIDO Global Mercury Project - Removal of Barriers to the Introduction of Cleaner Artisanal Gold Mining and Extraction Technologies.

In order to identify sites with high concentration of mercury (hotspots) a sampling campaign of soils, sediments and biota was conducted, consisting of **647 samples**. The present report describes characteristics of environmental samples and results of mercury analyses in sediments, soils, tailings and dust from the Brazilian gold mining areas Creporizinho and São Chico. An attempt to describe the distribution of mercury and to achieve an environmental assessment of mercury pollution is presented, in order to provide a better understanding of the impacted environment.

A research team comprising 23 research scientists from CETEM (8 members) and IEC (15 members) proceeded to Itaituba, State of Para, Brazil, on 3<sup>rd</sup> of August 2003 and has accomplished the sampling campaign within 20 days.

Two two artisanal gold mining areas, São Chico and Creporizinho, have been selected for undertaking the Environmental and Health Assessment in the Artisanal Gold Mining Reserve of the State of Para, in accordance with the Project's Coordination Unit, after considering different criteria, as follows:

- Commitment of the miners with the project's objectives;
- Their association with local artisanal miners leaderships;
- Production potential and economic stability of the mining activity;
- Representativeness relative to regional standards of technologies and practices;
- Accessibility;
- Spreading potential relative to the project's achievements.

### São Chico - General Description

The São Chico mining site (06° 25'31"S and 56° 02'99"W) is just 2 km distant from a landing strip and in 5 km distance from the *Transgarimpeira* road, which during the dry season (June-September) can be used for transportation of equipments and supply from Itaituba, the main town in this region with 150,000 inhabitants. Due to the bad conditions of this road, it should be used just for transportation of goods, since the 350 km distance from Itaituba needs some 20 hours to be overcome. The São Chico village consists only of 63 houses and 134 individuals, being 41% of garimpeiros, 6% of machinery owners, 30% of dealers, 9% of cooks, among others. The only public service in the village is a health post for malaria diagnosis from the National Foundation of Health (1 health assistant).

Sao Chico Creek was dammed up forming a reservoir behind the village from which water is used for mining activities that generate mining tailings to waterways. Few families have backyards in the village, where herbs, fruits, roots, medicinal teas and creeping plants are cultivated. Primary forest was replaced by pasture in hillsides. Grassland species and some small trees occur at reservoir's banks.

From the beginning of the very first gold mining activity in 1963, the São Chico village has shown two main periods of prosperity, one in the end of the 80's after the opening of the *Transgarimpeira* road, and other in the end of the 90's, when gold rich primary deposits were discovered. According to cross-checked estimations, about three tons of gold were produced from the beginning of the gold rush, corresponding to an estimated mercury emission of 7.5 tonnes to the environment. Since the primary gold ore has been crushed in hammer mills and directly amalgamated in copper plates, and no retorts have been used, the estimated Hg: Au (lost:produced) emission ratio is about 2.5 for this type of operation.

Nowadays, exploitation of primary gold ore is over, being gold production in São Chico almost restricted to the reprocessing of tailings produced during the 80's, when alluvial and laterite deposits (*baixões*) were worked using just sluice box for gravity concentration, without crushing. Tailings are now being concentrated through sluice boxes while the concentrate follows the same processing circuit as for the former primary ore, while mercury is widely used in both mineral processing steps, gravity concentration and amalgamation.

### **Creporizinho –General Description**

Creporizinho (S 06° 50' 14,1" – W 56° 35' 00,0") is a typical gold mining village with 238 wooden residences for an estimated population of 1000 inhabitants. There are grocery shops, pharmacies and a hotel. Two hundred children go to a primary school, where 5 teachers are working. Few families have backyards in the village, where herbs, fruits, roots, medicinal teas and creeping plants are cultivated.

In Creporizinho, located at km 145 on the *Transgarimpeira*, the Tolentino mining area is located 10 km NNW from the village and represents 3 different types of small scale gold mining activities: inactive alluvial deposits (including rework of former tailings and residues) – explored by hydraulic monitor (*garimpo de baixão*), lateritic deposits – explored through open pit and primary deposits – explored through open pit or shaft (*garimpo de filão*). Samples were taken in and around this area, in the village, as well as in the drainage basins nearby and remote, including samples from Crepori River, Creporizinho River and waterbodies in abandoned open pits.

The study sites in Creporizinho are ca. of 10 to 15 km far from the village. Creporizinho stream flows nearby the village and is used for water supply water to mining activities. Overbank deposits are common along its banks. There are many flooded open pits, drains of mining tailings forming small streams along mining sites. Also herbs sprout up over mining tailings and wastes, and pastures also replace primary forest, but forest fragments still remain in some places. Old flooded open pits have macrophytes growing in water.

At Crepori River mining activities have been performed with dredges and hydraulic jets at riversides. The low-water season exposes alluvial pits originated from dredge activities during high-water season.

Since 1999 novel operations have been introduced in the Tolentino area (S 06° 47' 46,9" – W 56° 36' 27,0"), considering they have reached a sub-surface level (about 10 meters depth) with gold veins, being 2001 identified as the higher production (said to reach 6,000 kg/year). The owner of the Tolentino area established a partnership with a group of entrepreneurs who assembled a plant using mainly hammer/crusher mill, hydraulic jet pumps and centrifuge concentrators.

### Environmental assessment of the mining sites ("mining hotspots")

In order to address the identification and location of mercury hotspots a sampling campaign of soils and sediments was performed. Amalgamation tailings dumped into drainage systems originate hotspots of metallic mercury (*mining hotspot*), where abnormally high concentrations are to be found in the heavy fraction of sediments. Due to its typical heterogeneous distribution, one may face enormous difficulties in locating mining hotspots of mercury in a given mining site, as conventional geochemical exploration techniques have been used unsuccessfully.

Simple sampling methods, consisting of pan concentrates for mercury analysis were also used for locating mining hotspots. Another strategy, consisting of a sociological approach, enables the reconstruction of the local mining history and the identification of amalgamation tailings, through establishing a relationship of confidence among miners and researchers.

The "Geoaccumulation Index" (Igeo) of mercury in bottom sediments has been selected for quantitative evaluation of contamination levels in aquatic systems (Müller, 1979). Since the enrichment process of metals in sediments, caused by a given emission, generally follows an exponential accumulation in fine fractions, the "Igeo" uses a log function for classifying distinct order of magnitude of contamination, as follows:

$$I_{geo} = \log_2 C_n / 1.5 \cdot B_n \quad \text{where,}$$

$C_n$  is the measured Hg concentration in the fraction -200 # and  $B_n$  is the *background* Hg concentration. Moreover, the Igeo is divided into 7 classes, from 0 to 6, being class 0 indicative of null contamination while class 6 represents an extreme contamination.

### São Chico

An open pit, comprising an area of about 60.000 m<sup>2</sup>, located at the northern slope of the valley in São Chico, represents a typical primary gold-ore deposit, as it is recently observed in the Tapajós Gold Mining Reserve. Superficial lateritic soils got removed in the range of 2 to 10 meters in order to provide access to gold-bearing quartz-veins. Hammer mills and Hg coated copper plates were placed and constructed in situ. At the eastern margin a very crude cyanidation plant was constructed, operating from 1999 to 2001. Amalgamation tailings and other wastes were poured into São Chico reservoir during this period of time. In general, material comprise silt and sand, as a result of mineral processing of lateritic soils and weathered rock, mainly of red and yellow colour, originated from Fe-, Mn-, and Al-oxides and -hydroxides.

In the immediate vicinity of São Chico village, 2 km downstream, some "virgin" areas without any recent and past mining activities were encountered – well suitable for determination of natural background of mercury in sediments and soil. A sediment core,

divided into 6 sections, was taken in the bed of the small clear water bearing brook in the forest area, where no former mining activity have been taken place.

The sediment core was 30 cm deep and revealed that Hg levels decreases with depth. The lowest background values of the -200# fraction ( $< 74 \mu\text{m}$ ) was around  $0.15 \mu\text{g/g}$  in the lowest 15 cm, corresponding to an Igeo class 0, and up to  $0.84 \mu\text{g/g}$  at the surface, or Igeo class 2. This is probably a result of the contribution from atmospheric Hg released from anthropogenic sources. It has been assumed that the lowest section of the core represents the Hg background level of this region (around  $0.15 \mu\text{g/g}$ ), since this procedure has been successfully adopted elsewhere (Rodrigues-Filho et al, 2002; Rodrigues-Filho and Maddock, 1997).

Mineralogy of fine sediment fractions in tropical waterways, draining lateritic terrains, present a general composition of secondary minerals like kaolinite, gibbsite and Fe hydroxides, and quartz. Significant variations on mineralogy are to be found in the heavy fraction of sediments rather than in the more mobile, fine fractions.

Between reservoir and village, the valley floor is covered by mining tailings, extending through an area of approximately  $50.000 \text{ m}^2$  with an average thickness of 5 meters, originated from prior alluvial processing and former mining activities in primary ore veins from magmatic, partially weathered rocks. This tailings pile has been deposited during a period of some 40 years.

A total of 38 composite samples of tailings from this part of the mining area were taken. Following a typical heterogeneous distribution in tailings, Hg levels in this site confirm the occurrence of a mining hotspot, reaching concentrations of up to  $300 \mu\text{g/g}$ , whereas 34% of the samples present an Igeo class 6, corresponding to Hg concentrations higher than  $7.5 \mu\text{g/g}$  in the -200# fraction, and averaging an Igeo class 4.

São Chico Creek flows into Conrado River, 2 km downstream from the village, where its water gets mixed with drainages from other mining sites, showing high turbidity. The entire region is drained by the Conrado River, Novo River (15 km from the village) and Jamanxin River (20 km from the village).

São Chico Creek was dammed up in 1989 at the end of a narrow valley, located around São Chico village forming a reservoir for supplying the mining site with water to carry out mining activities. Water covers an area of approximately 50 to 150 m width to 700 m length ( $85,000 \text{ m}^2$  surface) with an overall depth of less than 5 meters only. Outflow from this reservoir (during dry season) amounts to less than 5 liters/second.

Since 1989, tailings from both amalgamation and cyanidation activities have been poured into the reservoir. Due to lack of stream and turbulence nearly all of this material, in particular suspended load, entering the reservoir could settle down and accumulate. A very small outflow with nearly clear water feeds the São Chico creek, which drains the entire mining site and flows through Conrado River, Novo River and Jamanxim into the Tapajós River.

A total of 17 composite samples composed of tailings mixed with sediments - including settled suspended solids - were taken from reservoir bottom and margins. In general, sediments comprise sand and silt, covered with a thin layer ( $< 5 \text{ mm}$ ) of clay or suspended load and abundant organic matter. Close to amalgamation wastes and to a former cyanidation plant Hg levels in sediments reach Igeo classes 5 and 6 (47% of the samples), corresponding to Hg concentrations higher than  $7.5 \mu\text{g/g}$  in the -200# fraction, while for samples collected in other parts of the reservoir concentrations decrease to Igeo classes from 3 to 4 (53% of the samples).

Considering that these samples were composed of organic-rich clayey sediments, not directly originated from amalgamation wastes, these values indicate that São Chico reservoir represents both a *mining hotspot*, due to its proximity to amalgamation wastes, and an *environmental hotspot*, as the distribution of Hg throughout the reservoir's bottom is relatively homogeneous.

Although a less intense activity of amalgam roasting could be observed in the São Chico village during the sampling campaign - presently just one gold shop is in operation - dust and soil are sought to be efficient indicators of atmospheric Hg contamination. The maximum Hg concentration (1,280 µg/g) was observed in a sample of spider web collected inside the gold shop of the village, where no exhausting system exists. The others samples, composed of dust, have been collected inside houses of its immediate neighborhood. Since all of them present extremely high Hg levels, being the lowest one 20 µg/g, this suggests the need of urgent measures towards the protection of the population living in this village.

### **Creporizinho**

The mining sites of Papagaio and Areal are located circa of 15 kilometres in southeastern direction from Creporizinho village, where alluvial gold has been explored, and from the middle of the 90's exploration of primary started. Nowadays, alluvial mining is very rare, being mining of lateritic soil, primary ore and reworking of tailings common all over the area.

A total of 30 composite samples composed of tailings mixed with sediments and soils from this part of the mining area were collected. Except 12 samples of amalgamation wastes (A510 to A518 in Papagaio and A521, A522 and A531 in Areal), which fall in the Hg Igeo class 6, the general distribution of Hg throughout both Creporizinho mining sites indicates an expressive lower level of Hg contamination, comparing with the ones from São Chico.

The mining sites Tabocal and Bofe present a similar picture in terms of mineral processing techniques and waste disposal as in Papagaio. A total of 16 samples of tailings and sediments were collected. Nevertheless, Hg levels in sediments and tailings are significantly lower than in Papagaio, indicating either less intense Hg losses or a lower mobility of Hg from a given mining hotspot, resulting in Igeo classes close to the background, except for 3 samples reaching the Igeo class 4, revealing a low degree of Hg contamination in inorganic samples.

Tolentino mining site is located circa 5 km in southeastern direction from Creporizinho village, on the way to Papagaio. This is the only garimpo visited in Creporizinho area that works with "modern" equipment, like ball mills and centrifuges. The majority of processed material comes from primary ore deposits, extracted from gold-bearing quartz veins in magmatic rocks in the nearby surroundings and transported by trucks to the processing unit, while amalgamation is applied to gravity concentrates. Only a smaller part of the gold production comes from secondary material, both, lateritic soils and tailings, resulting from former mining activities in the entire area.

A total of 12 composite samples of sediments mixed with tailings from this site were collected. Although one single sample reaches Igeo class 6, the whole data set, averaging an Igeo class 2, indicates that Hg contamination is less significant than in other areas considered in this study.

### **Evaluate the nature and extent of the mercury pollution in agricultural produce, especially in those being part of the main diet**

At São Chico mining sites 27 samples of herbs and vegetable foodstuffs were collected close to mining tailings and backyards of the village. No aquatic plants could be found in flooded open pits, neither in the lake at São Chico mining site. At Creporizinho mining sites 29 samples of herbs, macrophytes and vegetable foodstuffs were collected in the village and close to the mining sites.

Total mercury values for soil samples at São Chico study area are significantly higher than background value - 0.15 µg/g - for this area. Although mean values in soils samples from São Chico (1.7 µg/g) are higher than soils samples from Creporizinho (0.99 µg/g), no significant differences between them at  $\alpha < 0.05$  were obtained.

Data on produces and wild plants were combined with aboveground and root plant parts for both study areas to compare mean total mercury concentrations. Only aboveground of produces samples from the São Chico mining site presents significantly higher values for mercury levels than samples from Creporizinho area (mean of 2.55 µg/g *vs.* 0.12 µg/g). Since Hg concentrations are much higher in aboveground parts of vegetable produces at São Chico study area than in Creporizinho, the uptake in produce plants is likely to occur through atmospheric deposition, as a result of amalgam burning. This makes the vegetables produced in backyards of the village, particularly leaves, a further potential pathway of Hg exposure to the population, besides fish consumption and inhalation of Hg vapour.

The present results also indicate that mercury concentrations in wild plants parts from Creporizinho study area increased with mercury concentrations in soil. Apparently, they function as a excluder, restricting transport of metal upwards to aerial parts. Since Hg concentrations are much higher in aboveground of produces at São Chico study area than in Creporizinho, the uptake in produce plants is likely to occur through atmospheric deposition, but further studies with a larger sample set are necessary to confirm this hypothesis.

In foodstuffs other than fish mercury exists mainly in inorganic form, while the gastrointestinal absorption is close to 7%. The average total contents of mercury in edible parts (leaves and stems of cabbage and chive, pulp of cassava and “cara” roots, and pulp of cashew fruit) were  $0.21 \pm 0.26$  µg/g w wt (n = 13) for São Chico, and  $0.01 \pm 0.01$  µg/g w wt (n = 7) for Creporizinho. We estimate the average dietary daily intake of vegetables and roots close to 100 g, for an adult with 70 kg. Considering 0.3mg the provisional tolerable mercury intake per person weekly (PTWI), the ingestion of total mercury from those foodstuffs falls close to the PTWI in São Chico area, whereas in Creporizinho area the estimated Hg ingestion falls in a range much lower than the PTWI. However, it should be taken into account the small gastrointestinal absorption of inorganic mercury, which results in 0.017 mg/week for São Chico and 0.0007 mg/week for Creporizinho.

The translocation of mercury from soil through roots to aboveground in produce plants was not significant in both studies areas.

### **Nature and extent of mercury pollution in the river system adjacent to the hot spot area**

Sampling and analysis of total suspended solids (TSS) and bioindicators in aquatic systems play a pivotal role in assessing mercury mobility and the nature of pollution. Mercury transported onto suspended particles may be deposited in riverside deposits forming mercury

sinks, which are potential sources for mercury remobilization, since mercury is adsorbed onto fine particles and prone to form soluble complexes, mainly in the presence of humic substances.

Since metallic mercury can be transported downstream onto particulate matter, it is assumed that mercury can be oxidized and promptly form soluble complexes in the presence of organic substances. Therefore, the accumulation of these organic-rich sediments receiving loads of soluble-mercury complexes may account for an *environmental hotspot*, since mercury bioavailability increases. High contents of organic matter in sediments have been sought during sampling.

Since sampling of TSS by filtering through 0.45  $\mu\text{m}$  membranes has been reported as controversial, due to its inefficiency of recovering enough material for analysis, it was sought naturally settled TSS samples where favorable hydrodynamic conditions were to be found.

### **São Chico**

According to the present results, the estimate of 7.5 tonnes of mercury released into the environment in São Chico is consistent. High mercury levels were found not only near amalgamation tailings, which are mining hotspots with up to 300  $\mu\text{g/g}$  of Hg, but also associated with suspended solids inside the reservoir and up to at least 20 km downstream, as indicated by the high Hg levels averaging an Igeo class 4 along the São Chico Creek, and further up to the mouth of the Novo River into the Jamanxin River, where Hg levels reach Igeo classes from 4 to 6. This is an indication that the mercury load released in São Chico is becoming mobile and prone for transportation onto suspended particles downstream.

A likely explanation for this particular mercury behaviour in São Chico, associated with suspended particles, is due to the introduction in 2001 of cyanidation by heap leaching from amalgamation tailings, which was undertaken at the margin of the dam reservoir situated upstream of the main mining site in São Chico, the so-called *Montanha*. Therefore, the formation of cyanide-mercury complexes into the reservoir is likely to be responsible for increasing mercury mobility downstream. This type of chemical treatment is being prepared to be undertaken once more through the storage of amalgamation tailings.

Similarly, another important factor contributing to Hg mobilization in São Chico is likely to be related to fires yearly practiced for cleaning up pasture throughout the study area, as it could be observed during the sampling campaign, when the surrounding pasture, very close to the reservoir and tailings, has been burned three days long. The sudden elevation of the soil temperature is likely to be very effective in releasing Hg from mining hotspots in soils to the atmosphere, thus enhancing its mobility. The extension of the area impacted by pasture fires is also visible from the satellite image in detailed scale of São Chico mining site.

The cyanidation attempt of amalgamation tailings together with the physical and chemical features of the dam reservoir, a semi-closed aquatic system with high organic contents in sediments and anoxic conditions in the bottom, make this environment a promising field opportunity for a better understanding of the behavior of mercury in aquatic systems in the presence of cyanide, and surrounded by pasture fires. Therefore, a more detailed investigation in the São Chico reservoir is enthusiastically recommended.

The physiochemical parameters in the water column of the São Chico reservoir are consistent with usual water parameters of Amazonian rivers, and fall in the range of near-neutral pH and low electrical conductivity (low salinity). Lower values of dissolved oxygen are due to anoxic conditions in the bottom of the reservoir. Those physiochemical conditions are

favourable to the stability of elemental mercury. Thus, one may realize that further factors are likely being responsible for Hg mobility in this aquatic system, such as biochemical processes through microbiological activity and/or anthropogenic ones, among which the cyanidation attempt and pasture fires are to be highlighted.

Veiga et al. (1994) indicated the significant role that deforestation plays among the most important emission sources of Hg in tropical countries, where forest fires are contributing to increase Hg emissions worldwide through the release of Hg baselevels present in biomass.

Further downstream, a total of 15 composite sediment samples were collected from the Conrado River, Novo River and Jamanxin River, in order to evaluate to which extension the Hg load released from São Chico is influencing the sediment chemical composition. In general, sediments comprise a thin layer of settled suspended load and organic matter covering riverine deposits in overbanks and riversides.

Since the main contribution in terms of Hg emissions to the Novo River comes from the São Chico region, showing its high turbidity, one may realize that due to its indicated association onto suspended particles, Hg released from São Chico is prone to be transported downstream up to a distance at least as long as 20 km. However, a further in-depth study is required to verify this indication.

A general distribution of Igeo classes of Hg in sediments, tailings and soils throughout the whole São Chico area is presented in a satellite image of the study area. It is to be highlighted the occurrence of significantly high Hg levels associated with fine sediments (< 200# fraction) up to 20 km downstream from the São Chico mining area, where 5 of 15 samples fall in the range of Igeo classes 3 to 6.

### **Creporizinho**

The most downstream area along the Crepori River, close to the mouth of the Creporizinho River, which drains the mining sites considered in this study lies circa of 40 km from the mining sites. Although among 11 samples there are significant indications of Hg contamination in fine sediments, pointing that Hg is being transported onto suspended particles downstream, one may face in this case severe difficulty in tracing the source of Hg. This difficulty is due to the existence of several mining operations throughout the Crepori river basin.

On the other hand, the highest values of Igeo classes – averaging class 5 - are represented by samples collected in the Creporizinho River that drains the mining sites considered in this study. This is an indication of Hg contamination whose source is related to mining activities located 40 km upstream, but further studies are required to confirm this hypothesis.

Additionally, the so-called Porto Alegre site and the mouth of a clear stream to the Crepori River are located upstream of the investigated mining areas, but downstream of other existing mining sites along the Crepori River. There, a less intense Hg contamination in inorganic samples is to be reported for the Crepori River, where Igeo classes of Hg range from 0 to 4, being predominant values close to the background, with Igeo classes from 0 to 1.

### **Mercury in Fish**

Fish sampling was conducted in August 2003, at São Chico and Creporizinho mining sites, where the mining activities are distributed along the tributaries of the Tapajós River. These

two areas belong to two distinct hydrographic basins: Jamanxin river basin and Crepori river basin, respectively.

It was investigated the mercury levels in fish from 11 sites: 4 in São Chico and 7 in Creporizinho. A total of **234 fish** specimens of 16 species were collected: 73 specimens belonging to 13 species in São Chico and 161 specimens of 11 species in Creporizinho. A total of 9 common species could be collected in both areas (acari, cará, curimatã, lambari, mandi, piau, piranha and traíra).

It is well known that freshwater biota is able to accumulate Hg from natural and anthropogenic sources. Maximum background levels for Hg in uncontaminated freshwater fish are in the range of 0.1 to 0.3  $\mu\text{g/g}$ , although considerably higher levels can be found in large predators. The mean concentration of Hg (1.04 $\mu\text{g/g}$ ) in fish species from this work was similar to those observed in other contaminated Amazonian rivers (Lacerda & Solomons, 1991; Akagi et al, 1994, Malm et al., 1996; Bidone et al., 1997; Castilhos et al., 1998).

However, São Chico area has shown Hg levels in fish that are considered abnormally high (2.53 $\mu\text{g/g} \pm 3.91$ ; n=73), compared with results from previous studies. In Creporizinho area (n=161), mercury levels in fish resulted in 0.36 $\pm$ 0.33 $\mu\text{g/g}$ . Additionally, the results show that the minimum values for Hg in fish are similar between areas (0.027 $\mu\text{g/g}$  and 0.025 $\mu\text{g/g}$ ), whereas the maximum values are one order of magnitude higher in São Chico (21.90 $\mu\text{g/g}$ ) than in Creporizinho area (2.10 $\mu\text{g/g}$ ). Among the analyzed fish in both areas, 82 specimens (35% of the total) from 6 species (37,5% of the total) presented Hg concentrations above 0.5  $\mu\text{g/g}$ , the Hg concentration in fish recommended by WHO (1990). Whereas in Creporizinho 22% of fish samples showed Hg levels above that limit, in São Chico this percentage increases to more than 60%. This is a further indication that *mining hotspots* in São Chico are becoming *environmental hotspots*, strengthening the results and conclusions obtained in the geochemical survey.

Additionally, the results show that the minimum values for Hg in fish are similar between areas, whereas the maximum values are one order of magnitude higher in São Chico than in Creporizinho area.

Comparisons with global means of Hg in fish, however, may result in a certain misinterpretation, since observations on given species of marine and freshwater fish indicate that Hg concentrations in fish tissue increase with increasing age, as inferred from length (WHO, 1990); it is also strongly affected by fish species and size (length and weight) and, in addition, it is generally agreed that Hg concentrations in carnivorous fish are higher than in non-carnivorous species (e.g., Watras and Huckabee 1994), due to the indirect Hg bioaccumulation or biomagnification. It was investigated a relationship between fish length and Hg levels, by correlation analysis with log-transformed and non-transformed data and, also, by using the mean values of the length intervals. The objective was to assess the Hg contamination in those sites and to find an indicator of Hg bioavailability by using fish species.

The present results show that fish from São Chico are more contaminated, heavier and larger than those from Creporizinho area. However, no correlation was found between fish Hg concentration and weight or length when analyzing all specimens in both areas. Comparing mercury levels in fish from each site within each study area (São Chico and Creporizinho) the results showed that fish from the São Chico Reservoir present the highest mercury levels in São Chico and are smaller than fish from the other sites.

In order to assess the Hg biomagnification processes in the ichthyofauna of the study areas, data were worked out whereby distinct food habits and their correspondent Hg concentrations were taken into account and analyzed. The fish were classified as carnivorous (arraia, bocudo, lambari, piranha, pirarara, surubim e traíra) and noncarnivorous. The non-carnivorous fish species were classified into (i) detritivorous (acari and curimatã); (ii) herbivorous (pacu and piau), (iii) insectivorous (ituí), (iv) macrophagous (sairu), (v) microphagous (cará) and omnivorous (candiru and mandi). As expected, carnivorous species showed higher Hg concentrations than in non-carnivorous species for total data and for both studied areas.

In São Chico area, the Hg levels in carnivorous species are higher than in detritivorous. When this analysis is performed considering only noncarnivorous, the microfagous species are different of the herbivorous, detritivorous and insectivorous species. In Creporizinho, the species of detritivorous, herbivorous and macrofagous showed different Hg levels of the carnivorous, microfagous and omnivorous ones, being macrofagous species different of detritivorous ones. This results is very interesting and one could suggest that mercury transfer in the trophic chain in those studied areas could be distinct, since in Creporizinho, omnivorous showed higher Hg levels than carnivorous.

In Creporizinho area, fish from the site A8 showed higher Hg levels than all the other sites (A5, A6, A7, A9, A10 and A11), and the specimens are also smaller than fish from the most of the other sites (A6, A9, A10 and A11). However, significant positive correlation between Hg in muscles and length were found in sites A6, A7 and A9, and a negative correlation in A11, whereas no significant correlation was found for A2 nor to A8.

Carás and Traíras from São Chico have higher mercury levels than the ones from Creporizinho, whereas others species (Piranha, Acari, Curimatã, Piau and Mandi) did not show any difference between areas. The ratio of total mercury levels in Traíras and Carás from several sites of two study area ranged from about 2 to 4, meaning that the carnivorous specie accumulates Hg from 2 to 4 times more than noncarnivorous species. In addition, the results showed that Hg levels only in Traíras from A2 are higher than Traíras from the other sites, which are similar one each other. Mercury levels in Carás from A1 and A2 are higher than Carás from A5, A6, and A8. Mercury levels in Carás from A5 and A6 are similar each other and lower than levels in Carás from A8.

A toxicological approach has been used for the risk assessment to human health. Hazard Quotient (HQ) results show for all study sites values above one, from 1.5 to 28.5, except for A11, which is considered a reference area. The São Chico reservoir (A2) showed the higher values of HQ, followed by A1, A4, and A3. In Creporizinho area, the HQ values are close to 2 for all sites, except in A8, where the HQ attained 3.3.

It should be stressed that the present modeling is an evaluation tool, and therefore its uncertainty should be taken into account for interpretation of results and conclusions. From the present results, however, one could indicate that possibly in all sites, except in A11, and depending on their dietary habits, populations are subject to potential hazards and health effects due to fish consumption, being site A2 the most evident case of mercury pollution. Therefore, further in-depth studies on Hg bioavailability are highly recommended for the overall study area, while an awareness campaign should address to the local population the risk of consuming fish from the site A2.

According to the correlation analyses, there is correlation between Hg and length and/or weight, in Creporizinho area, with Curimatã and Piranha' species, and in São Chico area, the species Curimatã and Ituí showed positive and significant correlation between Hg and length. The other species, including Traíra species, did not show any correlation in both areas. Considering specific species collected from different sites, Curimatã from A1 and Acari from A9 showed significant correlation between Hg and length and Piranha from A11 showed significant correlation between Hg and weight.

Although Traíras and Carás did not show any correlation between mercury levels and length or weight when total data were analyzed in São Chico and/or Creporizinho and, even, when data from each site was considered, we decided to investigate the correspondence between log of length and log of mercury levels in muscles, as advised by the UNIDO Protocol. We have chosen these species because they are distributed throughout the studied aquatic systems, have different food habits and the number of specimens collected is large enough. The data analyzed showed very low correlation between parameters for all Traíras from São Chico and Creporizinho, as well as for Traíras from different sites. Carás also did not show any correlation in São Chico and Creporizinho, neither in sites of those areas. Other species, like as Sairu from Creporizinho, A5, A6, A7; Piau from A11 and Piranha from A11 did not show any correlation. The results showed strong positive correlation between log length and log mercury levels only for Curimatã from A1 (São Chico area), Acari and Piranhas from A9 (Creporizinho area), showing the same tendency found with non-transformed data.

Considering the low correlation coefficient resulting from analysis of log transformed data for most part of species studied, we decided to investigate the correspondence between length intervals and the average mercury levels in fish muscles, trying to decrease the high variability in data, considering, firstly, data not log transformed and, secondly, log transformed data. The linear equation for Traíras from A2 with log transformed data shows a positive and significant correlation. It is very interesting result, but it should be considered that changes in length intervals could change this linear relationship. However, considering the present results, one could suggest that Traíras can be used as indicator organism for mercury contamination, at least in Amazonian contaminated sites.

Although Traira does not show good correlation between Hg and length, it should be used as a Hg bioindicator for the following reasons: It shows the fairly highest Hg levels; it has the most widespread distribution in tropical drainages; in contrast to other species it is easily adapted to adverse conditions in impacted areas and, it is appreciated for eating. Although the indication of absence of correlation shows that this species do not fit well with the modelling proposed in the Protocol, this has a potential negative effect in the human population (easy to catch and appreciated as food). In addition, Piranhas, Curimatã and Acari are also good indicators for specific sites, suggesting that, in order to find an indicator of Hg contamination, a search for a site-specific fish species, with more than one species for different sites, could bring better results.

The relationship between Hg levels in fish and Hg in sediments can be used as an indicative of bioavailability of Hg in aquatic system. In order to investigate this availability, we performed the ratio between Hg levels in fish and Igeo classes of Hg in sediments. Traíra and Piranha (carnivorous species) and Cará and Curimatã (non carnivorous species) were chosen because they were collected in São Chico and Creporizinho areas and represent different food habits. All sites showed this ratio below 0.5 considering all species, except A2 and A7 for Traíra,

which resulted in 1.5 and 1.8, respectively. The results suggest that A2 and A7 showed higher mercury bioavailability than the other sites.

In order to assess the potential ecological effects in Amazonian fish from aquatic systems influenced by gold mining, Hg in tissue and its hematological and biochemical responses were measured in each fish specimen. The results of total Hg in fish muscles and fish blood and biochemical parameters were used as effects biomarkers in ecological risk assessment. It was investigated biochemical parameters as enzyme activities, such as amino-alanina transferase-ALT; amino- spartate transferase-AST; creatina kinase and creatinine, and hematological parameters, such as hematocrit, hemoglobin, erythrocytes and total leukocyte count; trombocytes-leukocytes count in blood of fish from São Chico and Creporizinho.

A total of 42 fish specimens of those species (Carás and Traíras) were collected: 27 specimens in São Chico (18 Carás and 9 Traíras) and 15 specimens in Creporizinho (11 Carás and 4 Traíras).

All biochemical parameters measured in the present work did not show any difference between both areas, probably as a result of the low number of specimens, which did not permit performing the correlation analysis. In addition, those biochemical parameters could not be sensible as mercury biomarkers. However, the data are important because they can be used as biochemical reference values for Amazonian fish, considered as rare data.

Traíras and Carás from Creporizinho showed higher globular volume and erythrocytes number and/or mean globular volume than the ones from São Chico. Mercury levels and globular volume showed significant negative correlation for both species, suggesting that mercury levels may cause decrease in number of erythrocytes, which are smaller than normal ones and are characteristic of regenerative anemia.

## 1. Introduction

The present report describes the results achieved in two small scale gold mining areas in the Brazilian Amazon - São Chico and Creporizinho - as part of the environmental and health assessment (E&HA) conducted by the Centre for Mineral Technology (CETEM) with the collaboration of the Evandro Chagas Institute (IEC), under the general coordination of the United Nations Industrial Development Organization (UNIDO).

In order to identify sites with high concentration of mercury (hotspots) a sampling campaign of water, soils, sediments and biota was conducted, consisting of **658 samples**. The present report describes characteristics of environmental samples and results of mercury analyses in samples from the Brazilian gold mining areas Creporizinho and São Chico. An attempt to describe the distribution of mercury and to achieve an environmental assessment of mercury pollution is presented, in order to provide a better understanding of the impacted environment.

A research team comprising 23 research scientists from CETEM (8 members) and IEC (15 members) proceeded to Itaituba, State of Para, Brazil, on 3<sup>rd</sup> of August 2003. On the same day, a meeting has been organized by the Local Association of Miners (AMOT) with CETEM's team, the Municipal Secretaries of Environment and Health (SEMMA and SEMS), and a representative of the State Secretary of Science, Technology and Environment (SECTAM), since the local authorities required a comprehensive explanation about the activities to be performed during the field work of the Environmental and Health Assessment for the Global Mercury Project (GMP).

The following benefits should be seen as a voluntary contribution from UNIDO, CETEM and IEC to the mining community of Itaituba through this E&HA work, in addition to the project objectives themselves:

- Gratuitous medical assistance including diagnosis, treatment recommendation and medicines for the whole mining communities of São Chico and Creporizinho, encompassing 700 people;
- Restoration of a local laboratory in Itaituba for implementing an innovative semi-quantitative method for mercury analysis in fish samples, including training of 5 technicians from the local Secretaries (SEMS, SEMMA and SECTAM) during two weeks;
- Improvements on the installations of both schools, in São Chico and Creporizinho, which served as field laboratories for CETEM's team.

The Global Mercury Project, funded by GEF and co-funded by UNDP and UNIDO, is complemented by a suite of ongoing activities that are financed either through the participating countries' resources and/or bilateral programs. The main goals of the GMP are (Veiga and Baker, 2003):

- Reduce mercury pollution caused by artisanal miners on international waters;
- Introduce cleaner technologies for gold extraction and train miners;
- Develop capacity and regulatory mechanisms within local governments that will enable the sector to minimize mercury pollution;
- Introduce environmental and health monitoring programs;

- Build capacity in local laboratories to assess the extent and impact of mercury pollution.

The monitoring component of the Global Mercury Project (GMP) has specific goals described in the Objective 3 of the project proposal: “*identify hotspots in project demonstration sites, conduct geochemical and toxicological studies and other field investigations in order to assess the extent of environmental (mercury) pollution in surrounding water bodies and devise intervention measures*”.

Small-scale or artisanal gold mining is an essential activity in many developing countries as it provides an important source of livelihood, particularly in rural regions where economic alternatives are critically limited. Artisanal mining encompasses small, medium, informal, legal and illegal miners who use rudimentary processes to extract more than 30 different mineral substances worldwide. Artisanal mining activities are not necessarily limited to small-scale mining activities. When a large number of individuals excavate a single site, the resulting pit diameter can be as large as 2 km. This is the case of Serra Pelada, an infamous ASM site in the Brazilian Amazon where, during the 1980's, more than 80,000 miners gathered to manually extract about 90 tonnes of gold from the same open pit. The International Labour Organization (ILO, 1999) estimates that the number of artisanal miners is currently around 13 million in 55 countries and rising, which suggests that 80 to 100 million people worldwide depend on this activity for their livelihood. Gold is easy to transport across borders and easily sold, and is by far the main metal being extracted. Worldwide it is estimated that more than 2.5 million women and 250,000 children are directly employed in artisanal mining (Hinton *et al*, 2003).

Although the use of mercury in mineral processing is illegal in most countries, mercury amalgamation is the preferred method employed by ASM. When used correctly, mercury is an effective, simple and very inexpensive reagent to extract gold (e.g., 1kg of Hg costs from 1 to 2g of Au). A variety of mining and amalgamation methods are used in artisanal mining operations and they must be primarily surveyed to establish a reliable environmental assessment (Veiga and Baker, 2003).

The extent of mercury losses from a specific site is defined by Au-Hg separation procedures; mercury often is discharged with contaminated tailings and/or volatilized into the atmosphere. Typical amalgamation methods used by ASM are listed below (Veiga and Meech, 1995):

- Whole ore is amalgamated: mercury is mixed with the whole ore in pump boxes or introduced in sluices during gravity concentration or amalgamated when copper plates are used.
- Only gravity concentrates are amalgamated: mercury is mixed with concentrates in blenders or barrels and separation of amalgam from heavy minerals is accomplished by panning in waterboxes, in pools or at creek margins.

Many miners are nowadays amalgamating only gravity concentrates. This is an important improvement in artisanal mining methods, resulting in significant decreases in Hg consumption and emissions. Using this method approximately 14 grams of mercury is required to amalgamate 1 kg of concentrate (ratio Hg:Concentrate » 1:70). Amalgamation is efficient for particles coarser than 200 # (0.074 mm) and for liberated or partially liberated gold (Wenqian & Poling, 1983).

Although artisanal mining has shown some positive contributions worldwide, it has also suffered negative conceptualization as a misnomer to mineral sector development by host Governments. Whereas some countries choose to ignore the existence of such activities, others

lack adequate legal frameworks to regulate them. As a result, the activities are carried out illegally thus denying the host Governments the badly needed revenues (Beinhoff, 2002).

The increasing societal demand for actions and strategies towards sustainability of small-scale gold mining in developing countries has led experts to face the challenge of managing the hazards associated with mercury contamination from active and abandoned mine sites. Mercury contamination in drainage systems and its health effects are the most frequent subjects on environmental researchs dealing with small-scale gold mining worldwide. Also, filling of river beds with mineral matter originated from runoff of abandoned mining waste piles and tailings generally causes both silting of waterways and elevation of Hg concentrations in the environment.

From the end of the 80's onwards the extraction of gold in rain forest areas and wetlands worldwide, in the form of SSGM operations, are receiving increased attention from scientists and public planners. Moreover, the formidable impacts caused by mercury usage in industrial activities, be it in chemical factories or energy production, as it is inherent in coals used in thermal power plants, and in agriculture as part of herbicides compounds are well documented in the literature. As well teeth amalgams are an old concern, recently revived in the scientific literature (Villas-Bôas, 2001).

Inhalation of mercury vapor is the primary exposure pathway to miners, gold shop workers and people living near areas where mercury is handled. High methylmercury concentrations in fish in waterways contaminated by mercury released from mining sites is the main means of exposure to local residents in rural communities. Because fish are plentiful and inexpensive fish are the main protein source for community residents, but can also result in consumption of greater amounts of methylmercury than health authorities advise (Veiga and Baker, 2003).

Biota is the ultimate indicator of bioavailability of any form of Hg. Mercury, particularly MeHg, is highly biomagnified in the food web and reaches its highest concentrations in fish, especially fish-eating, carnivorous fish. Mercury concentration in fish is usually expressed on a wet weight basis as parts per million (ppm) which is equivalent to mg/kg or µg/g. The natural background in fish has been estimated to be between 0.05 to 0.3 ppm Hg and may be less than 0.01 ppm Hg in small, short-lived herbivorous species (Suckcharoen *et al*, 1978).

By employing toxicological methods for the risk assessment to human health, significance of the contamination can be ascertained. At a screening level, a Hazard Quotient (HQ) approach (USEPA, 1989), assumes that there is a level of exposure (i.e., RfD = Reference of Dose) for non-carcinogenic substances, like mercury, below which it is unlikely for even sensitive populations to experience adverse health effects.

There are three physiological responses regarding the translocation of metals to aboveground plant tissues. The excluder response, where aboveground tissues concentrations are low until a critical soil concentration is reached, and an unrestricted transport occur with toxicity results. The indicator response, when tissues and environmental concentrations are proportional, with a passively regulated transport and uptake. The accumulator response, when metal is actively accumulated through a highly specialized physiology (e.g. hyperaccumulators species). Shoot : root ratios could be a measure of the degree of metal transport, a higher amount of metal in above-ground than in roots could indicate an no restricted metal uptake (Windham *et al*, 2003).

Assimilation through plants plays a major role in the entry of mercury into terrestrial food chain (WHO, 1990). The assimilation of mercury by plants does not depend only on its concentration in soil, but also on the ratio of soil and air mercury contamination, on biochemical conditions of soil and on meteorological conditions. The assimilation from the soil by roots depends on soil type, content of humic acid, microbiological activity, pH, and redox potential. The assimilation through leaves depends on type of plant, air contamination and atmospheric aerosol deposition (Vecera et al., 1999). Bryophytes and lichens without any roots, assimilate mercury only from air and water and can be used as active biomonitors (Fernández et al., 2002). Further studies show that certain plant species, such as carrots, lettuce and mushrooms in particular, are likely to assimilate more mercury than other plants growing at the same place, but on the other hand, they show that mercury levels in plants bear little relationship to the mercury content of soils (Nichols et al., 1997).

Mercury toxicity and sources of exposure depends on its chemical form. For organic and inorganic mercury compounds, diet is the most important source for the majority of organisms. In terrestrial food webs, mercury exists in an inorganic form, and accumulates in plants. However, it does not biomagnify in the organisms that feed on them (Nichols *et al.*, 1997). Concentrations of mercury in most foodstuffs are often below the detection limit, usually less than 20 ng.g<sup>-1</sup> wet weight, with mercury mainly in the inorganic form (WHO, 1991, as cited by UNEP, 2002), with gastrointestinal absorption close to 7%. WHO (1990, as cited by UNEP, 2002) estimates an average daily intake of inorganic mercury of 3.6 µg/day, for populations not occupationally exposed, whereas its retention in the body averages 0.25 µg/day, as a result of consumption of foodstuffs other than fish.

A Joint FAO/WHO Expert Committee on Food Additives (1972, as cited by IPCS, 1976) established a provisional tolerable weekly intake (PTWI) of 0.3 mg of total mercury/person (of which 0.2 mg should be in methylmercury form), being these amounts equivalent to 5 µg /kg of body weight, and 3.3 µg/kg relative to methylmercury.

## 2. Study Areas in Brazil

Two artisanal gold mining areas, São Chico and Creporizinho, have been selected for undertaking the Environmental and Health Assessment in the Artisanal Gold Mining Reserve of the State of Para, in accordance with the Project's Coordination Unit, after considering different criteria, as follows:

- Commitment of the miners with the project's objectives;
- Their association with local artisanal miners leaderships;
- Production potential and economic stability of the mining activity;
- Representativeness relative to regional standards of technologies and practices;
- Accessibility;
- Spreading potential relative to the project's achievements.

**São Chico** (06° 25'31"S and 56° 02'99"W)

The garimpo São Chico is just 2 km distant from a landing strip and in 5 km distance from the *Transgarimpeira* road, which during the dry season (June-September) can be used for transportation of equipments and supply from Itaituba, the main town in this region with 150,000 inhabitants. Due to the bad conditions of this road, it should be used just for transportation of goods, since the 350 km distance from Itaituba needs some 20 hours to be overcome (Figure 1).

The São Chico village consists only of 63 houses and 134 individuals, being 41% of garimpeiros, 6% of machinery owners, 30% of dealers, 9% of cooks, among others. The only public service in the village is a health post for malaria diagnosis from the National Foundation of Health (1 health assistant)(Armin Mathis, Sociological Report, July 2003).

At São Chico mining site a small village has been established on the bottom of a valley. The topography is undulating with mean altitudinal differences between plateaus and stream valleys of 10-20 m.

Sao Chico stream was dammed up forming a reservoir behind the village from which water is used for mining activities that generate mining tailings to waterways (Figure 2). Few families have backyards in the village, where herbs, fruits, roots, medicinal teas and creeping plants are cultivated. Primary forest was replaced by pasture in hillsides. Grassland species and some small trees occur at reservoir's banks.

From the beginning of the very first gold mining activity in 1963, the São Chico village has shown two main periods of prosperity, one in the end of the 80's after the opening of the *Transgarimpeira* dirt road, and other in the end of the 90's, when gold rich primary deposits were discovered. According to revised estimations, about two tons of gold were produced during the last gold rush, while a total estimated mercury emission to the environment reaches three tons since 1963.





**Figure 2 - Main tailing deposit in São Chico: lies at the slope of a valley, between the village (to the right) and a dam reservoir (on the left)**

**Creporizinho** (S 06° 50' 14,1" – W 56° 35' 00,0")

Creporizinho is a typical gold mining village with 238 wooden residences for an estimated population of 1000 inhabitants. There are grocery shops, pharmacies and a hotel. Electricity is based on diesel engines. The 200 children go to a primary school, where 5 teachers are working. Gold is bought at any corner. Few families have backyards in the village, where herbs, fruits, roots, medicinal teas and creeping plants are cultivated.

Both study sites, Tolentino and Papagaio, were said to start its prospective/extraction activities since 1968 (manual extraction). From 1985 on started to work with machinery consisting basically on processing alluvial – colluvial terraces. They have privileged the using of hydraulic jet pumps coupled with riffled or carpeted sluice boxes in order to concentrate gold prior to amalgamation.

Creporizinho study sites are ca. 10 km far from the village. Creporizinho stream flows nearby the village and is used for water supply water to mining activities. Overbank deposits are common along its banks. There are many flooded open pits, drains of mining tailings forming small streams along mining sites. Also herbs sprout up over mining tailings and wastes, and pastures also replace primary forest, but forest fragments still remain in some places. Old flooded open pits have macrophytes growing in water.

From 10 to 15 kilometres in southeastern direction from Creporizinho village lies the mining area of "Luis Preto", comprising the Garimpos Papagaio (Figure 3), Tapocal an Areal Alluvial gold has been mined and from the middle of the 90's exploration of primary ore began, more or less successfully. Nowadays, alluvial mining is very rare, mining of lateritic soils, primary ore and reworking of residues and tailings from former mining activities became common all over the area.



**Figure 3 - Panoramic view of the Papagaio area in Creporizinho**

In the Papagaio mining site (S 06° 47' 00,2" - W 56° 40' 03,2"), primary ore from open pits and from shafts is extracted, transported to the processing unit, located on top of a hill, where material gets ground and undergoes amalgamation through mercury-coated copper plates. In the neighbouring Tapocal, Bofe and Areal areas, prevailing mining activities concentrate on reprocessing of tailings and residues mainly located along recent or past courses of creeks or small rivers. Amalgam is usually roasted locally.

At Crepori River mining activities were performed with dredges and hidraulic jets at riversides. The low-water season exposes alluvial pits originated from dredge activities during high-water season.

Since 1999 novel operations have been introduced in the Tolentino area (S 06° 47' 46,9" - W 56° 36' 27,0"), considering they have reached a sub-surface level (about 10 meters depth) with gold veins, being 2001 identified as the higher production (said to reach 6,000 kg/year). The owner of the Tolentino area established a partnership with a group of entrepreneurs who assembled a plant using mainly hammer/crusher mill, hydraulic jet pumps and centrifuge concentrators (Figure 4).



**Figure 4 - Processing plant at Tolentino mining site**

In order to address the identification and location of mercury hotspots a sampling campaign of soils and sediments was performed. Amalgamation tailings dumped into drainage systems originate hotspots of metallic mercury (*mining hotspot*), where abnormally high concentrations are to be found in the heavy fraction of sediments. Due to its typical heterogeneous distribution, one may face enormous difficulties in locating mining hotspots of mercury in a given mining site, as conventional geochemical exploration techniques have been used unsuccessfully. Therefore, the introduction of novel sampling and analytical methods was required, including *in situ* mercury analyses by a semi-quantitative colorimetric method.

Sampling and analysis of total suspended solids (TSS) and water in aquatic systems play a pivotal role in assessing mercury mobility and the nature of pollution. Mercury transported either in solution or onto suspended particles may be deposited in riverside deposits forming mercury sinks, which are potential sources for mercury remobilization, since mercury is adsorbed onto fine particles and prone to form soluble complexes, mainly in the presence of humic substances.

Since metallic mercury can be transported downstream onto particulate matter, it is assumed that mercury can be oxidized and promptly form soluble complexes in the presence of organic substances. Therefore, the accumulation of these organic-rich sediments receiving loads of soluble-mercury complexes may account for an *ecological hotspot*, since mercury bioavailability increases. High contents of organic matter in sediments have been sought during sampling.

Simple sampling methods, consisting of pan concentrates for mercury analysis were also used for locating mercury hotspots. Another strategy, consisting of a sociological approach, enables the reconstruction of the local mining history and the identification of amalgamation tailings, through establishing a relationship of confidence among miners and researchers.

Some physico-chemical parameters are considered important for assessing the fate of mercury in the environment, and its eventual bioaccumulation and/or biomagnification in fish, mainly as methylmercury. Therefore, besides the investigation of natural and/or anthropogenic mercury concentrations in sediments and water, the physiochemical parameters of water, such as temperature, electrical conductivity, pH and dissolved oxygen were determined in the drainage waters by multi-electrodes.

Since sampling of TSS by filtering through 0.45  $\mu\text{m}$  membranes has been reported as controversial, due to its inefficiency of recovering enough solid material for analysis, it was sought naturally settled TSS samples where favorable hydrodynamic conditions were to be found. An example of settled TSS on the São Chico Creek is illustrated in Figure 5.



**Figure 5 - Fine layer of settled TSS on São Chico Creek margins**

The “Geoaccumulation Index” (Igeo) of mercury in bottom sediments has been selected for quantitative evaluation of contamination levels in aquatic systems (Müller, 1979). Since the enrichment process of metals in sediments, caused by a given emission, generally follows an exponential accumulation in fine fractions, the “Igeo” uses a log function for classifying distinct order of magnitude of contamination, as follows:

$$I_{geo} = \log_2 C_n / 1.5 \cdot B_n \quad \text{where,}$$

$C_n$  is the measured Hg concentration in the fraction -200 # and  $B_n$  is the *background* Hg concentration.

Moreover, the Igeo is divided into 7 classes, from 0 to 6, being class 0 indicative of null contamination while class 6 represents an extreme contamination.

Preparation of sediment, soil and tailing samples consisted of homogenization followed by wet sieving for separating grain size fractions above and below 200 # (74  $\mu\text{m}$ ). After that, each fraction has been dried at 40 °C for analysis.

The analytical method used in the field was undertaken by a portable atomic absorption for mercury analysis (LUMEX), which allows simple and direct determinations in different matrixes without acid digestion.

The method used in the laboratory for the determination of total mercury in environmental samples (soils, sediments, fish) follows the methodology developed by Akagi and Nishimura (1991) (Speciation of Mercury in the Environment, in: Advances in Mercury Toxicology, edited by T.Suzuki et al.). It involves sample digestion with strong acids followed by reduction to elemental mercury, aeration and measurement of mercury absorption with cold vapor atomic absorption spectrometry.

The sample digestion procedure insures complete digestion of organic materials and at the same time avoiding mercury loss by use of a combination of acids and oxidizing agents. This combination involves a mixture of nitric, perchloric and sulfuric acids. Additionally, water is

added to protein-rich samples, to avoid frothing upon heating. The sample is then heated at 250 °C for 20 minutes.

The sample solution is reduced by stannous chloride, generating elemental mercury vapor, which is then circulated in a closed system. Absorbance is measured when equilibrium of mercury vapor between gas and liquid phases is reached. The use of a syringe with needle when adding the reducing agent avoids loss of mercury by vaporization. The detection limit of the method is 0.5 ng Hg. The flowchart below shows a scheme of the procedure.

Hg was analyzed in the fish muscle through Atomic Absorption Spectrophotometer (KK.Sanso SS) using a Vapor Generation Accessory-VGA (CVAAS). For the analysis of Hg-total, approximately 0.5 g of tissue was weighed in 50-ml-vol flasks, to which was added 2 ml of HNO<sub>3</sub>-HClO<sub>4</sub> (1:1), 5 ml of H<sub>2</sub>SO<sub>4</sub>, and 1 ml of H<sub>2</sub>O (Hg free), and heated on a hot plate to 230-250°C for 20 minutes. After cooling, the digested sample solution was made up to 50 ml with water. An aliquot (5 ml) of digested sample solution was introduced in the Automatic Mercury Analyzer Hg 3500. The difference in duplicate sample analyses was less than 10% (precision of measurements was 90%). The accuracy of analyses was estimated with analyses of biological tissue standard reference materials from International Atomic Energy Agency. The results indicated that the sample preparation and analytical procedures consistently produced accurate measures of Hg concentrations.

Statistical differences between Hg concentrations and allometric parameters among different sites and garimpos areas (São Chico and Creporizinho) were tested using parametric Student's T-test after Levene's test for equality of variance, or, if the underlying assumptions for parametric testing are not met, a nonparametric test of significance, the Mann-Whitney U-test was employed. The significant level considered was the probability level  $\leq 0.05$ . Correlation analyses were determined with both the Pearson correlation coefficient and/or the Spearman rank correlation coefficient. Significance of the correlation was determined with a two-tailed Student's *t* test. One-way ANOVA followed by Duncan pos-hoc were performed when appropriate for testing differences among groups.

Plant samples, collected manually or using a shovel to dig out the roots, were washed several times, labeled, stored in plastic bags and frozen. Approximately three replicates of each specimen were collected. In laboratory, plants samples were washed with tap water and cleaned with a small brush to remove potential aerial superficial mercury contamination. Roots, stems and leaves were analyzed separately. Wet materials were used to obtain total mercury concentrations in plant parts. Plant samples water content percentages were utilized to transform wet weight concentration to dry weight concentration.

Individual and composite substrate (soil and sediment) samples were collected with an plastic shovel, labeled, and stored in plastic bags. Composite samples were obtained mixing sub-samples in the plastic bags.

To evaluate the relationship between the mercury contamination in soil and plants, single variable regressions were performed, using natural-log transformed of mercury concentration in both soil and plants prior to regression analyses (BJC, 1998). Measurements of Hg concentrations in plants and soils were compared among studies areas, plant types and parts, and soil fractions (+200# and -200#), by *t*-test for independent samples and *U* Mann-Whitney test ( $n \leq 8$ ) (Siegel, 1975).

The estimate of total mercury weekly dietary intake were calculated by the product of the upper-bound range of mercury concentration ( $C_{\text{plant}}$ ) obtained in edible plant parts and the consumption rate (CR) of those foodstuffs ( $Hg_i = C_{\text{plant}} \times CR$ ).

Produce plants identifications were obtained from the Brazilian Ministry of Agriculture, while wild plants were identified by Dra. Rafaela Campostroni Forzza from the *Instituto de Pesquisas Jardim Botânico do Rio de Janeiro*.

Quality assurance/quality control (QA/QC) concerns were addressed through the use of analytical duplicates. Analytical duplicates were included with each sample, and duplicate analyses for each sample were checked to assure that the relative percent difference between duplicates was no greater than 10%.

Fish samples were collected usually by gill-netting, fishing line with a fish-hook and fishing line with several hooks (“espinhel”). After fish caught, still alive, the blood was drawn by caudal puncture with a EDTA containing syringe (Figure 6). All specimens were subjected to blood collection, while just for 60 specimens the collection was successful. The total blood was kept in Eppendorf tubes and haematological exams were performed. In the field, the manual methods for counting erythrocytes were performed as the same time as the total leukocyte count. Smears, two slides per individual, were prepared from fresh and without anticoagulant substances blood, air dried, fixed in methanol, and stained with Giemsa’s solution. The hematocrit (or globular volume) was performed by microhematocrit method, using small capillary tubes, which were filled approximately two-thirds full with anticoagulated blood and centrifuged. The percentage of packed cells to total volume is determined by direct measurement.

After blood collection, each specimen was weighed (Wt), and its length (Lt) was measured at the time of collection. After removing the individual axial muscle (fillet) each sample was placed in polyethylene bags and on ice as soon as possible, and frozen (Figure 7). The samples were delivered to Mercury lab at CETEM to carry out the total Hg measurement in the axial muscles of fish.



**Figure 6 - Fish blood collection by caudal puncture.**



**Figure 7 - Individual axial muscle (fillet) of fish**

#### **4. Results and Discussion**

A sampling campaign was conducted in August 2003, at two study areas: São Chico and Creporizinho mining areas. Table 1 shows the study sites in each area. These areas are located inside of the Tapajós Gold Mining Reserve, State of Para, between the cities of Jacareacanga and Itaituba, where the mining sites are distributed alongside the tributaries of the Tapajós River. However, these two areas belong to two distinct hydrographic basins: Jamanxin river basin and Crepori river basin, respectively.

For correlation purposes, results of Hg in sediments and fish are presented according to 11 study sites, A1 to A11, while site A1 has been used exclusively for fish sampling (Table 1).

**Table 1 - Study sites in São Chico (A1-A4) and Creporizinho (A5-A11) study areas**

Study Site	
A1	Flooded open pit, clear water, near to Conrado River
A2	São Chico Reservoir
A3	Flooded open pit, mining wastes, high turbidity, near Rosa stream, sandy area
A4	Inflow Conrado River to Novo River
A5	Papagaio mining site; stream with high turbidity
A6	Flooded open pit at Tabocal mining site
A7	Flooded open pit at Bofe mining site
A8	Tolentino mining site
A9	Porto Alegre site in Crepori River, upstream of Creporizão village
A10	Inflow of clear stream to Crepori River
A11	Inflow of Chico Chimango, a clear water stream, near the inflow of Creporizinho River to Crepori River

#### 4.1 São Chico

In São Chico, located at km 51 on the Transgarimpeira, the main mining area lies at the slope of a valley, between the village (see also report of Armin Mathis, July 2003) and a dam reservoir, which supplies the pumps for mining and milling activities with water (Figure 2).

In the same process material from primary deposits is mixed with residues of former mining activities and milled. The gold is concentrated on mercury coated copper plates. Samples were taken (see detailed list) in and around this area, in the village as well as in the drainage basins nearby and remote, including samples from Jamanxim, Rio Novo and Conrado, in which via igarapé São Chico and Sta. Rosa the mining area is drained.

From the beginning of the very first gold mining activity in 1963, the São Chico village has shown two main periods of prosperity, one in the end of the 80's after the opening of the *Transgarimpeira* road, and other in the end of the 90's, when gold rich primary deposits were discovered. According to cross-checked estimations, about three tons of gold were produced from the beginning of the gold rush, corresponding to an estimated mercury emission of 7.5 tons to the environment. Since the primary gold ore has been crushed in hammer mills and directly amalgamated in copper plates, and no retorts have been used, the estimated Hg:Au (lost:produced) emission ratio is about 2.5 for this type of operation.

Nowadays, exploitation of primary gold ore is over, being gold production in São Chico almost restricted to the reprocessing of tailings produced during the 80's, when alluvial and laterite deposits (*baixões*) were worked using just sluice box for gravity concentration, without crushing. Tailings are now being concentrated through sluice boxes while the concentrate follows the same processing circuit as for the former primary ore, while mercury is widely used in both mineral processing steps, gravity concentration and amalgamation. Mercury emission ratio becomes therefore even higher, since "old" mercury is mixed with "new" mercury.

This typical artisanal mining site can be briefly characterized as follows:

- Actually there is not too much prospective work. All activities are based on reprocessing the old tailings. Each processing plant operates with hydraulic monitors, 4 inches diameter, pumping very diluted pulp (around 5 - 10% solids) to carpeted sluice boxes.
- Gold production in 2003 was informed to be about 1.10 - 1.20 kg/monthly, so far.
- Hammer mills operate circa 10 hours daily (7 am to 5 pm) showing typical dimensions of 30 x 45 cm, being common to generate particles < 2 inches. Depending on the opening chamber mills, processing capacity can vary from 1 ton/hour to 2 ton/hour.
- After milling, all particulate material is repulped again with plenty of water and fed up to the amalgamated copper plates (sizes corresponding to about 600 x 2000 mm, width x length).
- Those devices are not expensive being informed that the whole set (hammer mill and amalgamated copper plates) would cost circa 100 grams of gold.
- Mercury use was informed to obey a traditional ratio used in such region corresponding to 2 - 4 kg Hg : 1 kg Au produced for both methods, using copper plates and gravity concentration.
- If concentrates are amalgamated, the main Hg emission source derives from amalgam burning in open pans. This operation, normally, produces a gold doré that contains 2 to

5% residual Hg. When the doré is melted at gold shops, most commonly located in urban areas, further release of mercury vapors takes place.

- When gravity concentrates are amalgamated, the mineral portion is separated from amalgam by panning, forming a tailing that is usually dumped into a stream generating a “mining hotspot”. Panning is usually done in water-boxes or in pools excavated in the ground or at creek margins. Hg excess is removed by squeezing it through a piece of fabric and is generally recycled.
- Since the estimated ratio  $Hg_{\text{lost}} : Au_{\text{produced}}$  is 2.5 for processing plants using copper plates and 1.5 for gravity concentration, the average ratio for this area is 2.0.
- Processing techniques practiced consist in to reprocess old tailings that resulted from the “fofocas” ages (that means, from 1999-2001), when there was a greater activity, which enabled garimpeiros to produce about 2000 kg over such period.

#### 4.1.1 São Chico reservoir and creek (sampling site A2)

The São Chico Creek was dammed up in 1989 at the end of a narrow valley, located around São Chico village forming a reservoir (Figure 2) for supplying the mining site with water to carry out mining activities. Water covers an area of approximately 50 to 150 m width to 700 m length (85,000 m<sup>2</sup> surface) with an overall depth of less than 5 meters only. Outflow from this reservoir (during dry season) amounts to less than 5 liters/second.

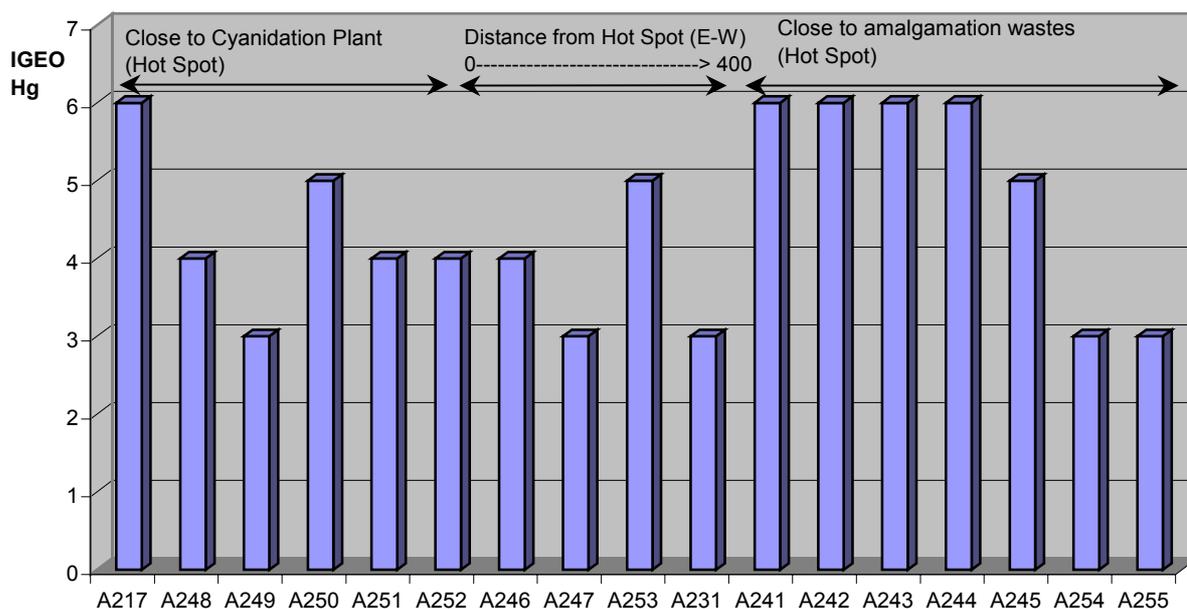
The small São Chico Creek, about 1 meter wide and only a few centimetres deep (Figure 5), having its source at Sao Chico reservoir, drains the mining site and the village. Very clear water could be observed during the survey campaign, indicating a low intensity of mining activity.

Since 1989, tailings from both amalgamation and cyanidation activities have been poured into the reservoir. Due to lack of stream and turbulence nearly all of this material, in particular suspended load, entering the reservoir could settle down and accumulate. A very small outflow with nearly clear water feeds the São Chico creek, which drains the entire mining site and flows through Conrado River, Novo River and Jamanxim into the Tapajós River.

A total of 17 composite samples (tailings mixed with sediments - including settled suspended load) were taken from reservoir bottom and margins. In general, sediments comprise sand and silt, covered with a thin layer (< 5 mm) of clay or suspended load and abundant organic matter.

Close to amalgamation wastes and to the former cyanidation plant Hg levels reach an Igeo class 6, while samples collected in other parts of the reservoir concentrations decrease to Igeo classes from 3 to 5, which are still very high considering that these samples were composed of organic-rich clayey sediments, not directly influenced by amalgamation wastes (Figure 8).

Since Hg concentrations in sediments and tailings have been transformed into Igeo classes throughout the present report, a table containing all data of Hg concentrations is presented in Appendix 1.

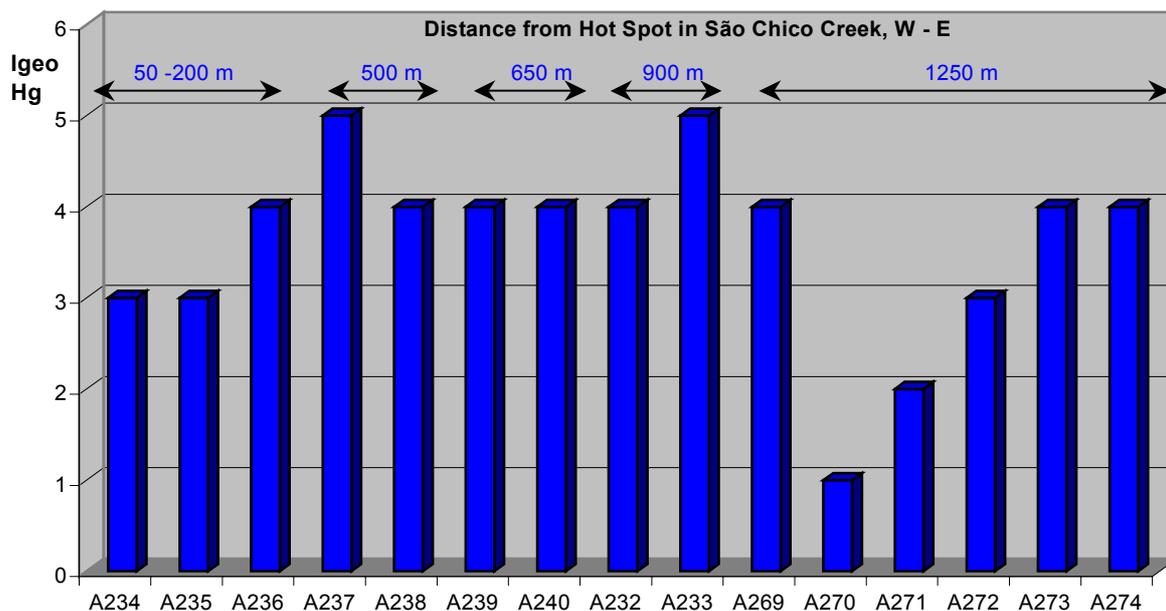


**Figure 8 - Distribution of IGEO Classes of Hg in sediments (< 74  $\mu\text{m}$ ) of the São Chico Reservoir**

According to the present results, the estimate of 7.5 tonnes of mercury released into the environment is consistent. High mercury levels were found not only near amalgamation tailings, which are mining hotspots with up to 300  $\mu\text{g/g}$  of Hg, but also associated with suspended solids inside the reservoir and up to 1 km downstream, as indicated by the high Hg levels averaging an IGEO class 4 along the São Chico Creek. Among the 15 TSS samples collected along the creek, up to 800 m from the main tailing deposit, there is no decreasing pattern of Hg concentrations from the main source (Figures 9 and 10). This is an indication that the mercury load released in São Chico is becoming mobile and prone for transportation either in solution or onto suspended particles downstream.

Moreover, a total of two water samples collected downstream from the main source, in the Conrado River and Jamanxim River, present slightly higher Hg concentrations in the filtered phase, averaging 1.25  $\mu\text{g/L}$ , than the limit, of 1  $\mu\text{g/L}$  for drinking water established by the Brazilian Ministry of Health. It is to be highlighted that Hg concentrations in water samples from gold mining sites generally fall in the range from 0.10 to 2.80  $\mu\text{g/L}$  (Rodrigues-Filho and Maddock, 1997).

A possible explanation for this particular mercury behaviour in São Chico, associated with suspended particles, is due to the introduction in 2001 of cyanidation by heap leaching from amalgamation tailings which was undertaken at the margin of the dam reservoir situated upstream of the main mining site in São Chico, the so-called *Montanha*. Therefore, the formation of cyanide-mercury complexes into the reservoir could be responsible for increasing mercury mobility downstream. An additional factor that likely enhances Hg mobility is due to pasture fires close to amalgamation tailings.



**Figure 9 - Distribution of Igeo Classes of Hg in sediments (TSS) of the São Chico Creek - up to 1.25 km downstream**

The cyanidation attempt of amalgamation tailings together with the physical and chemical features of the dam reservoir, a semi-closed aquatic system with high organic contents in sediments and anoxic conditions in the bottom, make this environment a promising field opportunity for a better understanding of the behavior of mercury in aquatic systems together with cyanide.

Table 2 shows the physiochemical parameters in the water column of the São Chico reservoir, which are consistent with usual water parameters of Amazonian rivers, with neutral pH and very low electrical conductivity (low salinity). Lower values of dissolved oxygen are due to anoxic conditions in the bottom of the reservoir. Those physiochemical conditions are favourable to the stability of elemental mercury. Thus, one may realize that further factors are responsible for Hg mobility in this aquatic system, such as biochemical processes through microbiological activity and/or anthropogenic ones, among which the cyanidation attempt and forest fires are to be highlighted.

Veiga et al. (1994) indicated the significant role that deforestation plays among the most important emission sources of Hg in tropical countries, where forest fires are contributing to increase Hg emissions worldwide through the release of Hg baselevels present in biomass.

Accordingly, another important factor contributing to Hg mobilization in São Chico is likely to be related to forest fires yearly practiced for cleaning up pasture throughout the study area, as it could be observed during the sampling campaign (Figure 10), when the surrounding pasture close to the reservoir and tailings has been burned three days long. The sudden elevation of the soil temperature is likely to be very effective in releasing Hg from mining hotspots in soils to the atmosphere, thus enhancing its mobility. The area impacted by fires in pasture is also visible from the satellite image in detailed scale of São Chico mining site (Figure 11).

**Table 2 - Physiochemical parameters in the water column - São Chico reservoir**

Sample-Nr.	pH	DO (mg/l)	Conduct. (µS/cm)	Temp (°C)	Depth (m)
W 1	5.1	5.71	114	29	0.5
W 2	5.1	7.62	142	28	0
W3	6.1	7.60	163	28	0
W4	6.2	7.61	113	28	0
W5	6.5	4.82	163	30	1
W6	5.1	5.75	105	29	1
W7	6.0	2.48	204	27	1

**Figure 10 - Former shaft in São Chico with burned pasture**

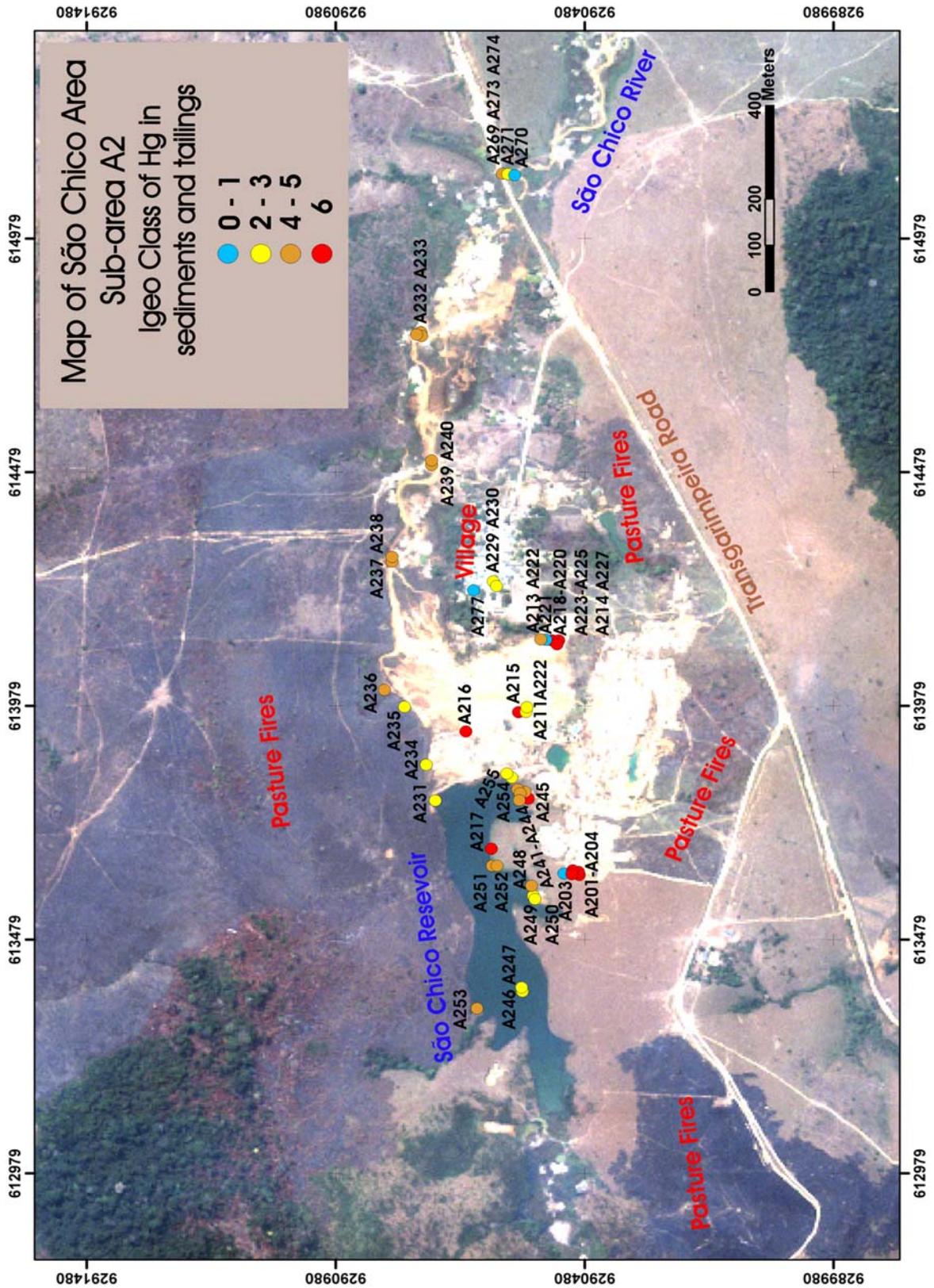
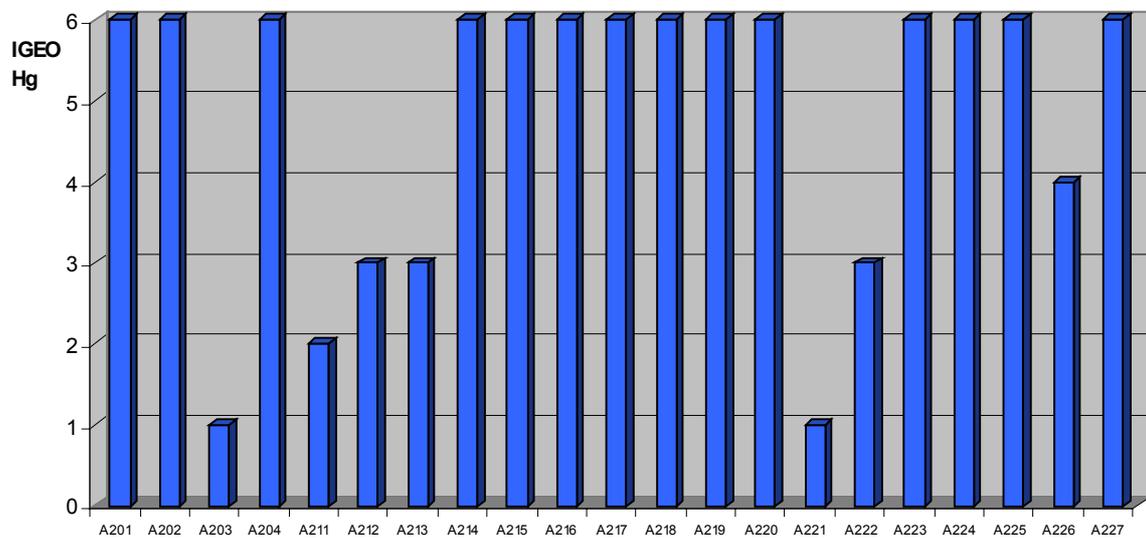


Figure 11 -Distribution of Igeo classes of Hg in the vicinities of the São Chico Village (Hg hotspots in red dots) and marks of pasture fires

#### 4.1.2. Mining area (tailings pile and open pit – site A2)

Between lake and village, the valley floor is covered by mining tailings, extending through an area of approximately 50.000 m<sup>2</sup> with an average thickness of 5 meters, coming from prior alluvial processing and former mining activities in primary ore veins from magmatic, partially weathered rocks. This tailings pile has been deposited during a period of some 40 years.

A total of 38 composite samples of tailings from this part of the mining area were taken. In general, material comprises silt and sand, due to former grinding procedures, mainly of red colour, origin from Fe-oxides and -hydroxides from lateritic soil. Following a typical heterogeneous in tailings, Hg levels in this site confirm the occurrence of a mining hotspot, reaching concentrations of up to 300 µg/g, or a maximum Igeo class 6 (Figure 12).



**Figure 12 - Distribution of Igeo Classes of Hg in tailings (< 74 µm) of the São Chico mining site**

An open pit, comprising an area of about 60.000 m<sup>2</sup>, located at the northern slope of the valley, represents a typical primary gold-ore deposit, as it is recently observed in the Tapajós Gold Mining Reserve (Figure 13). Superficial lateritic soils got removed in the range of 2 to 10 meters in order to provide access to gold-bearing quartz-veins. Several shafts, up to 20 m deep (Figure 10) have been dug, trying to follow the inclined quartz veins. Hammer mills and Hg coated copper plates were placed and constructed in situ. At the eastern margin a very crude cyanidation plant was constructed (Figure 14), operating from 1999 to 2001. Amalgamation tailings and other wastes were poured into São Chico reservoir during this period of time. In general, material comprise silt and sand, due to origin from lateritic soils and weathered rock, mainly of red and yellow colour, origin from Fe-, Mn-, and Al-oxides and -hydroxides.



**Figure 13 - Panoramic view of the open pit in São Chico**



**Figure 14 - A former cyanidation heap leaching close to the reservoir**

The general distribution of Igeo classes of Hg in sediments, soils and tailings throughout the study site A2, in a detailed scale, is presented from a satellite image of the study area. It is to be highlighted the occurrence of Hg hotspots represented by the red dots (Figure 11).

#### 4.1.3. Surrounding area and Conrado River (sampling site A3)

In the immediate vicinity of São Chico village, 4 km downstream, there are some small active and abandoned garimpos along the Conrado River and its creeks – little mining activity could be observed during the field survey period in July/ August 2003. Predominately tailings of past mining activities are reprocessed in those areas, while Hg levels in those tailings are moderately high, averaging an Igeo class 3 (Figure 15).

However, close to this site, some “virgin” areas along the Rosa Stream, without any recent and past mining activities were encountered – well suitable for determination of natural background of mercury in sediments and soil. A sediment core, divided into 6 sections, was taken in the bed of the small clear water bearing brook in the forest area, where obviously no former mining activity have been taken place. Sediment consists of nearly pure grey clay with some organic matter, like rotten leaves.

The sediment core was 30 cm deep and revealed that Hg levels decreases in depth. The lowest background values of the -200Mesh fraction ( $< 74 \mu\text{m}$ ) was around  $0.15 \mu\text{g/g}$  in the lowest 15 cm, corresponding to an Igeo class 0, and up to  $0.84 \mu\text{g/g}$  at the surface, or Igeo class 2 (Figure 14). This probably a result of the contribution from atmospheric Hg released from anthropogenic sources. It has been assumed that the lowest section of the core, samples A305 to A307, represents the Hg background level of this region (around  $0.15 \mu\text{g/g}$ ), since this procedure has been successfully adopted elsewhere (Rodrigues-Filho et al, 2002; Rodrigues-Filho and Maddock, 1997).

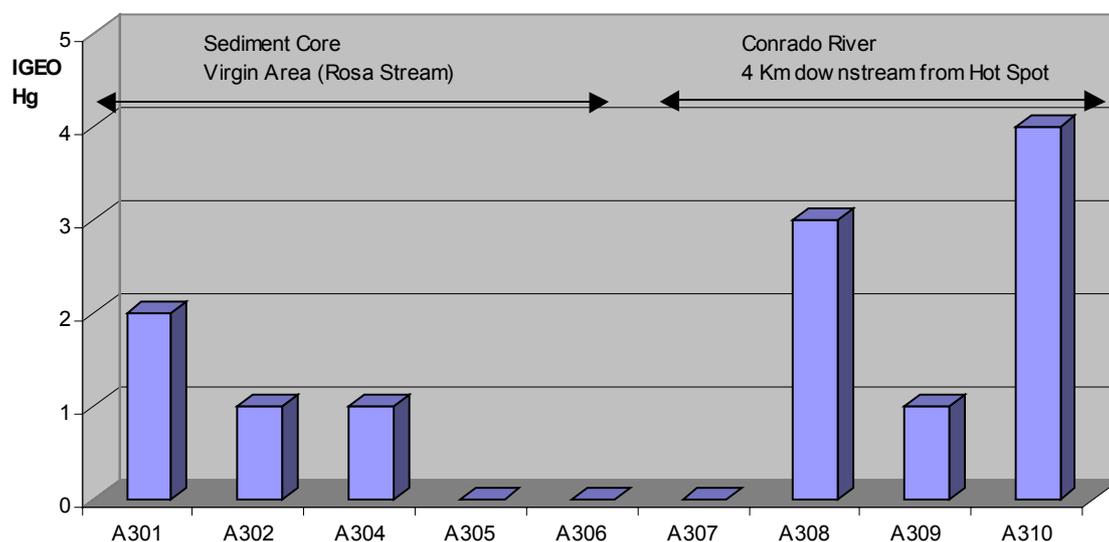


Figure 15 - Distribution of Igeo Classes of Hg in sediments ( $< 74 \mu\text{m}$ ) of the Conrado River and in a sediment core (Rosa Stream)

#### 4.1.4. São Chico Village

Although a less intense activity of amalgam roasting could be observed in the village of São Chico during the sampling campaign, presently just one gold shop is in operation, dust and soil are sought to be efficient indicators of atmospheric Hg contamination.

The maximum Hg concentration (1,280  $\mu\text{g/g}$ ) corresponds to an Igeo of 12 and was found in a sample of spider web collected inside the gold shop of the village, where no exhausting system exists. The others samples, composed of dust, have been collected inside houses of its immediate neighborhood. Since all of them present extremely high Hg levels, with a minimum Igeo of 6, it is suggested the need of urgent measures towards the protection of the population's health (Figure 16).

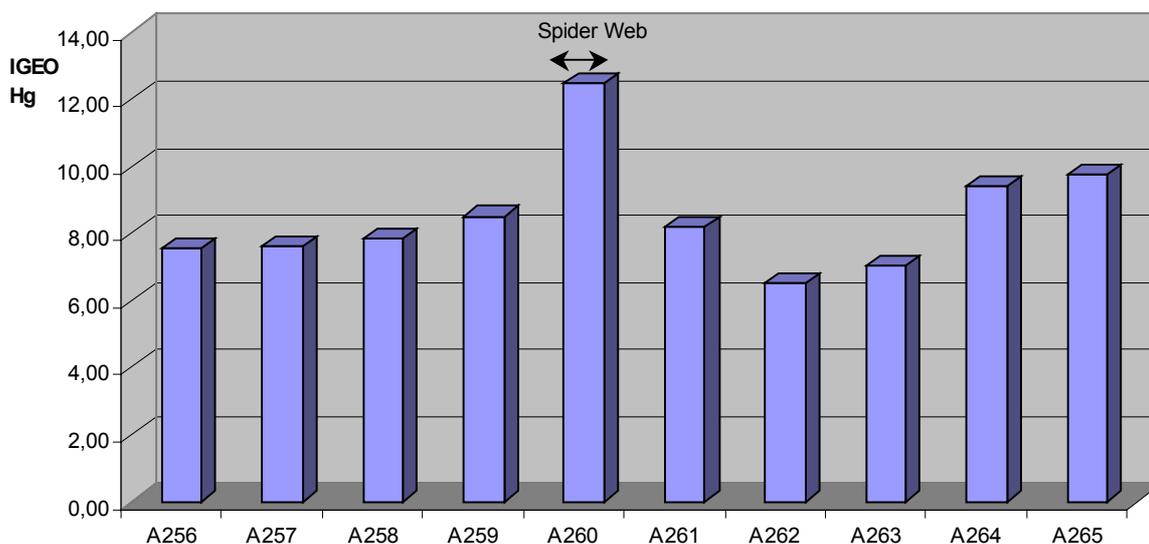


Figure 16 - Distribution of Hg Igeo in dust and spider web samples from São Chico village

#### 4.1.5. Remote drainages (site A4)

São Chico Creek flows into Conrado River, 2 km downstream from the village, where its water gets mixed with drainage from other mining sites, showing high turbidity. The entire region is drained by the Conrado River, Novo River (15 km from the village) and Jamanxin River (20 km from the village)(Figure 17).

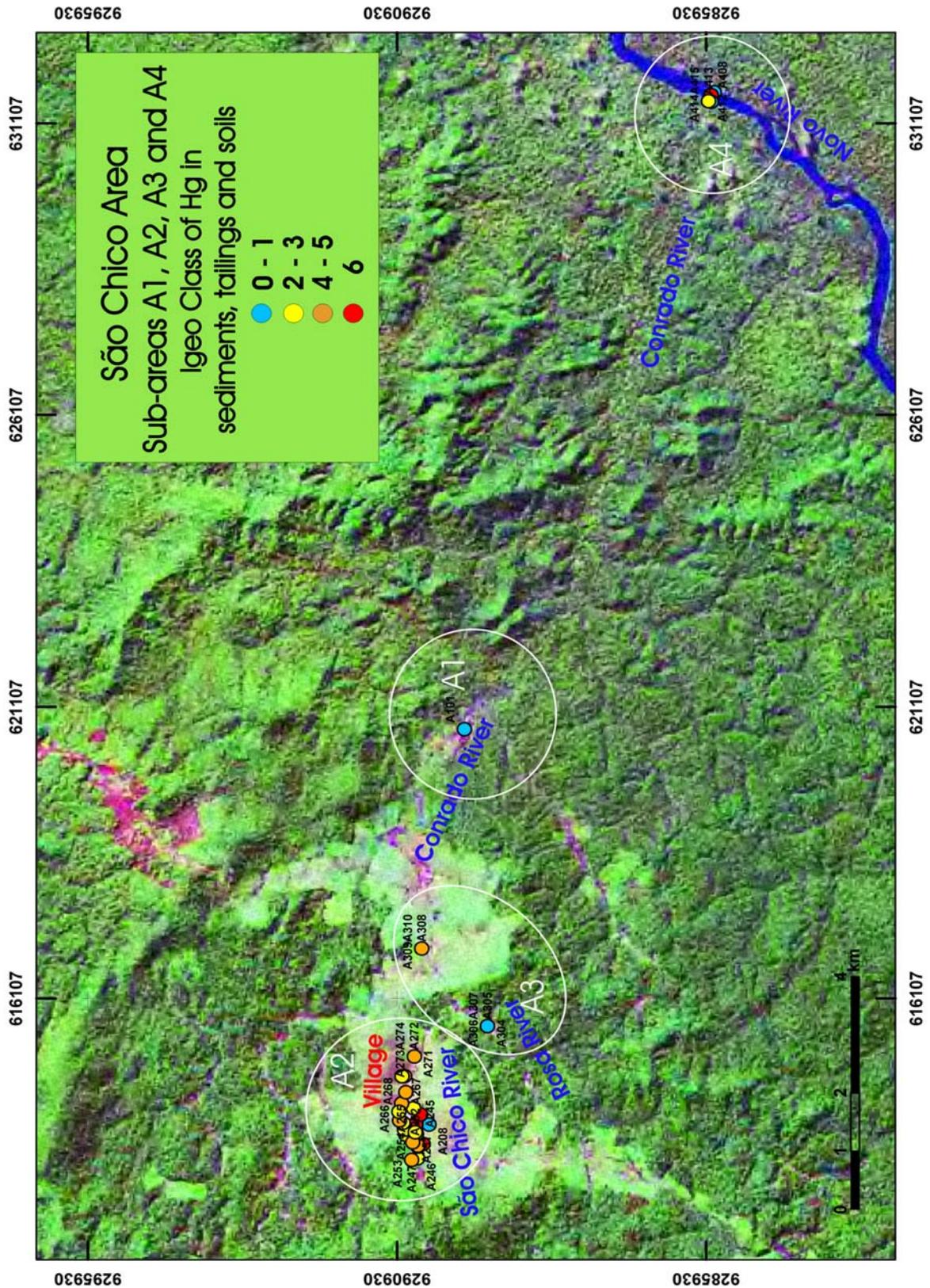


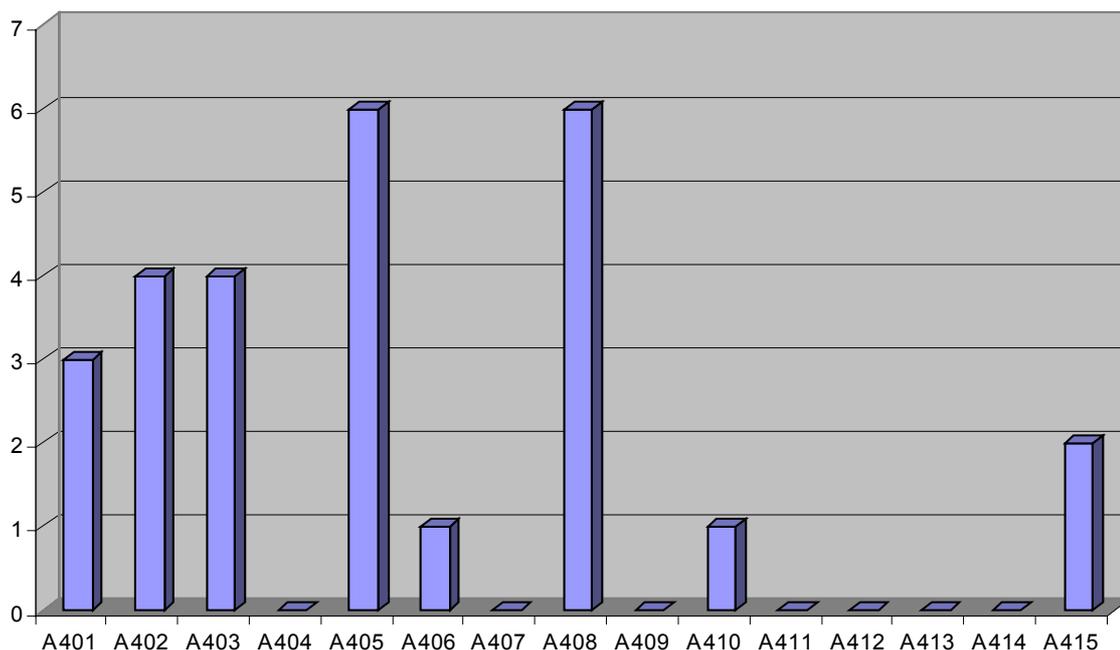
Figure 17 - Regional distribution of Igeo classes of Hg in sediments, tailings and soils from São Chico mining site and surrounding areas

A total of 15 composite sediment samples were taken from the Conrado River, Novo River and Jamanxin River, in order to evaluate to which extension the Hg load released from São Chico is influencing the sediment chemical composition downstream. In general, sediments comprise a thin layer of settled suspended load and organic matter covering riverine deposits in overbanks and riversides.

Since the main contribution in terms of Hg emissions to the Novo River comes from the São Chico region, showing its high turbidity (Figure 18), one may realize that due to its indicated association onto suspended particles, Hg released from São Chico is prone to be transported downstream up to a distance at least as long as 20 km, as indicated by results reaching Igeo classes 6 and 4 (Figure 19).



Figure 18 - Mouth of the Novo River to the Jamanxin River



**Figure 19 - Distribution of Igeo Classes of Hg in sediments (< 74  $\mu\text{m}$ ) of surrounding drainages (up to 20 km downstream - site A4)**

A general distribution of Igeo classes of Hg in sediments, tailings and soils throughout the whole São Chico area is presented, in a regional scale, from a satellite image of the study area. It is to be highlighted the occurrence of significantly high Hg levels associated with fine sediments (< 200 $\mu$ ) up to 20 km downstream from the São Chico mining area, in the site A4 (Figure 17).

#### **4.2. Creporizinho area**

Creporizinho is a typical gold mining village with 238 wooden residences for an estimated population of 1000 inhabitants. There are grocery shops, pharmacies and a hotel. Electricity is based on diesel engines. The 200 children go to a primary school, where 5 teachers are working. Gold is bought at any corner.

In Creporizinho, located at km 145 on the Transgarimpeira, the Tolentino mining area chosen for sampling is located about 5 to 10 km NNW from the village and represents 3 different types of small scale gold mining activities: inactive alluvial deposits (including rework of former tailings and residues) - explored by hydraulic monitor (*garimpo de baixão*), lateritic deposits - explored through open pit and primary deposits - explored through open pit or shaft (*garimpo de filão*). Samples were taken in and around this area, in the village, as well as in the drainage basins nearby and remote, including samples from Rio Crepori, Creporizinho, waterbodies in abandoned open pits and the draining *igarapés*.

#### 4.2.1. Papagaio and Areal (site A5)

From 10 to 15 kilometres in southeastern direction from Creporizinho village lies the mining area of “Luis Preto”, comprising the Garimpos Papagaio (Figure 3) and Areal where alluvial gold has been mined and from the middle of the 90’s exploration of primary ore began, more or less successfully. Nowadays, alluvial mining is very rare, mining of lateritic soil, primary ore and reworking of residues and tailings from former mining activities became common all over the area.

In the Papagaio mining site, primary ore from open pits and from shafts is extracted, transported to the processing unit, located on top of a hill, where material gets ground and amalgamated over mercury-covered copper plates. In the neighbouring site Areal, prevailing mining activities concentrate on reprocessing of tailings and residues mainly located along recent or past courses of creeks or small rivers. Amalgam is usually roasted locally.

A total of 30 composite samples (residue, sediments and soils) from this part of the mining area were taken. In general, material comprise silt and sand, due to origin of grinding activities from lateritic soils and weathered rock, mainly of red and yellow colour, origin from Fe-, Mn-, and Al-oxides and -hydroxides.

Except samples from amalgamation wastes (mining hotspots), A510 to A518 in Papagaio and A521, A522 and A531 in Areal, which show very high Hg concentrations, the general distribution of Hg throughout both Creporizinho mining sites indicates an expressive lower level of Hg contamination, comparing with the ones from São Chico (Figure 20).

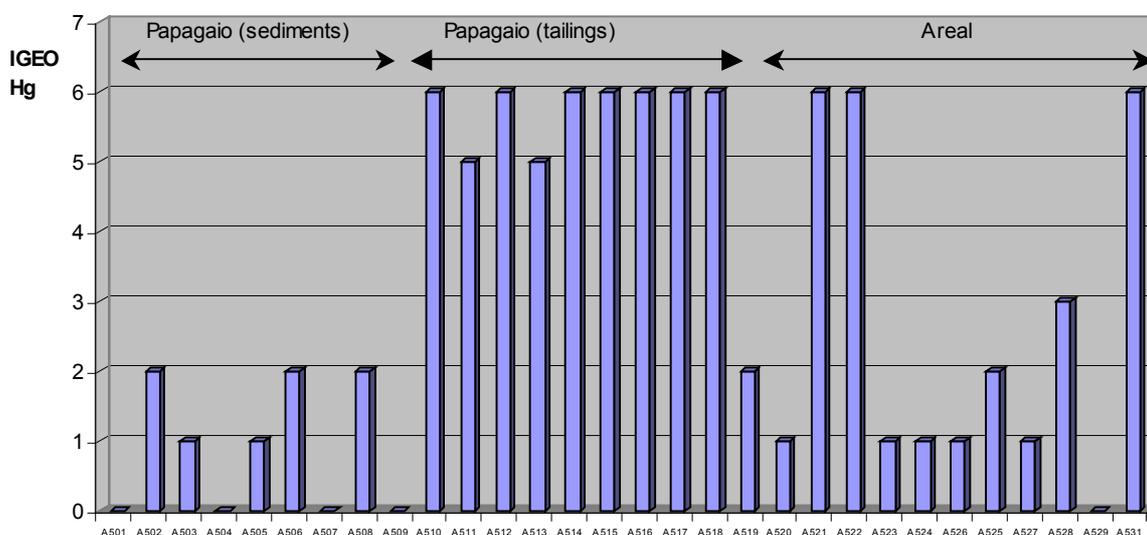


Figure 20 - Distribution of IGEO Classes of Hg in sediments and tailings (< 74 µm) of site A5

#### 4.2.2. Tabocal (A6) and Bofe (A7)

The mining sites Tabocal (A6) and Bofe (A7) present a similar picture in terms of mineral processing techniques and waste disposal as in Papagaio (A5). Nevertheless, Hg levels in sediments and tailings are significantly lower in A6 and A7 than in A5, indicating either less intense Hg losses or a lower mobility of Hg from a given mining hotspot, resulting in Igeo classes close to the background, except for 3 samples reaching the Igeo class 4, revealing a low degree of Hg contamination in inorganic samples (Figures 21 and 22).

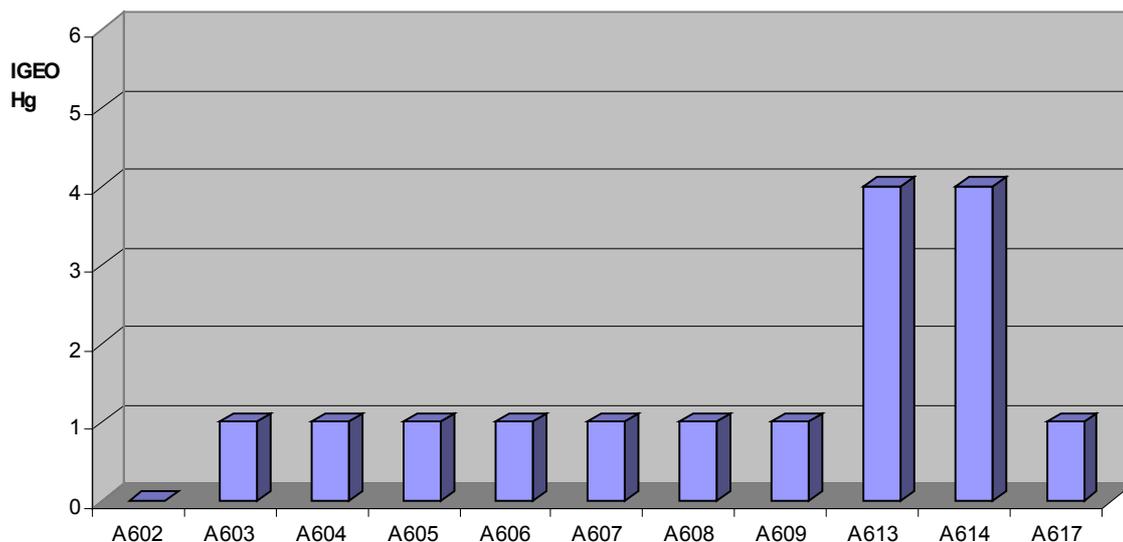


Figure 21 - Distribution of Igeo Classes of Hg in sediments and tailings (< 74 μm) of site A6

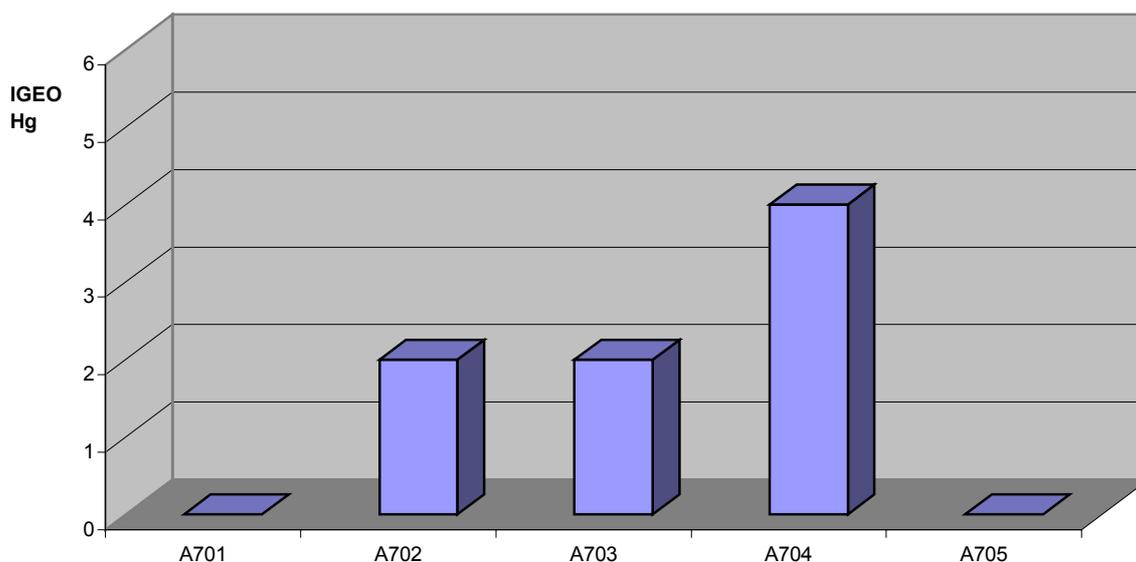


Figure 22 - Distribution of Igeo Classes of Hg in sediments and tailings (< 74 μm) of site A7

### 4.2.3. Tolentino (A8) and remote areas (A9 to A11)

Tolentino mining site (A8) is located circa 5 km in southeastern direction from Creporizinho, on the way to Papagaio. This is the only garimpo visited in Creporizinho area, which works with “modern” equipment, as it was being used successfully in Poconé for years, like ball mills and centrifuges (Figure 4). The majority of processed material comes from primary ore deposits, extracted from gold-bearing quartz veins in magmatic rocks in the nearby surroundings and transported by trucks to the processing unit, while amalgamation is applied to gravity concentrates. Only a smaller part of the gold production comes from secondary material, both, lateritic soils and tailings, resulting from former mining activities in the entire area.

A total of 12 composite samples of sediments mixed with tailings from this site were taken. In general, material comprises silt and sand, due to former mining procedures, mainly of red color, origin from Fe-oxides and -hydroxides from lateritic soil.

Although one single sample reached Igeo class 6, the whole data indicate an overall situation in terms of Hg contamination less significant than in other areas considered in this study (Figures 23 and 24).

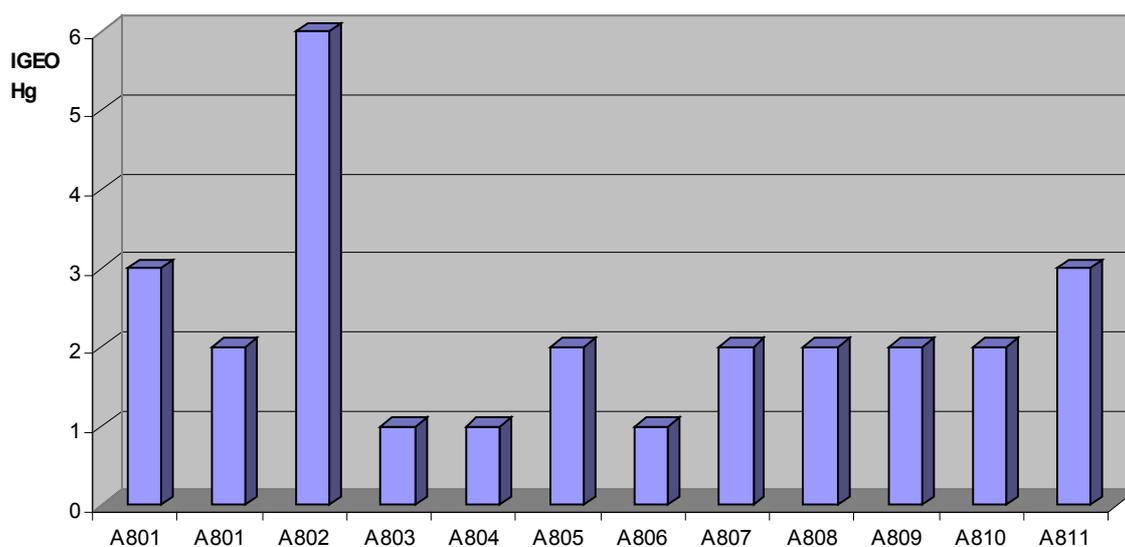


Figure 23 - Distribution of Igeo Classes of Hg in sediments and tailings (< 74 μm) of site A8

Sampling sites A9 and A10 represent the so-called Porto Alegre site and the mouth of a clear stream to the Crepori River, both located upstream of the investigated mining areas, but downstream of other mining sites along the Crepori River (Figure 25). A similar picture in terms of Hg contamination in inorganic samples, as in sites A6 and A7, is to be reported for A9 and A10, where Igeo classes of Hg range from 0 to 4, being predominant values close to the background, with Igeo classes from 0 to 1 (Figures 26 and 27).

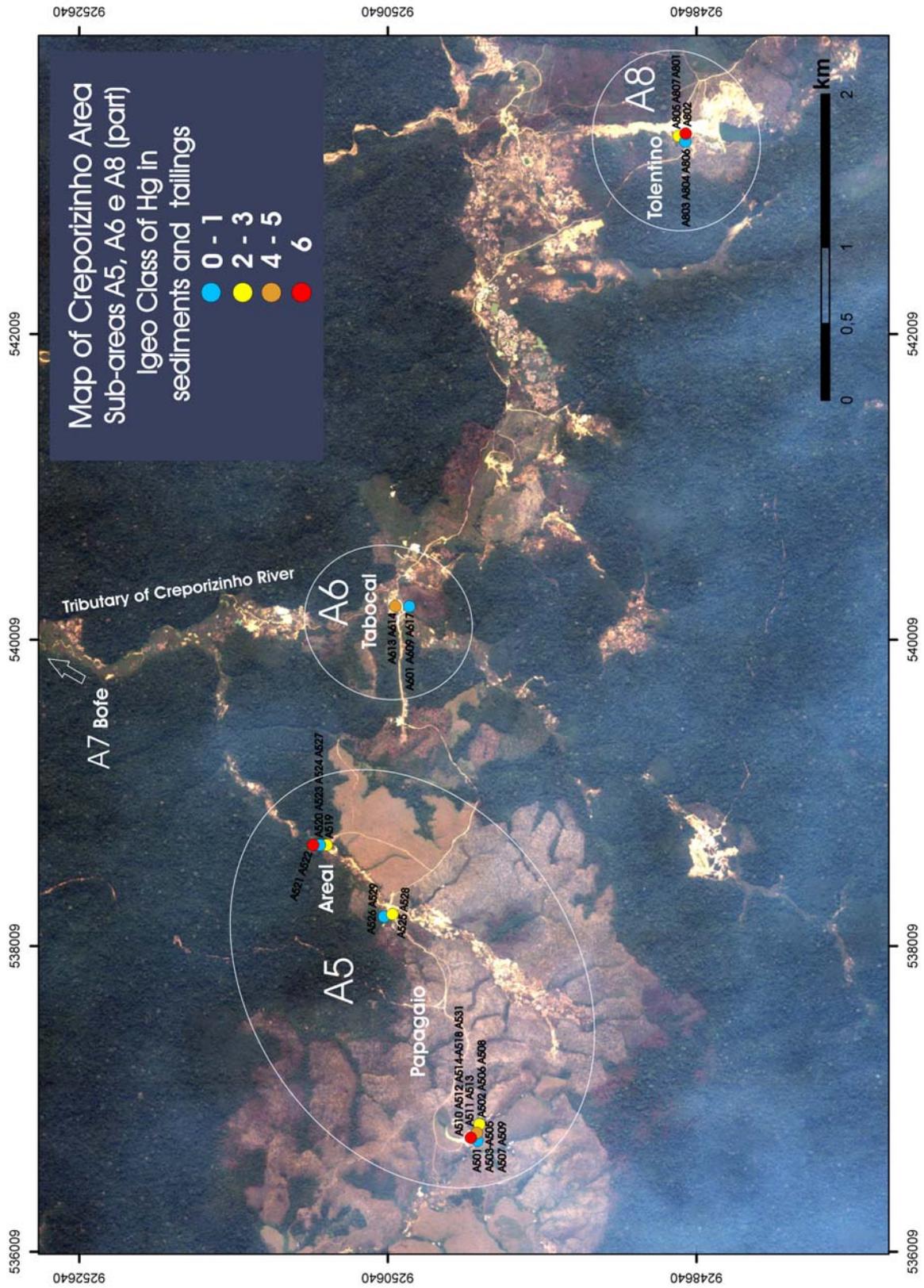


Figure 24 - Distribution of Igeo classes of Hg in the vicinities of the Creporizinho Village (Hg hotspots in red dots)

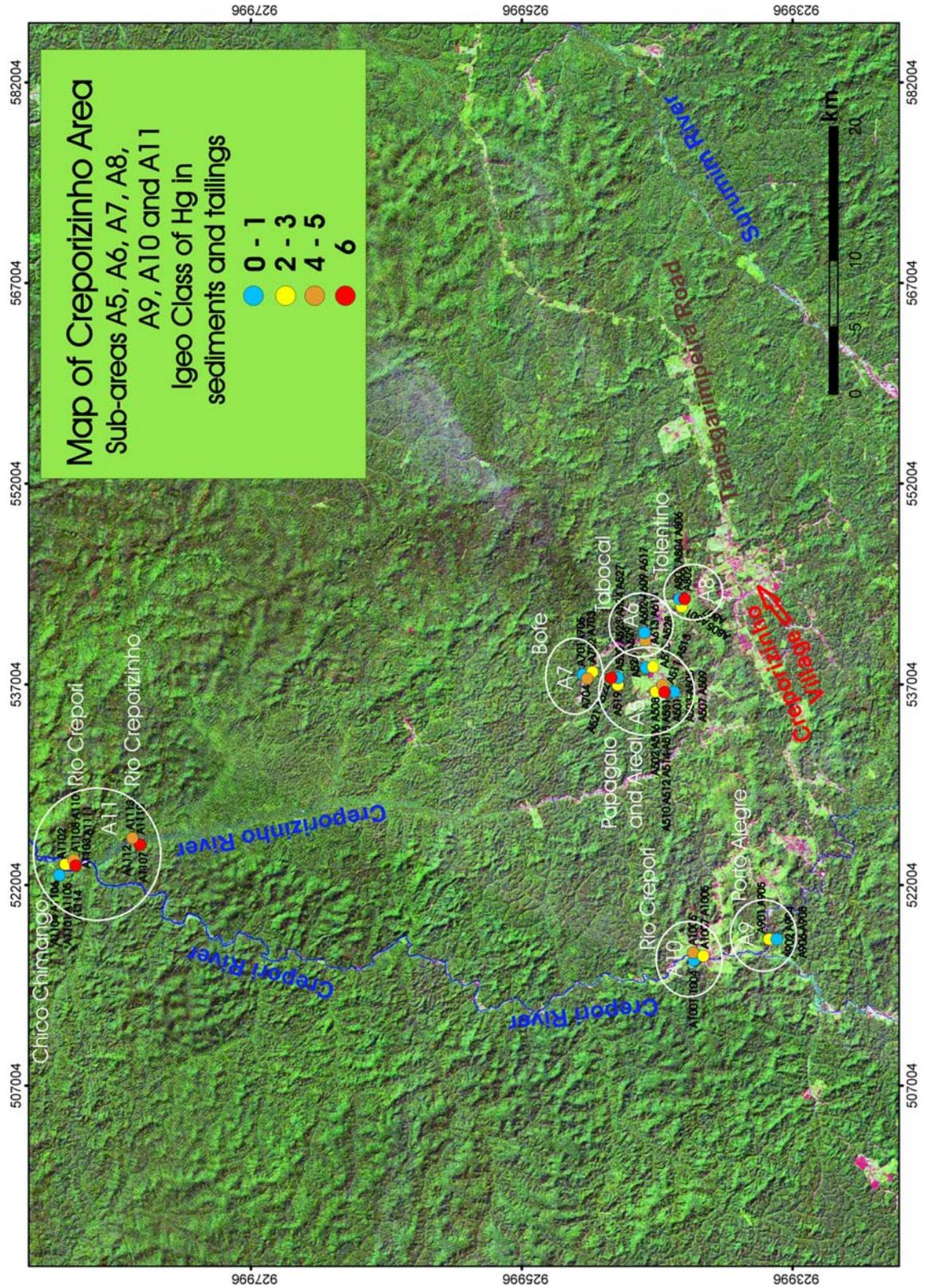


Figure 25 - Regional distribution of Igeo classes of Hg in sediments, tailings and soils from Creporizinho mining site and surrounding areas

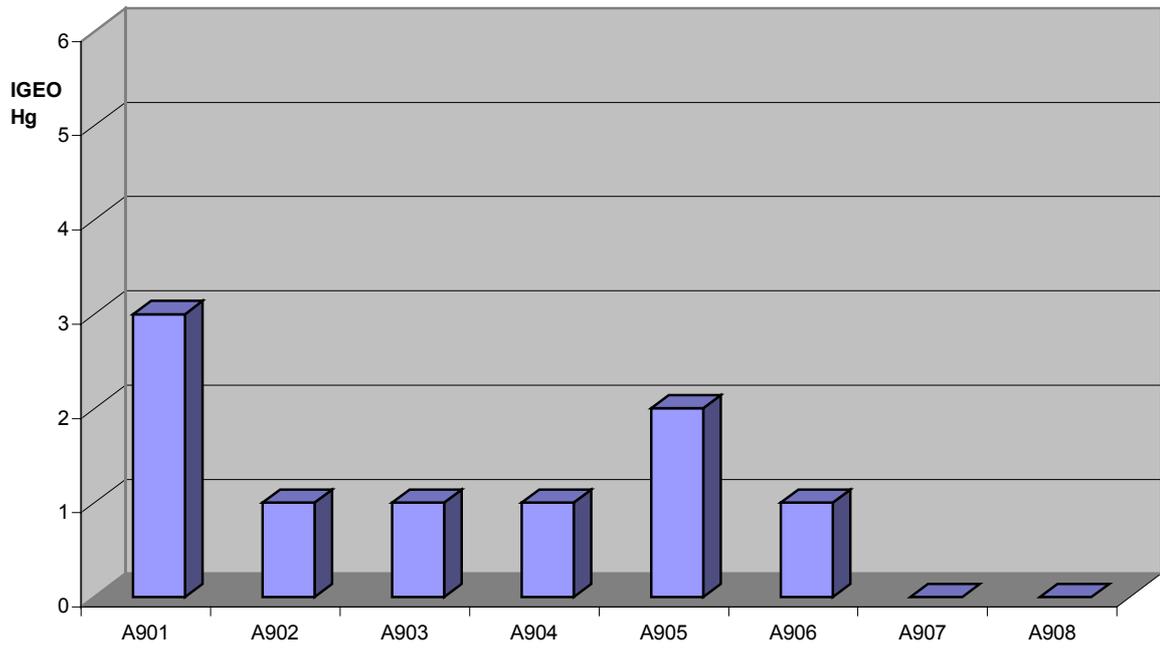


Figure 26 - Distribution of Igeo Classes of Hg in sediments and tailings (< 74 μm) of site A9

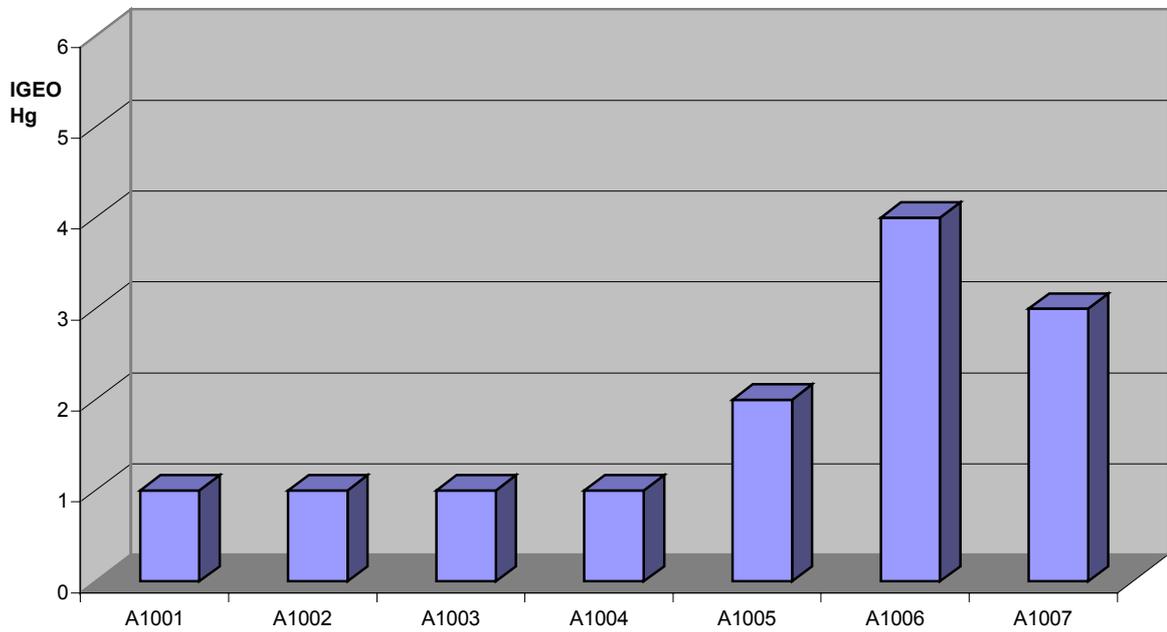
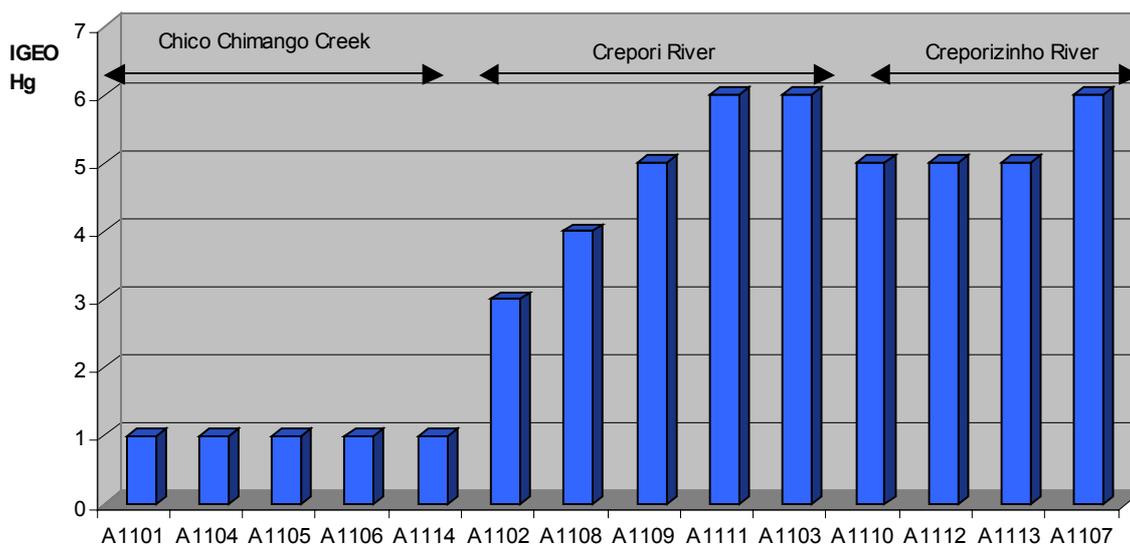


Figure 27 - Distribution of Igeo Classes of Hg in sediments and tailings (< 74 μm) of site A10

Sampling site A11 represents the most downstream area along the Crepori River, close to the mouth of the Creporizinho River, which drains the mining sites of Papagaio (A5), Tabocal (A6), Bofe (A7) and Tolentino (A8). This sampling site lies circa of 40 km from the mining sites downstream (Figure 28).

A total of 9 water samples were collected in the Creporizinho and Crepori River. Their results show Hg levels from 0.10 to 3.44  $\mu\text{g/L}$ , averaging 1.55  $\mu\text{g/L}$ , which is slightly higher in the filtered phase than the limit, of 1  $\mu\text{g/L}$  for drinking water established by the Brazilian Ministry of Health. It is to be highlighted that Hg concentrations in water samples from gold mining sites generally fall in the range from 0.10 to 2.80  $\mu\text{g/L}$  (Rodrigues-Filho and Maddock, 1997).

Although among 9 sediment samples there are significant indications of Hg contamination in fine sediments, as shown in Figure 33, indicating that Hg is being transported onto suspended particles downstream, one may face in this case severe difficulties in tracing the source of Hg. This difficulty is due to the existence of several mining operations throughout the Crepori river basin. In contrast to the clear water Chico Chimango Creek, the high values of Igeo classes are represented by the samples from both Crepori and Creporizinho River that drains several mining sites not considered in this study.



**Figure 28 - Distribution of Igeo Classes of Hg in sediments and tailings (< 74  $\mu\text{m}$ ) of site A11**

Creporizinho has been a strategic important village in the Tapajós Gold Mining Reserve since its foundation in 1962. The remaining 4 Gold shops, sharing turnovers of about 20 kg of gold per month, are operating with crude and primitive facilities for burning of amalgam. Vapour outlets exist in all of these shops, but none of them seems to work properly (Figure 29), so, contamination caused by mercury is to be found inside the shops as well as outside in the surroundings. Since during the past 40 years those types of shops were spread over the whole village area, soils and dust collected in the village might be a good indicator for accumulation of precipitated mercury.



**Figure 29 - Gold shop in Creporizinho**

The entire mining area around Creporizinho drains via small, partially unnamed watercourses leading to Creporizinho River, which flows into Rio Crepori, then into Tapajós and via Amazonas into Atlantic Ocean, in a distance of about 2,000 kilometres. Fine sediments are originally rare along the clear water drainages, although significant turbidity could be observed as a consequence of mining activities.

### **4.3. Mercury in Fish**

Fish sampling was conducted in August 2003, at two study areas: at São Chico and at Creporizinho mining sites or “garimpo” areas. These areas are located inside of the Mineral Tapajós Reserve, State of Para, between the cities of Jacareacanga and Itaituba, where the mining sites are distributed alongside the tributaries of the Tapajós River. These two areas belong to two distinct hydrographic basins: Jamanxin river basin and Crepori river basin, respectively.

The absence of a consistent relationship between Hg concentrations in water, sediment and various fish species, in general, illustrates the complexity and site-specific nature of mercury bioaccumulation. Thus, direct Hg determinations in the local biota appear to be crucial to adequately evaluating Hg sources, and, ultimately, the risk of the Hg exposure to human health (Peterson et al.1996).

It was investigated the mercury levels in fish from all 11 sites: 4 in São Chico and 7 in Creporizinho. A total of **234 fish** specimens of 16 species were collected: 73 specimens belonging to 13 species in São Chico and 161 specimens of 11 species in Creporizinho. A total of 7 common species could be collected in both areas (acari, cará, curimatã, mandi, piau, piranha and traíra). Table 3 shows the popular and scientific names of species collected in the Tapajós region; their food habits (FH), the number of specimens collected (n) in each site (A) and total number of fish collected.

**Table 3 - Study sites in São Chico (A1-A4) and Creporzinho (A5-A11) garimpo areas**

<b>Study Site</b>	
A1	Flooded open pit, clear water, near to Conrado River
A2	São Chico Reservoir
A3	Flooded open pit, mining wastes, high turbidity, near Rosa stream, sandy area
A4	Inflow Conrado River to Novo River
A5	Papagaio mining site; stream with high turbidity
A6	Flooded open pit at Bofe mining site
A7	Flooded open pit at Baieta/Tabocal mining site
A8	Buriti mining site; recent flooded open pit, near to Creporzinho River spring
A9	Porto Alegre site in Crepori River, upstream of Creporização village, with fluvial garimpo's areas
A10	Inflow of clear stream to Crepori River
A11	Inflow of Chico Chimango, a clear water stream to Crepori River, near the inflow of Creporzinho River to Crepori River

Table 4 shows the popular and scientific names of species collected in the Tapajós region; their food habits (FH), the number of specimens collected (n) in each site (A) and total number of fish collected. In Appendix 3 there are some photos of fish sampling sites and fish collected.

Table 4 - Popular and scientific names of species collected in the Tapajós river region; food habits (FH), number of specimens collected (n) in each site (A) and total number of fish collected

Popular name	Scientific name	FH	São Chico						CrepORIZINHO					Total			
			A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11				
Acari	<i>Hypostomus</i> sp	D			2								11			2	15
Arraia	<i>Potamotrygon motoro</i>	C				3											3
Bocudo	<i>Ageneiosus brevifilis</i>	C												1			1
Candiru	<i>Hemicetopsis candiru</i>	O											2	2			4
Cará	<i>Cichlasoma spectabile</i>	M	3	20				5	3	1	35						67
Curimatá	<i>Prochilodus nigricans</i>	D	8										3	1	2		14
Sairu	<i>Cyphocharax</i> sp	MF						10	7	29	1			3			50
Lambari	<i>Hemigrammus unilineatus</i>	C			4												4
Ituí	<i>Sternopygus macrurus</i>	I			5												5
Mandi	<i>Pimelodus blochii</i>	O	1			1			1								4
Pacu	<i>Myelus</i> sp	H	1														1
Piau	<i>Anostomoides laticeps</i>	H	1						1	1					13		16
Piranha	<i>Serrasalmus rhombeus</i>	C					2						6	2	8		18
Pirarara	<i>Phractocephalus hemiliopterus</i>	C				1											1
Surubim	<i>Pseudoplatystoma fasciatum</i>	C				1											1
Traíra	<i>Hoplias malabaricus</i>	C	1	13	5	1	1	2	3	2	2			1			30
	<b>Total</b>		15	33	16	9	9	17	15	33	39	22	10	25			<b>234</b>

carnivorous and/or ichthyophagous=C; herbivorous=H, insectivorous=I; microphagous=M; omnivorous=O; macrofauna=MF

Fish samples were collected usually by gill-netting, fishing line with a fish-hook and fishing line with several hooks (“espinhel”). Each specimen was weighed (Wt), and its length (Lt) was measured at the time of collection. After removing the individual axial muscle (filet), each sample was placed in polyethylene bags and cooled in ice box before being frozen for transportation.

The results of total mercury in fish, length and weight from São Chico and Creporizinho area are shown in Table 5.

**Table 5 - Results of total Hg in muscles (wet weight), length and weight of fish from both study areas (arithmetical mean and standard deviation)**

Garimpo area	N	Mercury ( $\mu\text{g/g}$ )	N	Length (cm)	N	Weight (g)
São Chico	73	2.53 $\pm$ 3.91*	73	18.75 $\pm$ 14.42*	32	934.3 $\pm$ 1,681.7*
Creporizinho	161	0.36 $\pm$ 0.33	161	11.62 $\pm$ 4.86	49	191.8 $\pm$ 186.0
Total	234	1.04 $\pm$ 2.42	234	13.84 $\pm$ 9.56	81	485.2 $\pm$ 1,118,0

N= number of specimens. Student's t-Test; \* p<0.0001

It is well known that freshwater biota is able to accumulate Hg from natural and anthropogenic sources. Maximum background levels for Hg in uncontaminated freshwater fish are in the range of 0.1 to 0.3  $\mu\text{g/g}$ , although considerably higher levels can be found in large predators. The mean concentration of Hg (1.04 $\mu\text{g/g}$ ) in fish species from this work was similar to that from species from some Amazonian rivers, mainly contaminated rivers (Lacerda & Solomons, 1991; Akagi et al, 1994, Malm et al., 1996; Bidone et al., 1997; Castilhos et al., 1998; Brabo, 2000). However, São Chico area has shown Hg levels in fish that are considered abnormally high, comparing then with results from previous works. Among the analyzed fish, 82 specimens (35% of total sampled fish) from 6 species (37,5% of total 16 species collected) presented Hg concentrations above 0.5  $\mu\text{g/g}$ , the Hg concentration in fish recommended by WHO (1990) as limit for human protection by Hg exposure by fish consumption. Whereas in Creporizinho 22% of fish samples showed Hg levels above that limit, in São Chico this percentage increases to more than 60%.

The results show that total mercury in fish from São Chico (Figure 30) is higher than in fish from Creporizinho area (Student's t-Test; t=4,75; p<0.0001), Figure 31. Table 6 shows that the minimum values for Hg in fish are similar between areas, but the maximum values are one order of magnitude higher in São Chico than in Creporizinho area.

**Table 6 - Results of total Hg in fish from both study areas (arithmetical mean  $\pm$  standard deviation and range -maximum and minimum values; wet weight)**

Garimpo area	N	Mercury ( $\mu\text{g/g}$ )	Range
São Chico	73	2.53 $\pm$ 3.91	0.027-21.90
Creporizinho	161	0.36 $\pm$ 0.33	0.025-2.10
Total	234	1.04 $\pm$ 2.42	0.025-21.90

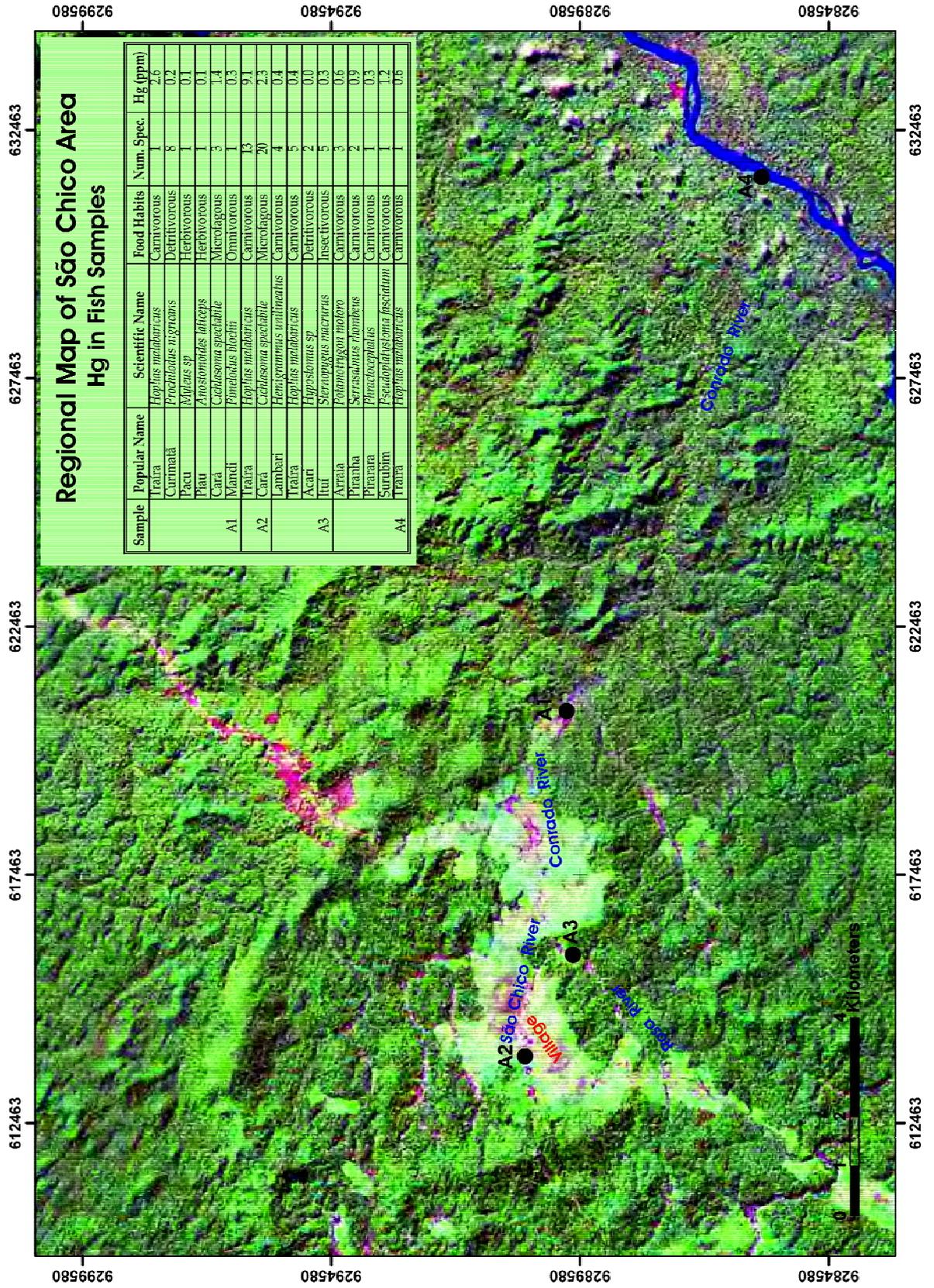


Figure 30 - Mercury distribution in fish from different sites in São Chico area

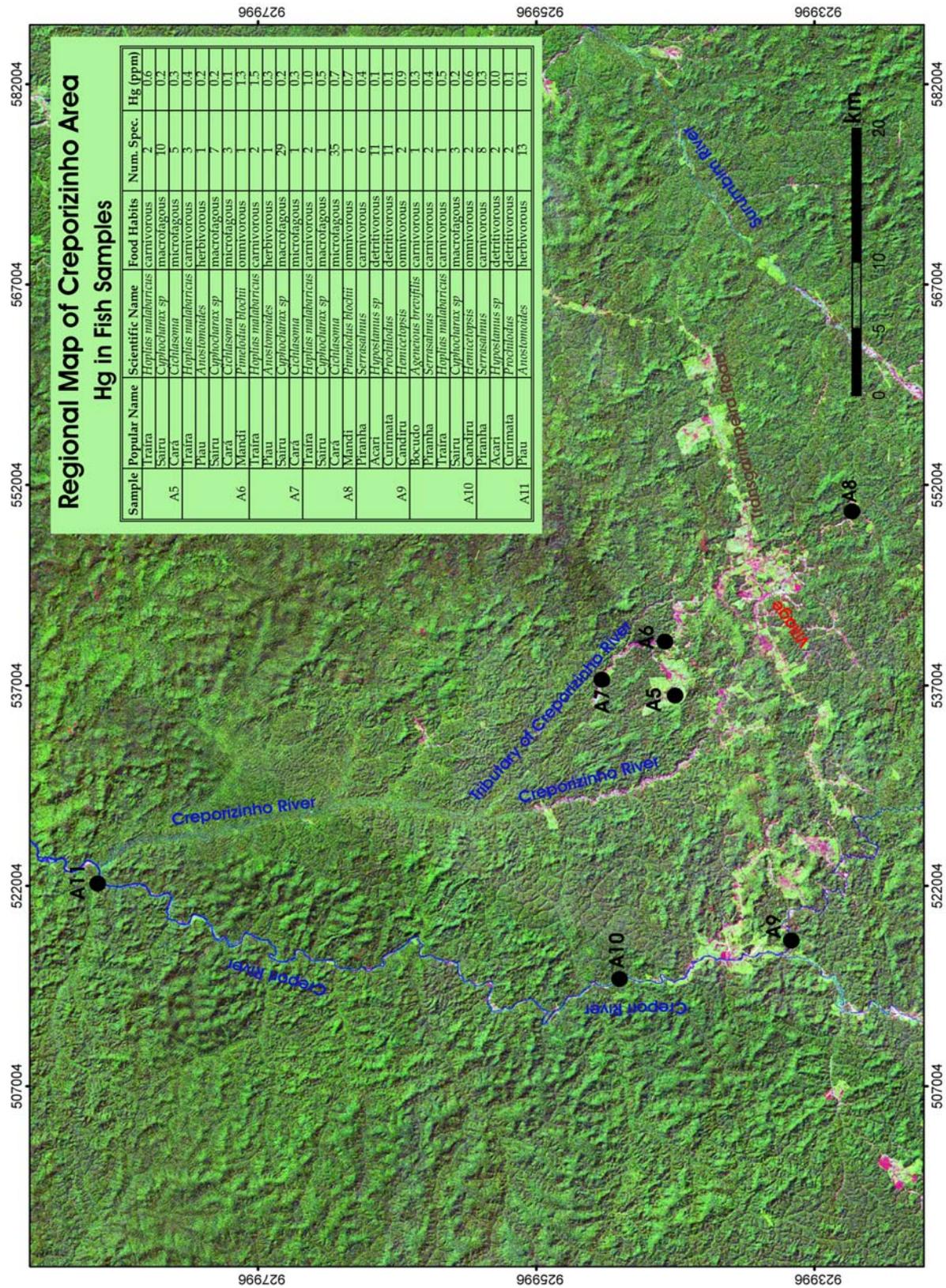


Figure 31 - Mercury distribution in fish from different sites in Creporizinho area

Comparisons with global means of Hg in fish, however, may result in a certain misinterpretation, since observations on given species of marine and freshwater fish indicate that all tissue concentrations of mercury increase with increasing age (as inferred from length) of fish (WHO, 1990); it is also strongly affected by fish species and size (length and weight) and, in addition, it is generally agreed that Hg concentrations in carnivorous fish are higher than in non-carnivorous species (e.g., Watras and Huckabee 1994), due to the indirect Hg bioaccumulation or biomagnification. Considering that, the data were compared, firstly, between garimpos' areas and among their sites; secondly, considering the different food habits of fish species collected and, after, by using Hg concentrations in individual species collected. It was investigated a relationship between fish length and Hg levels, by correlation analysis with log-transformed and non-transformed data and, also, by using the mean values of the length intervals. The objective was to assess the Hg contamination in those sites and to find an indicator of Hg bioavailability, by using fish species.

Fish from São Chico are also heavier and larger than those from Creporizinho area ( $t=2.49$ ;  $p<0.0001$  and  $t=4.12$ ;  $p<0.0001$ ; respectively). However, the present results showed no correlation between fish Hg concentration and weight or length when analyzing **all specimens in both areas**. The significant correlation between Hg levels and length is very low ( $0.13$ ;  $p<0.05$ ;  $n=234$ ) and the higher correlation between Hg levels and weight is not significant ( $-0.668$ ; n.s;  $n=81$ ). Maybe it is because we are dealing with many species within each group. Additionally, in this work, the weight measurements were not performed for fish lighter than 100 g, and this parameter were performed just for 35% of the specimens collected ( $n=81$ ).

Comparing mercury levels in fish from each site within each study area (São Chico and Creporizinho) the results (Table 7) showed that fish from A2 (São Chico Reservoir) have the highest mercury levels ( $4.97\pm 4.80\mu\text{g/g}$ ), whereas the other sites in São Chico area, A1, A3 and A4 present no significant difference to each other. Additionally, fish from A2 are smaller than fish from A3 and A4. Fish from A4 are heavier than the others sites. Furthermore, fish from A2 showed positive and significant correlation between Hg in muscles and length but not with weight ( $n=13$ ), whereas in the other sites (A1, A3 and A4) there was no significant correlation (Table I in Appendix 2).

**Table 7 - Total Hg in fish muscles (arithmetical mean  $\pm$  standard deviation; wet weight) from different sites of São Chico and Creporizinho garimpo's areas**

Garimpo area	N	Mercury ( $\mu\text{g/g}$ )	N	Length (cm)	N	Weight (g)
São Chico	73	$2.53\pm 3.91$	73	$18.75\pm 14.42$	32	$934.3\pm 1,681.7$
A1	15	$0.57\pm 0.75$	15	$12.33\pm 4.01$	1	
A2	33	$4.97\pm 4.80$	33	$13.11\pm 6.83$	13	$200.0\pm 81.64$
A3	16	$0.32\pm 0.15$	16	$22.04\pm 13.2$	9	$166.7\pm 66.1$
A4	9	$0.83\pm 0.43$	9	$43.61\pm 20.0$	9	$2,838.9\pm 2,294.5$
Creporizinho	161	$0.36\pm 0.33$	161	$11.62\pm 4.86$	49	$191.8\pm 186.0$
A5	17	$0.27\pm 0.16$	17	$9.53\pm 1.88$	-	
A6	15	$0.30\pm 0.30$	15	$13.4\pm 7.15$	5	$290.0\pm 134.2$
A7	33	$0.32\pm 0.35$	33	$9.80\pm 2.57$	3	$150.0\pm 86.6$
A8	39	$0.66\pm 0.33$	39	$8.57\pm 2.33$	2	$150.0\pm 70.7$
A9	22	$0.25\pm 0.28$	22	$13.2\pm 3.00$	12	$129.7\pm 62.0$
A10	10	$0.32\pm 0.17$	10	$15.75\pm 9.25$	6	$341.7\pm 196.4$
A11	25	$0.13\pm 0.10$	25	$16.06\pm 3.58$	21	$171.4\pm 48.9$
Total	234	$1.04\pm 2.42$	234	$13.84\pm 9.56$	81	$485.2\pm 1,118.0$

In Creporizinho area, fish from the site A8 showed higher Hg levels ( $0.66 \pm 0.33 \mu\text{g/g}$ ) than all the other sites (A5, A6, A7, A9, A10 and A11), but specimens are smaller than fish from other sites (A6, A9, A10 and A11). Also, fish from A7 showed higher Hg levels than fish from A11 and the others did not show significant differences among each other. It is indicated that A8 is the most contaminated site in Creporizinho area. Fish from this site have the highest Hg levels and are smaller than fish from the other sites. Significant positive correlation between Hg in muscles and length were found in sites A6, A7, A9 and significant negative correlation in A11. For A11 the negative and significant correlation was found also between Hg in muscles and weight (Table I in Appendix 2).

The indirect bioaccumulation or biomagnification is a phenomenon through which a chemical substance accumulates in a given species according to its trophic levels in a food chain (Bruggeman 1982). Noncarnivorous fish represents close to 75% of total sampled fish in this work ( $n=234$ ). Microfagous represents 36%, macrofagous 30%, detritivorous 15%, herbivorous 10%, omnivorous 5% and insectivorous, 3% approximately. In São Chico area, non-carnivorous and carnivorous fish represents close to 50% each, but at A1 and A2 sites in São Chico area non-carnivorous fish represents more than 60%, whereas at A3 and A4, carnivorous are predominant (56% and 88%, respectively).

In Creporizinho area, non-carnivorous fish represents close to 85% of collected fish, since from the A5 site to A11, non carnivorous fish are the majority (above 60%). Carnivorous species are placed at a higher trophic level than non-carnivorous species in a food chain. It is generally agreed that Hg concentrations in carnivorous fish are higher than in non-carnivorous species (e.g., Watras and Huckabee 1994). This was observed for results showed in Table II in Appendix 2, for total data (Student's t-Test;  $t=3.30$ ;  $p<0,005$ ) and for both studied areas (São Chico:  $t=2.84$ ;  $p<0,05$ ; Creporizinho:  $t=2.66$ ;  $p<0,01$ ).

The ratio between mercury levels in carnivorous: non-carnivorous fish resulted in 4.4 for total fish sampled, 4.3 for São Chico and 1,6 for Creporizinho, meaning that carnivorous fish showed from 1.6 to 4.4 times more mercury levels than non-carnivorous fish. Whereas the carnivorous fish are heavier and larger than non-carnivorous when total data are analyzed ( $t=5.21$ ;  $p<0.0001$ ), only the differences in length remains significant when the data are analyzed separately in each area ( $t=3.52$ ;  $p<0.001$  and  $t=3.99$ ;  $p<0.0001$  for São Chico and Creporizinho, respectively).

The correlation between Hg in muscles and length considering total data (Table III in Appendix 2) showed no correlation for carnivorous, and significant but lower correlation for non-carnivorous and its correlation between Hg in muscles and weight resulted positive and significant. However, its important to consider the few number of specimens available for this analysis.

Considering the data in each area, the results showed that the correlation only between Hg in muscles and length were significant. Non-carnivorous showed a negative and significant correlation in both areas, São Chico and Creporizinho. In Creporizinho, carnivorous fish showed positive and significant correlation for Hg in muscles and length (Table I in Appendix 2).

In order to assess the Hg biomagnification processes in the ichthyofauna of the studied areas, the data were worked out whereby distinct food habits and their correspondent Hg concentrations were taken into account and analyzed. The fish were classified as carnivorous (arraia, bocudo, lambari, piranha, pirarara, surubim e traíra) and non-carnivorous. The non-carnivorous fish species were classified into (i) detritivorous-D- (acari and curimatã); (ii) herbivorous-H- (pacu and piau), (iii) insectivorous-I- (ituí), (iv) macrophagous-Mf- (sairu), (v)

microphagous-M- (cará) and omnivorous-O- (candiru and mandi). The results of mercury, length and weight in these groups are shown in Table IV in Appendix 2.

The carnivorous fish species are pelagic and they are active in water column. Adults feed mainly on freshwater shrimps and fish. The detritivorous fish have as basic food source algae, bacteria and other organisms living in lime or mud and detritus. The herbivorous fish feed on fruits, roots, seeds and other important parts of the plant material. For these species, the flooded forest is an important food source. The insectivorous fish feed mainly on insects and the macrophagous have the macrofauna (ex. poliquetas; crustaceans; gastropoda; bivalvia) as the principal food item. The microphagous feed mainly on microorganisms as amoebas, small hidros, clams, briozoas and seas-squirt and the omnivorous fish can feed on either animal food or vegetable source, they have high capacity for feeding different kinds of food.

In São Chico area, the carnivorous species showed mercury levels different of the detritivorous. When this analysis is performed considering only non-carnivorous, the microfagous species are different of the herbivorous, detritivorous and insectivorous species ( $M > H = D = I$ ). In Creporizinho, the species of detritivorous, herbivorous and macrofagous showed mercury levels different of the carnivorous, microfagous and omnivorous ones, being macrofagous species different of detritivorous ones ( $D < O > C = M > H = Mf$ ;  $H = D < Mf$ ).

Hg levels were investigated in distinct fish species from studied areas, as shown in Table 8.

The results showed that Carás and Traíras from São Chico have higher mercury levels than from Creporizinho. Others species (Piranha, Acari, Curimatã, Piau and Mandi) did not show any difference between areas. Besides these results, it should be considered that Traíras and Carás were present in almost all of the studied aquatic systems. Then, they may be used as indicator species for mercury contamination in Amazonian aquatic ecosystems.

According to the correlation analyses, there are correlations between Hg and length and/or weight, in Creporizinho area, with Curimatã' and Piranha' species. The Curimatã specimens showed positives and significant correlation between Hg and length and between Hg and weight. The Piranha specimens showed strong positive and significant correlation between Hg and weight. In São Chico area, the species Curimatã and Ituí showed positive and significant correlation between Hg and length. The other species, including Traíra specie, did not show any significant correlation in both areas. The correlation coefficients were shown in Table I in Appendix 2.

**Table 8 - Total Hg concentrations (arithmetical mean ± standard deviation) in individual fish species (µg/g) from studied areas**

Popular name	Scientific name	Mercury (µg/g)			
		N	São Chico	N	Creporizinho
<b><i>Carnivorous</i></b>					
Arraia	<i>Potamotrygon motoro</i>	3	0.63±0.27		
Bocudo	<i>Ageneiosus brevifilis</i>			1	0.266
Lambari	<i>Hemigrammus unilineatus</i>	4	0.43±0.14		
Piranha	<i>Serrasalmus rhombeus</i>	2	0.93±0.38	16	0.34±0.13
Pirarara	<i>Phractocephalus hemiliopterus</i>	1	0.28		
Surubim	<i>Pseudoplatystoma fasciatum</i>	1	1.20		
Traíra**	<i>Hoplias malabaricus</i>	20	6.11±5.93	10	0.80±0.55
<b><i>Non-carnivorous</i></b>					
<b><i>Detritivorous</i></b>					
Acari	<i>Hypostomus sp</i>	2	0.03±0.01	13	0.05±0.02
Curimatã	<i>Prochilodus nigricans</i>	8	0.17±0.04	6	0.12±0.04
<b><i>Herbivorous</i></b>					
Pacu	<i>Myleus sp</i>	1	0.09		
Piau	<i>Anostomoides laticeps</i>	1	0.14	15	0.08±0.07
<b><i>Insectivorous</i></b>					
Ituí	<i>Sternopygus macrurus</i>	5	0.30±0.06		
<b><i>Macrofagous</i></b>					
Sairu	<i>Cyphocharax sp</i>			50	0.23±0.08
<b><i>Microfagous</i></b>					
Cará**	<i>Cichlasoma spectabile</i>	23	2.21±1.28	44	0.55±0.35
<b><i>Omnivorous</i></b>					
Candiru	<i>Hemicetopsis candiru</i>			4	0.73±0.21
Mandi	<i>Pimelodus blochii</i>	2	0.92±0.95	2	0.98±0.46
Total		73	2.53±3.91	161	0.36±0.33

N=number of specimens; Student-t Test \*\* p<0.0001

In Tables 9 and 10 are shown the average Hg concentrations in individual fish species (µg/g) from different sites in São Chico and Creporizinho, respectively.

**Table 9 - Total Hg concentrations (arithmetical mean±standard deviation) in individual fish species (µg/g) from São Chico garimpo area**

Popular name	Scientific name	Mercury (µg/g)			
		A1(n)	A2 (n)	A3 (n)	A4 (n)
<b><i>Carnivorous</i></b>					
Arraia	<i>Potamotrygon motoro</i>				0.63±0.27 (3)
Lambari	<i>Hemigrammus unilineatus</i>			0.43±0.13 (4)	
Piranha	<i>Serrasalmus rhombeus</i>				0.93±0.38 (2)
Pirarara	<i>Phractocephalus hemiliopterus</i>				0.27 (1)
Surubim	<i>Pseudoplatystoma fasciatum</i>				1.2 (1)
Traíra	<i>Hoplias malabaricus</i>	2.6 (1)	9.01±5.4*(13)	0.39±0.09 (5)	0.60 (1)
<b><i>Non-carnivorous</i></b>					
<b><i>Detritivorous</i></b>					
Acari	<i>Hypostomus sp</i>			0.03±0.003 (2)	
Curimatã	<i>Prochilodus nigricans</i>	0.16±0.04(8)			
<b><i>Herbivorous</i></b>					
Pacu	<i>Myleus sp</i>	0.09 (1)			
Piau	<i>Anostomoides laticeps</i>	0.14(1)			
<b><i>Insectivorous</i></b>					
Ituí	<i>Sternopygus macrurus</i>			0.30±0.06(5)	
<b><i>Microfagous</i></b>					
Cará	<i>Cichlasoma spectabile</i>	1.36±0.15(3)	2.34±1.33 (20)		
<b><i>Omnivorous</i></b>					
Mandi	<i>Pimelodus blochii</i>	0.25 (1)			1.6 (1)
Total		15	33	16	9

N=number of specimens; \* Student's-T test (t=5.73) p<0.0001

In São Chico area, all fish species were collected only in one site, or in very few number in more sites than one, except Traíras and Carás. Traíras are similar in length and weight, but Hg levels are higher in specimens from A2 than from A3. Carás did not show Hg levels significant differences between A1 and A2, but specimens from A1 are bigger than ones from A2. It is possible that Carás from A2 have less exposure time for mercury than A1, and, if the time exposure were similar, the mercury levels would be higher. In addition, it should be considered that there is few specimens in A1.

**Table 10 - Total Hg concentrations (arithmetical mean±standard deviation) in individual fish species (µg/g ) from Creporizinho garimpo area**

Popular name	Mercury (µg/g)						
	A5 (n)	A6 (n)	A7 (n)	A8 (n)	A9 (n)	A10 (n)	A11 (n)
<b>Carnivorous</b>							
Bocudo						0.266 (1)	
Piranha					0.44±0.15 (6)	0.38±0.01 (2)	0.25±0.06 (8)
Traíra	0.61±0.29 (2)	0.38±0.03 (3)	1.54±0.78 (2)	1.04±0.36 (2)		0.46 (1)	
<b>Non-carnivorous</b>							
<i>Detritivorous</i>							
Acari					0.05±0.01 (11)		0.04±0.02 (2)
Curimatã					0.11±0.06 (3)	0.15 (1)	0.12±0.04 (2)
<i>Herbivorous</i>							
Piau		0.19 (1)	0.30 (1)				0.06±0.02 (13)
<i>Macrofagous</i>							
Sairu	0.20±0.04 (10)	0.20±0.06 (7)	0.24±0.07 (29)	0.51 (1)		0.15±0.04 (3)	
<i>Microfagous</i>							
Cará	0.25±0.06 (5)	0.11±0.07 (3)	0.27 (1)	0.65±0.33 (35)			
<i>Omnivorous</i>							
Candiru					0.91±0.64 (2)	0.56±0.07 (2)	
Mandi		1.3 (1)		0.65 (1)			
<b>Total</b>	<b>17</b>	<b>15</b>	<b>33</b>	<b>39</b>	<b>22</b>	<b>10</b>	<b>25</b>

N= number of specimens

In Creporizinho area, Piranha specie showed no differences in length and weight, but Hg levels are higher in specimens from A9 than from A11. Traíra specie showed no differences in mercury levels, length or weight for specimens from A5, A6, A7 and A8. Cará specimens from A8 are smaller but showed higher mercury levels than ones from A5 and A6 (Kruskall-Wallis One-Way ANOVA and Mann-Whitney U-test).

It was performed the correlation analysis considering specific species collected from different sites, when the number of specimens were enough (more than 4). Traíras from A2 showed very low and no significant correlation between Hg and length or weight. Traíras from A3 showed relatively high but no significant negative correlation between Hg and length and no correlation between Hg and weight. Lambari from A3, Cará from A2, A5 and A8 and Sairu from A5, A6 and A7 did not show any correlation between Hg and length.

Curimatã from A1 and Acari from A9 showed significant correlation between Hg and length and Piranha from A11 showed significant correlation between Hg and weight. The correlation coefficients were shown in Table I in Appendix 2.

In Table 11 are shown total mercury levels in Traíras and Carás from several sites of two study area and the ratio of mercury between these species, a carnivorous and a non-carnivorous species. The ratio ranged from about 2 to 4, which means that Hg accumulates from 2 to 4 times more in Traíras than in Carás.

In addition, the results showed that Hg levels only in Traíras from A2 are higher than Traíras from the other sites, similar one each other (Kruskall-Wallis One-Way ANOVA and Mann-Whitney U-test). Mercury levels in Carás from A1 and A2 are higher than Carás from A5, A6, and A8 ( $p < 0.005$ ). A7 has one specimen. Mercury levels in Carás from A5 and A6 are similar each other and lower than levels in Carás from A8 ( $p < 0.05$ ; Kruskal-Wallis One-Way ANOVA and Mann-Whitney U-test).

**Table 11 - Ratio of total mercury in muscles of Traíras and Carás from different study sites in both Garimpo's areas, São Chico and Creporizinho**

Study sites	Traíras (T)		Carás (C)		Ratio Hg T/C
	N	Mercury ( $\mu\text{g/g}$ )	N	Mercury ( $\mu\text{g/g}$ )	
A1	1	2.6	3	1.36 $\pm$ 0.15	
A2	13	9.00 $\pm$ 5.42	20	2.34 $\pm$ 1.33	3,8
A3	5	0.39 $\pm$ 0.09	-	-	
A4	1	0.61	-	-	
A5	2	0.60 $\pm$ 0.29	5	0.25 $\pm$ 0.06	2,4
A6	3	0.38 $\pm$ 0.03	3	0.11 $\pm$ 0.07	3,45
A7	2	1.54 $\pm$ 0.78	1	0.27	
A8	2	1.04 $\pm$ 0.35	35	0.65 $\pm$ 0.33	1,6
A10	1	0.46	-	-	

Although Traíras and Carás did not show any correlation between mercury levels and length or weight when total data were analyzed in São Chico and/or Creporizinho and, even, when data from each site was considered, we decided to investigate the correspondence between log of length and log of mercury levels in muscles, as advised by Protocol. We chosen these species because they are distributed throughout the studied aquatic systems, have different food habits and the number of specimens collected are large enough. The data analyzed showed very low correlation between parameters for all Traíras from São Chico and for Traíras from A2, as shown in Figures I and II in Appendix 2.

The analysis were also performed with species from all sites, when adequate number of specimens was available, but there was no strong correlation for: Traíras from São Chico, from A2, from A3 and from Creporizinho; Cará from São Chico, from A2, from Creporizinho; from A5 and from A8; Sairu from Creporizinho, from A5, from A6, from A7; Piau from A1 and Piranha from A11. The results showed strong positive correlation between log length and log mercury levels only for Curimatã from A1 (São Chico area), Acari and Piranhas from A9 (Creporizinho area). These results are shown in Figures 32, 33 and 34.

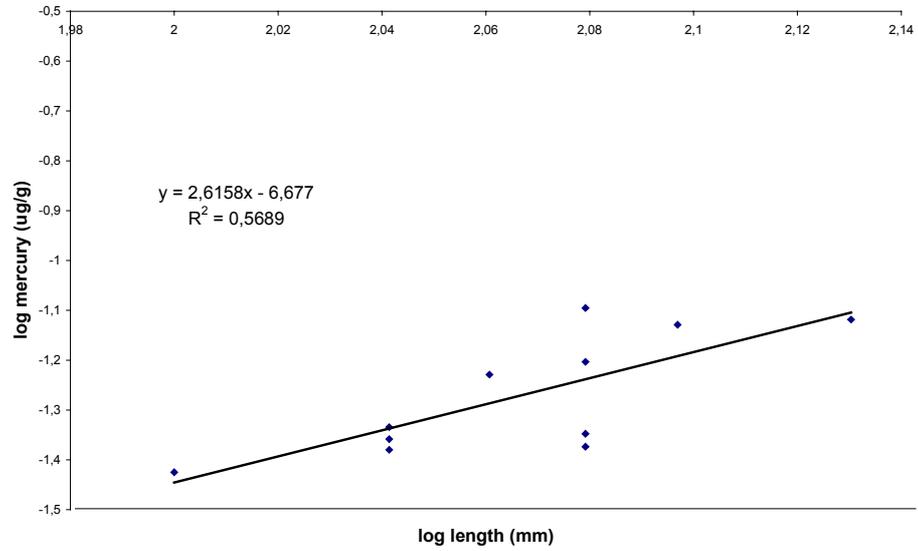


Figure 32- Log fish length versus log Hg in Acari from A9 (n=11) from Creporizinho Garimpo's area.

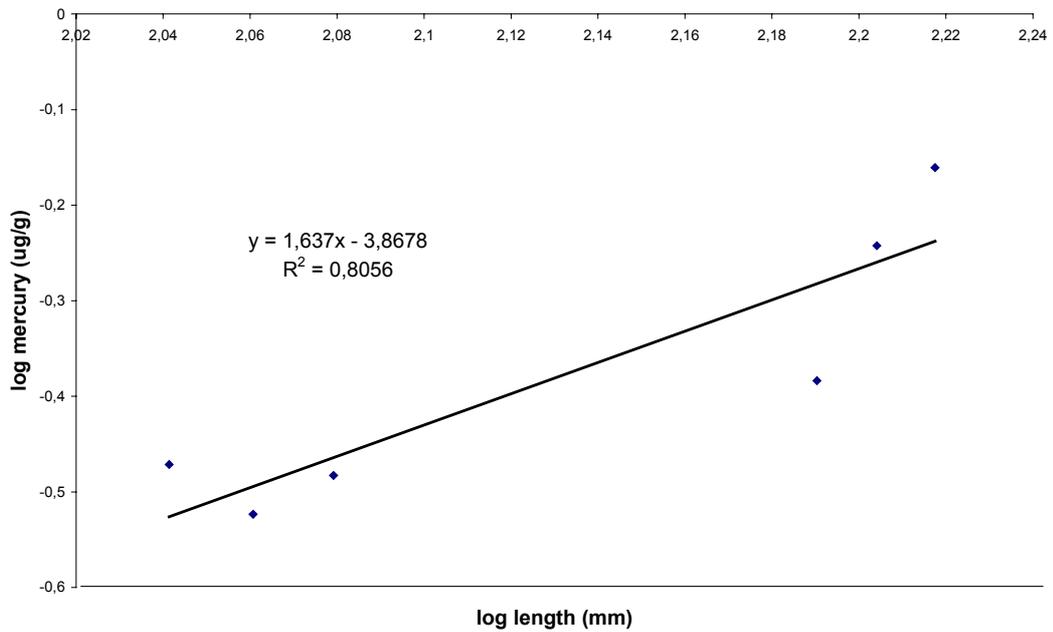
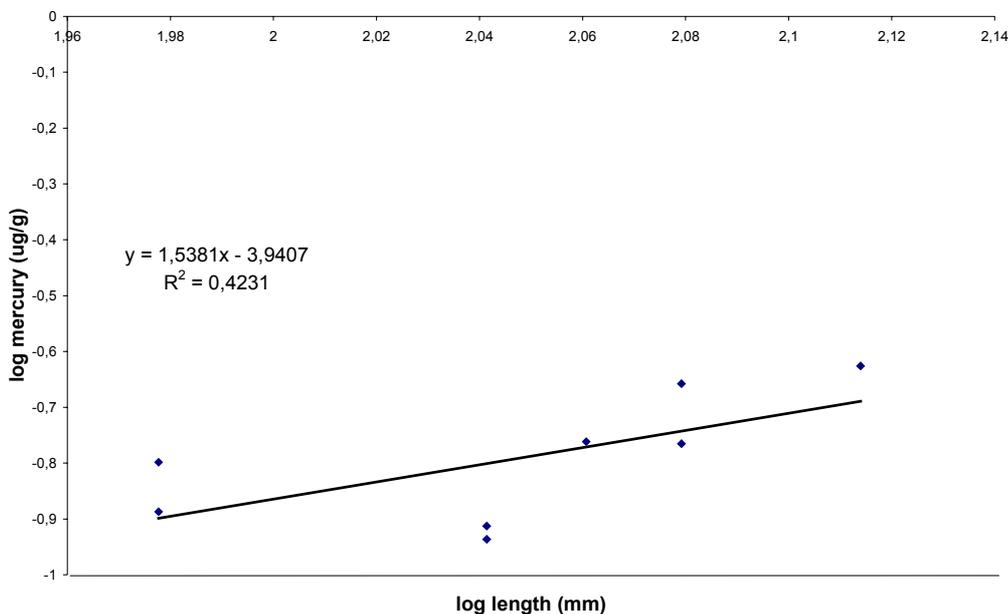


Figure 33 - Log fish length versus log Hg in Piranhas from A9 (n=6) from Creporizinho Garimpo's area



**Figure 34 - Log fish length versus log Hg in Curimatã from A1 (n=8) from São Chico Garimpo's area**

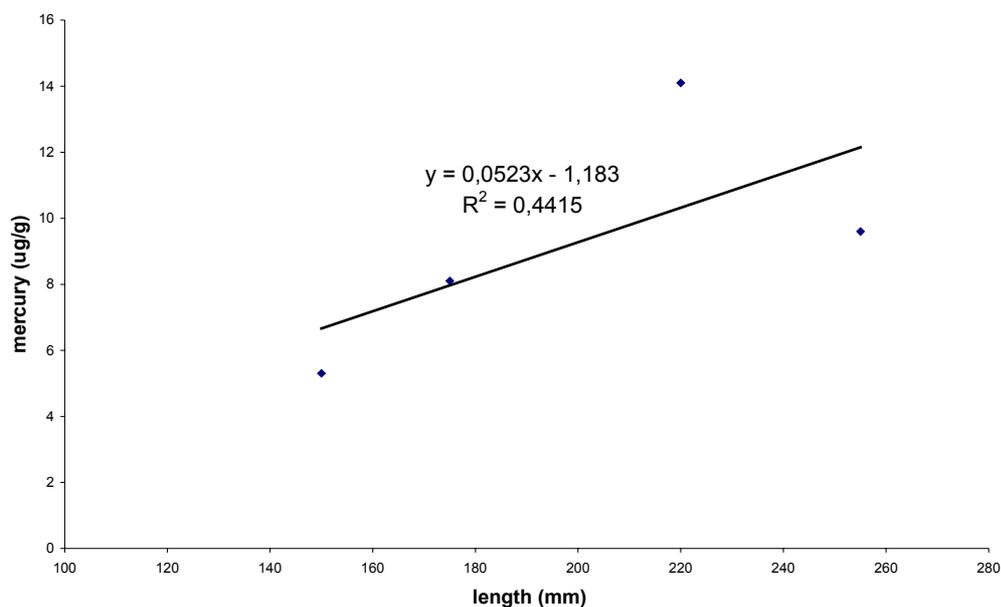
Considering the low correlation coefficient resulting from analysis of transformed data for most part of species studied, we decided to investigate the correspondence between length intervals (close to 10cm to Traíras and 5cm to Carás, as for other species, when available) and the average mercury levels in fish muscles, trying to decrease the high variability in data, and considering data not log transformed. In addition, these data were log transformed and the correlation coefficient were also investigated. The results are shown in Table V in Appendix 2. It could be notice that there are no significant differences between the analysis, except for Piau from Creporizinho, where the log values showed stronger negative correlation coefficient ( $y = -4.0512x + 7.9362$ ;  $R^2 = 0,5544$ ) than values not log transformed, and for Acari from Creporizinho, where the results from not transformed data were stronger. The other results showed the same tendency.

Traíras from A2 showed a significant correlation between Hg levels and length considering non log transformed (as shown in Table 12 and Figure 35) and for log transformed data, which the linear equation resulted as:  $y = 1.3316x - 2.1111$ ;  $R^2 = 0.6$ . In Creporizinho, the relationship between Hg levels and length considering non log transformed resulted in negative correlation (as shown in Table VI and Figure III in Appendix 2).

We should consider that changes in intervals of length could change the linear relationship found for Traíras from A2. However, considering the present results, one could suggest that Traíras can be used as indicator organism for mercury contamination, at least in Amazonian heavily contaminated sites.

**Table 12 - Total mercury in muscles, weight and length intervals (arithmetical means) of Traíras from A2; São Chico Garimpo's area.**

Length intervals	Length mean (mm)	Mercury ( $\mu\text{g/g}$ )	N
150	150	5.3	1
175	175	8.1	3
215-225	220	14.1	2
245-265	255	9.6	4



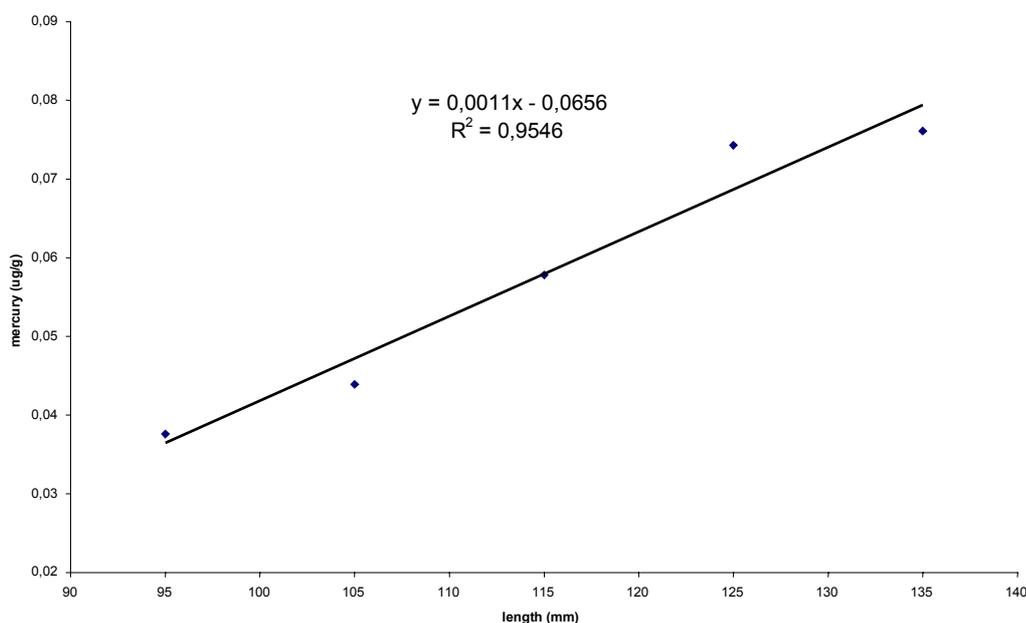
**Figure 35 - Total mercury in muscles and length intervals (arithmetical means) of Traíras from A2; São Chico Garimpo's area.**

Carás from A2, São Chico area, showed a strong negative correlation between length and Hg levels, as shown in Table VII and Figure IV in Appendix 2. Carás from A8, Creporizinho area showed very low linear relationship between length intervals and Hg levels ( $y = 0.0228x + 0.4795$ ;  $R^2 = 0.072$ ).

Other fish species from Creporizinho and its sites were also tested: Acari, Sairu, Piau and Piranha. The best results are shown in following Tables and Figures. Acari from A9 showed a strong positive relationship between Hg levels and length intervals of 100mm ( $y = 0.0107x - 0.0656$ ;  $R^2 = 0.9546$ ). The results are shown in Table 13 and Figure 36.

**Table 13 - Total mercury in muscles and length intervals (arithmetical means) of Acari from A9 -CrepORIZINHO Garimpo's area.**

Length intervals	Length mean (mm)	Mercury ( $\mu\text{g/g}$ )	N
9-10	90.5	0.04	1
10-11	105.0	0.04	3
11-12	115.0	0.06	5
12-13	125.0	0.07	1
13-14	135.0	0.08	1

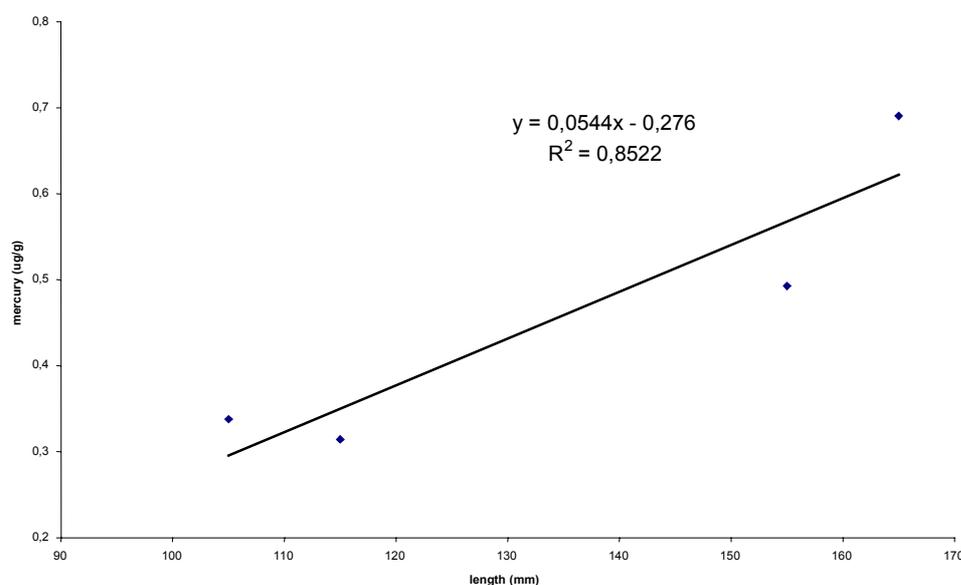


**Figure 36 - Total mercury in muscles and length intervals (arithmetical means) of Acari from Creporizinho Garimpo's area.**

Sairu showed weak correlation between Hg levels and length intervals for data from A5 and taken into account all of 50 specimens from Creporizinho area, the relationship was not strong. However, Sairu from A6 (Baixão do Bofe), showed stronger positive relationship between Hg levels and length intervals ( $y = 0.0325x - 0.0846$ ;  $R^2 = 0.557$ ). Piau from A11 (n=13). Finally, Piranhas from A9, A10 and A11, with total number of 16 specimens showed strong positive relationship between Hg levels and both length intervals, 50mm and 100mm,  $y = 0.0435x - 0.2115$ ;  $R^2 = 0.4399$  and  $y = 0.0422x - 0.1718$ ;  $R^2 = 0.4447$ , respectively. However, when analyzed specimens from A11 and A9 individually, Piranhas from A11 did not show any correlation with 50mm of intervals, but show stronger relationship with 100mm of intervals ( $y = 0.0302x - 0.11$ ;  $R^2 = 0.4125$ ). On the other hand, Piranhas from A9 showed strong relationship between mercury levels and both length intervals, 50mm and 100mm ( $y = 0.0552x - 0.3182$ ;  $R^2 = 0.7737$  and  $y = 0.0544x - 0.276$ ,  $R^2 = 0.8522$ , respectively). The best results, concern to Piranhas from A9 with 100mm of length intervals are shown in Tables 14 and Figure 37.

**Table 14 - Total mercury in muscles and length intervals (arithmetical means) of Piranhas from A9 -Creporizinho Garimpo's area.**

Length intervals	Length mean (mm)	Mercury ( $\mu\text{g/g}$ )	N
100.0-110.0	105.0	0.34	1
110.0-120.0	115.0	0.31	2
150.0-160.0	155.0	0.49	2
160.0-170.0	165.0	0.69	1



**Figure 37 - Total mercury in muscles and length intervals (arithmetical means) of Piranha from A9 -Creporizinho Garimpo's area.**

Although Traira does not show good correlation between Hg and length, it should be used as a Hg bioindicator for the following reasons: it shows the fairly highest Hg levels; it has the most widespread distribution in tropical drainage, in contrast to other species, it is easily adapted to adverse conditions in impacted areas and, it is appreciated for eating. Although the indication of absence of correlation shows that this species do not fit well with the modeling proposed in the Protocol, this has a potential negative effect in the human population (easy to catch and appreciated as food). In addition, Acari, Curimatã, Ituí, Piranha and Sairu are also good indicators for specific sites, suggesting that in order to find a Hg contamination indicator organisms, search for a site-specific fish species, with more than one species for several sites, could be a better approach in tropical aquatic ecosystems.

The relationship between mercury levels in fish and mercury in sediments can be used as an indicative of bioavailability of mercury in aquatic system. In order to investigate this availability, we performed the ratio between mean mercury levels in fish and IGEO, which is a contamination classification system, explained previously. Traíra and Piranha (carnivorous species) and Cará and Curimatã (non carnivorous species) were chosen because they were

collected in São Chico and Creporizinho areas and represent different food habits. The results are shown in Figure 38. All sites showed the ratio below of 0.5 considering all species, except A2 and A7 for Traíra, which resulted in 1.5 and 1.8, respectively. The results suggest that A2 and A7 showed the highest mercury bioavailability for fish from sediments.

By using the indicator fish species, we have chosen for A1, Curimatã specie; A2, Traíras and Carás; A3, Ituí; A4, Arraia; A5, A6 and A7, Sairu; A8, Carás; A9, Acari and Piranhas, A10, Sairu and A11, Piranhas. The results are shown in Figure 39. All sites showed the ratio below of 0.5 considering all species, except A2 (for Traíra). These results confirm the previous one, suggesting that A2 showed higher mercury bioavailability than the other sites, but, in contrast, A7 showed ratio below 0.5, similar to the other sites.

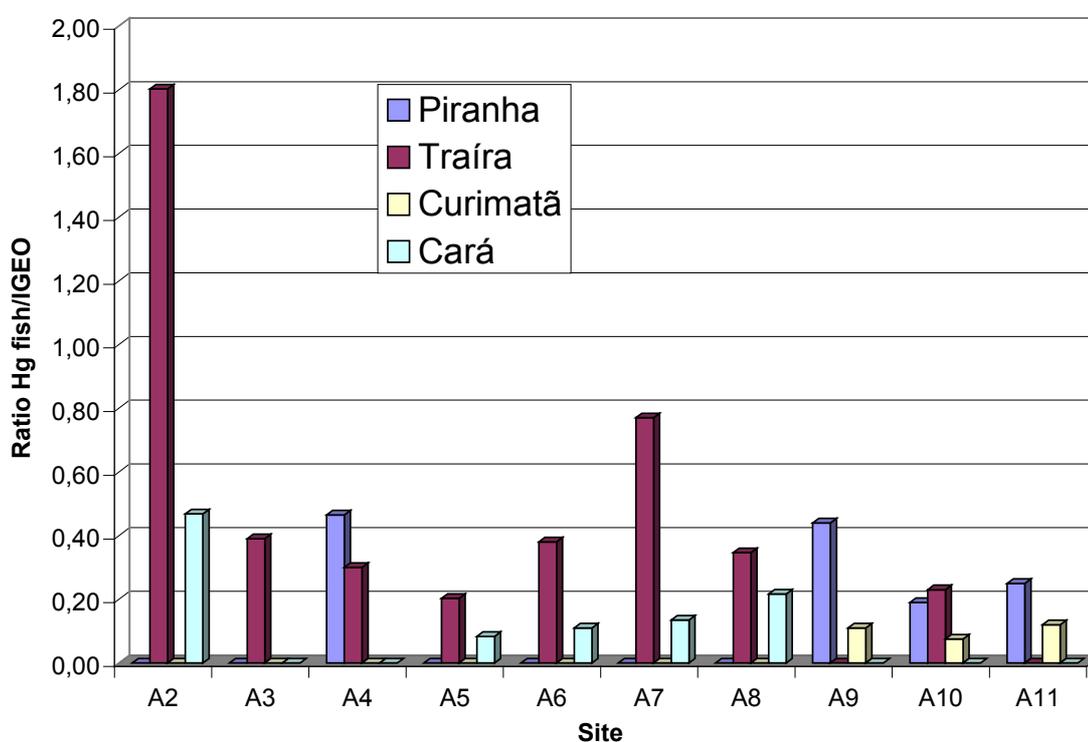


Figure 38 - Ratio between total mercury in muscles of some fish species and IGEO for all sites in São Chico and Creporizinho Garimpo's area.

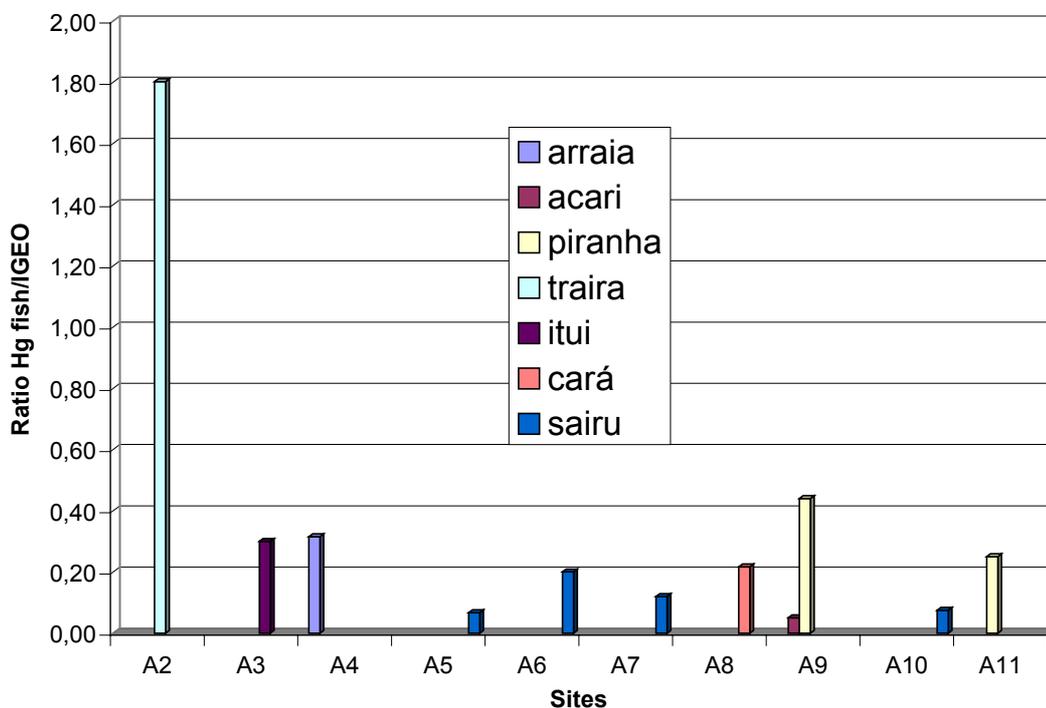


Figure 39 - Ratio between total mercury in muscles of some indicator fish species and Igeo of Hg in sediments for all sites in São Chico and Creporizinho Garimpo's area.

#### 4.3.1. Human exposure to mercury due to fish consumption

By employing toxicological methods for the risk assessment to human health, significance of the contamination can be ascertained. At a screening level, a Hazard Quotient (HQ) approach (USEPA, 1989), assumes that there is a level of exposure (i.e., RfD = Reference of Dose) for non-carcinogenic substances, like mercury, below which it is unlikely for even sensitive populations to experience adverse health effects.

The MeHg RfD value is  $1E-04$  mg.Kg<sup>-1</sup>.d<sup>-1</sup> (IRIS 1995) with an uncertainty factor of 10 and its confidence level is medium. Uncertainties of the RfD statistics have been reported, suggesting an under-estimation of RfD for Hg presented in IRIS, 1995 (Smith and Farris 1996). However, other authors suggest that there is no safe human exposure to MeHg and that of all living species, human appear to have weakest defenses against MeHg (Clarkson 1996). However, considerable gaps remain in our knowledge on that. Our approach therefore is to use the human risk assessment proposed by USEPA, at screening level. HQ is defined as the ratio of a single substance exposure level (E) to a reference of dose (E/RfD). When HQ exceeds the value of one, there may be concern for potential health effects.

The estimated exposure level was obtained by multiplication of 95th percentil upperbound of mean Hg concentration (see Table 7) considering all fish as suggested by USEPA (1989), by the adult human ingestion rate for local populations, Table 15. Most of the studies on

riverside population assume consumption rate close to 0.2 Kg.d-1. However, the Sociological Study from the São Chico community reported that close to 57% of the population consume fish just once a week and 90% consume fish twice weekly. Thus, it has been considered reasonable, and more conservative, a consumption rate close to 0.02 Kg.d-1 in those study areas, considering that fishing is not usual and fish is not caught easily.

Finally, the intake dose is estimated by dividing that product by 70 kg, considering the average weight of a human adult. Although total mercury was quantified in fish, it has been demonstrated elsewhere that about 75-95% of total mercury in fish muscles is methylmercury. Thus, it has been assumed that total mercury in fish represents methylmercury. The resultants HQ for MeHg are shown in Table 15.

**Table 15 - MeHg Hazard Quotient due to fish ingestion in São Chico and Creporizinho garimpo's areas and sites**

<b>Garimpo's area</b>	<b>RfD</b>	<b>Intake Dose</b>	<b>HQ</b>
São Chico	1 E-04	9,8E-03	14.8
A1	1 E-04	2.7E-03	4.1
A2	1 E-04	1.9E-02	28.5
A3	1 E-04	1.1E-03	1.7
A4	1 E-04	3.2E-03	4.8
Creporizinho	1 E-04	1,2E-03	1.8
A5	1 E-04	9.9E-04	1.5
A6	1 E-04	1.3E-03	1.9
A7	1 E-04	1.3E-03	1.9
A8	1 E-04	2.2E-03	3.3
A9	1 E-04	1.1E-03	1.6
A10	1 E-04	1.2E-03	1.8
A11	1 E-04	4.9E-04	0.7
<b>Total</b>	1 E-04	3,9E-03	5.8

HQ results show for all study sites values above one, from 1.5 to 28.5, except for A11, which is considered a reference area. The São Chico reservoir (A2) showed the higher values of HQ, followed by A1, A4, and A3. In Creporizinho area, the HQ values are close to 2 for all sites, except in A8, where the HQ attained 3.3.

It should be stressed that the present modeling is an evaluation tool, and therefore its uncertainty should be taken into account for interpretation of results and conclusions. From the present results, however, one could indicate that possibly in all sites, except in A11, and depending on their dietary habits, populations are subject to potential hazards and health effects due to fish consumption, being site A2 the most evident case of mercury pollution. Therefore, further in-depth studies on Hg bioavailability are highly recommended for the overall study area, while an awareness campaign should address to the local population the risk of consuming fish from the site A2.

In a previous study (Bidone et al. 1997) showed the estimates of Hg concentration in blood and in hair from contaminated site, using the single-compartment model (WHO 1990) through which the steady-state Hg concentration in blood (C) in  $\mu\text{g.l}^{-1}$  is related to the average daily dietary intake (d) in  $\mu\text{g}$  of Hg, as follows:  $C = 0.95 * d$ . Hair concentrations of Hg are proportional to blood concentrations at the time of the formation of the hair strand, and blood-to-hair ratio in humans is about 1 to 250, but appreciable individual differences have been found (WHO, 1990). A synthesis of the estimates to Hg concentration in blood and in hair using the single-compartment model for São Chico and Creporizinho areas is shown in Table 16.

**Table 16 - Hg concentration in fish; estimated average Hg daily intake (d); estimated blood Hg concentration (b) and estimated hair Hg concentration(h).**

Garimpo's areas	Hg in fish* ( $\mu\text{g.g}^{-1}$ )	d ( $\mu\text{g.d}^{-1}$ )	b ( $\mu\text{g.l}^{-1}$ )	h ( $\mu\text{g.g}^{-1}$ )
São Chico	3.44	103.3	98.2	24.5
Creporizinho	0.41	12.3	11.7	2.9
Total	1.35	40.6	38.7	9.7

\* = 95 percent upper confidence limit on the arithmetic mean

The estimated blood and hair Hg concentration in São Chico ( $98.2 \mu\text{g.l}^{-1}$  and  $24.5 \mu\text{g.g}^{-1}$ ) do not agree with the observed  $21.6 \mu\text{g.l}^{-1}$  and  $3.16 \pm 2.63 \mu\text{g.g}^{-1}$  ( $n=136$ ) total Hg concentration, respectively. However, it should be taken into account that there are some individuals with higher levels of mercury in blood (as  $141 \mu\text{g.l}^{-1}$ ) and hair ( $15 \mu\text{g.g}^{-1}$ ) in this area.

Considering only A1, A3 and A4, the estimated Hg in blood and hair are closer to the verified values:  $23.5 \mu\text{g.l}^{-1}$  and  $5.9 \mu\text{g.g}^{-1}$ . As a result, one could suggest that consumption of fish from A2 appears to be uncommon within the local community. This has been confirmed through interviews with the local population, probably as a result of a general perception towards Hg contamination in the reservoir (A2). On the other hand, it is highlighted that the estimated blood and hair Hg concentration in Creporizinho fall closer to the observed  $23.21 \pm 27.11 \mu\text{g.l}^{-1}$  and  $1.82 \pm 1.53 \mu\text{g.g}^{-1}$  of total Hg concentration, respectively.

The estimated and verified blood and hair Hg concentrations are lower than those values ( $\sim 200 \mu\text{g.l}^{-1}$  and  $50 \mu\text{g.g}^{-1}$ ) associated with adverse effects on nervous system, manifested as an approximately 5% increase in the incidence of paraesthesia. Clinical observations in Iraq suggest that women are more sensitive to the toxic effects of MeHg during pregnancy; pregnant women may suffer effects at lower methylmercury exposure than non-pregnant adults, suggesting a greater risk for pregnant women and, especially for their offspring. (WHO, 1991).

#### **4.3.2. Preliminary assessment of physiological effects in fish caused by Hg exposure**

Whereas potential human health effects from Hg exposure have received considerable attention, relatively few studies have explored effects of realistic environmental Hg concentrations on fish or have attempted to use wild fish collected from polluted site where interactions among factors including diet, water chemistry and other variables could be important. Physiological biomarkers may identify effects at a tissue/organ before they are apparent at a clinical/pathological level.

Biological markers, or biomarkers, are observable properties of an organism that indicate biochemical components, structure, or function and that can be measured biologically. Biomarkers can be used to estimate prior exposure, to identify changes and effects on organisms, and to assess underlying susceptibility of an organism. Markers of internal dose are direct measures of a toxic chemical and integrate multiple portals of entry and fluctuating exposure dose. Markers of biologically effective dose assess the internal molecular targets, and markers of early biological effect assess the molecular sequelae (es.epa.gov/ncer/fra/2004).

Some studies have been shown that MeHg has affinity for red blood cells (WHO 1990). So, hematology might be an important diagnostic test related to Hg exposure. It is possible to classify and evaluate fish anemias and this can be particularly important in fish, since clinical signs of anemia are often masked until quite late in the pathogenesis of the disease (Stoskopf 1993). In fish's erythrocytes, about 90% of the Hg is in the organic form (Olson, 1973), as the same ratio presented in muscles. Additionally, experimental Hg poisoning in fish showed marked hematological anomalies (Gill and Pant 1984). However, in order to evaluate the contaminant's adverse effects on ichthyofauna and other wildlife, one should establish the normal or reference values, overall to Amazonian species (Almosny and Santos 2001), since the information is limited.

The main objective of this approach is to assess biochemical and hematological parameters in Amazonian fish from aquatic systems influenced by gold mining areas. Both the level of Hg in tissue and the hematological and biochemical responses were measured in each specimen. The results of total Hg in fish muscles and fish blood and biochemical parameters were used as effects biomarkers in ecological risk assessment.

It was investigated biochemical parameters as enzyme activities, such as amino-alanina transferase-ALT; amino- spartate transferase-AST; creatina kinase and creatinine, and hematological parameters, such as hematocrit, hemoglobin, erythrocytes and total leukocyte count; trombocytes-leukocytes count in blood of fish from São Chico and Creporizinho.

A total of 49 fish specimens from São Chico (30) and Creporizinho (19) were examined: Bocudo (1), Cará (29), Mandi (1), Piau (2), Piranha (1), Pirarara (1), Surubim (1) and Traíra (13). Considering that only Traíras and Carás were collected in reasonable number, the following analysis of the results are related with these two species. A total of 42 fish specimens of those species (Carás and Traíras) were collected: 27 specimens in São Chico (18 Carás and 9 Traíras) and 15 specimens in Creporizinho (11 Carás and 4 Traíras).

After fish were caught, still alive, the blood was drawn by caudal or heart puncture with an EDTA containing syringe. In the field, the manual methods for counting erythrocytes were performed at the same time as the total leukocyte count, as recommended by Almosny et al.(1993) and Almosny and Santos (2001). A specific dilution of the blood was made with a diluent Gowers and Giemsa staining solutions, and the Newbauer,(Improved) cell counting chamber was flooded. Smears, two slides per individual, were prepared without anticoagulant substances from fresh blood, air dried, fixed in methanol, and stained with Giemsa's solution. Blood corpuscles were examined by immersion microscopy and photographed. The hematocrit (or globular volume) was performed by microhematocrit method, using small capillary tubes, which were filled approximately two-thirds full with anticoagulated blood and centrifuged for five minutes at 14,000G. The percentage of packed cells to total volume was determined by direct measurement. The mean globular volume (MGV), a Wintrobe erythrocyte index, was calculated as follows:  $MGV = [(\text{hematocrit}) \times 100] / \text{Total erythrocyte count}$ .

The modified Cyanometahaemoglobin method (Murachi, 1959) was used for hemoglobin measurement, because this method is considered the most appropriate to determine haemoglobin in fish (Campbell & Murru, 1990; Stoskopf, 1993; Canfield et al ,1994). The procedure was performed in field, with a Spectrophotometer 800M Analyser®, by using 20µl of blood collected with EDTA, until 12h after blood collection. For biochemical analyses, plasma was collected after centrifugation and the elements measured were: Urea (BUN- Blood Urea Nitrogen), Creatinine, Ammonia, and CK - Creatine Kinase , ALT - Alanine Transferase, Aspartato Transferase AST - Aspartate Transferase. The procedure was performed in laboratory using biochemical-dry analyzer, an Ektachem DT60 II System -Ortho-Clinical Diagnostics, Johnson & Johnson®.

Statistical differences on Hg concentrations, physical, hematological and biochemical parameters between different sites were tested using parametric tests (Student's t-Test) or a nonparametric test of significance (the Mann-Whitney U-test). One-way ANOVA followed by Duncan pos-hoc were performed when appropriate. The significant level considered was the probability level  $\leq 0.05$ . Correlations were determined with both the Pearson correlation coefficient and the Spearman rank correlation coefficient on the original data.

The results are shown in Tables 17 and 18.

**Table 17 - Total mercury in muscles, biochemical and hematological parameters of Traíras from Garimpo's area**

Parameters	N	São Chico	N	Creporizinho
Mercury	9	7.71±6.20*	4	0.73±0.43
Length	9	24.11±7.23	4	18.63±9.80
Weight	9	400.00±493.71	3	316.67±202.1
ALT	2	32.50±4.95	1	47.00
AST	2	219,500±99.70	2	225,000±247.50
CK	2	5,380.00±1,909.2	2	5,147.50±3,885.5
Creatinine	2	0.25±0.071	1	0.30
CHCG	2	19.86±0.44	-	-
Amonia	3	866.67±119.30	2	585.0±70.71
Ureia	2	2.00±1.41	1	3.0
Hb	2	5.45±0.58	-	-
Erythrocyte count	7	2,177,142±401,111*	4	2,785,000±455,814
GV	7	26.86±5.50**	4	40.75±5.25
MGV	7	123.40±15.35	4	148.87±26.53
Trombocyte-leukocyte count	-	-	-	-

Student's t-Test: \*p<0.05; \*\* p<0.005

**Table 18 - Total mercury in muscles, biochemical and hematological parameters of Carás from Garimpo's area.**

Parameters	N	São Chico	N	Creporizinho
Mercury	18	2.16±1.02	11	0.42±0.26
Length	18	8.25±0.60	11	8.68±0.79
Weight	-	-	-	-
ALT	-	-	-	-
AST	-	-	-	-
CK	-	-	-	-
Creatinine	-	-	-	-
CHCG	16	23.75±4.9	-	-
Amonia	-	-	-	-
Ureia	-	-	-	-
Hb	16	5.85±1.05	-	-
Erythrocyte count	17	1,971,176±329,125	11	2,080,909±215,102
GV	18	24.83±4.02**	11	29.27±3.13
MGV	17	128.43±19.47	11	141.68±17.95
Trombocyte-leukocyte count	16	19.5±6.46	10	22.0±10.38

It should be noted that by macroscopic clinic observation of fish specimens, they did not show any significant alteration, except in Traíras from A2, which showed very high number of muscles parasites in all samples. It has been suggested that wild population in equilibrium with its environment shows up to 30% of organisms with visible number of parasites, while in stressed population, a higher number of parasites are to be found in higher percentage of organisms, as observed in Traíras from A2.

All biochemical parameters measured in the present work did not show any difference between sites. These data maybe resulted due to low number of specimens with biochemical parameters measured, available to compare between areas, which did not permit perform the correlation analysis. In addition, those biochemical parameters could not be sensible as mercury biomarkers. However, the data are important because they can be used as biochemical reference values for Amazonian fish, considering as rare data .

Traíras from Creporizinho showed higher globular volume and erythrocytes number than Traíras from São Chico. Carás from Creporinho showed higher globular volume and mean globular volume than those from São Chico. Mercury levels and globular volume showed significant negative correlation for both species (Traíras: -0.82;  $p < 0.005$   $n = 11$ ; Carás: -0.37;  $p < 0.05$   $n = 29$ ). These results suggest that mercury levels may cause decrease in number of erythrocytes, which are smaller than normal ones, characteristics of regenerative anemia.

### 4.3.3. Bioindicators other than fish

Very few samples of earthworms, a number of 5, could be obtained in the field, due to severe physical impacts caused by silting of drainages that likely prevented the availability of invertebrates in the study sites, while some samples were lost during the depuration period, due to dehydration or by physical damages during washing or handling. Thus, earthworm specimens could not be used as a bioindicator of methylation potential of Hg in sediments and soils.

At São Chico mining sites 27 samples of herbs and vegetable foodstuffs were collected close to mining tailings and backyards of the village. No aquatic plants could be found in flooded open pits, neither in the lake at São Chico mining site.

At Creporizinho mining sites 29 samples of herbs, macrophytes and vegetable foodstuffs were collected in the village and close to the mining sites.

The concentration of total mercury in plant parts (aboveground and roots), and corresponding substrates are shown in Appendix 2. Total mercury values for soil samples at São Chico study area are higher than background values for this area (about 0.15 to 0.20 mg./kg) Table 19. Although mean values in soils samples from São Chico are higher than soils samples from Creporizinho, no significant differences between them at  $\alpha < 0.05$  were obtained.

Data on produces and wild plants were combined with aboveground and root plant parts for study area to compare mean total mercury concentrations. Only aboveground of produces samples from the São Chico mining site presents significantly higher values for mercury levels than samples from Creporizinho area (means 2.5517 vs. 0.1183;  $t = 2.6023$ ,  $P = 0.0159$ , Table 20). The non-parametric *U* Mann Whitney test were used to identify the produce species with significant values. Only above-ground parts of cabbage present samples size to perform the test, and significant values for mercury levels (São Chico,  $n = 3$ , Creporizinho,  $n = 3$ ,  $U = 0$ ,  $P = 0.050$ ).

To obtaining the relationship between the mercury contamination in soil fractions and plants, the same data arrangements to compare means were used in regression analysis (Table 21). Data of São Chico wild plants aboveground and roots parts were insufficient for the construction of models. Regression of mercury concentrations in plants versus soil produced significant model fits for five of 12 analyses performed (Table 21). The slopes of nine regression models were positive, including of five significant regression models (Figures 40 to 44). Intercept differed from zero in nine of the regression models. Determination coefficients ( $r^2$ ) for significant models ranged from 0.5549 to 0.9963. Over all regression models of produce samples generated, only soil-root produce regression model from the Creporizinho's study area were significant, and the slope were negative (Figure 40). Over all regression models of wild plants samples generated, of both aboveground and root plant parts, from Creporizinho's study area were significant, and the slopes were positive (Figures 45 to 48).

Aboveground : root ratios were higher than 1 in all of the produce samples of São Chico ( $n = 5$ ), and in only one of Creporizinho study area ( $n = 3$ ) (Table 22). The translocation of mercury from soil through roots to aboveground in produce plants was not significant in both studies areas (Table 21), and mercury uptake probably occurs through stomata by atmospheric mercury deposition. Aboveground : root ratios were lower than 1 in wild plants (São Chico,  $n = 3$ ; Creporizinho,  $n = 11$ ), except samples A5-13 and A5-14 V of Creporizinho (Table 22). Nevertheless, the translocation of mercury from soil through roots to aboveground in wild plants were significant in samples of Creporizinho (Table 21), suggesting that a significant

proportion of Hg uptake occurs through roots, with higher concentrations in root tissues and lower translocation to aboveground tissues.

The present results indicate that mercury concentrations in wild plant parts from Creporizinho study area increase with mercury concentrations in soil. Apparently, they function as a excluder, restricting transport of metal upwards to aerial parts.

Since Hg concentrations are much higher in aboveground of produces at São Chico study area than in Creporizinho (Tables 23 and 24, and *U* Mann-Whitney test result), the uptake in produce plants is likely to occur through atmospheric deposition, but further studies with a larger sample set are necessary in other to confirm this hypothesis.

In foodstuffs other than fish mercury exists mainly in inorganic form, while the gastrointestinal absorption is close to 7%. The average total contents of mercury in edible parts (leaves and stems of cabbage and chive, pulp of cassava and “cara” roots, and pulp of cashew fruit) were  $0.21 \pm 0.26 \mu\text{g/g w wt}$  ( $n = 13$ ) for São Chico, and  $0.01 \pm 0.01 \mu\text{g/g w wt}$  ( $n = 7$ ) for Creporizinho. We estimate the average dietary daily intake of vegetables and roots close to 100 g, for an adult with 70 kg. Considering 0.3mg the provisional tolerable mercury intake per person weekly (PTWI), the ingestion of total mercury from those foodstuffs falls close to the PTWI in São Chico area, whereas in Creporizinho area the estimated Hg ingestion falls in a range much lower than the PTWI. However, it should be taken into account the small gastrointestinal absorption of inorganic mercury, which results in 0.017 mg/week for São Chico and 0.0007 mg/week for Creporizinho.

**Table 19 - Comparison of total mercury values for substrates samples at São Chico and Creporizinho studies areas**

Substrate	Mesh	São Chico			Creporizinho			t	P
		n	Mean	SD	n	Mean	SD		
soil	# 200	7	1.9571	1.4305	4	0.9963	0.5152	1.2718	0.2353
	# - 200	7	1.5041	1.1247	4	0.9401	0.3950	0.9520	0.3659
sediment	# 200	-	-	-	4	0.4921	0.5663		
	# - 200	-	-	-	4	0.6773	0.8361		

**Table 20 - Data on total mercury concentrations in produces and wild plants, aboveground and root plant parts at São Chico and Creporizinho studies areas (Hg concentrations in  $\mu\text{g/g dw}$ )**

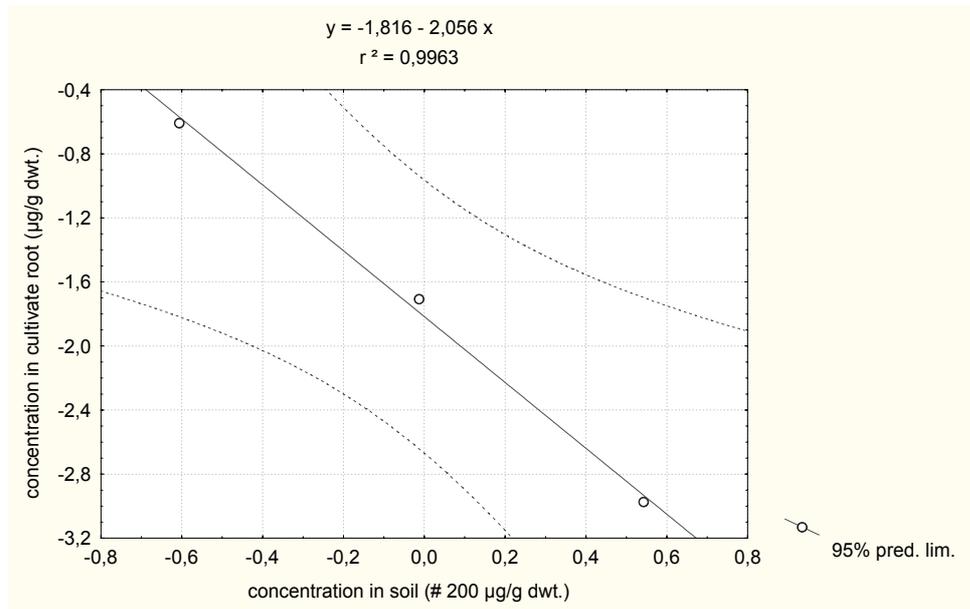
Plant parts	Types	São Chico			Creporizinho			t	P
		n	Mean	SD	n	Mean	SD		
Above-ground	Produces	14	2.5517	3.0855	11	0.1183	0.1100	2.6023	0.0159*
	Wild plants	4	0.3838	0.1455	15	0.3090	0.6161	0.2363	0.8160
Root	Produces	5	0.4141	0.3005	3	0.2588	0.2554	0.7428	0.4856
	Wild plants	4	0.4594	0.2221	11	0.2233	0.2594	1.6085	0.1317

**Table 21 - Results of regression of the natural log of total mercury concentrations in produces and wild plants, aboveground and root plant parts versus natural log of total mercury concentrations in soil fractions at São Chico and Creporizinho studies areas**

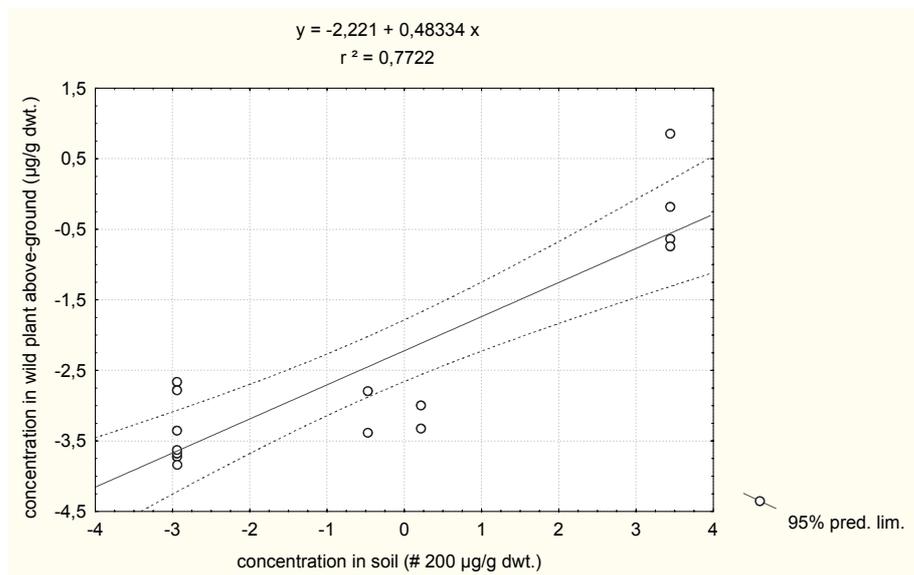
Study Area	Plant parts	Type	Soil fractions	n	r <sup>2</sup>	P
São Chico	Above ground	Produces	+200#	13	0.0270	< 0.5916
			-200#	13	0.0695	< 0.3841
	Roots	Wild plants	+200#	4	-	-
			-200#	4	-	-
		Produces	+200#	5	0.1493	< 0.5205
			-200#	5	0.0105	< 0.8692
		Wild plants	+200#	4	-	-
			-200#	4	-	-
Creporizinho	Above ground	Produces	+200#	11	0.0349	0.5819
			-200#	11	0.1025	0.3371
	Roots	Wild plants	+200#	15	0.7722	0.00002*
			-200#	15	0.7999	0.00001*
		Produces	+200#	3	0.9963	< 0.0382*
			-200#	3	0.6891	< 0.3764
		Wild plants	+200#	11	0.5890	< 0.0058*
			-200#	11	0.5549	< 0.0085*

**Table 22 - Ratios of above-ground : root for each plant species of São Chico and Creporizinho studies areas**

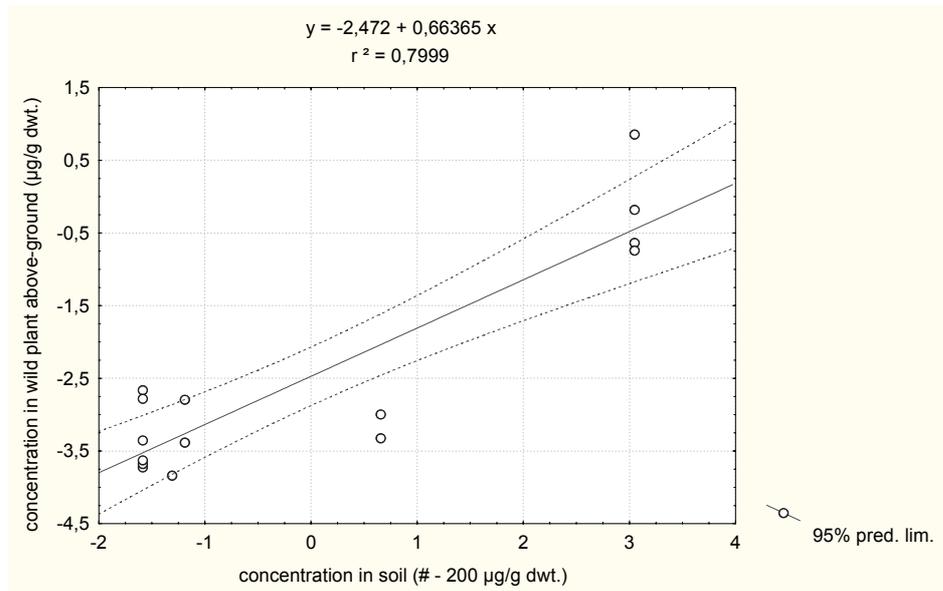
Study Area	Sample area - Field number	Type	Above-ground : root ratio
São Chico	A2-1	cabbage	9.9302
	A2-1	chive	1.4057
	A2-3	cabbage	3.1460
	A2-3	chive	5.3474
	A2-4	mango shoot	1.4541
	A2-4	Poaceae sp.1	0.4655
	A2-4	Poaceae sp.2	0.5963
	A2-6	sweet potato	6.6521
Creporizinho	A5-12	Cyperaceae sp. 1	0.5954
	A5-13	Poaceae sp.3	2.8535
	A5-14	<i>Hypolytrum</i> sp.1 (Cyperaceae)	1.4996
	A6-15	Poaceae sp.4	0.6313
	A6-16	Cyperaceae sp. 2	0.3144
	A6-17	Cyperaceae sp. 3	0.0645
	A6-17	macrophytes	0.2539
	A8-18	cassava	0.6914
	A8-19	cabbage	3.5597
	A8-21	cabbage	0.4283
Crepori river	A9-22	Poaceae sp.5	0.2304
	A9-22	herbaceous species	0.3839
	A9-22	herbaceous species	0.1838
	A11-23	Cyperaceae sp. 4	0.3111



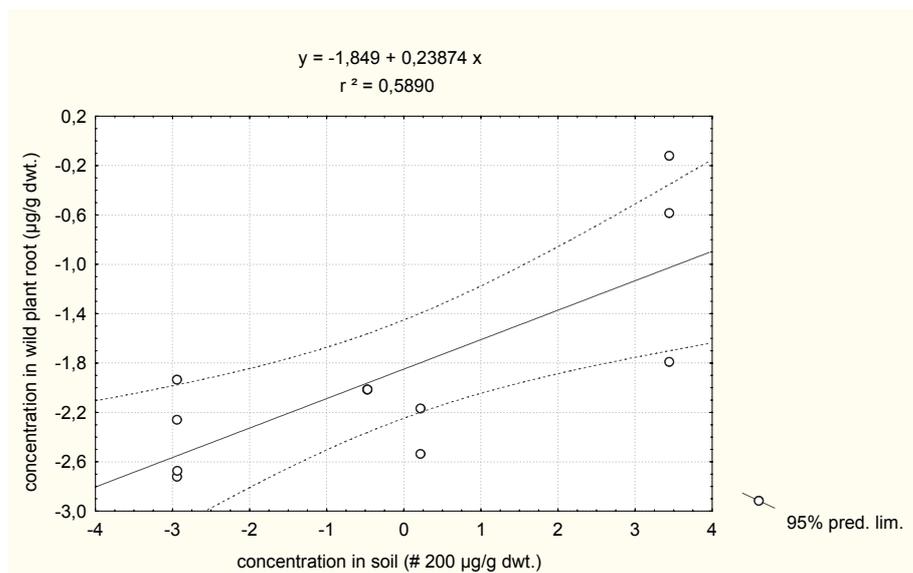
**Figure 40 - Significant scatterplots of soil-plant regressions models and the 95% upper prediction limit of produce plants roots. Hg concentrations ( $\mu\text{g/g}$ ) were expressed on dry weight basis. Samples from Creporizinho study area**



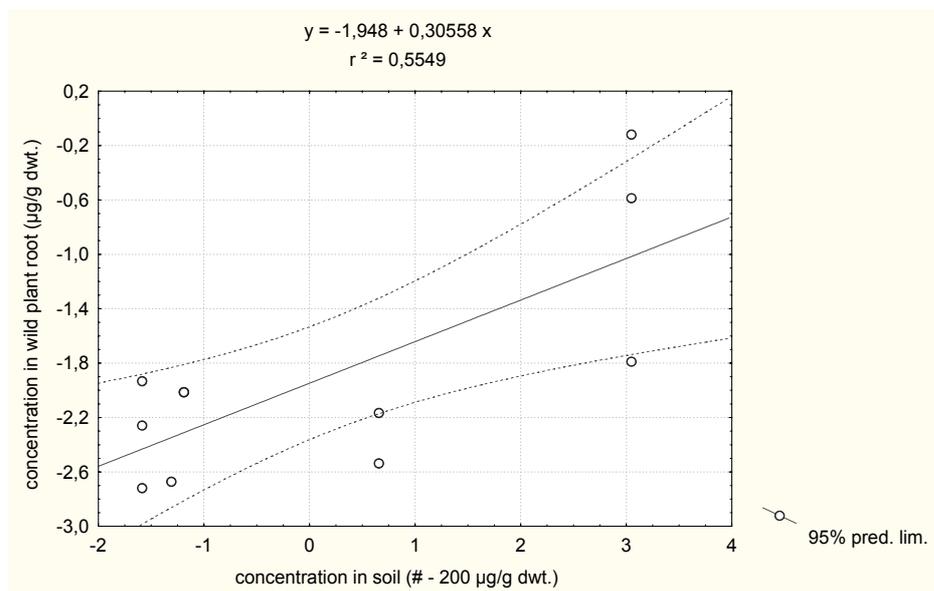
**Figure 41 - Significant scatterplots of soil-plant regressions models and the 95% upper prediction limit of wild plants above grounds. Hg concentrations ( $\mu\text{g/g}$ ) were expressed on dry weight basis. Samples from Creporizinho study area.**



**Figure 42 - Significant scatterplots of soil-plant regressions models and the 95% upper prediction limit of wild plants above grounds. Hg concentrations (µg/g) were expressed on dry weight basis. Samples from Creporizinho study area**



**Figure 43 - Significant scatterplots of soil-plant regressions models and the 95% upper prediction limit of wild plants above grounds. Hg concentrations (µg/g) were expressed on dry weight basis. Samples from Creporizinho study area**



**Figure 44 - Significant scatterplots of soil-plant regressions models and the 95% upper prediction limit of wild plants above grounds. Hg concentrations (µg/g) were expressed on dry weight basis. Samples from Creporizinho study area**

#### **4.4. Mining Technology and Hg Use Issues (Veiga, 2004)**

Amalgamation is a preferred method used by artisanal miners to extract fine gold. It has been known that mercury is an avid collector for gold forming an amalgam paste that can be easily separated from other solid material in an ore. There are many methods and devices used to contact mercury with an ore, each of which have their own specific efficiency, effectiveness and impact on the environment. Mercury is relatively inexpensive. It is commonly sold in Brazilian “garimpos” (artisanal mining sites).

Artisanal miners use a variety of mining and amalgamation methods. Together with the fate of contaminated tailings and Au-Hg separation procedures, these methods define the extent of mercury losses from a specific site. If concentrates are amalgamated, the main emission source derives from burning amalgam in open pans. This operation, normally, produces a gold doré that contains 2 to 5% residual Hg. When the doré is melted at gold shops most commonly located in urban areas, further release of mercury vapor takes place.

When gravity concentrates are amalgamated, the mineral portion is separated from amalgam by panning, forming a tailing that is usually dumped into a stream generating a “hot spot”. Panning is usually done in water-boxes or in pools excavated in the ground or at creek margins. Excess mercury is removed by squeezing it through a piece of fabric. The excess is generally recycled but some is lost to the tailing.

Amalgam usually contains about 60% gold and so must be retorted or burned in an open pan. When retorts are not used, atmospheric emissions represent as much as 50% of the total mercury introduced into the process. However, when amalgamation is conducted properly and retorts are used, losses are very low – as little as 0.05%. This recycling practice suggests one of the first approaches to reduce the Hg burden to the environment.

#### 4.4.1. Alternative Processes (Veiga, 2002)

Amalgamation is applied in “garimpos” for two purposes: to cover fine gold from the whole ore and to extract the gold from concentrates to a very high grade product. The first application is the one, which must be stopped. This will avoid mercury emissions directly to the aquatic environment with tailings. To stop the second application is extremely unlikely. So, our goal should be to encourage use of amalgamation only for gravity concentrates and to see that it is conducted in a sensible and controlled way.

Amalgamation of the total ore is attractive since the gravity process is easily adaptable to amalgamation. Mercury can be added directly to the primary extraction operations without requiring a second processing stage. To eliminate mercury use for the total ore, we must find alternative methods to recover fine gold. In the initial stages of a “rush”, fine gold is rarely an issue – the attraction of a site generally is due to the presence of “easy-to-recover” coarse gold nuggets. As the ore becomes depleted, the miners will turn to amalgamation to maintain their gold production by recovering fine gold. Alternatively, some miners may begin reprocessing old tailings or waste dumps using mercury for fine gold.

Attempts to introduce new gravity concentration equipment, such as shaking tables, spirals, automatic panners etc, to eliminate amalgamation, have not been very successful. Mercury use has declined, but never eliminated. The principle of these methods is based on using gravity to clean an initial (rougher) concentrate to obtain a rich final concentrate for smelting. Instead of amalgamation, the tables work as cleaners to produce a concentrate that is smelted and sold. A gold-rich concentrate is produced which must be amalgamated to extract very fine gold, but this material is very low in weight relative to the ore and so a significant decrease in mercury consumption results.

**Centrifuges**, such as Falcon or Knelson Concentrators, have potential as primary gravity concentrators for fine gold as well as for cleaning ordinary gravity concentrates. A new model of the Falcon Super Bowl uses a fluidized bed spinning-bowl that can process up to 60 tonnes of solids/h, applying a centrifugal force of 200G. Concentrates can reach grades above 20,000 g Au/ton in two stages (rougher and cleaner), which can be directly smelted, potentially avoiding an amalgamation step. Knelson Concentrators has developed a continuous high-G force unit as well.

Centrifuges have been manufactured in Brazil (MacKnelson) and are in use by many artisanal miners. Despite being rough copies of the Knelson Concentrator, they do provide improvement in gold recovery and a reduction in mercury use.

Froth flotation, has been tried in a few South American artisanal operations to concentrate fine gold. But even with concentrate grades as high as 3000 g Au/ton, the product still requires amalgamation or cyanidation – it is not easy to directly smelt such concentrates. Using xanthate collectors, concentrates were upgraded from 13 g Au/ton to 3,000 g Au/ton at 82% recovery. Flotation of coarse gold (<0.43mm) is inefficient so a two-stage process is

necessary. Flotation cannot compete economically with amalgamation as used by artisanal miners.

Experiments with **coal-oil agglomeration** show some promise. Agglomerates of coal and oil (5mm) are formed and contacted with a gravity concentrate pulp. Recoveries of 90% are possible. Envi-tech Inc., Edmonton, Canada has developed a novel agglomeration process using a proprietary adsorbent. Following 5 to 10 minutes of intense agitation, gold-loaded adsorbent is separated by froth flotation achieving 70% recovery.

A **salt-electrolytic process** to leach gold has been developed by the Center of Mineral Technology (CETEM) in Rio de Janeiro and tested in a pilot plant in the Tapajos region of Brazil. This process has the potential to replace amalgamation of gravity concentrates. Material with as little as 1 µg Au/g is mixed with a sodium chloride solution (1.0M), which is transformed by electrolysis into a mixture of sodium hypochlorite-chlorate. More than 95% of the gold dissolves within 4 hours and is collected on a graphite cathode. The solution is recycled, minimizing effluent discharge. Plastic tanks are used, reducing investment and replacement costs and so the process may be relatively inexpensive in some cases. The main drawback is the need for trained personnel to control operating variables (pH, current density etc.).

Cyanidation is a process beginning to appear in artisanal mining operations in Andean countries and, to a lesser extent, in Brazil. Numerous organized mining companies have adopted cyanidation of ores and flotation concentrates widely. The establishment of effluent discharge standards that are difficult, if not impossible has essentially banned the use of amalgamation, to meet when amalgamation is used. With ores that contain extremely fine gold or gold in solid solution, cyanidation has replaced amalgamation as the preferred method in order to obtain high recovery. As coarse gold requires long retention time for cyanide leaching, it is generally, a gravity process prior to submitting the material to flotation and/or cyanidation generally removes it.

Despite high gold recoveries, cyanidation needs much more skill and investment than simple amalgamation. In such cases, artisanal miners need constantly technical support. A small cyanidation plant can be set up for use by a small mining community, but this is not a general solution for all cases of artisanal mining. Another important issue is the occupational risk operator. Although part of the residual cyanide is naturally degraded by sunlight and heat, total cyanide destruction requires a method such as the INCO SO<sub>2</sub>/air process. These processes are not simple. Although the environmental impacts of cyanide are usually lower than those of mercury, the consequences of occupational exposure can be rapid and very dramatic. Cyanide does not bioaccumulate like mercury, rather it may kill-off food sources in the food-web.

The possibility of replacing amalgamation with other processes is remote, but must be pursued. For an artisanal miner, mercury is an easy and efficient way to extract fine gold. When amalgamation is applied to gravity concentrates, more than 90% of the gold is generally recovered. Alternative processes must be investigated, but no extraordinary breakthrough should be expected.

## **5. Alternative low cost method for mercury semiquantitative determination in fish: training of local users**

### **5.1 Colorimetric Method for Hg Semiquantitative Analysis of Fish**

The usual analytical method to determine mercury content in biological samples is the cold vapor technique connected to an atomic absorption spectrometer. Although simple, it requires qualified technicians and infrastructure, which are not suitable for most of the locations, where a continuous monitoring of mercury content in fish is to be accomplished, like in the Amazon region. The lack of laboratory infrastructure and the difficult access to these places, associated to the high cost of analysis by conventional methods, has inspired the development of a low cost and easy operational method which attends the WHO recommendations (Yallouz, 1997; Yallouz et al, 2000 and Yallouz et al, 2002). A brief description of the method and some results about its quality assurance can be find at Appendix 4.

### **5.2 Adapting the minilab for mercury analysis in fish samples**

The minilab for semiquantitative mercury determination in fish was adapted in a building that was used in former times by the Companhia de Recursos Minerais (CPRM), nowadays belonging to the National Health Foundation (FUNASA). Some restoration works (painting, exhaustion installation) were performed before our starting the training. Equipments of air-conditioned and freezer were rent for the period of our stay. The technical activities were developed in the period from 08/04 to 08/22/2003 Allegra Viviane Yallouz and Débora Maia Pereira.

### 5.3. Developed activities

#### 5.3.1 Background

At the meeting with Dra Amélia Ayako Kamagari Araújo, Municipal Secretary of Health, it was made a brief exhibition of the objectives of the work. Dra Amélia showed its concern in relation to the repercussion of studies disclosed by the press that aimed the evaluation of mercury contamination in babies born in Itaituba. Despite being not conclusive, it mobilized the public opinion.

The practical work started on 08/08/2003. In the occasion the materials of the kit were adapted and installed. The equipments (balances and heating plate) and reagents were organized by the team composed of two trainees.

Since the first moment it was strengthened to the collaborators the need of care with comments and the ethics related to the popularization of the results, independent of the texts, seeking to avoid any situation of misunderstanding.

An intensive training of 5 technicians (Table 23) was performed in the use of the method and quality assurance of analytical results. The training was done strenghtening theoretical concepts and safe lab practices. Each participant received the detailed work instructions and the copy of the transparencies used in the seminar.

**Table 23 - Users indicated for the training**

Name	Institution
Lúcia Fátima Cruz Bezerra	AMOT
José Arnóbio Lima Linhares	Municipal Secretary of Agriculture
José Sales of Medeiros	City Hall of Itaituba
Kátia Cilene Silva Peão	Municipal Secretariat of Health
Telma Lúcia Matias of Araújo	SECTAM

#### 5.3.2. Training new users

The theoretical concepts were taught in two steps:

- 1) Informal discussions using median posters placed on the lab walls were used (Figure 45).

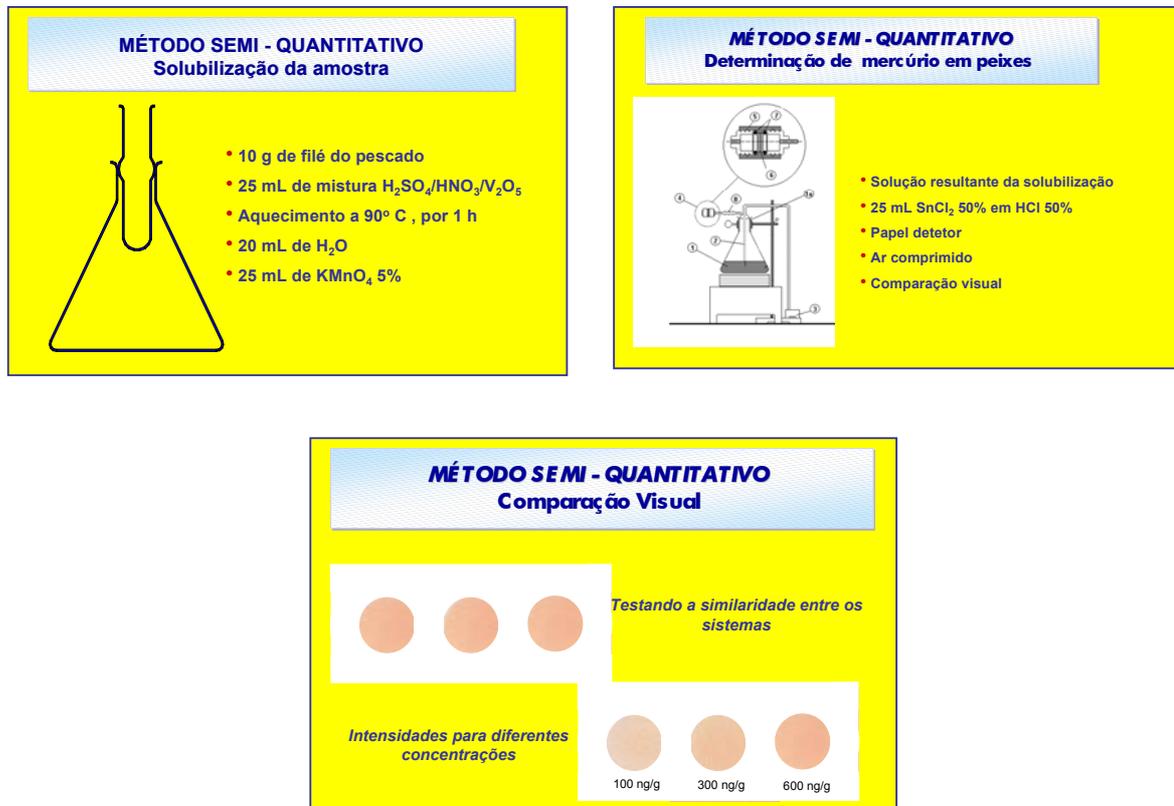


Figure 45 - Examples of miniposters used as a didactic material in the minilab

2) A lecture with discussions that was done on the third day of training during four hours, with discussions with all trainees and two invited researchers from local IBAMA. The lecture was done in AMOT Chemical concepts of the method, and practical details could be discussed at this moment. Important topics were discussed as:

- Comparison with usual methods
- The importance of the mercury determination in fish
- The different toxicology of mercury species
- The chemical ways of the mercury in the environment
- Method's applicability
- Method's advantages and limitations
- WHO recommendations and the Brazilian Laws regarding mercury level in fish,
- Quality assurance of the results
- Possible applications.

During the lecture (Figure 46), we had the opportunity to hear the explanation about the garimpos' techniques for the concentration of the material extracted by José Sales, using the models in exhibition in AMOT. They were also presents in this lecture, Alexandre Bezerra of Carvalho (biologist) and Vera Christiana Pereira Pastokino (chemist), that work in IBAMA demonstrated interest in participating at the training program. The schedules were not adequate, and it was only possible to attend the lecture.



**Figure 46 - Lecture presented at AMOT**

The practical training program (Figure 47) was performed giving individual training for each participant beginning with a practical demonstration of the use. After demonstration of the use, each operator participated of an exhaustive practical training in the use of the determination system until the complete domain of the system using mercury aqueous solutions with well-known concentration. For the digestion step, three samples acquired in the local market were used.



**Figure 47 - Some views of the training program**

The best trainee Kátia, was submitted to test, using a control sample supplied by Canadian Food Inspection Agency. The obtained results were in agreement with the expected values (Table 24).

**Table 24 - Results from the performance test**

Sample	Expected Value (ng/g)	Found Value (ng/g)
MQAP 300	142-334	<300
MQAP 329	285-465	300-600

It was also promoted a discussion about the work instructions with the users to clear doubts and the users' contribution was considered..

### 5.4. Application study

A short application study was performed to demonstrate the applicability of the method. When it was possible, it was chosen to work with 3 different sizes from the same species. 28 samples could be analysed by the recently trained team, under our supervision and the results are shown in Table 25. Fish samples were recorded through pictures and stored and frozen in plastic bags (Figure 48). The sampling criteria were based on fish habits, size, and preferences of the population for consumption.



**Figure 48 - Some samples analysed by the recently trained group**

The samples were analysed in duplicate nad where no correspondence were observed in triplicate. A control sample was used. All the team worked together with exception of Sra

Telma, from Belém, that return after the training was finished. It was a good opportunity to review every detail with the group.

**Table 25 - Results of the analysis of an application study of the method**

Sample	Size(cm)/weight(g)	Result
Tucunaré-1	59 / 2500	<100
Tucunaré-2	40/1170	300-600
Tucunaré-3	30/467	~ 300
Tucunaré-4	~1000g*	~600
Filhote-1	41/1600	100-300
Filhote-2	~5000	100-300
Surubim	~1000g*	600-1000
Pirarucu-1	~170/80Kg	~600
Pirarucu-2	~74 Kg	>1000
Pescada-1	37/805	100-300
Pescada-2	# / 750	100-300
Pirapitinga-1	46/2600	<100
Pirapitinga-2	36/1600	<100
Pacu-1	27/ #	<100
Pacu-2	20/ #	<100
Pacu-3	15/140	<100
Acari-1	#	<100
Acari-2	#	<100
Acari-3	#	<100
Tamuatá-1	10/54	<100
Tamuatá-2	13/92	<100
Tamuatá-3	15/150	<100
Mapará-1	35/355	<100
Mapará-2	37/368	100-300
Mapará-3	528/40	100-300
Aracu(piau)-1	16/106	<100
Aracu(piau)-2	25/319	<100
Aracu(piau)-3	27/412	<100

The results confirm the literature description about the difference of accumulation on carnivorous fishes. The species popularly known as surubim, pirarucu e tucunaré shown a higher mercury content. Other samples must be analysed for a complete conclusion, but our intention was to demonstrate how the method can be applied by a simple and low cost way.

## 5.5. Further applications

Further applications may be done comparing preference intake of the different groups of fish eaters and the mercury content, to evaluate the risk of contamination. The results may be used to tranquilize the population or to give guidelines about safer consumption. The Health Secretary of Itaituba demonstrated willingness to further applying this methodology. A questionnaire to check the population preferences regarding fish consumption should be applied by health agents (there are about 85 ones, each one covering about 100 families). Following this step, the most consumed species and the most vulnerable ones should be analysed by the alternative method and the results be used for an awareness campaign. The experience in Itaituba was very useful to evaluate the positive response of the local community in this regard.

## 6. Health Assessment

### 6.1. Introduction

The Health Assessment part of the Global Mercury Project is designed to complement the Environmental Assessment providing indications of the level of mercury poisoning and their health effects on ASM communities. This exposure may be caused either by mercury vapor inhalation or by ingestion of contaminated food, in particular fish as the most accessible protein in riparian communities, or both. Based on the assessment of pathways and bioavailability of mercury vapor and methylmercury to the mining communities, the Health Assessment combines information from biological samples associated with medical exams to evaluate the level of impact that the pollutant caused or may cause to individuals residing in “mining and environmental hot-spots” (Veiga and Baker, 2003).

A Health Assessment is an epidemiological research and therefore includes an evaluation of the physical and neurological conditions of individuals and possible influences of external factors that may or may not contribute to the aggravation of their health. Medical exams were designed to establish a relationship between biomonitoring materials (analysis of hair, urine and blood) and symptoms of poisoning (Veiga and Baker, 2003).

The main pathways through which mercury is bioaccumulated in humans are the inhalation of metallic mercury vapor from amalgam burning (and gold melting) and the oral ingestion of fish contaminated with methylmercury. Other pathways may include inhalation of Hg evaporated from amalgamation tailings, ingestion of contaminated vegetables or consumption and dirt ingestion by children (Veiga and Baker, 2003).

The Evandro Chagas Institute, through its Environment Department, responding to a request by the Centre for Mineral Technology (Centro de Tecnologia Mineral - CETEM/MCT) to participate as a contracted party in the “Removal of Barriers to Introduction of Cleaner Artisanal Gold Mining and Extraction Technologies” project, under the sponsorship of the United Nations Industrial Development Organization (UNIDO), performed field and laboratory activities in the two selected areas to accomplish the study (the “São Chico” gold mining and the “CrepORIZINHO” gold mining) located in the Tapajós region in the municipality of Itaituba-Pa.

As part of the investigation of the general health of the local populations and the long term exposure to mercury, specially by the gold miners and their families, a comprehensive physical structure has been set up in the two locations to support the activities which included a field laboratory to collect material, the conditioning of the samples and processing of some hematological biochemical e parasitologic determinations, a space to fill out the epidemiological questionnaire and a medical office.

## **6.2. Area Of Study And Population**

The survey about the social-economical conditions of the two working areas: the "São Chico" gold mining and the "CrepORIZINHO" gold mining was performed by Dr. Armin Mathis of the "Universidade Federal do Pará" and are summarized in the "Report referring to the prospecting of "São Chico and Creporizinho", presented by the author to the other Institutions involved in the Project. The information served to fund the subsequent activities of a comprehensive health survey.

### **6.2.1. "São Chico" Gold Mining Area**

The access to the São Chico community is done, preferably, by air in a freighted airplane, by land this is only possible during summer time. The villa is located along an old prospecting landing field.

In the "São Chico" community 246 people were attended who fulfilled the necessary requirements to participate in the research, submitting them to all the steps and procedures planned in the protocol. The field work steps involved in the filling out of the epidemiological questionnaire, collecting of material (blood and urine), receiving the standard containers with preservative for the parasitologic test of feces and doctor service (clinical and neurological). Table 26 shows the distribution by sex and age of the population resiofnt in this and nearby locations. About 20% of the population are children up to 10 years old.

There is a predominance of male individuals (n=151) against 95 of the female sex. The biggest percentages, including men and women, were verified in the age ranges 31-35 and 36-40 with 13.8% and 13.0% of the population considered in the study, followed by individuals of age range between 46 and 50 with 11,0%. This distribution corresponds to the one expected in communities such as the São Chico.

The information referring to the origin and occupation of the individuals who participated in the research in the community of "São Chico" indicate that 43.1% (n=106) come from the Maranhão State, followed by Pará with 34.1% (n=84), Piauí, Goiás and Ceará with 6.5% (n=16); 2.8% (n=7) and 2.4% (n=6), respectively. As to the occupation of 44.3% that corresponds to 109 individuals, it referred to prospectors or shop workers dealing with the purchase and sale of gold. Among the other occupations, businessmen 3.7% (n=9) and other activities 52.0% (n=128), which include cooks, housewives, cattle farmers, mechanics and salespeople, etc.

**Table 26 - Distribution by age and sex range of the population served at the "São Chico" gold mining, Itaituba, Pará Brazil. 2003.**

Age	Masculine	Feminine	Sub-Total	%
0 - 2	6	10	16	6,5
3 - 5	12	6	18	7,3
6 - 10	8	6	14	5,7
11 - 15	3	4	7	2,9
16 - 20	12	4	16	6,5
21 - 25	6	9	15	6,1
26 - 30	10	10	20	8,1
31 - 35	21	13	34	13,8
36 - 40	20	12	32	13,0
41 - 45	12	8	20	8,1
46 - 50	19	8	27	11,0
51 - 55	11	2	13	5,3
>55	11	2	13	5,7
<b>Total</b>	<b>151</b>	<b>95</b>	<b>246</b>	<b>100,0</b>

The educational level, evaluated through the number of years of study, is extremely low, with an average 2 years stay in school. Among the individuals who participated in the research 31.1% (n=77) referred to themselves as not literate. Among the participants of the study in the age range between 7 and 11, 20.1% (n=42) and those aged 12 (19.7%), which correspond to 42 individuals, are in this situation. It was also verified that in the first age range referred herein, there are 3 children who are out of school.

### 6.2.2. Laboratory Analysis for Mercury in Urine

Inhalation of Hg vapor is more significant for mining and gold shop workers directly involved in handling metallic mercury, but can also indirectly affect surrounding communities. Hg vapor is completely absorbed through the alveolar tissue. The biological half-life of Hg in blood absorbed as vapor is about 2-4 days when 90% is excreted mainly through urine (Veiga and Baker, 2003).

Mercury can accumulate in the central nervous system (CNS) and damage it irreversibly. Kidneys are the most affected organs in exposure of moderate duration to considerable levels, while the brain is the dominant receptor in long-term exposure to moderate levels (Suzuki, 1979 APUD Veiga and Baker, 2003).

Occupational Hg vapor exposure in humans indicates that neurotoxicity is the adverse effect most likely to occur at lowest exposure level (LOEL) and usually it is reversible. Elemental mercury is categorized as Group D, unable to be classified as to human carcinogen, according to USEPA Guideline for Carcinogen Risk Assessment (USEPA, 1986).

In general, it is difficult to find an association between exposure level and blood concentration due to confounding exposure to methylmercury from fish consumption, but this problem is not so important when analyzing urine, as only a very small fraction of absorbed methylmercury is excreted by urine (WHO, 1991) and one could assume that most part of Hg in

urine is due to Hg vapor exposure. Since inorganic mercury poisoning affects liver and kidneys, high levels in urine can indicate undue exposure to Hg vapor (Veiga and Baker, 2003).

Determination of total Mercury in the urine and blood samples were performed to evaluate the exposure to Mercury metallic steam, considered comparison parameters for the criteria adopted by the OMS. Determinations of Urinary creatinine in urine were also performed and the values were related to the content of mercury for the correction of the results and comparison with the data of the literature.

In the São Chico community, a total of 235 urine samples were analyzed, where 104 were those of prospectors and 131 of the control group (intern). The analysis results of blood and urine Mercury of the participants in the São Chico gold mining are summarized in Table 27. The research used the urine of the people considered as not prospecting as internal control of the studied population and the Mercury determinations are presented without correction with the values of creatinine. This correction is the one that has to be used for the comparison with the clinical results. The arithmetic average of total mercury contents in urine among the prospectors ( $17.37 \pm 36.55 \mu\text{g/l}$ ;  $n= 104$ ) represented three times the content found among the non-prospectors ( $5.73 \pm 8.65 \mu\text{g/l}$ ;  $n=131$ ). Other data such as maximum amplitude and the distribution by quarters, also showed the higher mercury levels among the prospectors. After readjusting the Mercury values by the creatinine values, the average contents of mercury represented about twice the values observed among the prospectors. Thus in general, a bigger impact was observed in the reduction of mercury levels in the prospecting group after the correction of values by Urinary creatinine which shows, in an indirect form, the occurrence of alteration in excretion of creatinine in this group. Therefore, this could be an adverse effect on normal kidney function.

WHO (1991) stated that effects of elemental mercury vapor on the kidney had been reported at lower exposure levels than those associated with the onset of CNS signs and symptoms.

WHO (1991) concluded that a person with a urine Hg level of 100  $\mu\text{g/g}$  creatinine has a high probability of developing symptoms such as tremors and erythema. For Hg levels between 30 and 100  $\mu\text{g/g}$  creatinine, the incidence of certain subtle effects on psychomotor performance. The occurrence of several subjective symptoms such as fatigue, irritability and loss of appetite can be observed. For Hg levels below 30-50  $\mu\text{g/g}$  creatinine, mild effects can occur in the sensitive individuals but it seems more difficult to observe symptoms.

**Table 27 - Descriptive statistics of Mercury levels in the researched population of the "São Chico" Gold mining. Itaituba, Pará-Brazil. 2003.**

<b>Variables</b>	<b>"Prospectors"</b>	<b>"Non-Prospectors"</b>	<b>Total</b>
<b>Hg Urine (µg/l)</b>			
No. Individual	104	131	235
Mean/Std. Deviat.	17,37±36,55	5,73±8,65	10,88±25,75
Amplitude	0,157 - 301,17	0,118 - 73,06	0,118 - 301,17
1° quartil	4,63	1,33	1,78
3° quartil	15,51	6,54	11,22
<b>Corrected Values Urine (µg/g of creatinine)</b>			
No. Individual	104	129	233
Mean/Std. Deviat.	9,29±13,59	5,13±13,59	6,99±11,09
Amplitude	0,087 - 78,505	0,090 - 55,000	0,087 - 78,50
1° quartil	2,178	1,064	1,442
3° quartil	9,316	5,396	7,665
<b>Hg Blood (µg/l)</b>			
No. Individual	106	128	234
Mean/Std. Deviat.	27,74±23,19	16,50±10,46	21,60±18,26
Amplitude	3,90 - 141,00	2,92 - 63,00	2,92 - 141,00
1° quartil	15,42	10,37	10,90
3° quartil	35,23	19,26	24,39
<b>Hg Hair (µg/g)</b>			
No. Individual	1	136	137
Mean/Std. Deviat.	3,92	3,157±2,63	3,16±2,62
Amplitude	-	0,14 - 14,97	0,14 - 14,97
1° quartil	-	1,55	1,56
3° quartil	-	3,79	3,84

OBS: The normal values of 10 µg/g creatinine, and Limit of Biological Tolerance (LBT) of 50 µg/g creatinine, in urine, according to the World Health Organization (1990). Methylmercury. Geneva. Environmental Health. 101-144. For blood the values are: up to 8 µg/l, normal and the Limit of Biological Tolerance (LBT) of 30 µg/l. For hair, up to 2 µg/g for not exposed individuals, while 6 µg/g is the Limit of Biological Tolerance (LBT).

In addition, WHO (1991) concluded that a person with a urine Hg levels of 100 µg/g creatinine has a high probability of developing symptoms such as tremors and erythema. For Hg levels between 30 and 100 µg/g creatinine, the incidence of certain subtle effects on psychomotor performance. The occurrence of several subjective symptoms such as fatigue, irritability and loss of appetite can be observed. For Hg levels below 30-50 µg/g creatinine, mild effects can occur in the sensitive individuals but it seems more difficult to observe symptoms.

However, Drasch et al (2001) have found that miners from gold mining area, with median levels of 11.0 and max. 294 µg/l showed classical symptoms of mercury intoxication such as tremor, ataxia, metallic taste, bluish line in the gums. The authors diagnosed chronic mercury intoxication based on high blood/urine and/or hair mercury levels together with

abnormal medical examination results. They also found that individuals not directly involved with Hg handling had high Hg levels in urine (median 4.1, max 76.4  $\mu\text{g}/\text{l}$ ), relative to an outside control group (median 1.7, max. 7.6  $\mu\text{g}/\text{l}$ ). These results are very consistent with the present work. The control group, which is not involved directly with Hg handling, presented Hg in urine close to 6  $\mu\text{g}/\text{l}$  and max. 73.06  $\mu\text{g}/\text{l}$ .

In Brazilian Amazon, gold shop workers with high levels of Hg in urine (average around 270  $\mu\text{g}/\text{l}$ ) exhibited some signs of mercurialism, such as dizziness, headache, palpitations, tremors, pruritus and insomnia (Malm et al., 1995).

Another study with 20 amalgamation workers, 8 individuals presented high mercury levels in urine (exceeding 50  $\mu\text{g}/\text{g}$  creatinine) and 4 of them with symptoms of poisoning such as stomach irritation, nausea, sexual dysfunction, headache and character alteration. Mercury levels in urine as high as 460  $\mu\text{g}/\text{g}$  creatinine were observed (Schulz-Garban, 1995; as cited in Veiga and Baker, 2003).

A positive correlation has been established between the daily time-weighted exposure to Hg vapor and the daily mercury in blood and urine (Roels, 1987 apud WHO, 1991). Urinary levels about 50  $\mu\text{g}/\text{g}$  creatinine were seen occupational exposure to about 40  $\mu\text{g}/\text{m}^3$  in the air. Such exposure would correspond to about 17  $\mu\text{g}/\text{l}$  of blood. So, values for air concentration (in  $\mu\text{g}/\text{m}^3$ ) are approximately the same as those for urine mercury concentration (expressed in  $\mu\text{g}/\text{g}$  creatinine) (WHO, 1991).

The ratio of urine to air concentrations was re-evaluated by WHO (1980) to be closer to 2.0-2.5. However, USEPA 2001, using experiments with animals, indicates continuous exposure to Hg above 0.3  $\mu\text{g}/\text{m}^3$  of air may present a health hazard. The critical effects related to human exposure to elemental mercury are reported as hands tremor, increases in memory disturbances, slight subjective and objective evidence of autonomic dysfunction.

At the São Chico gold mining, 106 blood samples of individuals referring to themselves as prospectors were analyzed and 128 of the non-prospectors group (control). The average mercury concentration in the group of gold miners reaches 27.74  $\mu\text{g}/\text{l}$ , varying from 3.90 to 141.00  $\mu\text{g}/\text{l}$ . In the second group, the average mercury level reaches 16.50  $\mu\text{g}/\text{l}$ , varying from 2.92 to 63.00  $\mu\text{g}/\text{l}$ . In blood samples, the average mercury concentration among the prospectors was almost the double of those observed in non-prospectors.

The mercury levels in hair were analyzed among the non-prospectors and presented an average of 3.15  $\mu\text{g}/\text{g}$  with a variation of 0.14 to 14.97  $\mu\text{g}/\text{g}$ , the majority remaining (third quarter - 75%) below the LTB (6  $\mu\text{g}/\text{g}$ ) and near the normal limits for those not exposed (2  $\mu\text{g}/\text{g}$ ).

The mean concentration of total mercury in whole blood (in the absence of consumption of fish with high methylmercury levels) is probably of the order of 5-10  $\mu\text{g}/\text{l}$ , and the hair about 1-2  $\mu\text{g}/\text{g}$ . The average mercury concentration in urine is about 4  $\mu\text{g}/\text{l}$ . One source of the variation in urine levels seems to be exposure from dental amalgams while for blood and hair levels fish consumption is the major source of exposure (WHO, 1991).

The background level in hair falls in the range of 1-2  $\mu\text{g}/\text{g}$  (WHO, 1991). Hazardous effects on fetus are likely when 20  $\mu\text{g}/\text{g}$  is analyzed in the hair of pregnant women (Krenkel, 1971). WHO (1990) reports that 50  $\mu\text{g}/\text{g}$  Hg in hair is an adequate threshold to observe clinical effects and that child-bearing women with Hg concentrations in hair above 70  $\mu\text{g}/\text{g}$  exhibit more than 30% risk of having neurological disorder in the offspring. Levels of 10  $\mu\text{g}/\text{g}$  must be considered as the upper limit guideline for pregnant women (Skerfving, 1973). Recent evaluation considers 5  $\mu\text{g}/\text{g}$  Hg in hair a safety guideline for pregnant women (Yagev, 2002)

### 6.2.3. Analysis of Some Variables Contained in the Index Cards (Preliminary Results). São Chico, Itaituba, Pará-Brazil. 2003.

The general working conditions with mercury (Table 28) show that 84.1% of the prospectors have been using mercury directly in their activities, as an average, for 15 years, performing the burning of gold-mercury amalgam in open recipient, characterizing an chronic occupational exposure. Only 11.2% use a retort for the process of burning amalgam, which is a recent improvement for mercury handling in this area.

**Table 28 - Occupational conditions of the use of mercury in the São Chico gold mining. Itaituba, Pará-Brazil. 2003.**

Variables	São Chico n = 109		
	N° of gold miners	%	Average working time (years)
Work with Hg	90	84,1	14,9
Hg burning in open air	82	76,6	-
Use of retort	12	11,2	2,1

The diagnosis of the main diseases in the region is shown on Table 29. As expected, the highest incidence refers to malaria, with 4 cases detected and treated at the moment of the research. Past cases of malaria were reported by 94.5% of the prospectors (an average of 6 past episodes) and 71.5% of the non-prospectors (average of 4 past episodes). Other diseases were also pointed out, such as tuberculosis, hanseniasis and hepatitis of unspecified origin, all with one current case. Therefore, malaria is spread all over the study area, being almost all the local population infected by this endemic disease. This makes malaria a potential confounder parameter when analyzing health effects due to mercury.

**Table 29 - Analysis of the Main Diseases of the Region - São Chico. Itaituba, Pará-Brazil. 2003.**

Variables	Prospectors (N=109)	Non-Prospectors (N=137)	Total
<b>Malária</b>			
Current	1 (0,9%)	3 (2,1%)	4 (1,6%)
Past	103 (94,5%)	98 (71,5%)	201 (81,7%)
Mean incidence	6,0	4,0	5,0
<b>Tuberculosis</b>			
Current	-	1 (0,7%)	1(0,4%)
Past	2 (1,8%)	1 (0,7%)	3 (1,2%)
<b>Hanseníase</b>			
Current	-	1 (0,7%)	1 (0,4%)
Past	1 (0,9%)	-	1 (0,4)
<b>Hepatitis</b>			
Current	-	1 (0,7%)	1 (0,4%)
Past	12 (11,0%)	20 (14,6%)	32 (13,0)

The existence of intestinal parasitism in the São Chico god mine showed the occurrence of parasite agents presented in Table 30, where the presence of *Ancilostomidis* and the *Ascaris*

*lumbricoiops* were more prevailing among the helmintos and *Giardia lamblia* and *Entamoeba histolytica* are noted among the protozoa.

**Table 30 - The prevailing of Intestinal Parasites in the São Chico community. Itaituba, Pará-Brazil. 2003.**

Helmintos e Protozoan	Prospectors (N=109)		Non-Prospectors (N=137)		Total (N=246)	
	n	(%)	n	(%)	n	(%)
<i>Ascaris lumbricoiops</i>	13	11,9	27	19,7	40	16,3
<i>Trichuris trichiura</i>	1	0,9	1	0,7	2	0,8
<i>Strongiloiofs stercoralis</i>	0	-	1	0,7	1	0,4
<i>Ancilostomiofos</i>	42	38,5	29	21,2	71	28,9
<i>Giardia lamblia</i>	22	20,6	42	30,7	64	26,0
<i>Entamoeba histolytica</i>	23	21,5	32	23,4	30	21,2

WHO (1991) concluded that a person with a Hg level in urine of 100 µg/g creatinine has a high probability of developing symptoms such as tremors and erythism. For Hg levels between 30 and 100 µg/g creatinine, the incidence of certain subtle effects on psychomotor performance. The occurrence of several subjective symptoms such as fatigue, irritability and loss of appetite can be observed. For Hg levels below 30-50 µg/g creatinine, mild effects can occur in the sensitive individuals but it seems more difficult to observe symptoms.

Occupational exposure of mercury has resulted on effects on CNS. Acute exposure has cause delirium, hallucinations and suicidal tendency as well as erithism (exaggerated emotional response), excessive shyness, insomnia and muscular tremors. The latter symptoms are associated with long-term exposure to high levels of Hg vapor. In milder cases, erithism and tremors regress slowly over a period of years following removal from exposure pathways (WHO, 1991).

Long-term, low-level Hg vapor exposure has been characterized by less pronounced symptoms of fatigue, irritability, loss of memory, vivid dreams and depression (WHO, 1991).

Some signs and symptoms of interest were investigated to evaluate the mercury exposure, as demonstrated in Tables 31 and 32.

**Table 31 - Some Signs and Symptoms of the Prospecting Population of São Chico. Itaituba, Pará-Brazil. 2003**

Symptoms	Never		once/month		once/week		once/day	
	n	%	n	%	n	%	n	%
Metallic Taste	91	83,5	7	6,4	2	1,8	9	8,3
Sialorrhoea	78	71,6	14	12,8	4	3,7	13	11,9
Náusea	83	76,1	19	17,4	5	4,6	2	1,8
Cefaléia	55	50,5	33	30,3	8	7,3	13	11,9
Palpitation	63	57,8	29	26,6	5	4,6	12	11,0
Paresthesia	56	51,4	14	12,8	7	6,4	32	29,4

**Table 32 - Some Signs and Symptoms of the Non-Prospecting Population of São Chico. Itaituba, Pará-Brazil. 2003.**

Symptoms	never		once/month		once/week		once/day	
	n	%	n	%	n	%	n	%
Metallic Taste	131	95,6	2	1,5	-	-	4	2,9
Sialorrhoea	127	92,7	6	4,4	1	0,7	3	2,2
Náusea	109	79,6	22	16,1	3	2,2	3	2,2
Cefaléia	95	69,3	20	14,6	7	5,1	15	10,9
Palpitation	107	78,1	20	14,6	8	5,8	2	1,5
Paresthesia	120	87,6	12	8,8	3	2,2	2	1,5

In general, the occurrence of these symptoms was more frequent among the prospectors rather than among the non-prospectors, mainly for symptoms cited as once a month or once a day. The frequency of paraesthesia is pretty higher in gold miners than in control group, as well as other important symptoms, as metallic taste and palpitations. These findings suggest effects due to mercury exposure in gold miners.

Certain symptoms such as nausea (that can be associated to digestive disturbance and to parasitism) and headache (associated to many causes) are similar in the two groups.

Although pulmonary problems and dermatitis due to high levels of Hg vapor were the main symptoms reported in a population exposed to Hg vapor in the Peruvian Yanacocha mine (Veiga and Baker, 2003), in Table 33 we observe the predominance of skin mucus paleness, which represents n= 130 (52.8%) of the population, the non-prospectors category prevailing with 77 (56,2%). This situation is the consequence of the anemic parasitism syndrome, common to other communities of the rain forest, investigated by the Environment Department of the Evandro Chagas Institute.

**Table 33 - Analytical Results of Skin - São Chico. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=109)		Non-Prospectors (n=137)		General (n=246)	
	n	% Cases	n	% Cases	n	% Population
Skin paleness	53	48.6%	77	56.2%	130	52.8%
Skin Itch	7	6.4%	18	13.1%	25	10.2%
Hypochromatic Spots	3	2.8%	9	6.6%	12	4.9%
Hyperchromatic Spots	3	2.8%	11	8.0%	14	5.7%
Piodermatitis	1	0.9%	-	-	1	0.4%
Impetigo	1	0.7%	-	-	1	0.4%

Symptoms typically associated with high, short-term exposure to Hg vapor (1000 to 44,000 µg/m<sup>3</sup>), such as those miners are subject to when burning amalgam in open pans, are chest pains, dyspnoea, cough, haemoptysis, impairment of pulmonary function and interstitial pneumonitis (Veiga and Baker, 2003).

Table 34 shows the results of digestive system analysis in gold mining workers and control group.

**Table 34 - Analytical Results of the Digestive System - São Chico. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=109)		Non-Prospectors (n=137)		General (n=246)	
	n	% Cases	n	% Cases	n	% Population
Anorexia	8	7.3%	20	14.6%	28	11.4%
Hepatomegaly	4	3.7%	1	0.7%	5	2.0%
Diarrhea	4	3.7%	7	5.1%	11	4.5%
Intestinal Obstipation	1	0.9%	-	-	1	0.4%
Esplenomegaly	3	2.8%	1	0.7%	4	1.6%
Abdominal Pain	41	37.6%	48	35.0%	89	36.2%
Dispepsia	28	25.7%	13	9.5%	41	16.7%
Pelvic Pain	2	1.8%	22	16.1%	24	9.8%
Icterícia	2	1.8%	-	-	2	0.8%
Vomit	4	3.7%	9	6.6%	13	5.3%
Weight Loss	2	1.8%	3	2.2%	5	2.0%
Nutrition Disturbance	2	1.8%	1	0.7%	3	1.2%

The frequency of hepatomegaly, splenomegaly and dispepsia in gold mining workers is close to 5, 4 and 3 times higher than in control group, respectively. These results are consistent, since inorganic mercury poisoning affects liver and kidneys.

The results of Table 35 refer to the frequency in which one finds infections in the upper airways, probably due to the climate conditions and the high diversity of viral and bacterial agents in the region, associated to the general health and environmental conditions.

**Table 35 - Analytical Results of the Respiratory System - São Chico. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=109)		Non-Prospectors (n=137)		General (n=246)	
	n	% Cases	N	% Cases	n	% Population
Crackling Stertors	1	0.9%	2	1.5%	3	1.2%
Sub-crackling Stertors	7	6.4%	17	12.4%	24	9.8%
Sibilos	2	1.8%	3	2.2%	5	2.0%
Epistaxe	1	0.9%	-	-	1	0.4%
Rinorrhea	-	-	10	7.3%	10	4.1%
Nasal Obstruction	1	0.9%	1	0.7%	2	0.8%
Pharynx Hiperemia	-	-	4	2.9%	4	1.6%
Amygdala Hipertrofy	-	-	5	3.6%	5	2.0%
Dispnea	8	7.3%	8	5.8%	16	6.5%
Cough	7	6.4%	20	14.6%	27	11.0%
Lung Disturbance	7	6.4%	19	13.9%	26	10.6%

The frequency for the most symptoms showed in Table 36, was similar between groups, except arterial hypertension, for which the gold miners showed frequency close to 3 times higher than the control group.

**Table 36 - Analytical Results of the Cardiovascular System - São Chico. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=109)		Non-Prospectors (n=137)		General (n=246)	
	n	% Cases	n	% Cases	n	% Population
Cardiac Disturbance	1	0.9%	1	0.7%	2	0.8%
Arterial Hypertension	7	6.4%	4	2.9%	11	4.5%
Taquycardia	-	-	3	2.2%	3	1.2%
Bradycardia	1	0.9%	-	-	1	0.4%
Precordial Pain	1	0.9%	2	1.5%	3	1.2%

Table 37 shows similar frequency for most of the symptoms in both groups. However, it was detected higher frequency of muscular and articular pain in the control group.

**Table 37 - Analytical Results of the Osteomuscular System - São Chico. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=109)		Non-Prospectors (n=137)		General (n=246)	
	n	% Cases	n	% Cases	n	% Population
Backbone Pain	4	3.7%	3	2.2%	7	2.8%
Spine Pain	36	33.0%	26	19.0%	62	25.2%
Fatigue	26	23.9%	31	22.6%	57	23.2%
Astenia	26	23.9%	32	23.4%	58	23.6%
Muscle Pain	55	50.5%	41	29.9%	96	39.0%
Thorax Pain	14	12.8%	9	6.6%	23	9.3%
Articular Pain	55	50.5%	39	28.5%	94	38.2%

#### 6.2.4. Mercury Burden

This section provides analysis of clinical and neurological signs and symptoms and their possible association with mercury concentrations in prospectors and non-prospectors of São Chico. The common manifestation of chronic exposure to excessive levels of Hg vapor is the metallic taste and gum diseases, such as gingivitis, ulcers and formation of a blue line at gum margins (Stopford, 1979).

The self-perception survey as to health and sickness in the group of prospectors obtained very similar answers, i.e., 51% of the individuals feel healthy, while 49% feel they are not healthy (Table 38). However, in the non-prospectors group these percentages are 73 and 27%, respectively.

The mercury levels in urine of the prospectors presented a difference in relation to the health complaints, such as metal taste, hair loss and breathing problems as well as renal illness. This difference however did not prevail after the statistics evaluation ( $p > 0.05$ ). In the case of tremors related, and its interference in work, a significant difference has been observed (T-test=-2.69,  $p = 0.004$ ). The worsening of the health did not show a significant variation in relation to the mercury exposure ( $p > 0.05$ ).

**Table 38 – Average mercury contents in prospectors and non prospectors according to health self-perception and the presence of certain health complaints, São Chico gold mining, Itaituba, Pará-Brazil, 2003.**

Self-Perception of Health	Prospectors (104)		Non-Prospectors (129)	
	n	Mean of Hg Corrected Values Urine ( $\mu\text{g/g}$ of creatinine)	n	Mean of Hg Corrected Values Urine ( $\mu\text{g/g}$ of creatinine)
<b>Feel Healthy</b>				
Yes	53	8,65 $\pm$ 13,49	94	5,35 $\pm$ 9,18
No	51	9,97 $\pm$ 13,79	35	4,54 $\pm$ 4,36
<b>Perception of Health Worsening</b>				
Not Exposed	37	6,59 $\pm$ 8,43	88	4,67 $\pm$ 8,56
Exposed (No)	33	10,90 $\pm$ 18,96	25	6,09 $\pm$ 7,82
Exposed (Yes)	34	10,69 $\pm$ 11,73	16	6,15 $\pm$ 6,36
<b>Tremors</b>				
No	54	5,94 $\pm$ 7,35	101	5,12 $\pm$ 8,76
Yes	50	12,92 $\pm$ 17,43	28	5,17 $\pm$ 5,57
<b>Metallic Taste</b>				
Yes	17	12,45 $\pm$ 16,03	6	5,00 $\pm$ 6,08
No	87	8,68 $\pm$ 13,07	123	5,14 $\pm$ 8,26
<b>Sialorrhea</b>				
Yes	30	8,53 $\pm$ 9,75	10	3,60 $\pm$ 4,90
No	74	9,60 $\pm$ 14,91	119	5,26 $\pm$ 8,37
<b>Appetite</b>				
Yes	72	9,51 $\pm$ 13,07	32	4,71 $\pm$ 7,89
Disturbed	32	8,82 $\pm$ 14,89	17	7,91 $\pm$ 9,49
<b>Weight Loss</b>				
Yes	15	9,41 $\pm$ 19,57	5	9,20 $\pm$ 16,36
No	89	9,28 $\pm$ 12,45	124	4,97 $\pm$ 7,73
<b>Hair Loss</b>				
Yes	9	4,94 $\pm$ 5,83	30	5,45 $\pm$ 7,66
No	95	9,71 $\pm$ 14,05	99	5,03 $\pm$ 8,33
<b>Cough</b>				
Yes	2	1,53 $\pm$ 1,47	3	1,78 $\pm$ 0,78
No	102	9,45 $\pm$ 13,67	126	5,21 $\pm$ 8,23
<b>Renal Sickness</b>				
Yes	16	6,34 $\pm$ 5,09	3	1,08 $\pm$ 0,56
No	88	9,83 $\pm$ 14,57	126	5,23 $\pm$ 8,22
<b>Respiratory Disturbance</b>				
Yes	9	14,47 $\pm$ 24,59	6	4,46 $\pm$ 5,53
No	95	8,81 $\pm$ 12,16	123	5,16 $\pm$ 8,27

In relation to tests of static balance, 43.3% of the prospectors showed an alteration in at least one of the evaluation forms, while in the non-prospectors group this percentage was of 13.2%. The mercury levels however, in the prospectors with some variation were about twice the average of contents found in the non-prospectors (Table 39).

**Table 39 - Alterations registered in the static balance investigation in 104 prospectors and 129 non-prospectors, São Chico gold mining, Itaituba, Pará-Brazil, 2003.**

	Prospectors (N=104)				Non-Prospectors (N=129)			
	Altered		Normal		Altered		Normal	
	N	Mean Hg Urine (µg/g creatinine)	N	Mean Hg Urine (µg/g creatinine)	N	Mean Hg Urine (µg/g creatinine)	N	Mean Hg Urine (µg/g creatinine)
<b>Static Balance</b>	45	10,26±14,96	59	8,56±12,53	17	4,68±5,79	112	5,20±8,48
Stand (open eyes)	7	16,29±17,12	97	8,79±13,27	2	2,43±1,05	127	5,18±8,21
Stand (closed eyes)	39	11,13±15,90	65	8,19±12,00	15	4,82±6,11	114	5,18±8,41
Bend Down	30	9,94±16,04	74	9,03±12,58	5	8,76±8,31	124	5,06±8,18
Tremors	40	9,91±15,02	64	8,91±12,72	7	6,94±8,23	122	5,03±8,17

The evaluation of dynamic balance (Table 40) also showed variation in about 1.9% of the prospectors (alteration in at least one of the tests) and also 0.8% of the non-prospectors, with an average in the mercury levels well higher in the first group as compared to the second one.

**Table 40 - Alterations registered in the dynamic balance in 104 prospectors and 129 non prospectors, São Chico gold mining, Itaituba, Pará-Brazil, 2003**

	Prospectors (N=104)				Non-Prospectors (N=129)			
	Altered		Normal		Altered		Normal	
	N	Mean Hg Urine (µg/g creatinine)	N	Mean Hg Urine (µg/g creatinine)	N	Mean Hg Urine (µg/g creatinine)	N	Mean Hg Urine (µg/g creatinine)
<b>Dynamic Balance</b>	2	24,22±25,66	102	9,00±13,32	1	10,18	128	5,10±8,18
Walk Forward	1	42,37	103	8,97±13,26	-	-	129	5,14±8,16
Walk Backward	1	42,37	103	8,97±13,26	-	-	129	5,14±8,16
Feet tip Walking	-	-	104	9,29±13,59	1	10,18	128	5,10±8,18
Heel Walking	1	42,37	103	8,97±13,26	-	-	129	5,14±8,16
Joint Feet Jumping	-	-	104	9,29±13,59	-	-	129	5,14±8,16
Right Foot Jumping	-	-	104	9,29±13,59	-	-	129	5,14±8,16
Left Foot Jumping	-	-	104	9,29±13,59	-	-	129	5,14±8,16
Ataxia	-	-	104	9,29±13,59	-	-	129	5,14±8,16
Rigidity	1	6,07	103	9,33±13,66	-	-	129	5,14±8,16

Most prospectors answered negatively when questioned about physical fatigue (Table 41), no relevant differences were found in the levels of mercury among the prospectors

according to a positive or negative answer regarding physical fatigue. In the non-prospectors, the reports on physical fatigue as well as mercury levels were always lower.

**Table 41 - Physical fatigue evaluation in 104 prospectors and 129 non-prospectors, São Chico gold mining, Itaituba, Pará-Brazil, 2003.**

	Prospectors (N=104)				Non-Prospectors (N=129)			
	Altered		Normal		Altered		Normal	
	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)
Physical Fatigue	54	9,01 $\pm$ 10,70	50	9,60 $\pm$ 16,26	21	5,58 $\pm$ 8,95	108	5,05 $\pm$ 8,04
Easily Tired	46	8,90 $\pm$ 11,16	58	9,60 $\pm$ 15,34	18	6,31 $\pm$ 9,49	111	4,94 $\pm$ 7,95
Need more Rest	42	9,47 $\pm$ 11,51	62	9,17 $\pm$ 14,93	16	6,74 $\pm$ 9,98	113	4,91 $\pm$ 7,89
Sleepy	38	8,51 $\pm$ 11,41	66	9,74 $\pm$ 14,77	12	5,27 $\pm$ 10,79	117	5,12 $\pm$ 7,90
Disposition to Daily Tasks	31	8,71 $\pm$ 9,76	73	9,54 $\pm$ 14,98	12	2,37 $\pm$ 2,73	117	5,42 $\pm$ 8,48
Lack of Energy	39	8,11 $\pm$ 8,96	65	10,00 $\pm$ 15,76	13	4,34 $\pm$ 5,65	116	5,22 $\pm$ 8,41
Less Muscle Strength	45	8,61 $\pm$ 9,19	59	9,82 $\pm$ 16,23	15	4,52 $\pm$ 5,51	114	5,19 $\pm$ 8,38
Feel Weak	48	8,05 $\pm$ 8,73	56	10,36 $\pm$ 16,69	16	4,42 $\pm$ 5,37	113	5,24 $\pm$ 8,49
Good Disposition but Easily Tired	44	7,96 $\pm$ 9,00	60	10,27 $\pm$ 16,16	12	3,50 $\pm$ 5,08	117	5,30 $\pm$ 8,41

In the mental fatigue evaluation (Table 42) of the prospectors the negative answers were also predominant as to the survey carried on, however among the non prospectors there were less negative answers when compared to those of the prospectors, and mercury contents were also much lower.

**Table 42 -. Mental fatigue evaluation in 104 prospectors and 129 non-prospectors, São Chico gold mining, Itaituba, Pará-Brazil, 2003.**

	Prospectors (N=104)				Non-Prospectors (N=129)			
	Altered		Normal		Altered		Normal	
	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)
<b>Mental Fatigue</b>	52	11,07 $\pm$ 16,30	52	7,52 $\pm$ 10,06	36	4,01 $\pm$ 5,08	93	5,26 $\pm$ 9,09
Difficulty to be concentrated	29	9,12 $\pm$ 14,28	75	9,36 $\pm$ 13,42	20	4,29 $\pm$ 5,40	109	5,29 $\pm$ 8,62
Difficulty to think clearly	25	6,79 $\pm$ 8,14	79	10,09 $\pm$ 14,86	5	2,25 $\pm$ 2,43	124	5,25 $\pm$ 8,29
Difficulty to oral expression	24	18,91 $\pm$ 8,62	80	9,97 $\pm$ 14,74	3	2,54 $\pm$ 3,11	126	5,20 $\pm$ 8,23
Ocular Fadigue	45	10,64 $\pm$ 14,71	59	8,27 $\pm$ 12,71	27	4,10 $\pm$ 4,71	102	5,41 $\pm$ 8,45
Memory Disturbance	40	11,22 $\pm$ 15,40	64	8,09 $\pm$ 12,31	32	4,70 $\pm$ 4,99	97	5,28 $\pm$ 8,98

Table 43 shows several parameters related to muscular strength and reflex alterations.

**Table 43 – Muscular Strength and Reflex Alterations - São Chico, Itaituba, Pará-Brazil, 2003.**

		Prospectors (N=104)				Non-Prospectors (N=129)			
		Altered		Normal		Altered		Normal	
		Mean Hg		Mean Hg		Mean Hg		Mean Hg	
		Urine ( $\mu\text{g/g}$ creatinine)		Urine ( $\mu\text{g/g}$ creatinine)		Urine ( $\mu\text{g/g}$ creatinine)		Urine ( $\mu\text{g/g}$ creatinine)	
	Skin	n		n		n		n	
Abdominal Reflex		-	-	104	9,29±13,59	-	-	129	5,14±8,16
Mentolabial Reflex		66	10,73±15,71	38	6,41±8,42	45	4,71±5,04	84	5,36±9,43
Reflex of Babinski		2	11,92±3,92	102	9,24±13,72	5	5,58±5,88	124	5,12±8,25
Reflex of Hoffmann		1	9,15	103	9,30±13,66	3	7,08±7,24	126	5,09±8,20
Press Strength		67	10,78±15,79	37	6,59±8,43	50	5,39±6,76	79	4,97±8,97
SRP (Reflex of quadriceps)		21	13,49±19,00	83	8,23±11,77	6	4,71±5,64	123	5,16±8,28
BSR (Reflex of biceps braquial)		14	16,84±22,52	90	8,12±11,37	3	7,16±7,43	126	5,09±8,19
Radial Reflex		5	31,27±30,68	99	8,18±11,40	1	0,78	128	5,17±8,18
RA - Reflex									
Aquileu (triceps sural)		15	16,46±21,69	89	8,09±11,45	2	1,23±0,64	127	5,20±8,21
Yesetria facial		1	3,18	103	9,35±13,65	-	-	129	5,14±8,16
Muscular Strength		-	-	104	9,29±13,59	-	-	129	5,14±8,16
Ocular Movement		-	-	104	9,29±13,59	-	-	129	5,14±8,16
Tactile Sensitivity		-	-	104	9,29±13,59	-	-	129	5,14±8,16
Pain Sensitivity		-	-	104	9,29±13,59	-	-	129	5,14±8,16
Distinguishing Segmental Position		-	-	104	9,29±13,59	-	-	129	5,14±8,16
Distinguishing Colors		-	-	104	9,29±13,59	-	-	129	5,14±8,16
Distinguishing Geometric Forms		-	-	104	9,29±13,59	-	-	129	5,14±8,16
Intentional Tremor		21	10,00±16,72	83	9,12±12,80	1	0,35	128	5,17±8,18
Ataxia		3	16,01±22,83	101	9,09±13,36	-	-	129	5,14±8,16

For all parameters, gold miners showed higher frequency than non-gold miners, except for Reflex of Babinski and Reflex of Hoffman. In Mentolabial reflex, press strength, intentional tremor, the differences of frequency between groups were close to 20%, higher in gold miners. Ataxia close to 3% of frequency, was noted only in gold miners.

### 6.3. "CrepORIZINHO" Gold Mining

In the Creporizinho community, 451 individuals participated in all the steps of the protocol of the Project. However, a contingent of 208 people sought the IEC-SAMAM team and received medical service, be it with present and/or past clinical complaints. Table 44 shows a distribution of the population who was served in this location. About 15% of the population are children from zero to 10 years old.

**Table 44 - Distribution by age range and sex of the population served in the "CrepORIZINHO" gold mining. Itaituba, Pará-Brazil. 2003.**

Age	Masc.	Fem.	Sub-Total	%
0 - 2	6	5	11	2,4
3 - 5	13	7	20	4,4
6 - 10	15	16	31	6,9
11 - 15	5	13	18	4,0
16 - 20	5	3	8	1,8
21 - 25	4	11	15	3,3
26 - 30	13	13	26	5,8
31 - 35	32	18	50	11,1
36 - 40	60	18	78	17,3
41 - 45	51	24	75	16,6
46 - 50	36	16	52	11,5
51 - 55	20	6	26	5,8
>55	34	7	41	9,1
<b>Total</b>	<b>294</b>	<b>157</b>	<b>451</b>	<b>100,0</b>

The information referred to in the epidemiological inquiry related to origin showed that 48% (n=216) of the individuals are from Maranhão, followed by 29,1% (n=131) originating from the state of Pará. The rest of the individuals belong to Piauí 6,2% (n=28); Ceará 3,8% (n=17) and Goiás 2,4% (n=11). As to marital status, 27,6% (n=124) reported being single and 51,9% (n=233) said they were married or lived as a couple.

The epidemiological inquiry also showed that 51,2% (n=230) of the individuals participating in the survey were at the moment working as "prospectors" in the poor districts near the urban centers as businessmen 2,9% (n=13), salesclerks of shops buying and selling gold 0,7% (n=3). Other occupations 45,3%, which include housewives, cooks, sales people, etc.

As to schooling referred to by the individuals who participated in the survey, it was verified that the average time spent in school was 2 years. The level of the illiterate people is 21,8% (n=98) whereas in the age range between 6 and 11 and older than 12, these levels are 17,4 and 18,4%, respectively. There is also, out of a total of 29 children between 7 and 11 years old one out of school and the rest with 1 to 2 years of school attendance.

### 6.3.1 Laboratory Analysis for Mercury in Urine

In the Creporizinho community a total of 345 urine samples were analyzed, 170 of which belonging to prospectors and 175 to the control group (intern). The analysis results of Hg blood and urine of the Creporizinho gold mining participants are summarized in Table 45. Here too the urine of people considered non-prospectors was analyzed as an internal control of the studied population and the Hg determinations are presented with and with correction Hg Urinary creatinine. The arithmetic average of total Hg contents in urine among the prospectors ( $13.75 \pm 19.59 \mu\text{g/l}$ ; n= 170) represented 3.5 times the content found among the non-prospectors ( $3.91 \pm 4.87 \mu\text{g/l}$ ; n= 175). These values are similar to São Chico garimpo's area, showed previously. Other data such as the maximum amplitude and the distribution by quarters also showed the highest levels of Hg among the prospectors. After the adjustment of Hg values by

the values of creatinine, the average contents of Hg also represented about twice the contents observed among the prospectors. In general, a bigger impact was observed in the Hg level reduction in the prospectors group after the correction of values by the Urinary creatinine, which indirectly shows the occurrence of variation in Urinary excretion of creatinine in this group, as said previously for the same results from São Chico garimpo's area.

At the Creporzinho gold mining, 211 blood samples of individuals referring to themselves as prospectors were analyzed and 190 of the non-prospecting group (control). The average Hg concentration in the prospectors group was of 25.23 µg/l with a variation of 0.74 and 128.74 µg/l. In the second group, the average was of 20.97 µg/l with a variation of 1.11 and 171.75 µg/l. In this analyzed material the average mercury contents found among the prospectors was just a little lower than that observed in the non-prospectors while the other data presented in general, higher values among the prospectors except the maximum amplitude, where a bigger value was found among the non-prospectors. The Hg levels in hair were analyzed among the non-prospectors and presented an average of 1.82 µg/g with a variation of 0.23 to 10.48 µg/g, the majority remaining (third quarter - 75%) close to the normality limits of those not exposed (2µg/g).

**Table 45 - Descriptive statistic of Hg levels in the researched population at the Creporzinho gold mining. Itaituba, Pará-Brazil. 2003.**

<b>Variables</b>			
<b>Mean Hg Urine (µg/l)</b>	<b>"Prospectors"</b>	<b>"Non-Prospectors"</b>	<b>Total</b>
No. Individual	170	175	345
Mean/Std. Deviat.	13,75±19,59	3,91± 4,87	8,76± 14,99
Amplitude	0,030 - 147,00	0,21 - 36,19	0,030 - 147,00
1° quartil	3,20	1,38	2,11
3° quartil	16,45	4,48	2,11
<b>Corrected Values Urine (µg/g of creatinine)</b>			
No. Individual	169	175	344
Mean/Std. Deviat.	6,00±9,30	1,93±1,88	3,92±6,95
Amplitude	61,58 - 0,02	12,07 - 0,12	61,58 - 0,02
1° quartil	1,75	0,74	1,11
3° quartil	5,72	2,39	4,01
<b>Hg Blood (µg/l)</b>			
No. Individual	211	190	401
Mean/Std. Deviat.	25,23±25,59	20,97±28,61	23,21±27,11
Amplitude	0,74 - 128,74	1,11 - 171,65	0,74 - 171,65
1° quartil	8,14	6,27	7,27
3° quartil	32,00	19,09	27,36
<b>Hg Hair</b>			
No. Individual	-	116	116
Mean/Std. Deviat.	-	1,82±1,53	1,82±1,53
Amplitude	-	0,23 - 10,48	0,23 - 10,48
1° quartil	-	0,77	0,77
3° quartil	-	2,49	2,48

OBS: The normal values of 10 µg/g creatinine, and Limit of Biological Tolerance (LTB) of 50 µg/g creatinine, in urine, according to the World Health Organization (1990). Methylmercury. Geneva. Environmental Health. 101-144. For blood the values are: up to 8 µg/l, normal and the Limit of Biological Tolerance (LTB) equal to a 30 µg/l. For hair, up to 2 µg/g for not exposed individuals, 6 µg/g is the Limit of Biological Tolerance (LTB).

### 6.3.2 Analysis of Some Variables contained in Cards (preliminary results) Creporizinho

The general working conditions with Hg (Table 46) are similar with São Chico area, showing that the majority of the prospectors, i.e. 90,1%, has been using Hg directly in their activities for about 14 years, performing the gold amalgam - Hg burning in open recipient (84,5%). A small number of prospectors (6,0%) uses a retort in the amalgam burning process.

**Table 46 - Occupational Conditions of the use of Hg in the Creporizinho gold mining. Itaituba, Pará-Brazil. 2003.**

Variables	Garimpo Crepurizinho (n=233)		
	Nº of Prospectors	%	Mean of Time (anos)
Work with Hg	210	90,1	14,4
Amalgam Burning in open air	197	84,5	-
Use Retort	14	6,0	2,9

The analysis of the main diseases in the region show, as expected, that the biggest incidence is malaria, with 6 cases detected and treated at the moment of the research. Past cases of malaria were reported by 94,5% of the prospectors (an average of 7 past episodes) and 74,2% of the non-prospectors (average of 5 past episodes). Other diseases were also pointed out, such as tuberculosis (no current case) , hansenias (5 current cases) and hepatitis of unspecified origin, all with one current case (Table 47).

**Table 47 - Analysis of the Main Diseases of the Region - Creporizinho. Itaituba, Pará-Brazil. 2003.**

Variables	PROSPECTORS (n=233)	Non-Prospectors (n=217)	Total (n=450)
<b>Malária</b>			
Current	5 (2,1%)	1 (0,5%)	6 (1,3%)
Past	220 (94,5%)	162 (74,2%)	381 (84,7%)
Mean No. of Episodes	7,0	5,0	6,0
<b>Tuberculosis</b>			
Current	-	-	-
Past	3(1,3%)	1 (0,5%)	4 (0,9%)
<b>Hanseníase</b>			
Current	4 (1,7)	1 (0,5)	5 (1,1%)
Past	1 (0,4%)	2 (0,9)	3 (0,7)
<b>Hepatite</b>			
Current	-	1 (0,5%)	1 (0,2%)
Past	32 (13,7)	24 (11,2%)	56 (12,4)

The prevailing of intestinal parasitism in the Creporizinho gold mining showed the occurrence of parasite agents presented in Table 48, where the presence of Ancilostomídeos and the *Ascaris lumbricoides* were also the most prevailing among the helmintos, two cases of *Taenia sp* were still existing which is not common in other regions but are maybe due to the poor conditions existing on the swine and cattle farms. The *Giardia lamblia* and *Entamoeba histolytica* are noted among the protozoa.

**Tabela 48 - The Prevailing of Intestinal Parasitism in the Creporizinho community, Itaituba, Pará-Brazil. 2003.**

Helmintos and Protozoans	Prospectors (n=233)		Non-Prospectors (n=217)		Total (n=450)	
	n	(%)	n	(%)	n	(%)
<i>Ascaris lumbricoides</i>	27	11,9	40	18,4	67	14,9
<i>Trichuris trichiura</i>	5	2,1	10	4,6	15	3,3
<i>Taenia sp</i>	1	0,4	1	0,5	2	0,4
<i>Ancilostomídeos</i>	67	28,8	11	5,1	78	17,3
<i>Giardia lamblia</i>	79	34,9	93	42,9	172	38,2
<i>Entamoeba histolytica</i>	33	14,2	44	20,3	77	17,1

The evaluation of some interesting signs and symptoms of the exposure to Hg are shown in Tables 49 e 50. In general the occurrence of these symptoms were more frequent among the prospectors than the non-prospectors, including certain symptoms normally related to various causes such as nausea (that may be associated to digestive disturbance and to parasitism) and to headache (associated to various causes).

**Table 49 - Some Signs and Symptoms in prospectors from Creporizinho**

Symptoms	never		once/month		once/week		once/day	
	n	%	n	%	n	%	n	%
Metallic Taste	173	74,2	20	8,6	6	2,6	34	14,6
Sialorrhea	165	70,8	32	13,7	9	3,9	27	11,6
Náusea	154	66,1	46	19,7	25	10,7	8	3,4
Cefalea	87	37,3	64	27,5	48	20,6	34	14,6
Palpitation	120	51,5	63	27	14	6	36	15,5
Paresthesia	101	43,3	8	3,4	1	0,4	123	52,8

**Table 50 - Some Signs and Symptoms in non-prospectors from Creporizinho**

Sintomatologia	never		once/month		once/week		once/day	
	n	%	n	%	n	%	n	%
Metallic Taste	216	99,5	1	0,5	-	-	-	-
Sialorrhea	214	98,6	2	0,9	1	0,5	-	-
Náusea	216	99,5	-	-	1	0,5	-	-
Cefalea	214	98,6	1	0,5	1	0,5	1	0,5
Palpitation	213	98,2	3	1,4	-	-	1	0,5
Paresthesia	214	98,6	-	-	3	1,4	-	-

In general, the occurrence of these symptoms were more frequent among the prospectors rather than among the non-prospectors. The frequency of paraesthesia is pretty higher in gold miners than in control group, as well as all the other symptoms (metallic taste, excessive sweat,

palpitations, nausea and headache). These findings suggest that Hg exposure in gold miners could be in progress.

Table 51 shows the predominance of skin mucus paleness, which represents n= 217 (48.2 %) of all the studied population, contributed similarly between gold miners and control group. This situation is the consequence of the anemic parasitism syndrome, common to other communities of the rain forest, investigated by the Environment Department of the Evandro Chagas Institute.

**Tabela 51 - Analysis Results of Skin - Creporizinho. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=233)		Non-Prospectors (n=217)		General (n=450)	
	n	% Cases	n	% Cases	n	% Population
Skin paleness	109	46,2	108	49,8	217	48,2
Skin Itch	16	6,9	11	5,1	27	6,0
Hypochromatic Spots	10	4,3	10	4,6	20	4,4
Hyperchromatic Spots	8	3,4	13	6,0	21	4,7
Piodermite	4	1,7	-	-	4	0,9
Impetigo	-	-	-	-	-	-

The frequency of dispepsia in gold miners is close twice of control group's frequency, but no other symptoms are more frequent in gold mining workers comparing to control group (Table 52).

**Tabela 52 - Analytical Result of the Digestive System - Creporizinho. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=233)		Non-Prospectors (n=217)		General (n=450)	
	n	% Cases	N	% Cases	n	% Population
Anorexia	12	5,2	19	8,8	31	6,9
Hepatomegaly	1	0,4	3	1,4	4	0,9
Diarrhea	9	3,9	14	6,5	23	5,1
Intestinal Obstipation	2	0,9	2	0,9	4	0,9
Esplenomegaly	1	0,4	1	0,5	2	0,4
Abdominal Pain	89	38,2	89	41,0	178	39,6
Dispepsia	49	21,0	25	11,5	74	16,4
Pelvic Pain	3	1,3	20	9,2	23	5,1
Icterícia	1	0,4	2	0,9	3	0,7
Vomits	7	3,0	21	9,7	28	6,2
Weight Loss	4	1,7	6	2,8	10	2,2
Nutrition Disturbance	1	0,4	-	-	1	0,2

The results of Table 53 refer to the frequency in which one finds infections in the upper airways, probably due to the climate conditions and the big diversity of viral and bacterial agents in the region, associated to the general health and environment conditions.

**Table 53 - Analytical Results of the Respiratory System - Creporizinho. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=233)		Non-Prospectors (n=217)		General (n=450)	
	n	% Cases	n	% Cases	n	% Population
Crackling Stertors	1	0,4	-	-	1	0,2
Sub-crackling Stertors	8	3,4	15	6,9	23	5,1
Sibilos	-	-	2	0,9	2	0,4
Epistaxe	1	0,4	1	0,5	2	0,4
Rinorrhea	5	2,1	5	2,3	10	2,2
Nasal Obstruction	4	1,7	5	2,3	9	2,0
Pharynx Hiperemia	3	1,3	2	0,9	5	1,1
Amygdala Hipertrofy	4	1,7	3	1,4	7	1,6
Dispnea	6	2,6	8	3,7	14	3,1
Cough	9	3,9	19	8,8	28	6,2
Lung Disturbance	11	4,7	20	9,2	31	6,9

Table 54 shows the results of the cardiovascular system investigatrion.

**Table 54 - Analytical Results of the Cardiovascular System - Creporizinho. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=233)		Non-Prospectors (n=217)		General (n=450)	
	n	% Cases	n	% Cases	n	% Population
Cardiac Disturbance	11	4,7	5	2,3	16	3,6
Arterial Hypertension	21	9,0	16	7,4	37	8,2
Taquycardia	12	5,2	6	2,8	18	4,0
Bradycardia	-	-	-	-	-	-
Precordial Pain	10	4,3	7	3,2	17	3,8

The gold miners showed higher frequencies for all of the symptoms than control group, including hypertension, as seen in São Chico area.

Table 55 showed different frequencies of the most of the symptoms in gold miners and control group. Generally, all frequencies were from 2 to 5 times higher in gold miners group than in control one. Muscular and articular pains are the most frequent complains.

**Table 55 - Analytical results of the Osteomuscular System - Creporizinho. Itaituba, Pará-Brazil. 2003.**

Symptoms	Prospectors (n=233)		Non-Prospectors (n=217)		General (n=450)	
	n	% Cases	n	% Cases	n	% Population
Backbone Pain	3	1,3	-	-	3	0,7
Spine Pain	107	45,9	36	16,6	143	31,8
Fatigue	106	45,5	48	22,1	154	34,2
Asthenia	107	45,9	49	22,6	156	34,7
Muscle Pain	124	53,2	51	23,5	175	38,9
Thorax Pain	16	6,9	3	1,4	19	4,2
Articular Pain	125	53,9	50	23,0	175	38,9

### 6.3.3. Mercury Burden

*Some analysis of signs and symptoms compared to the contents of Hg found in prospectors and non-prospectors of the Creporizinho.*

In the case of the Creporizinho gold mining, the self-perception survey as to health and sickness in the group of prospectors obtained different answers, where 32.5% of the individuals feel healthy, while 67.5% think they are not in good health. However, in the non-prospectors group 97.7% reports feeling healthy (Table 56). The Hg levels in urine of the prospectors presented a difference in relation to the health complaints, such as metal taste, excessive sweat and breathing problems as well as tremors and renal illness, this difference however did not prevail in terms of significance in the statistics evaluation (T- student,  $p > 0.05$ ). The worsening of current health problems showed a significant variation in relation to the Hg exposure (Kwallis test=10,22  $p=0.006$ ).

**Table 56 - Average Hg concentrations in prospectors and non-prospectors according to health self-perception and the presence of certain health complaints, Creporizinho gold mining. Itaituba, Pará-Brazil. 2003.**

Self-Perception	Prospectors		Non-Prospectors	
	N	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	N	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)
<b>Feel Healthy</b>				
Yes	55	4,60 $\pm$ 7,02	171	1,90 $\pm$ 1,85
No	114	6,88 $\pm$ 10,59	4	3,90 $\pm$ 2,52
<b>Perception of Health Worsening</b>				
Not Exposed	24	2,64 $\pm$ 2,37	171	1,92 $\pm$ 1,87
Exposed without problems	52	8,10 $\pm$ 12,06	3	1,62 $\pm$ 0,67
Exposed with problems	93	5,95 $\pm$ 9,02	1	7,02
<b>Tremors</b>				
Yes	51	5,61 $\pm$ 8,75	170	1,91 $\pm$ 1,86
No	118	6,37 $\pm$ 9,99	5	3,34 $\pm$ 2,52
<b>Metallic Taste</b>				
Yes	46	7,53 $\pm$ 11,68	1	1,39
No	123	5,62 $\pm$ 8,72	174	1,95 $\pm$ 1,89
<b>Sialorrhea</b>				
Yes	51	7,11 $\pm$ 11,35	3	2,69 $\pm$ 1,99
No	118	5,72 $\pm$ 8,78	172	1,93 $\pm$ 1,89
<b>Appetite</b>				
Yes	50	6,55 $\pm$ 9,75	5	2,11 $\pm$ 1,62
No	119	5,97 $\pm$ 9,59	170	1,94 $\pm$ 1,90
<b>Weight Loss</b>				
Yes	19	7,12 $\pm$ 13,43	2	0,98 $\pm$ 0,15
No	150	6,02 $\pm$ 9,07	173	1,96 $\pm$ 1,89

**Table 56 (Cont.)- Average Hg concentrations in prospectors and non-prospectors according to health self-perception and the presence of certain health complaints, Creporizinho gold mining. Itaituba, Pará-Brazil. 2003.**

Self-Perception	Prospectors		Non-Prospectors	
	N	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	N	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)
<b>Hair Loss</b>				
Yes	37	6,84 $\pm$ 8,14	-	-
No	132	5,95 $\pm$ 10,01	175	1,95 $\pm$ 1,89
<b>Cough</b>				
Yes	5	4,22 $\pm$ 3,60	1	2,39
No	164	6,20 $\pm$ 9,74	174	1,94 $\pm$ 1,89
<b>Renal Sickness</b>				
Yes	15	8,61 $\pm$ 10,33	1	4,83
No	154	5,90 $\pm$ 9,54	174	1,93 $\pm$ 1,88
<b>Respiratory Disturbance</b>				
Yes	24	7,26 $\pm$ 11,86	1	1,39
No	145	5,95 $\pm$ 9,23	174	1,95 $\pm$ 1,89

In relation to tests of static balance, 74,0% of the prospectors showed an alteration in at least one of the evaluation forms, while in the non-prospectors group this percentage was only of 3.4%. The Hg levels however, in the prospectors with some variation were about twice the average of contents found in the non-prospectors (Table 57).

**Table 57 - Alterations registered in the static balance investigation in 169 prospectors and 175 non-prospectors, Creporizinho gold mining. Itaituba, Pará-Brazil..**

	Prospectors (N=169)				Non-Prospectors (N=175)			
	Altered		Normal		Altered		Normal	
	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)	n	Mean Hg Urine ( $\mu\text{g/g}$ creatinine)
<b>Static Balance</b>	125	6,24 $\pm$ 9,78	44	5,31 $\pm$ 7,82	6	2,93 $\pm$ 2,47	169	1,90 $\pm$ 1,85
Stand (open eyes)	5	5,48 $\pm$ 4,61	164	6,01 $\pm$ 9,41	1	1,09	174	1,94 $\pm$ 1,88
Stand (closed eyes)	110	6,71 $\pm$ 10,32	59	4,67 $\pm$ 6,88	5	3,35 $\pm$ 2,52	170	1,89 $\pm$ 1,85
Bend down	103	6,28 $\pm$ 9,78	66	5,55 $\pm$ 8,54	5	3,24 $\pm$ 2,63	170	1,89 $\pm$ 1,85
Tremors	99	5,81 $\pm$ 9,87	70	7,26 $\pm$ 6,48	6	2,93 $\pm$ 2,47	169	1,90 $\pm$ 1,85

The evaluation of dynamic balance (Table 58) also showed variation in about 4.1% of the prospectors (alteration in at least one of the tests), there were no variations found in the non-prospectors, with an average in the Hg levels well higher in the first group as compared to the second one.

**Table 58 – Alterations registered in the investigation of the dynamic balance in 169 prospectors and 175 non-prospectors, Creporizinho. Itaituba, Pará-Brazil. 2003.**

	Prospectors (N=169)				Non-Prospectors (N=175)			
	Altered		Normal		Altered		Normal	
	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)
<b>Dynamic Balance</b>	7	4,31±4,10	162	2,22±1,56	-	-	175	1,93±1,88
Walk Forward	1	1,88	168	6,02±9,32	-	-	175	1,93±1,88
Walk Backward	2	1,38±0,71	167	6,05±9,34	-	-	175	1,93±1,88
Feet tip Walking	1	1,88	168	6,02±9,32	-	-	175	1,93±1,88
Heel Walking	2	1,38±0,71	167	6,05±9,34	-	-	175	1,93±1,88
Joint Feet Jumping	2	1,38±0,71	167	6,05±9,34	-	-	175	1,93±1,88
Right Foot Jumping	2	1,38±0,71	167	6,05±9,34	-	-	175	1,93±1,88
Left Foot Jumping	2	1,38±0,71	167	6,05±9,34	-	-	175	1,93±1,88
Ataxia	4	5,03±5,46	165	6,02±9,38	-	-	175	1,94±1,88
Rigidity	7	4,31±4,10	162	6,07±9,46	-	-	175	1,94±1,88

Most prospectors answered affirmatively when questioned as to physical fatigue (Table 59), being the Hg levels generally higher among those prospectors who answered affirmatively to the physical fatigue question. In the non-prospectors, the data on physical fatigue as well as Hg levels were always well lower.

**Table 59 – Physical fatigue evaluation in 169 prospectors and 175 non-prospectors, Creporizinho gold mining. Itaituba, Pará-Brazil. 2003.**

	Prospectors (N=169)				Non-Prospectors (N=175)			
	Altered		Normal		Altered		Normal	
	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)
Physical Fatigue	129	6,58±9,20	40	4,12±9,48	6	2,13±2,47	169	1,90±1,85
Easily Tired	119	6,32±8,17	50	5,71±12,48	5	3,34±2,52	170	1,91±1,86
Need more Rest	122	6,72±9,44	47	4,62±10,01	5	3,34±2,52	170	1,91±1,86
Sleepy	121	6,51±9,06	48	5,22±10,94	5	3,34±2,52	170	1,91±1,86
Disposition to Daily Tasks	119	5,78±7,12	50	7,00±13,92	5	3,34±2,52	170	1,91±1,86
Lack of Energy	124	6,30±8,59	45	5,69±12,10	5	3,34±2,52	170	1,91±1,86
Less Muscle Strength	123	6,45±8,99	46	5,31±11,17	5	3,34±2,52	170	1,91±1,86
Feel Weak	123	6,45±8,99	46	5,31±11,17	5	3,34±2,52	170	1,91±1,86
Good								
Disposition but Easily Tired	123	6,42±9,00	46	5,41±11,16	6	2,13±2,47	169	1,90±1,85

In the mental fatigue evaluation of the prospectors the negative answers were predominant (Table 60), however among the non-prospectors the negative answers were much fewer when compared to those of the prospectors, with Hg contents also much more reduced.

**Table 60 - Mental fatigue evaluation in 169 prospectors and 175 non-prospectors, Creporizinho gold mining, Itaituba, Pará-Brazil. 2003.**

	Prospectors (N=169)				Non-Prospectors (N=175)			
	Altered		Normal		Altered		Normal	
	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)
<b>Mental Fadigue</b>	52	11,07±16,30	52	7,52±10,06	36	4,01±5,08	93	5,26±9,09
Difficulty to be concentrated	29	9,12±14,28	75	9,36±13,42	20	4,29±5,40	109	5,29±8,62
Difficulty to think clearly	25	6,79±8,14	79	10,09±14,86	5	2,25±2,43	124	5,25±8,29
Difficulty to oral expression	24	18,91±8,62	80	9,97±14,74	3	2,54±3,11	126	5,20±8,23
Ocular Fadigue	45	10,64±14,71	59	8,27±12,71	27	4,10±4,71	102	5,41±8,45
Memory Disturbance	40	11,22±15,40	64	8,09±12,31	32	4,70±4,99	97	5,28±8,98

Table 61 shows several parameters related alteration of reflex and muscular force in gold miners and control group.

**Table 61 - Alteration of Reflex and Muscular Force - Creporizinho. Itaituba, Pará-Brazil. 2003.**

	Prospectors (N=169)				Non-Prospectors (N=175)			
	Altered		Normal		Altered		Normal	
	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)	n	Mean Hg Urine (µg/g creatinine)
Abdominal Skin Reflex	3	4,25±2,43	166	6,03±9,37	-	-	175	1,93±1,88
Mentolabial Reflex	143	6,60±9,96	26	2,69±1,86	5	3,30±2,57	170	1,89±1,85
Reflex of Babinski	3	4,30±2,01	166	6,03±9,37	-	-	175	1,93±1,88
Reflex of Hoffmann	1	61,58	168	5,67±8,26	-	-	175	1,93±1,88
Press Strength	174	6,59±9,90	25	2,56±2,44	5	2,12±1,62	170	1,93±1,89
SRP (Reflex of quadriceps)	50	3,93±2,65	119	6,87±10,84	2	4,21±3,98	173	1,91±1,85
BSR (Reflex of biceps braquial)	39	3,89±2,82	130	6,63±10,41	2	4,21±3,98	173	1,91±1,85
Radial Reflex	7	3,90±3,04	162	6,09±9,47	-	-	175	1,93±1,88
RA - Reflex Aquileu (triceps sural)	49	3,75±2,49	120	6,91±10,80	-	-	175	1,93±1,88
Yesetria facial	1	2,82	168	6,02±9,32	-	-	175	1,93±1,88
Muscular Strength	-	-	169	6,00±9,29	-	-	175	1,93±1,88
Ocular Movement	3	6,67±1,41	166	6,04±9,37	-	-	175	1,93±1,88
Tactile Sensitivity	-	-	169	6,00±9,29	-	-	175	1,93±1,88
Pain Sensitivity	-	-	169	6,00±9,29	-	-	175	1,93±1,88
Distinguishing Segmental Position	-	-	169	6,00±9,29	-	-	175	1,93±1,88
Distinguishing Colors	-	-	169	6,00±9,29	-	-	175	1,93±1,88
Distinguishing Geometric Forms	-	-	169	6,00±9,29	-	-	175	1,93±1,88
Intentional Tremor	79	6,56±10,38	90	5,50±8,25	1	0,88	174	1,94±1,88
Ataxia	8	4,07±1,61	161	6,09±9,51	-	-	175	1,93±1,88

Gold miners showed higher frequencies for all parameters. Mentolabial reflex and intentional tremor were shown by 84 and 46% of gold miners. Ataxia was shown by 4.71 of gold miners.

The evaluation to Hg exposure included Hg determinations in blood and urine. Table 62 shows a summary of the analysis results of Hg in the group of individuals who are working at the moment or used to work as “prospectors” and the other occupations (“non-prospectors”) in both study areas.

With regard to Hg in urine, the higher exposure to inorganic mercury in São Chico is reflected by 20.2% of the gold miners with Hg levels in urine between 10 and 50 µg/g creatinine, while in Creporinho only 13% fall in this range. Moreover, 2.9% of the gold miners in São Chico and 1.2% in Creporizinho present Hg levels higher than 50 µg/g creatinine. This is an indication that the gold miners in São Chico are more intensively exposed not only to methylmercury, but also to inorganic mercury, in relation to Creporizinho (Table 62).

Within the control group, represented by the population not directly involved in gold mining activities, it is observed that 13.9% of the population in São Chico present Hg levels in urine higher than 10 µg/g creatinine, while in Creporizinho only 0.6% falls in this range. With regard to Hg levels higher than 50 µg/g creatinine in this group, only 1.5% of the population in São Chico falls in this range, whereas no individual in Creporizinho does (Table 62).

**Table 62 - Population distribution according to Hg levels in urine above normality and Limit of Biological Tolerance (LBT) in both areas**

Garimpo	PROSPECTORS					NON- PROSPECTORS					Total				
	n	10<Hg< 50 µg/g creatinine		Hg>50 µg/g creatinine		n	10<Hg< 50 µg/g creatinine		Hg>50 µg/g creatinine		n	10<Hg< 50 µg/g creatinine		Hg>50 µg/g creatinine	
		n	%	n	%		n	%	n	%		n	%	n	%
São Chico	104	21	20.2	3	2.9	129	18	13.9	2	1.5	233	39	16.7	5	2.1
Creporizinho	169	22	13.0	2	1.2	175	1	0.6	-	-	344	23	6.7	2	0.6

The use of blood as a bioindicator of exposure to inorganic mercury requires further investigations using either speciation techniques or the determination in plasma and erythrocytes in order to identify the contribution of inorganic and organic mercury. Although 27.3% of the gold miners in São Chico present Hg levels in blood higher than 50 µg/L, and in Creporizinho only 13% fall in this range, it is not possible to identify mercury sources that caused this exposure level (Table 63).

**Table 63 - Population distribution according to Hg levels in blood above normality and Limit of Biological Tolerance (LBT) in both areas**

Garimpo	PROSPECTORS					NON- PROSPECTORS					Total				
	n	10<Hg< 50 µg/l		Hg>50 µg/l		n	10<Hg< 50 µg/l		Hg>50 µg/l		n	10<Hg< 50 µg/l		Hg>50 µg/l	
		n	%	n	%		n	%	n	%		n	%	n	%
São Chico	106	65	61.3	29	27.3	128	85	66.4	15	11.7	234	150	64.1	44	18.8
Creporizinho	211	112	53.1	28	13.3	190	78	41.0	21	11.0	401	190	47.4	49	12.2

## 7. Conclusions

Since 1989, amalgamation tailings have been dumped into São Chico reservoir, originally built for water supply. As time plays an important role in the behaviour of mercury in the environment, and miners are additionally using cyanide for reworking amalgamation tailings, this has been increasing mercury mobility.

Moreover, pasture fires close to mining hotspots, as observed in São Chico, are likely to represent an important factor responsible for Hg mobilization from soils to the atmosphere. The widespread distribution of Hg contaminated soils in the vicinities of the mining site demonstrate that Hg is probably being precipitated from the atmosphere, after being released from amalgam burning, and remobilized again to the atmosphere during pasture fires.

Since formation of cyanide-mercury complexes into the São Chico reservoir could also be responsible for increasing mercury mobility downstream, as well as the usual practice of pasture fires, this site must be studied in detail to understand the behaviour of mercury species from cyanidation tailings.

High mercury levels have been detected all over the nearby water body, including sediments (averaging 4.10  $\mu\text{g/g}$ ) and aquatic organisms (averaging 4.97  $\mu\text{g/g}$  in fish). After several studies conducted by CETEM on assessment of mercury pollution in the Amazon, this is the first case where the dispersion of mercury from mining hotspots throughout an aquatic system is detected to such an extent. According to the present results, São Chico has shown clear indications of Hg dispersion from mining hotspots, reaching a distance at least as long as 20 km. This consists of a major environmental and health concern. The environmental factors responsible for this particular Hg behavior, marked by its high mobility, are likely to be linked to both the cyanidation attempt and pasture fires.

The present results reveal that the most of fish from São Chico present higher mercury levels than the ones from Creporizinho area. Additionally, in São Chico area, the highest levels of mercury bioaccumulation in fish was shown in Traíra species, a carnivorous and appreciated species for consumption by local residents, extending the environmental risk to a health issue.

Although Piranha and Acari could not be collected in all study sites, their positive correlation in terms of length and Hg concentration demonstrates the feasibility of their use as indicator organisms for mercury availability in tropical aquatic systems, besides Traíra, which showed advantage due to its widespread distribution in the study area.

Traíras from Creporizinho showed higher globular volume and erythrocytes number than Traíras from São Chico. Carás from Creporinho showed higher globular volume and mean globular volume than those from São Chico. Mercury levels and globular volume showed significant negative correlation for both species, suggesting that mercury levels may cause decrease in number of erythrocytes, which are smaller than normal ones, characteristics of regenerative anemia.

The present results also indicate that mercury concentrations in wild plants parts from Creporizinho study area increased with mercury concentrations in soil. Apparently, they function as a excluder, restricting transport of metal upwards to aerial parts. Since Hg concentrations are much higher in aboveground of produces at São Chico study area than in Creporizinho, the uptake in produce plants is likely to occur through atmospheric deposition, but further studies with a larger sample set are necessary to confirm this hypothesis. The

translocation of mercury from soil through roots to aboveground in produce plants was not significant in both studies areas.

Considering 0.3mg the provisional tolerable mercury intake per person weekly (PTWI), the ingestion of total mercury from those foodstuffs falls close to the PTWI in São Chico area, whereas in Creporizinho area the estimated Hg ingestion falls in a range much lower than the PTWI. However, it should be taken into account the small gastrointestinal absorption of inorganic mercury (7%), which results in 0.017 mg/week for São Chico and 0.0007 mg/week for Creporizinho.

Artisanal miners use a variety of mining and amalgamation methods. Together with the fate of contaminated tailings and Au-Hg separation procedures, these methods define the extent of mercury losses from a specific site. If concentrates are amalgamated, the main emission source derives from burning amalgam in open pans. When retorts are not used, atmospheric emissions represent as much as 50% of the total mercury introduced into the process. However, when amalgamation is conducted properly and retorts are used, losses are very low – as little as 0.05%. This recycling practice suggests one of the first approaches to reduce the Hg burden to the environment.

The successful training of new users for the semiquantitative method of mercury determination in fish encourages us to recommend the application of this methodology in all localities where mercury pollution presumably exists. New applications were developed during the last months, so that the same equipment can be used for Hg determinations in urine, soils and sediments. This means that in next training programs we will be able to offer training on semiquantitative mercury determination in fish, sediments, soils and urine samples. As an application of this training, local authorities would be able to manage their pollution problem, using the SMQ determination as a low cost tool for Hg pollution and health monitoring.

The general health conditions observed in both areas revealed to be very precarious, as demonstrated by extremely high incidence of malaria, parasitosis and other diseases not related to mercury exposure.

Since mercury burning in open air is a common practice in both areas since at least 1989, one could realize that a chronic exposure to inorganic mercury occurs. Moreover, pasture fires over Hg contaminated soils in São Chico characterizes a further exposure route to inorganic mercury for local population.

With regard to the exposure to methylmercury through fish consumption, as indicated by its high occurrence in fish from specific sites, one suggests that a possible explanation for increasing Hg bioavailability is related to the cyanidation attempt in São Chico.

The use of blood as a bioindicator of exposure to inorganic mercury requires further investigations using either speciation techniques or the determination in plasma and erythrocytes in order to identify the contribution of inorganic and organic mercury.

Although Hg levels in hair samples are relatively low, as 75% of both population investigated presented Hg concentrations lower than 4 µg/g, it is highlighted that the mean Hg concentration in hair samples from São Chico are the double of those from Creporizinho. This is consistent with the main results obtained by the environmental survey, through which a higher mercury mobility and potential bioavailability has been suggested.

With regard to Hg in urine, the higher exposure to inorganic mercury in São Chico is reflected by 20.2% of the gold miners with Hg levels in urine between 10 and 50 µg/g creatinine,

while in Creporinho only 13% fall in this range. Moreover, 2.9% of the gold miners in São Chico and 1.2% in Creporizinho present Hg levels higher than 50 µg/g creatinine. This is an indication that the gold miners in São Chico are more intensively exposed not only to methylmercury, but also to inorganic mercury, in relation to Creporizinho.

Within the control group, represented by the population not directly involved in gold mining activities, it is observed that 13.9% of the population in São Chico present Hg levels in urine higher than 10 µg/g creatinine, while in Creporizinho only 0.6% falls in this range. With regard to Hg levels higher than 50 µg/g creatinine in this group, only 1.5% of the population in São Chico falls in this range, whereas no individual in Creporizinho does.

In relation to symptoms potentially associated with mercury exposure, it is highlighted the significant incidence of metallic taste, paresthesia, tremors and palpitation in both areas. As for paresthesia, an incidence in the gold miners group as high as 30% in São Chico and 50% in Creporizinho has been observed, while within the control group in both areas this incidence decreases to 1.5% and 0.5% respectively. These results strengthen the need of a continuous monitoring on the health effects within the identified critical groups.

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# **APPENDIX 1**

## **Hg concentrations in sediments, tailings and soils**

Sample	Ref_Lab	Hg (µg/g) -200#	Hg (µg/g) +200#	Igeo	Igeo Class
A101	CC3	0.28		0.32	1
A201	01	122.40	43.50	9.09	6
A202	02	58.70	30.90	8.03	6
A203	03	0.27	0.27	0.26	1
A204	04	10.70	6.26	5.57	6
A205	05	303.50	137.80	10.40	6
A206	06	14.40	5.10	6.00	6
A207	07	151.70	11.30	9.40	6
A208	08	0.30	0.24	0.42	1
A209	09	0.11	0.12	-1.03	0
A210	10	16.30	2.57	6.18	6
A211	11	0.46	0.06	1.03	2
A212	12	1.47	0.47	2.71	3
A213	13	1.01	0.47	2.17	3
A214	15	95.80	54.20	8.73	6
A215	18	25.60	8.60	6.83	6
A216	19	8.27	18.00	5.20	6
A217	20	9.45		5.39	6
A218	A 21	21.10	31.30	6.55	6
A219	A01	122.40	43.50	9.09	6
A220	A02	58.70	30.90	8.03	6
A221	A08	0.25	0.09	0.15	1
A222	A23	1.17	0.49	2.38	3
A223	A24	25.50	6.12	6.82	6
A224	A25	23.00	5.45	6.68	6
A225	A26	21.10	31.30	6.55	6
A226	A27	3.16	1.32	3.81	4
A227	A30	23.00	5.45	6.68	6
A228	C90	10.80	0.05	5.58	6

Sample	Ref_Lab	Hg (µg) 200#	Hg (µg) +200#	Igeo	Igeo Class
A229	C91	0.58	0.42	1.37	2
A230	C92	1.19	0.29	2.40	3
A231	F 1	1.58		2.81	3
A232	F 10	2.49	1.06	3.47	4
A233	F 11	6.01	1.21	4.74	5
A234	F 2	1.46	1.51	2.70	3
A235	F 3	1.74	0.70	2.95	3
A236	F 4	2.63	1.70	3.55	4
A237	F 6	3.78	2.77	4.07	5
A238	F 7	1.88	1.56	3.06	4
A239	F 8	1.93	1.03	3.10	4
A240	F 9	3.01	2.68	3.74	4
A241	L 1	7.61		5.08	6
A242	L 1A	7.45		5.05	6
A243	L 1B	7.45		5.05	6
A244	L 2	8.79		5.29	6
A245	L 2B	5.50		4.61	5
A246	L 4	2.31		3.36	4
A247	L 4A	1.56		2.79	3
A248	L 5	2.33	0.82	3.37	4
A249	L 5A	1.63	0.75	2.86	3
A250	L 6	4.46	1.86	4.31	5
A251	L 7	2.22		3.30	4
A252	L 7A	2.14		3.25	4
A253	L3	4.03		4.16	5
A254	L8	1.20		2.42	3
A255	L8A	1.18		2.39	3
A256	P01	42.10		7.55	6

Sample	Ref_Lab	Hg ( $\mu\text{g}$ ) -200#	Hg ( $\mu\text{g}$ ) +200#	Igeo	Igeo Class
A257	P02	44.20		7.62	6
A258	P03	51.50		7.84	6
A259	P04	82.20		8.51	6
A260	P05	1286.80		12.48	6
A261	P06	65.40		8.18	6
A262	P07	20.30		6.50	6
A263	P08	29.20		7.02	6
A264	P09	152.70		9.41	6
A265	P10	196.50		9.77	6
A266	S 3	1.29	0.62	2.52	3
A267	S 5	5.68	1.93	4.66	5
A268	S 6	0.73	0.22	1.70	2
A269	Sta. Rosa 1	2.06	0.39	3.19	4
A270	Sta. Rosa 1A	0.35		0.64	1
A271	Sta. Rosa 2	0.50		1.15	2
A272	Sta. Rosa 3	1.56		2.79	3
A273	Sta. Rosa 4	2.28		3.34	4
A274	Sta. Rosa 5	2.08		3.21	4
A275	1Vc	0.89	0.45	1.98	2
A276	3Vc	0.54	3.84	1.26	2
A277	4V	0.33	0.19	0.55	1
A278	1Vc	2.48	1.88	3.46	4
A279	6V	0.47	0.29	1.06	2
A280	7V	2.80	1.70	3.64	4
A281	9Vc	4.44	2.88	4.30	5
A282	10V	0.54	3.84	1.26	2
A283	11Vcv	2.80	1.70	3.64	4
A301	Kern 1a	0.84	0.43	1.90	2

Sample	Ref_Lab	Hg (µg) -200#	Hg (µg) +200#	Igeo	Igeo Class
A302	Kern 1b	0.33	0.28	0.55	1
A304	Kern 1c	0.25	0.22	0.15	1
A305	Kern 1d	0.16	0.18	-0.49	0
A306	Kern 1e	0.18	0.15	-0.32	0
A307	Kern 1f	0.19	0.18	-0.24	0
A308	Rio Conrado 1	0.95	0.39	2.08	3
A309	Rio Conrado 2	0.31		0.46	1
A310	Rio Conrado 3	3.34	2.23	3.89	4
A401	Conr1	0.95	0.39	2.08	3
A402	Conr3	3.34	2.23	3.89	4
A403	ConrCava3	2.34	1.86	3.38	4
A404	J6	0.13		-0.79	0
A405	JX	13.10		5.86	6
A406	JX1	0.23		0.03	1
A407	JX2	0.22	0.06	-0.02	0
A408	JX3	15.80	2.02	6.13	6
A409	JX5	0.10		-1.17	0
A410	JX7	0.35	0.05	0.64	1
A411	JX8	0.21	0.03	-0.10	0
A412	JM1	0.07		-1.68	0
A413	JM1	0.07		-1.68	0
A414	JM2	0.15	0.59	-0.62	0
A415	JM2	0.68		1.60	2
A501	C02	0.21	0.03	-0.10	0
A502	C03	0.66	0.08	1.55	2
A503	C04	0.40	0.09	0.83	1
A504	C05	0.11	0.08	-1.06	0
A505	C06	0.32	0.08	0.51	1

Sample	Ref_Lab	Hg (µg) -200#	Hg (µg) +200#	Igeo	Igeo Class
A506	C07	0.82	0.05	1.87	2
A507	C08	0.15	0.04	-0.58	0
A508	C09	0.68		1.60	2
A509	C10	0.14	0.10	-0.73	0
A510	C11	29.30	1.65	7.02	6
A511	C12	4.53	0.66	4.33	5
A512	C14	48.30	2.82	7.75	6
A513	C15	5.57	0.88	4.63	5
A514	C16	26.20	4.18	6.86	6
A515	C17	8.29	5.08	5.20	6
A516	C18	10.40	2.15	5.53	6
A517	C19	11.40	1.08	5.66	6
A518	C21	21.10	31.30	6.55	6
A519	C23	0.57	0.14	1.34	2
A520	C24	0.38	0.04	0.76	1
A521	C25	23.00	5.45	6.68	6
A522	C30	17.60	2.82	6.29	6
A523	C31	0.29	0.25	0.37	1
A524	C32	0.25	0.22	0.15	1
A525	C33	0.57	0.14	1.34	2
A526	C34	0.37	0.04	0.72	1
A527	C35	0.26	0.24	0.20	1
A528	C36	1.54	0.50	2.77	3
A529	C37	0.10	0.09	-1.17	0
A530	CS2	0.60	0.52	1.42	2
A531	12V	21.10	31.30	6.55	6
A601	C40	0.39	0.21	0.79	1

Sample	Ref_Lab	Hg (µg) -200#	Hg (µg) +200#	Igeo	Igeo Class
A602	C41	0.14	0.39	-0.68	0
A603	C42	0.31	0.03	0.45	1
A604	C43	0.36	0.07	0.68	1
A605	C44	0.32	0.03	0.51	1
A606	C45	0.27	0.15	0.26	1
A607	C46	0.23	0.04	0.03	1
A608	C47	0.24	0.03	0.09	1
A609	C48	0.33	0.05	0.55	1
A610	C49	0.61	0.34	1.44	2
A611	C50	2.37	0.61	3.40	4
A612	C51	1.67	0.38	2.89	3
A613	15V	1.93	1.24	3.10	4
A614	16V	1.93	1.24	3.10	4
A617	17V	0.30	0.62	0.44	1
A701	C26	0.10	0.09	-1.17	0
A702	Bof02	0.48	0.12	1.09	2
A703	Bof2b	0.81	0.28	1.85	2
A704	C27	1.93	1.24	3.10	4
A705	Bof3	0.12	0.11	-0.91	1
A801	C01	0.95	6.41	2.08	3
A802	C80	151.90	64.40	9.40	6
A803	Pap1	0.42	0.48	0.89	1
A804	Pap2	0.38	0.00	0.76	1
A805	Paps	0.56	0.33	1.32	2
A806	SolA	0.43	0.36	0.93	1
A807	Tol2	0.51	0.19	1.18	2
A808	18V	0.86	0.54	1.93	2
A809	19V	0.52	1.72	1.20	2

Sample	Ref_Lab	Hg (µg) -200#	Hg (µg) +200#	Igeo	Igeo Class
A810	20V	0.52	1.72	1.21	2
A811	21V	0.92	0.98	2.03	3
A812	C52	0.80	0.64	1.83	2
A901	PA1	1.04	0.32	2.21	3
A902	PA2	0.29	0.05	0.37	1
A903	PA3	0.26	0.08	0.23	1
A904	PA4	0.23	0.19	0.03	1
A905	PA5	0.63	0.13	1.49	2
A906	PA6	0.28		0.32	1
A907	PA7	0.18		-0.32	0
A908	22V	0.20	0.05	-0.17	0
A1001	Cao1	0.32	0.03	0.51	1
A1002	Cao2	0.27		0.26	1
A1003	Cao3	0.23	0.04	0.03	1
A1004	Cao4	0.39	0.21	0.79	1
A1005	Cao5	0.61	0.34	1.44	2
A1006	Cao7	2.37	0.61	3.40	4
A1007	Cao8	1.67	0.38	2.89	3
A1008	Cao9	0.27	0.12	0.26	1
A1101	CME	0.29	0.16	0.34	1
A1102	GME	1.47	0.85	2.71	3
A1103	h	12.90		5.84	6
A1104	IC	0.43	0.26	0.93	1
A1105	ICMD	0.35	0.29	0.64	1
A1106	ICMEB	0.41	0.24	0.86	1
A1107	D	22.20		6.62	6
A1108	a	3.24		3.85	4
A1109	b	4.02		4.16	5
A1110	E13	4.74		4.40	5
A1111	C	13.50		5.91	6
A1112	F	5.87		4.71	5
A1113	G	6.52		4.86	5
A1114	23V	0.27	0.05	0.26	1

## **APPENDIX 2**

### **Tables and Figures of Fish Data**

**Table I - Significant correlation coefficients of correlation analysis between Hg levels in muscles and length and weight of fish from São Chico and Creporizinho garimpo's areas**

Garimpo's areas	São Chico		Creporizinho	
	Hg x Lt (n)	Hg x Wt (n)	Hg x Lt (n)	Hg x Wt (n)
A2	0.688 (33)	-	-	-
A6	-	-	0.54 (15)	-
A7	-	-	0.68 (33)	-
A9	-	-	0.57 (22)	-
A11	-	-	-0.53 (25)	-0.64 (21)
Carnivorous	-	-	0.40 (27)	-
Noncarnivorous	-0.35 (42)	-	-0.25 (134)	-
Curimatã	0.75 (8)	-	0.88 (6)	0.87 (5)
Ituí	0.90 (5)	-	-	-
Piranha	-	-	-	0.78 (10)
Curimatã, A1	0.75 (8)	-	-	-
Acari, A9	-	-	0.74 (14)	-
Piranha, A11	-	-	-	0.86 (6)

**Table II - Results of total Hg in fish muscles (arithmetical mean  $\pm$  standard deviation; wet weight), length and weight of fish from São Chico and Creporizinho areas, considering their food habits**

Garimpo area	N	Mercury ( $\mu\text{g/g}$ )	N	Length (cm)	N	Weight (g)
São Chico	73	2.53 $\pm$ 3.91	73	18.75 $\pm$ 14.42	32	934.3 $\pm$ 1,681.7
Carnivorous	31	4.16 $\pm$ 5.42	31	25.17 $\pm$ 15.79	27	1,038.8 $\pm$ 1,805.9
Noncarnivorous	42	1.33 $\pm$ 1.38	42	14.0 $\pm$ 11.32	5	370.0 $\pm$ 493.2
Creporizinho	161	0.36 $\pm$ 0.33	161	11.62 $\pm$ 4.86	49	191.8 $\pm$ 186.0
Carnivorous	27	0.50 $\pm$ 0.41	27	15.92 $\pm$ 6.49	19	234.2 $\pm$ 289.6
Noncarnivorous	134	0.32 $\pm$ 0.30	134	10.75 $\pm$ 3.95	30	165.0 $\pm$ 57.5
Total	234	1.04 $\pm$ 2.42	234	13.84 $\pm$ 9.56	81	485.2 $\pm$ 1,118.0
Carnivorous	58	2.46 $\pm$ 4.35	58	20.87 $\pm$ 13.12	46	706.52 $\pm$ 1,441.7
Noncarnivorous	176	0.56 $\pm$ 0.83	176	11.50 $\pm$ 6.60	35	194.28 $\pm$ 191.6

**Table III - Significant correlation coefficients of correlation analysis between Hg levels in muscles and length and weight of fish from São Chico and Creporizinho garimpo's areas**

<b>Garimpo's areas</b>	<b>Hg x L (n)</b>	<b>Hg x Wt (n)</b>
São Chico	-	-
Creporizinho	-	-
Total	0.13 (234)	-
Carnivorous	-	-
Noncarnivorous	-0.16 (176)	0.54 (35)

**Table IV - Total Hg in fish muscles (arithmetical mean±standard deviation; wet weight), length and weight of fish from São Chico and Creporizinho garimpo's areas, considering the different food habits**

<b>Garimpo area</b>	<b>N</b>	<b>Mercury (µg/g)</b>	<b>N</b>	<b>Length (cm)</b>	<b>N</b>	<b>Weight (g)</b>
<u>São Chico</u>	73	2.53±3.91	73	18.75±14.42	32	934.3±1,681.7
<i>Carnivorous</i>	31	4.16±5.42	31	25.17±15.79	27	1,038.8±1,805.9
<i>Noncarnivorous</i>	42	1.33±1.38	42	14.0±11.32	5	370.0±493.2
Detritivorous	10	0.13±0.06	10	11.40±1.23	-	-
Herbivorous	2	0.11±0.03	2	14.50±3.53	-	-
Insectivorous	5	0.30±0.06	5	40.20±6.1	4	150.0±40.8
Microfagous	23	2.21±1.28	23	8.13±0.61	-	-
Omnivorous	2	0.92±0.95	2	28.2±19.4	-	-
<u>Creporizinho</u>	161	0.36±0.33	161	11.62±4.86	49	191.8±186.0
<i>Carnivorous</i>	27	0.50±0.41	27	15.92±6.49	19	234.2±289.6
<i>Noncarnivorous</i>	134	0.32±0.30	134	10.75±3.95	30	165.0±57.5
Detritivorous	19	0.07±0.04	19	13.07±3.47	11	145.4±65.1
Herbivorous	15	0.08±0.07	15	18.7±2.07	14	196.42±36.5
Macrofagous	50	0.23±0.08	50	9.05±0.81	-	-
Microfagous	44	0.56±0.34	44	8.13±0.84	-	-
Omnivorous	6	0.81±0.28	6	16.91±1.46	5	12.00±44.5
Total	234	1.04±2.42	234	13.84±9.56	81	485.2±1,118.0

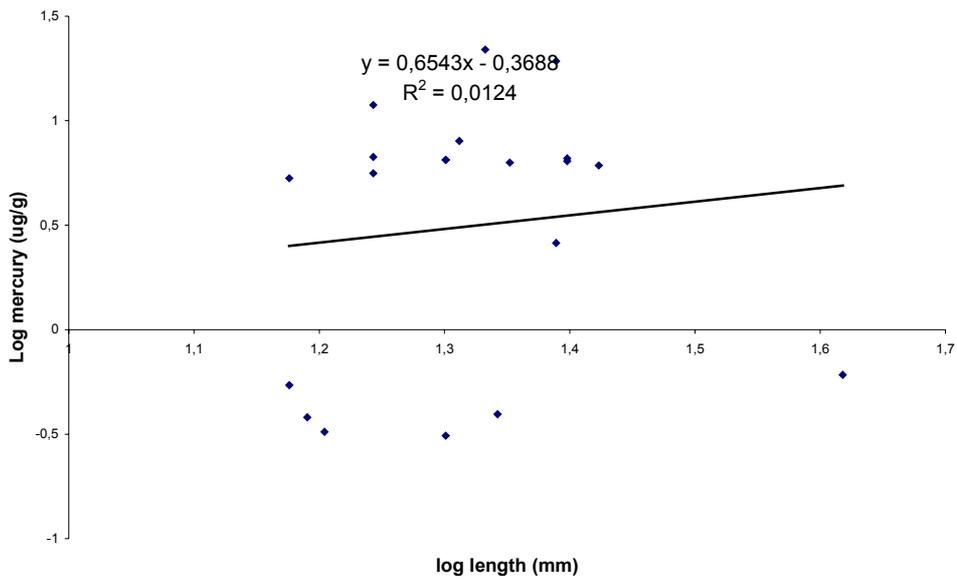


Figure I - Log fish length versus log Hg in Traíras (n=25) from São Chico Garimpo's area

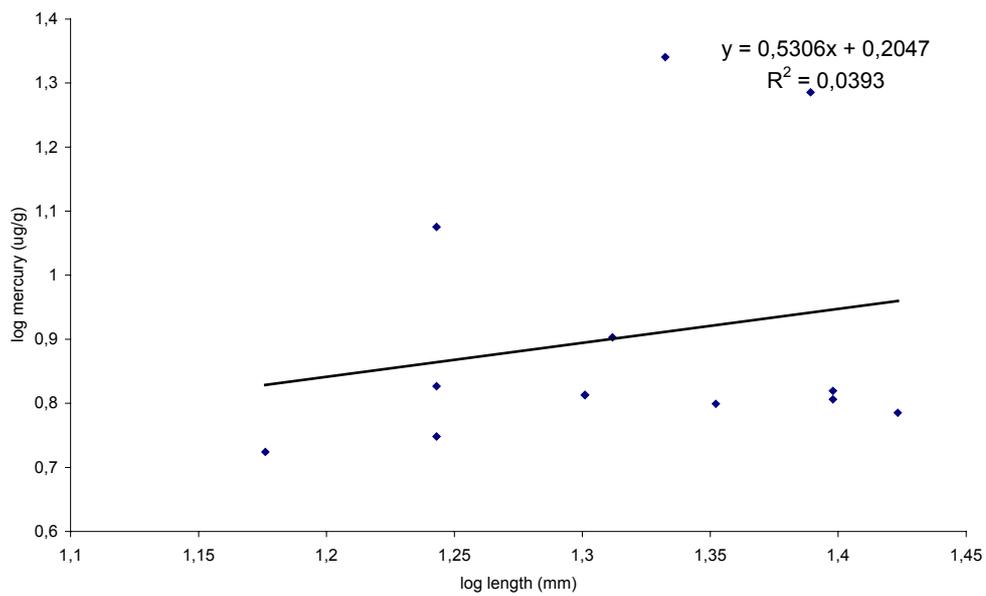


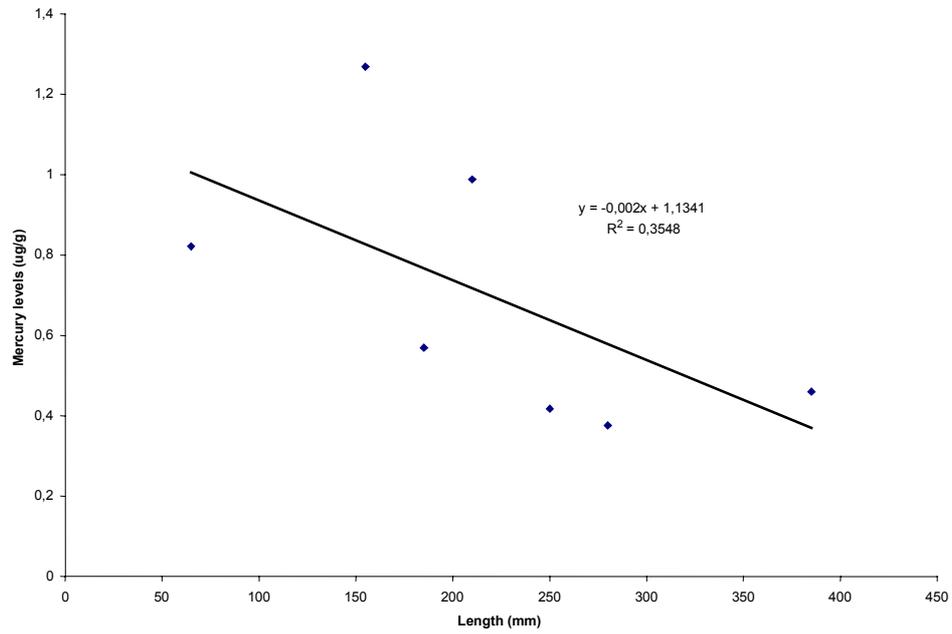
Figure II - Log fish length versus log Hg in Traíras from A2 (n=13) from São Chico Garimpo's area.

**Table V - Correlation coefficients from relationship between mercury in muscles and length intervals (arithmetical means), not transformed and log transformed data**

<b>Fish Specie</b>	<b>site</b>	<b>Log transformed</b>	<b>Not transformed</b>
Acari	A9	0.963	0.955
	Creporizinho	0.019	0.362
Cará	A2	0.620	0.642
	Creporizinho	0.060	0.029
Piau	A8	0.058	0.072
	Creporizinho	0.554	0.051
Piranha	A11	0.00002	0.0004
	Creporizinho	0.306	0.445
	A11	0.345	0.412
Traíra	A9	0.870	0.852
	São Chico	0.210	0.164
	A2	0.600	0.441
	A3	0.159	0.152
Sairu	Creporizinho	0.339	0.355
	Creporizinho	0.470	0.375
	A5	0.016	0.008
	A6	0.607	0.557
	A7	0.142	0.123

**Table VI - Total mercury in muscles and length intervals (arithmetical means) of Traíras Creporizinho Garimpo's area.**

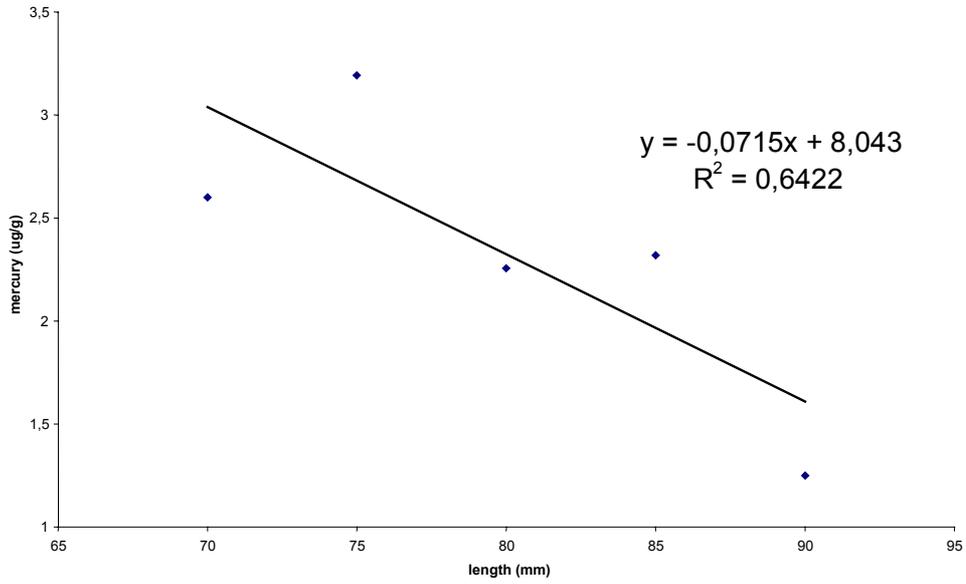
<b>Length intervals</b>	<b>Length mean (mm)</b>	<b>Mercury (µg/g)</b>	<b>N</b>
65	65	0.82	1
150-160	155	1.26	3
180-190	185	0.57	2
210	210	0.99	1
250	250	0.42	1
280	280	0.38	1
385	385	0.46	1



**Figure III - Total mercury in muscles and length intervals (arithmetical means) of Traíras from Creporizinho Garimpo's area.**

**Table VII - Total mercury in muscles, weight and length intervals (arithmetical means) of Carás from A2; São Chico Garimpo's area.**

Length mean (mm)	Mercury (µg/g)	N
70.0	2.60	2
75.0	3.20	2
80.0	2.26	12
85.0	2.32	3
90.0	1.25	1



**Figure IV - Total mercury in muscles and length intervals (arithmetical means) of Carás (A2) from São Chico Garimpo's area.**

## **APPENDIX 3**

**Photos of fish sampling sites and fish collected**

Fish sampling sites in São Chico (A1-A4) and Creporizinho (A5-A11) garimpo areas.

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Study Site	
A1	Flooded open pit, clear water, near to Conrado River
A2	São Chico Reservoir
A3	Flooded open pit, mining wastes, high turbidity, near Rosa stream
A4	Inflow Conrado River to Novo River
A5	Papagaio mining site; stream with high turbidity
A6	Flooded open pit at Bofe site
A7	Flooded open pit at Tabocal site
A8	Buriti mining site; recent flooded open pit, near to Creporizinho River spring
A9	Porto Alegre site in Crepori River, upstream of Creporização village
A10	Inflow of clear stream to Crepori River
A11	Inflow of Chico Chimango, a clear water stream to Crepori River, near the inflow of Creporizinho River to Crepori River

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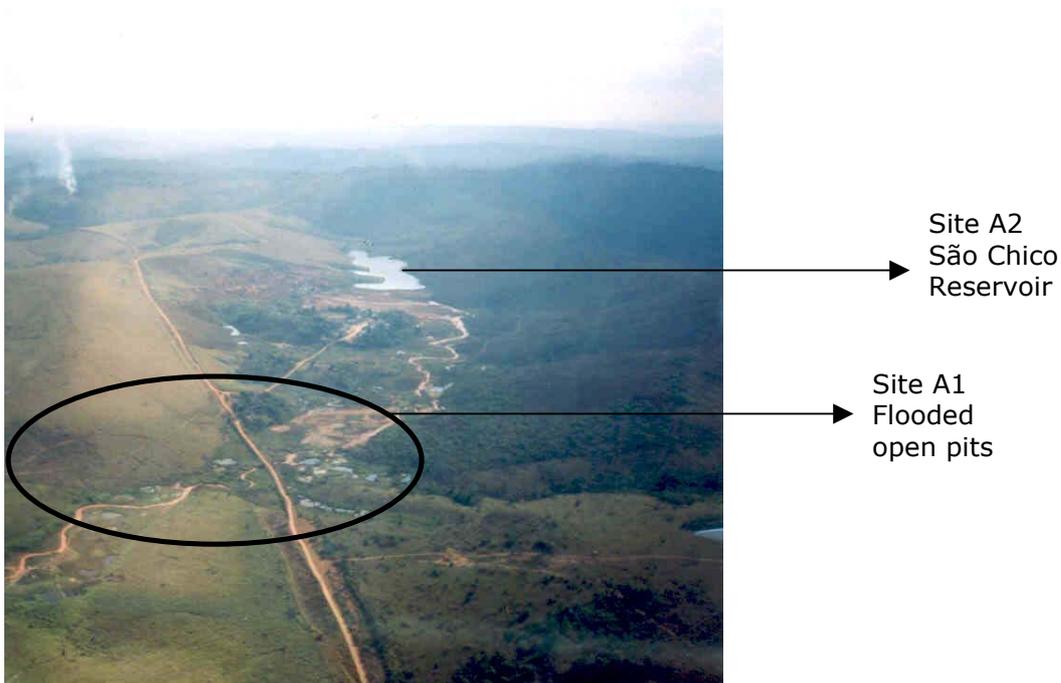


Photo 1. São Chico garimpo area, where can be see the Transamazônica road, the São Chico reservoir, and several flooded open pits along of the secondary roads.



Photo 2. São Chico reservoir, mining sites and São Chico village.



Photo 3. Flooded open pit, mining wastes, high turbidity, near Rosa stream (A3)



Photo 4. Conrado River. It is near A1, but fish are scarce there, due to high turbidity.



Photo 5. Inflow of Conrado River to Novo River (A5).



Photo 6. Flooded open pit at Bofe site



Photo 7. Flooded open pit in Baieta/Tabocal site (A7)



Photo 8. Flooded open pit in Buriti site (A8)



Photo 9. Crepori River, Porto Alegre site (A9), upstream of Creporzinho inflow.

**Fish collected**



Photo 10. Fish collected: Acari

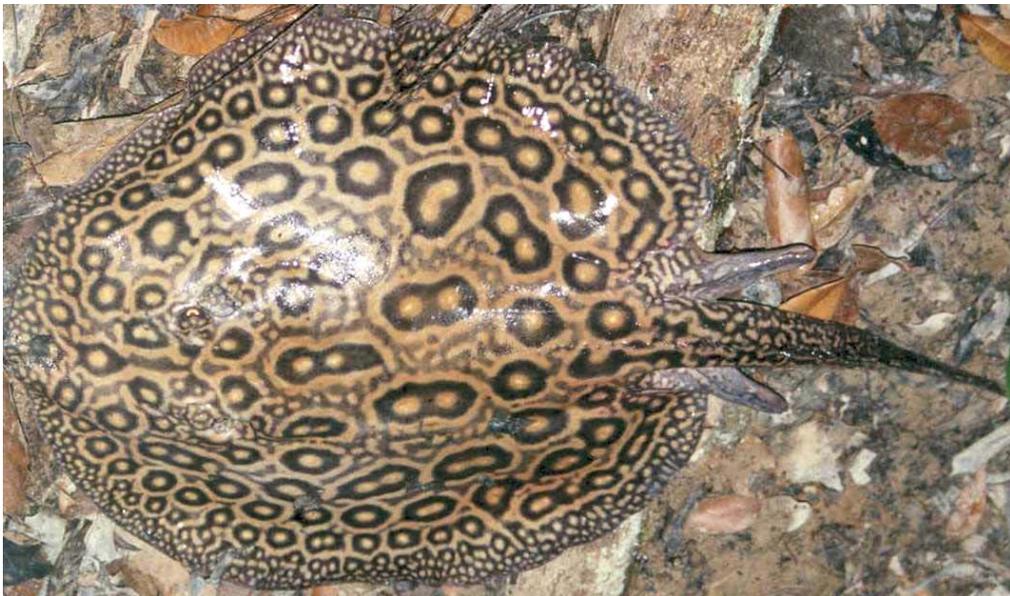


Photo 11. Fish collected: Arraia



Photo 12. Fish collected: Candiru



Photo 13. Fish collected: Lambari

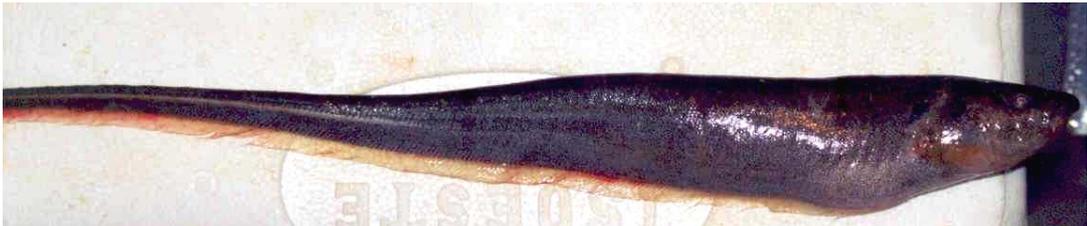


Photo 14. Fish collected: Ituí



Photo 15. Fish collected: Mandi



Photo 16. Fish collected: Pacu



Photo 17. Fish collected: Piau



Photo 18. Fish collected: Piranha



Photo 19. Fish collected: Pirarara



Photo 20. Fish collected: Surubim



Photo 21. Fish collected: Traíra

## **APPENDIX 4**

**Hg concentrations in bioindicators other than fish**

Study Area	Sample area – Field number	Type	Plant parts	Hg Concentrations µg/g ww (µg/g dw)	Substrate	Hg Concentration (µg/g)		Place	
						200#	-200#		
São Chico	A2-1M	earthworms			soil			Mr. Valdomiro's farm Rosa stream Mr. Paulo Arara's farm Mr. Valdomiro's backyard Village	
	A3-2M	earthworms			soil				
	A2-3M	earthworms			soil				
	A2-4M	earthworms			soil				
	A2-1sl	cabbage*	stem+leaves	0.1943 (1.85)		soil	0.4485	0.8906	
	A2-1r		root	0.0149 (0.1863)					
	A2-1l	chive+	leaves	0.0708 (0.6607)		soil	1.88	2.48	
	A2-1r		root	0.0282 (0.4700)					
	A2-3sl	cabbage*	stem+leaves	0.3664 (2.86)		soil <sup>c</sup>	3.84	0.5439	Village
	A2-3r		root	0.1100 (0.9091)					
	A2-3l	chive+	leaves	0.0995 (0.9898)					
	A2-3r		root	0.0161 (0.1851)					
	A2-4sl	mango shoot *	stem+leaves	0.2053 (0.5985)		mining tailings <sup>c</sup>	0.1913	0.3315	Montanha mining site
	A2-4r		root	0.1247 (0.4116)					
	A2-4sl	Poaceae sp.1	stem+leaves	0.0940 (0.3172)					
	A2-4r		root	0.1391 (0.6814)					
	A2-4sl	Poaceae sp.2	stem+leaves	0.0770 (0.3422)					
	A2-4r		root	0.1010 (0.5739)					
	A2-5sl	vine	stem+leaves	0.0594 (0.2776)					Montanha mining site
	A2-5sl	herbs	stem+leaves	0.0224 (0.1483)		rocks	-	-	
	A2-5r		root	0.0227 (0.1707)					
	A2-6p	cashew fruit *	pulp	0.1370 (1.11)		soil <sup>c</sup>	0.2917	0.4752	Tent in Montanha mining site
	A2-6r	sweet potato <sup>o</sup>	root	0.0301 (0.3202)					
	A2-6p		pulp	0.0039 (0.0148)					
	A2-6sl		stem+leaves	0.2365 (2.13)					
	A2-7k	"cara" *	skin	0.3286 (2.04)		soil	1.70	2.80	Village
	A2-7p		pulp	0.0767 (0.2710)					
	A2-8k	cassava	skin	0.2627 (1.20)		soil	-	-	Village
	A2-8p		pulp	0.1627 (0.4593)					
	A2-8sl		stem+leaves	0.9205 (3.79)					
	A2-8l	chive+	leaves	0.0834 (0.7651)		soil	-	-	
	A2-8r		root	0.0161 (0.1388)					
A2-9sl	cabbage*	stem+leaves	0.9605 (8.5)		soil <sup>c</sup>	2.88	4.44	Village	
A2-9l	chive+	leaves	0.0526 (0.5260)						
A2-10k	cassava <sup>o</sup>	skin	0.5170 (2.7)		soil	3.84	0.5439	Village	
A2-10p		pulp	0.4540 (1.33)						
A2-10sl		stem+leaves	2.3700 (10.5)						
A2-11l	chive+	leaves	0.0239 (0.2570)		soil	1.70	2.80	Village	
CrepORIZINHO	A5-5M	earthworms			soil			Papagaio mining site	
	A5-12sl	Cyperaceae sp. 1	stem+leaves	0.1115 (0.5284)	minig tailings <sup>c</sup>	31.30	21.10	Papagaio mining site	
	A5-12r		root	0.1207 (0.8875)					
	A5-13sl	Poaceae sp.3	stem+leaves	0.1250 (0.4771)					
	A5-13r		root	0.0204 (0.1672)					
	A5-14sl	<i>Hypolytrum</i> sp.1 (Cyperaceae)	stem+leaves	0.1253 (0.8353)					
	A5-14r		root	0.0440 (0.5570)					
	A5-14f		flower	0.5411 (2.35)					
	A6-15sl	Poaceae sp.4	stem+leaves	0.0054 (0.050)	sediment <sup>c</sup>	1.24	1.93	Tabocal flooded open pit	
	A6-15r		root	0.0047 (0.0792)					
	A6-16sl	Cyperaceae sp. 2	stem+leaves	0.0042 (0.0360)					
	A6-16r		root	0.0094 (0.1145)					
	A6-17r	<i>Hypolytrum</i> sp.2 (Cyperaceae)	root	0.0131 (0.1335)	sediment <sup>c</sup>	0.6228	0.3042	Tabocal flooded open pit	
	A6-17f		flower	0.0015 (0.0087)					
	A6-17sl	Cyperaceae sp. 3	stem+leaves	0.0081 (0.0613)					
A6-17r		root	0.0172 (0.95)						
A6-17sl	macrophytes	stem+leaves	0.0035 (0.0339)						

Study Area	Sample area – Field number	Type	Plant parts	Hg Concentrations µg / g ww (µg / g dw)	Substrate	Hg Concentration (µg / g)		Place
						200 #	-200 #	
Crepori river	A6-17r	cassava <sup>∞</sup>	root	0.0083 (0.1335)	soil	0.5452	0.8570	Village
	A8-18sl		stem+leaves	0.0801 (0.3761)				
	A8-18r		root	0.0767 (0.5440)				
	A8-18p	cabbage*	pulp	0.0026 (0.0080)	soil <sup>c</sup>	1.72	0.5158	Village
	A8-18k		skin	0.0243 (0.1509)				
	A8-19sl		stem+leaves	0.0172 (0.1819)				
	A8-19r	chive <sup>+</sup>	root	0.0082 (0.0511)	soil <sup>c</sup>	0.7335	1.47	Village
	A8-19l		leaves	0.0001 (0.0894)				
	A8-20sl	cabbage*	stem+leaves	0.0192 (0.2043)	soil	0.9868	0.9177	Village
	A8-20l	chive <sup>+</sup>	leaves	0.0049 (0.0609)				
	A8-20sl	cassava <sup>∞</sup>	stem+leaves	0.0280 (0.1346)	soil	0.9868	0.9177	Village
	A8-20k		skin	0.0014 (0.0071)				
	A8-20p	cabbage*	pulp	0.0034 (0.0107)	soil	0.9868	0.9177	Village
	A8-21sl		stem+leaves	0.0092 (0.0777)				
	A8-21r	root	0.0283 (0.1814)	sediment <sup>c</sup>	0.0527	0.2049	Porto Alegre rapids	
	A9-22l	herbaceous species	leaves					0.1480 (1.42)
	A9-22sl	Poaceae sp.5	stem+leaves	0.0056 (0.0241)	sediment <sup>c</sup>	0.0539	0.2702	Right bank
	A9-22r		root	0.0094 (0.1046)				
	A9-22l	herbaceous species	leaves	0.0113 (0.0698)	sediment <sup>c</sup>	0.0539	0.2702	Right bank
	A9-22l		leaves	0.0059 (0.0253)				
	A9-22r	herbaceous species	root	0.0183 (0.0659)	sediment <sup>c</sup>	0.0539	0.2702	Right bank
	A9-22l		leaves	0.0053 (0.0266)				
	A9-22r	herbaceous species	root	0.0275 (0.1447)	sediment <sup>c</sup>	0.0539	0.2702	Right bank
A9-22sl	stem+leaves		0.0082 (0.0349)					
A9-22l	herbaceous species	leaves	0.0094 (0.0619)	sediment <sup>c</sup>	0.0539	0.2702	Right bank	
A11-23sl	Cyperaceae sp. 4	stem+leaves	0.0245 (0.0215)					
A11-23r	root	0.0691 (0.0691)	sediment <sup>c</sup>	0.0539	0.2702	Right bank		

c composite sample

\* *Brassica oleracea* L. var. *acephala* DC. (Brassicaceae)

+ *Allium fistulosum* L. (Linaceae)

◆ *Mangifera indica* L. (Anacardiaceae)

● *Anacardium occidentale* L. (Anacardiaceae)

° *Ipomoea batatas* (L.) Lam. (Convolvulaceae)

♣ *Discorea cayenensis* Lam. (Disconiaceae)

∞ *Manihot esculenta* Crantz (Euphorbiaceae)

## **APPENDIX 5**

**Semiquantitative mercury determination in fish**

### A brief description of semiquantitative mercury determination in fish samples

To determine mercury concentration in fish, 10 g of sample is digested with an oxidant mixture, containing sulfuric acid, nitric acid and vanadium pentoxide (Figure Ia). To the clear solution obtained, containing ionic mercury, a reduction reagent (acid solution of stannous chloride) is added and elemental mercury formed is forced by an air stream (Figure Ib). The mercury steam is forced to go covered with emulsion containing cuprous iodide. The color intensity formed by the complex is proportional to the mercury concentration in the sample.

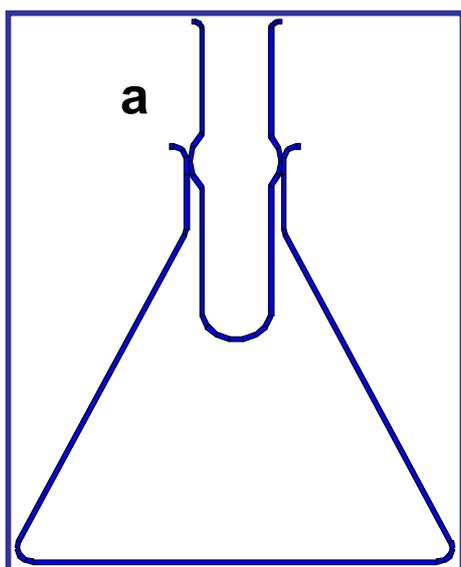


Figure Ia: digestion system

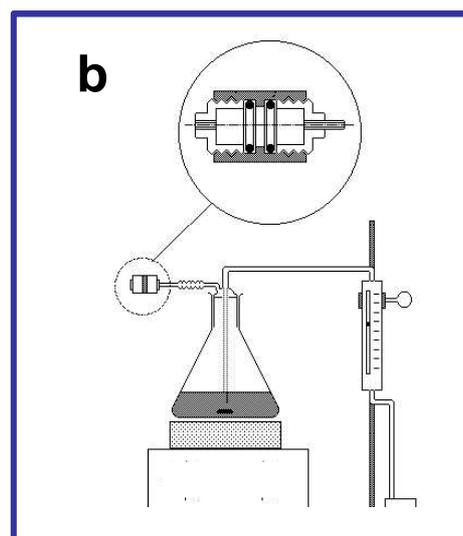


Figure Ib: determination system

At the end of the operation, the operator is capable to classify the sample according to the WHO recommendations, by comparing it with the color developed in similar analytical systems, containing standard solutions. Figure II shows the range of colors resulting from the analytical tests.

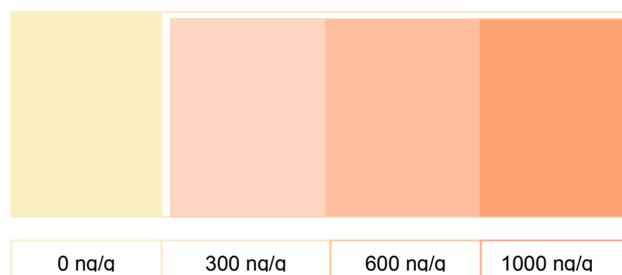


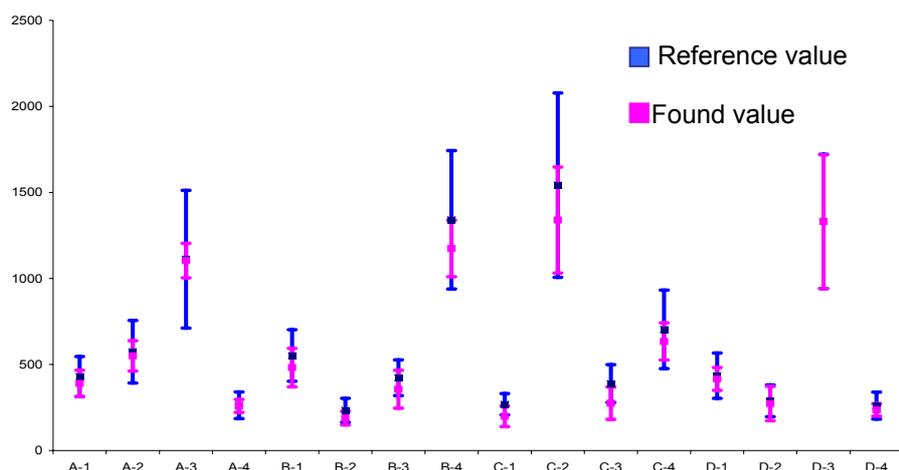
Figure II- Similar colors to those developed in the detecting papers

After determination, fish samples can be classified into 3 groups according to Table I.

**Table I - Table classification according to mercury content and the WHO recommendations**

Classification	Mercury content (ng/g) of fish
Proper for frequent consumption	Lower than 300
Proper for eventual consumption	Between 300 and 600
Not proper for consumption	Higher than 600

The semiquantitative method was compared to the conventional analytical method (CVAAS), whose performance was checked using Standard Reference Materials of fish muscle and liver fish (*Squalus acanthias*) produced and distributed by National Research Council Canada (NRC-CNRC), named DORM-1 and DOLT-2. Participation on the Mercury Quality Assurance Program (MQAP), coordinated by Canadian Food Inspection Agency has been used for the quality assurance of the quantitative method since January 2000. Some results are shown in Figure III which confirmed the method accuracy.



**Figure III - Quality assurance results for interlaboratorial the quantitative method (CV-AAS).**

Since February 2002 the semiquantitative results are being accompanied by quarterly performance evaluations coordinated by the Canadian Food Inspection Agency (Table II). The results obtained showed that the method is sufficiently accurate even in a semiquantitative level.

**Table II - Comparison of semiquantitative results for interlaboratory rounds coordinated by the Canadian Food Inspection Agency**

MQAP	Found value ng/g (n)	Reference Value ng/g (N)
MQAP 308	300-600 (3)	190 to 374 (43)
MQAP 309	300-600 (3)	286 to 494 (42)
MQAP 310	>1000 (3)	1433 to 2975 (43)
MQAP 311	300-600 (3)	197 to 381 (42)
MQAP 312	300-600	301 to 481 (42)
MQAP 313	600-1000	465 to 757 (42)
MQAP 314	300-600	306 to 474 (42)
MQAP 315	>1000	707 to 1495 (43)
MQAP 316	300-600	349 to 605
MQAP 317	300-600	282 to 478
MQAP 318	600-1000	794 to 1438
MQAP 319	<300	199 to 365
MQAP 320	<300	147 to 283
MQAP 321	<300	283 to 527
MQAP 322	300-600	288 to 588
MQAP 323	300-600	442 to 818

n= number of replicates ; N=number of participants in the round