

## Preliminary study on mercury distribution in soil profiles from Serra do Navio, Amapá, using radiochemical neutron activation analysis

C. Gonçalves,<sup>\*1</sup> D. I. T. Fávaro,<sup>\*2</sup> S. M. B. De Oliveira,<sup>\*\*</sup> R. Boulet,<sup>\*\*\*</sup> M. B. A. Vasconcellos,<sup>\*</sup> M. Saiki<sup>\*</sup>

<sup>\*</sup> Radiochemistry Division - IPEN/CNEN-SP, CP 11049 - CEP 05422-970, São Paulo, Brazil

<sup>\*\*</sup> Instituto de Geociências - IGUSP, São Paulo, Brazil

<sup>\*\*\*</sup> Nupegel, USP/ORSTOM, São Paulo, Brazil

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This study presents preliminary results on mercury distribution, released by gold mining activities, in soils from Vila Nova River region, an area located in Serra do Navio, Amapá, in the Brazilian Amazon. The soil samples were separated in two grain sizes, sand (between 2 and 0.063 mm) and silt+clay (<63 µm), and have been analysed by radiochemical neutron activation analysis. The precision and accuracy of the method were verified by means of the reference material analysis GXR-5 (USGS).

### Introduction<sup>12</sup>

Mercury is considered to be the most potentially dangerous of the metal pollutants<sup>1</sup> and in spite of this fact, it has been used in several activities by humans for at least 3500 years.<sup>2</sup> Mercury contamination and its effects upon the environment and human beings only became a real concern after the tragic accident which occurred in the Japanese bay of Minamata in 1956. At the village of this bay, a chemical plant employing Hg<sup>2+</sup> as a catalyst in a process that produced polyvinyl chloride discharged mercury-containing residues into Minamata Bay; the methylmercury that subsequently formed then bioaccumulated in the fish, which were the main component of the diet for many local residents. The fish contained up to 100 mg·kg<sup>-1</sup> mercury. By contrast, the current North American recommended limit for mercury in fish destined to be consumed by humans is 0.5 mg·kg<sup>-1</sup>. Thousands of people in Minamata were affected by mercury poisoning from this source and hundreds of them died from it. Symptoms in humans arise from dysfunctions of the central nervous system, since the target organ for methylmercury is the brain. They include numbness in arms and legs, blurring and even loss of vision, loss of hearing and muscle coordination, and lethargy and irritability.<sup>3</sup> The worst catastrophe involving mercury took place in Iraq in 1971/72. More than 500 people died after eating flour made from grain that had been treated with methylmercury fungicide.<sup>4</sup>

Although mercury was used in the past, problems still exist today, mainly on the ecosystem of Amazonian forest, where it is employed to amalgamate fine gold particles. In recent years these activities have been widely spread in the Amazon Basin and the potential mercury contamination has become an important issue. The amalgamation process is conducted using metallic

mercury, and mercury losses to the environment occur at two distinct stages: (1) through manipulation of metallic mercury in the separation of gold from gravel, after which a significant amount of metallic mercury finds its way into the rivers and soils and (2) through the separation of gold by burning, which releases elemental mercury vapour into the atmosphere.<sup>5</sup> PFEIFFER and LACERDA<sup>6</sup> described the entire gold mining process through mercury amalgamation in the Brazilian Amazon and estimated mercury losses for the production of 1 kg of gold as 1.32 kg of mercury, being 0.72 kg to the atmosphere as mercury vapour and 0.60 kg directly to rivers as metallic mercury.

In this study, soil profile samples from Vila Nova river Basin, in the Brazilian Amazon, were collected to evaluate the anthropogenic impact upon the environment caused by the gold mining activities. Samples from Igarapé Pedra Preta Basin – out of the influence of ‘garimpos’ (informal mining in small scale) – were also collected for comparison. The location of the studied areas, in Amapá, Brazil, is presented in Fig. 1. In Vila Nova river region (gold mining area), in the Southern part of Serra do Navio, there were lots of ‘garimpos’. However, this activity has been decreasing, and nowadays there are only two active ‘garimpos’.

The samples were submitted to a radiochemical separation procedure in order to determine levels of total mercury in soil profile samples from both the affected and unaffected areas. This procedure was employed to remove interferences caused by background radiation from 511 keV photopeak of <sup>64</sup>Cu and 279 keV photopeak of <sup>75</sup>Se, which are elements generally present in geological samples, and to isolate the element of interest before measurement by gamma-ray spectrometry. In order to avoid these interferences, bismuth diethyldithiocarbamate (Bi(DDC)<sub>3</sub>) was introduced to extract mercury by solvent extraction after sample irradiation.

<sup>1</sup> E-mail: crisgon@net.ipen.br

<sup>2</sup> E-mail: defavaro@ih0.ipen.br

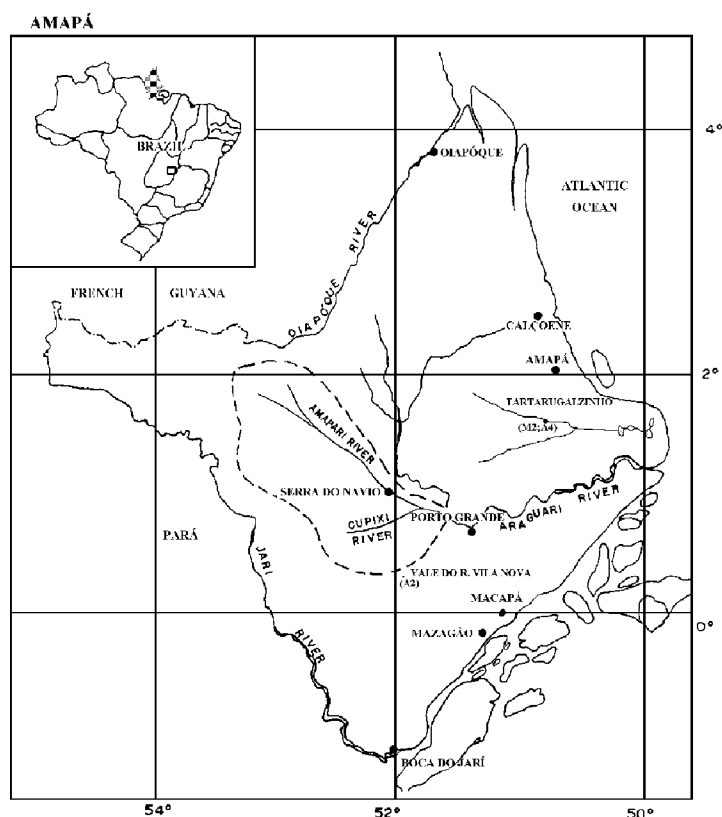


Fig. 1. Map of the studied area

Table 1. Soil profile samples analysed in this work

Location	Sampling code	Depth, cm	Description	Sampling campaign
Serra do Navio (Igarapé Pedra Preta basin)	SN1	0-10	top of	1994, July
		40-50	toposequency I	
		160-170		
	SN5	0-20	bottom of	1996, July
		200	toposequency I	
	SLPP0201			
	SLPP0202		superficial soils	
	SLPP0203	0-2	from source of	1995, March
	SLPP0204		Igarapé Pedra Preta	
	SLPP0205			
Vila Nova river Basin	VN2	0-7	soil over alluvium	1994, July
		40-50	of Vila Nova river –	
		60-70	“garimpo do Chicão”	
	VN3	0-10	soil over bedrock –	
		200	“garimpo do Vicente” – shast	
	VN4	0-10	soil over bedrock –	
		100	“garimpo do Vicente” – drill	

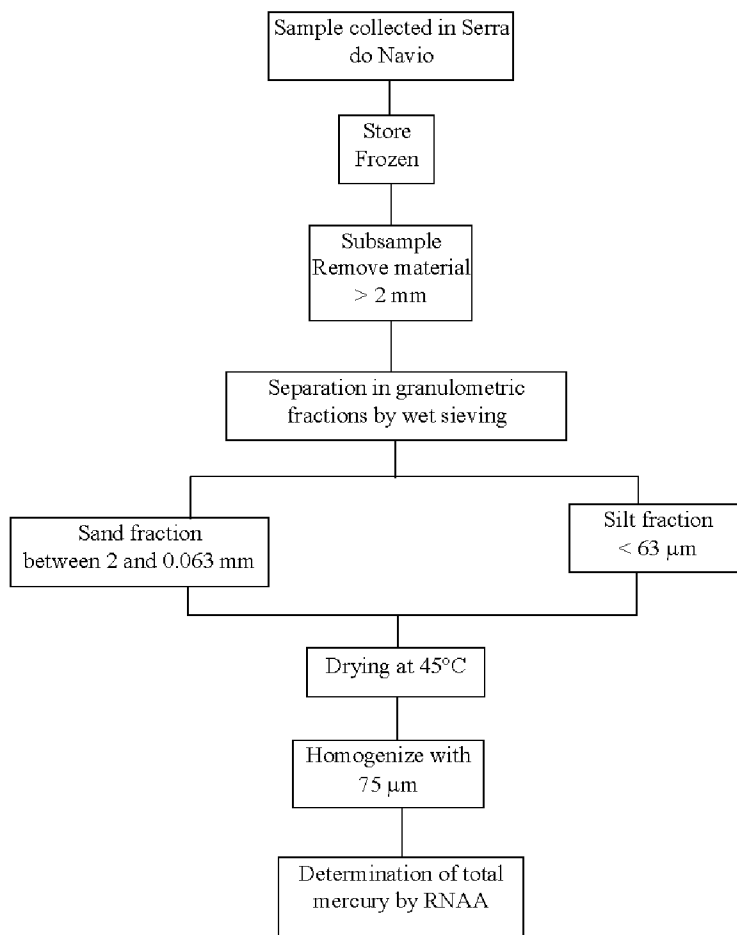


Fig. 2. Sample preparation for total mercury determination

## Experimental

### Reagents

All chemicals were of analytical reagent quality and only distilled and deionized water was used.

The reagent  $\text{Bi}(\text{DDC})_3$  was prepared by reacting an excess of  $\text{Bi}(\text{NO}_3)_3$  with  $\text{NaDDC}$  as described earlier.<sup>7</sup>

The mercury stock solution was prepared by dissolving mercury(II) oxide in diluted nitric acid, followed by dilution with distilled water to 25 ml. Working standard solution ( $21.904 \mu\text{g}\cdot\text{ml}^{-1}$ ) was prepared by dilution with 10 ml concentrated  $\text{HCl}$  and the volume was adjusted with distilled water to 100 ml.

All containers used in this study were cleaned by immersing in diluted  $\text{HNO}_3$  for few days and then rinsed thoroughly with deionized water.

### Samples

The soil profile samples were collected in three fields trips from 1994 to 1996. In 1995 five superficial soil samples from Igarapé Pedra Preta basin, in Serra do

Navio, were also collected. The samples description is presented in Table 1.

All samples were packed in polyethylene bags and frozen in the field for transportation to the General Geology Laboratory (IGUSP – SP, Brazil). In the laboratory, the samples designated for mercury analysis were defrosted and homogenized while still wet and then the coarse material  $>2$  mm was removed. The sampling collected during the first campaign (1994) were separated, by wet sieving, in two different granulometric fractions to verify if the chemical composition changed with the grain size. Thus the remaining material was sub-fractioned through a  $63 \mu\text{m}$  sieve, obtaining the grain size classes SILT, which includes silt (between  $63$  and  $2 \mu\text{m}$ ) and clay ( $<2 \mu\text{m}$ ), and SAND (between  $2$  and  $0.063$  mm). Mercury concentrations were determined in both fractions.

As mercury is sensitive to drying, all samples were dried at  $45^\circ\text{C}$  in an oven to avoid the loss of any volatile mercury. Figure 2 illustrates schematically the laboratory sequence for the determination of total mercury concentration in soil samples.

### Analytical procedure

About 200 mg of sample and an aliquot of mercury standard solution were irradiated for 16 hours, under a  $10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$  thermal neutron flux, in the IEA-R1 reactor from IPEN/CNEN – SP, Brazil, in quartz vials.

After a ten day decay period, the samples were transferred to teflon vessels, and 100  $\mu\text{g}$  mercury carrier and 4 ml of aqua regia were added. The sealed vessels were placed in a domestic microwave oven for one minute at 70% power (280 W) for soils. The irradiated samples and standard+inactive sample were processed in the same way.

Digested solutions were cooled and transferred to beakers, and the residue was separated by filtration.

The pH of the solution was adjusted to about 1.5 with ammonia.

Solutions were placed in separatory funnels, where mercury was extracted with 25 ml  $5\cdot 10^{-3}\text{M}$   $\text{Bi}(\text{DDC})_3$  in chloroform, and were shaken for five minutes. The aqueous phase was discarded and the organic one was transferred to counting vials for the subsequent determination of total mercury by using the  $^{203}\text{Hg}$  and  $^{197}\text{Hg}$  radioisotopes activities.

The chemical yield of this separation procedure was determined by means of using  $^{203}\text{Hg}$  tracer and inactive sediment and soil samples and the average was  $95\pm 5\%$ . Figure 3 illustrates schematically the established procedure for total mercury analysis.

Table 2. Results obtained for mercury (in  $\text{mg}\cdot\text{kg}^{-1}$ ) in the reference material GXR-5 (USGS)

This work	Certified value <sup>9</sup>	Standard deviation, %	Relative error, %	Detection limit
$0.161 \pm 0.003^*$	0.158	1.86	1.90	0.054

\* Mean of two determinations.

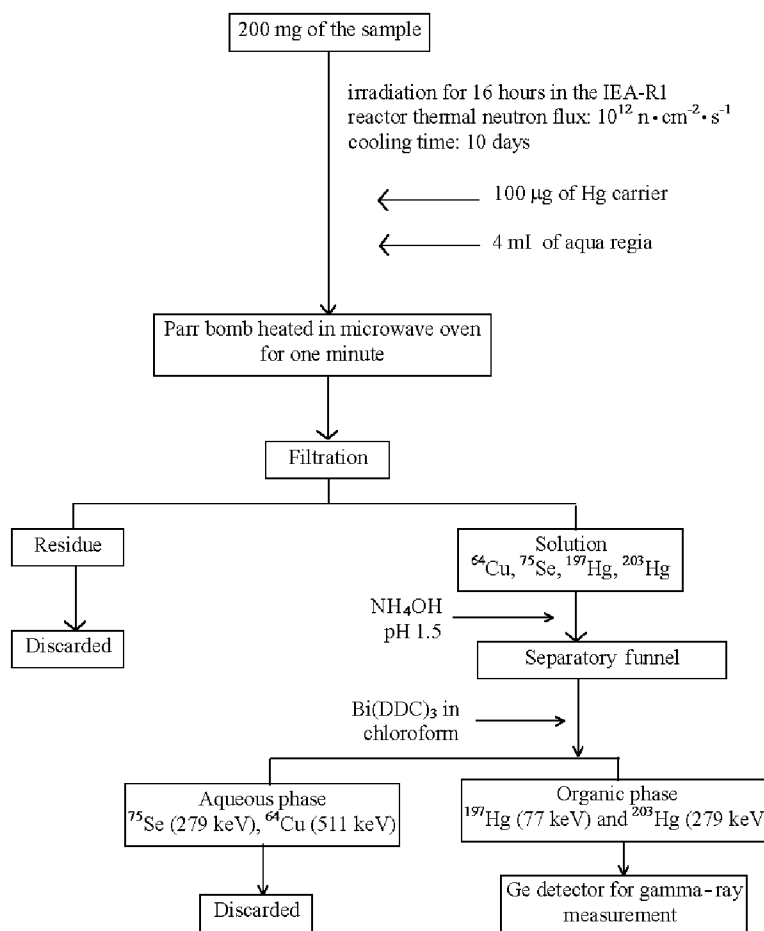


Fig. 3. Schematic diagram of radiochemical separation procedure

Table 3. Results obtained for mercury (in  $\text{mg}\cdot\text{kg}^{-1}$ ) in soil profile samples by radiochemical neutron activation analysis (mean of 2 determinations)

Location/samples	Depth, cm	Fraction	Mercury
Top of toposequency I – SNI	0-10	silt	$0.38 \pm 0.03$
		sand	$0.21 \pm 0.02$
Bottom of toposequency I – SN5	160-170	<2 mm	$0.281 \pm 0.005$
		silt	$0.158 \pm 0.013$
SLPP0201	0-20	sand	$0.189 \pm 0.015$
		<2 mm	$0.26 \pm 0.01$
SLPP0202	200	<2 mm	$0.30 \pm 0.02$
		<2 mm	$0.26 \pm 0.02$
SLPP0203	400	<2 mm	$0.124 \pm 0.007$
		<2 mm	$0.275 \pm 0.008$
SLPP0204	0-2	<2 mm	$0.173 \pm 0.013$
		<2 mm	$0.097 \pm 0.008$
SLPP0205	0-7	<2 mm	$0.094 \pm 0.006$
		silt	$18.1 \pm 1.4$
VN2 – soil over alluvium of Vila Nova river, “garimpo do Chicão”	duricrust at the water table	sand	$26.7 \pm 2.1$
		<2 mm	$0.45 \pm 0.04$
VN3 – soil over bedrock, “garimpo do Vicente” – shast	60-70	silt	$0.39 \pm 0.02$
		sand	$0.185 \pm 0.019$
VN4 – soil over bedrock, “garimpo do Vicente” – drill	0-10	silt	$0.183 \pm 0.017$
		sand	$0.29 \pm 0.02$
	200	silt	$0.22 \pm 0.01$
		sand	$0.179 \pm 0.015$
	0-10	silt	$0.206 \pm 0.018$
		sand	$0.30 \pm 0.01$
	100	silt	$0.27 \pm 0.01$
		sand	$0.23 \pm 0.02$

### Radioactivity measurements

Each sample was counted for 50000 seconds in a GEM 20190P detector coupled to an ORTEC ACE 8K card plus IBM/PS2 microcomputer with a resolution of about 0.98 keV at the 121.97 keV gamma ray of  $^{57}\text{Co}$  and 1.81 keV for the 1332.49 keV gamma-ray of  $^{60}\text{Co}$ . The gamma-rays 77.6 keV ( $^{197}\text{Hg}$ ) and 279.2 keV ( $^{203}\text{Hg}$ ) were used for mercury determination. Spectrum analysis was performed by means of the VISPECT2 software, developed by Dr. D. PICCOT, from Saclay, France in TURBO BASIC.

### Results and discussion

The validation of the developed method was carried out by using the reference material GXR-5 (USGS). The results are given in Table 2, which shows a good agreement between RNAA results and the certified value of the reference material, indicating a high accuracy of RNAA technique. The detection limit of the method was determined according to CURRIE,<sup>8</sup> reaching  $0.054 \text{ mg}\cdot\text{kg}^{-1}$ .

Table 3 presents the results obtained for mercury concentrations in the soil profile samples. Comparing mercury levels in the studied areas, it is clear that mercury concentrations in Igarapé Pedra Preta basin are

lower than in ‘garimpo do Chicão’, a contaminated area, where mercury levels have reached up to  $18 \text{ mg}\cdot\text{kg}^{-1}$  at the surface.

Soil samples from Serra do Navio, considered to be a control area (without direct effect of mercury contamination), have presented levels around  $0.3 \text{ mg}\cdot\text{kg}^{-1}$ . No significant differences can be observed between Serra do Navio and ‘garimpo do Vicente’.

In all sampling no significant relationship has been found between the different depths and the content of mercury. It is clear that mercury distribution is independent of grain size.

Usually, the trace metal concentrations increase with decreasing grain size of the material. This is because the host minerals of the elements and the surface area of the particles change with the grain size.<sup>10</sup> On the other hand, adsorption of mercury still depends on other factors, including the chemical form of mercury introduced, the nature and amount of inorganic and organic soil colloid, the soil pH, and the redox potential. In addition,  $\text{Hg}^{2+}$  may be fixed in the form of low-solubility precipitates, in particular the sulphide and the selenide.<sup>11</sup>

The results presented however are still preliminary, and other samples should be collected before a generalization can be made, although the evidence

available suggests a contamination in Vila Nova river region, mainly in 'garimpo do Chicão'.

### Conclusions

The Parr bomb mixed acid digestion system has proven to be a fast and accurate method for Mercury leaching in soils. This method is very useful for volatile elements, such as mercury, which can be lost during decomposition procedures.

The extraction constant of  $\text{Hg}(\text{DDC})_2$  is much larger than that of  $\text{Se}(\text{DDC})_2$ ,  $\text{Cu}(\text{DDC})_2$  or  $\text{Bi}(\text{DDC})_3$ .<sup>12</sup> Thus, mercury can be selectively extracted into chloroform solution of  $\text{Bi}(\text{DDC})_3$  and no interference by  $^{75}\text{Se}$  and  $^{64}\text{Cu}$  radioisotopes is observed in the gamma-spectrum for all samples analysed.

The levels of mercury at the surface of the soil collected in 'garimpo do Chicão' have shown anomalous values, compared with the local background levels (Igarapé Pedra Preta). The existing results on mercury concentration and distribution in Vila Nova river region affected by gold mining are, however, too preliminary; it is necessary to analyse more samples so that Mercury behavior can be understood.

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