

Evaluation of mercury levels in sediment and soil samples from Vila Nova river basin, in Amapá State, Brazil, using radiochemical neutron activation analysis

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In the present work, results from a survey on mercury concentration in sediments and soils from a gold mining area along the Vila Nova river, in Amapá State, Brazil, are presented. These values were compared with those from the Igarapé Pedra Preta basin, an area unaffected by mining activities. Total mercury contents were determined in the muddy (silt+clay) fraction of the sediments and in the <2 mm fraction of the soils using radiochemical neutron activation analysis (RNAA). The detection limit of the method was $54 \mu\text{g}\cdot\text{kg}^{-1}$ for soils and $14 \mu\text{g}\cdot\text{kg}^{-1}$ for sediments when 200 mg of sample were analysed. The Hg results obtained from a comparison between our current method (RNAA) and CV AAS are also presented. Mercury levels showed to be very high in the soils and sediments collected in the Vila Nova river (up to $2 \text{ mg}\cdot\text{kg}^{-1}$) when compared to background values ($0.3 \text{ mg}\cdot\text{kg}^{-1}$) for this region. An enrichment factor was calculated, using Al as a normalizing factor. It showed values up to 8 in sediments of the Vila Nova river basin, indicating a relatively high degree of pollution as compared to the values of about 1 for the samples of the Igarapé Pedra Preta basin.

Introduction

The pollution caused by mercury is one of the causes of the forest environmental degradation process in the Amazonian region. Gold mining activities are quite widespread in the Amazonian region and the potential contamination by mercury used for collecting alluvial gold has become a matter of great concern.¹

In Brazil, several studies about mercury pollution have been carried out during the last few years.^{1–13} PFEIFFER et al.⁴ studied the Hg distribution in sediments and fishes for the Madeira river watershed, Rondonia State. Hg contamination was clearly detected in some sites along the Madeira river, where Hg concentration levels reached values as high as $19.8 \text{ mg}\cdot\text{kg}^{-1}$ in bottom sediments and up to $2.7 \text{ mg}\cdot\text{kg}^{-1}$ in fish.

RODRIGUES FILHO and MADDOC⁷ also studied two gold mining areas in the Brazilian Amazon in order to determine mercury pollution in sediments and soils, from regions unaffected and affected by gold mining. They concluded that the concentrations of Hg in bottom sediments and soils of the drainage subbasins studied in the Poconé region showed anomalous values, compared to the local background values for sediments and soils. On the other hand, some studies are indicating contamination in remote areas not directly affected by mining activities.^{14,15}

It becomes necessary to carry out studies in order to assess the contribution of mining and other anthropogenic or natural sources for mercury pollution in the Amazon environment. Within this context, in the present work we studied an area, in the midst of alluvial/elluvial ways of gold exploration. As a background to quantitative balances, an area located near Serra do Navio (Amapari river) was chosen, where the forest is found totally preserved from any anthropogenic contribution. The location of the areas studied in Amapá, Brazil, is presented in Fig. 1. Soil and sediment samples from both regions were collected and analyzed by radiochemical neutron activation analysis (RNAA).

The irradiated samples were leached with aqua regia in a microwave oven and subsequent selective Hg extraction with bismuth diethyldithiocarbamate ($\text{Bi}(\text{DDC})_3$). The developed radiochemical separation procedure allowed as to determine low and high levels of mercury concentrations both in soil and sediment samples. The results obtained hereby were compared to those achieved by cold vapor atomic absorption spectrometry (CV-AAS) technique.

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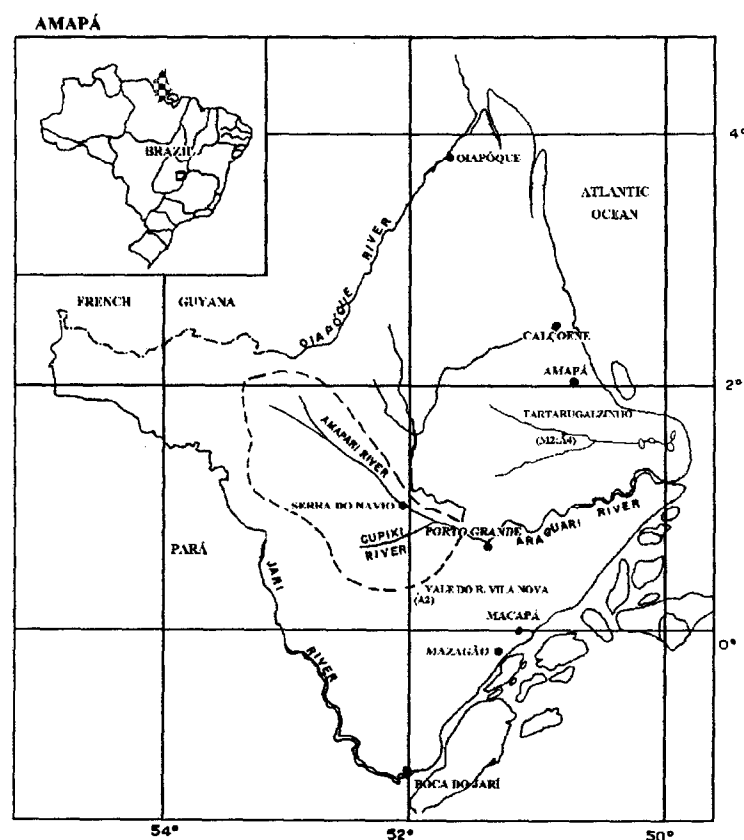


Fig. 1. Map of the area studied

Table 1. Description of the sediment samples analyzed in this work

Location	Sampling code	Description	Sampling campaign
Serra Do Navio	SDPP001	Bottom sediment from Igarapé Pedra Preta	1994, July
	SDAP001	Bottom sediment from Amapari river	1994, July
	SDAP002	Bottom sediments from Amapari river	1995, March
	SDAP003 SDAP004		
Vila Nova River Basin	SDVN004 SDVN006	Bottom sediments from Vila Nova river, upstream 'garimpo do Chicão'	1995, March
	SDVN007	Bottom sediment from Vila Nova river, downstream a mining site	1995, March
	SDVN001A 20–30 cm depth	Core sediment from margin at Vila Nova river, within a mining site	1994, July
	SDVN001B 10–20 cm depth		
	SDVN001C 0–10 cm depth		

Experimental

Sampling

The study areas are located in the Amapá State, Brazilian northeastern Amazon, approximately at the latitude of 00°00' (Fig. 1). The area chosen as reference, out of influence of "garimpos" (informal mining in small scale), is a small catchment (Pedra Preta Creek) in the Amapari valley, near Serra do Navio village, in the central part of the State. Two soil profiles were sampled. The SN10 and SN5 profiles are separated by about 300 m, being at 100 and at 30 m altitude, respectively. Also soil samples from Vila Nova river basin were collected (VN2, VN3 and VN4). Description of the soil samples analyzed in this work is given in our previous work.¹⁶

Sediment samples were collected by using Eckman dredge. Table 1 shows the description of the samples. All samples (about 1 kg) were stored in polyethylene bags and immediately frozen. In the laboratory, samples were defrosted and homogenized while still wet and the coarse material (>2 mm) was removed. For sediments the remaining material was sub-fractioned through a 63 µm sieve, obtaining sand (between 2 and 0.063 mm) and muddy, which includes silt (between 63 and 2 µm) and clay (<2 µm). For soil samples only the <2 mm fraction was prepared for analysis, although some previous analysis has already been made in both fractions of the investigated soils.

As mercury is sensitive to high temperatures, all samples were dried at 45 °C in an oven to avoid the loss of any volatile mercury. Chemical and mineralogical determinations were performed after pulverizing the 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.

The analytical procedure for soil samples is described in our previous work.¹⁶ For leach processing, the sealed vessels were placed in a domestic microwave oven for one minute at 50% power (200 watts) for sediments and 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. After this, mercury was extracted with 25 ml $5\cdot 10^{-3}\text{M}$ (Bi(DDC)₃) in chloroform and the organic phase was transferred to counting vials for the

subsequent determination of total mercury by using the ²⁰³Hg and ¹⁹⁷Hg radioisotopes activities.

Iron concentration was evaluated in all samples by instrumental neutron activation analysis, whereas aluminum was determined in the sediment samples by X-ray fluorescence method at IPEN/CNEN-SP.

For the sake of comparison, the samples were also submitted to cold vapor atomic absorption spectrometry (CVAAS) for total Hg, after digestion with a mixture of nitric and sulfuric acid and potassium permanganate^{17,18} at the Laboratório de Química Analítica of CENA/USP and IPEN/CNEN-SP.

Radioactivity measurements

Each sample was counted for 50 000 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 ⁵⁷Co and 1.81 keV for the 1332.49 keV gamma-ray of ⁶⁰Co. The gamma-rays 77.6 keV (¹⁹⁷Hg) and 279.2 keV (²⁰³Hg) 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.

Reference materials analysis

The precision and accuracy of the method were verified by means of analysis of reference materials Lake Sediment (BCR-CRM 280) and Buffalo River Sediment (NIST SRM 2704) for sediments and GXR-5(USGS) for soil samples.

Results and discussion

The validation of the developed method was carried out by using reference materials analysis. The results are given in Table 2, which shows a good agreement between RNAA results and the certified values of the reference materials, indicating a high accuracy and precision of this technique for total mercury analysis in soil and sediment samples. The detection limits of the method were determined according to CURRIE,¹⁹ reaching $0.054 \text{ mg}\cdot\text{kg}^{-1}$ for soil and $0.014 \text{ mg}\cdot\text{kg}^{-1}$ for sediment samples.

Chemical data for mercury (Hg) and iron (Fe) are displayed in Tables 3 and 4, for sediment and soil samples, respectively. Also the results obtained for Hg by using CV AAS technique are presented.

It can be concluded that the radiochemical procedure developed for Hg determination in sediment and soil samples is a very reliable method and the results are in agreement to those obtained by the CV AAS technique.

Table 2. Results obtained for total Hg (in $\text{mg}\cdot\text{kg}^{-1}$) in the reference materials Lake Sediment (BCR-CRM 280), Buffalo River Sediment (NIST SRM 2704) and GXR-5 (USGS), by using RNAA technique

Reference material	Obtained values	Certified values	R.S.D.	R.E.	Detection limit, $\text{mg}\cdot\text{kg}^{-1}$
Lake sediment	0.69 ± 0.03^2	0.670 ± 0.019	4.8	2.7	0.014
Buffalo river sediment	1.50 ± 0.03^3	1.47 ± 0.07	2.0	2.0	0.014
GXR-5	0.161 ± 0.003^2	0.158	1.9	1.9	0.054

ⁿ Number of determinations.

Table 3. Results obtained for total Hg (in $\text{mg}\cdot\text{kg}^{-1}$) by using RNAA and CV AAS, Al (X-ray fluorescence) and Fe (INAA) analysis in sediments from Serra do Navio and Vila Nova river basin

Location	Sample	Fraction	Al, %	Fe, %	Hg RNAA*	Hg CV-AAS
Serra Do Navio	SDPP0101	Mud	n.d.	9.90	0.46 ± 0.03	n.d.
		Sand	1.99	1.60	0.022 ± 0.003	n.d.
	SDAP001	Mud	29.3	2.85	0.21 ± 0.01	0.25
		Sand	4.30	1.1	0.041 ± 0.001	0.045
	SDAP002	Mud	n.d.	4.6	0.377 ± 0.005	0.42
Vila Nova River Basin	SDAP003	Mud	29.9	3.3	0.19 ± 0.02	0.54
	SDAP004	Mud	32.6	2.9	0.25 ± 0.01	n.d.
	SDVN004	Mud	28.9	2.13	0.27 ± 0.02	0.39
		Mud	28.7	2.10	0.24 ± 0.01	0.27
	SDVN001A (20–30 cm)	Mud	23.4	5.0	2.98 ± 0.04	3.2
		Sand	5.4	2.1	1.41 ± 0.05	1.40
	SDVN001B (10–20 cm)	Mud	24.2	1.96	1.03 ± 0.11	1.27
		Sand	10.2	2.20	0.70 ± 0.03	0.71
	SDVN001C (0–10 cm)	Mud	23.6	2.6	2.0 ± 0.1	2.09
		Sand	4.6	2.35	0.29 ± 0.03	0.35
	SDVN007	Mud	30.5	7.0	1.9 ± 0.1	1.46

n.d. – Not determined.

* Mean of two determinations.

Sediments

We can observe from the results obtained for Hg in sediments (Table 3) a correlation between grain size and Hg concentration: lower levels in the sandy fraction and higher levels in the muddy (silt + clay) fraction. Therefore, to verify the contamination, it is more suitable to analyze the muddy fraction in the sediments. According to FERREIRA and VEIGA,²⁰ this may be due to the fact that clay minerals show a great capacity of Hg adsorption, but with a weak link which is dependent of pH, electric conductivity etc. In fact the amorphous Fe and Mn oxides, at pH 4 to 10, are responsible for

Hg retention, because they have a great capacity of retention of heavy metal ions by precipitation or adsorption.²¹

The Pearson similarity correlation test was applied to the sediment samples in order to verify the correlation between Fe and Hg in these samples. It was observed that there is a positive correlation between Hg and Fe in sediments (Serra do Navio: $r_{xy}=0.88>r_{table}$ and Vila Nova $r_{xy}=1.00>r_{table}$).

RODRIGUES and MADDOCK²² also found a positive correlation between Hg and Fe ($r=0.72$, $n=16$) for contaminated sediments from Poconé region, Mato Grosso State, showing that the iron oxides are the main linkage of Hg in this region.

Table 4. Results obtained for Hg (in $\text{mg}\cdot\text{kg}^{-1}$) by using RNAA and CV AAS and Fe (INAA) analysis in soils from Serra do Navio and Vila Nova river basin

Location	Depth cm	Fraction	Fe, %	Hg RNAA	Hg CV-AAS
Top of toposequency – SN1	0–10	Mud	4.7	0.38 ± 0.03	0.355
		Sand	5.3	0.21 ± 0.02	0.222
	40–50	<2 mm	4.4	0.281 ± 0.005	0.247
	160–170	Mud	6.4	0.158 ± 0.013	0.158
		Sand	6.6	0.189 ± 0.015	0.110
Bottom of toposequency SN5	0–20	<2 mm	23.0	0.26 ± 0.01	0.26
	200	<2 mm	18.0	0.30 ± 0.02	0.306
	400	<2 mm	25.0	0.26 ± 0.02	0.216
Surface soils from Pedra Preta (0–2 cm)	SLPP0201	<2mm	4.5	0.124 ± 0.007	0.19
	SLPP0202	<2mm	6.3	0.275 ± 0.008	0.299
	SLPP0203	<2 mm	8.5	0.173 ± 0.013	0.211
	SLPP0204	<2 mm	6.6	0.097 ± 0.008	0.098
	SLPP0205	<2 mm	14.4	0.094 ± 0.006	0.115
VN 2- soil over alluvium of Vila Nova river	0–7	Mud	2.5	18.1 ± 1.4	19.8
		Sand	2.3	26.7 ± 2.1	29.6
		Duricrust at the water table	<2 mm	0.45 ± 0.04	0.43
	60–70	Mud	2.4	0.39 ± 0.02	0.41
		Sand	1.9	0.185 ± 0.019	0.189
VN3 – soil over bedrock - shaft	0–10	Mud	6.4	0.183 ± 0.017	0.182
		Sand	6.0	0.29 ± 0.02	0.22
	200	Mud	10.5	0.22 ± 0.01	0.216
		Sand	10.0	0.179 ± 0.015	0.136
VN4 – soil over bedrock - drill	0–10	Mud	5.4	0.206 ± 0.018	0.203
		Sand	5.9	0.30 ± 0.01	0.281
	100	Mud	7.6	0.27 ± 0.01	0.294
		Sand	6.6	0.23 ± 0.02	0.22

RAVICHANDRAM²³ also found a strong positive correlation between trace metals concentration, grain size and concentration of organic carbon and iron oxides. The correlation coefficients varied between 0.77 and 0.97 ($n=90$) for sediment cores.

Since the enrichment factor (EF)²⁴ which is convenient for discussing geochemical trends and making comparisons between two different areas was chosen to evaluate the contribution of Hg in the region studied. It can be calculated by the following expression:

$$EF = (X/Al)_{\text{sample}} / (X/Al)_{\text{crust}}$$

where X is the concentration of the metal of interest in the sample and the average content in earth crust and Al ,²⁹ aluminum concentration in the sample and the average content in earth crust. $EF=1$ means that the main source of metal is considered to be the terrestrial crust, $EF>1$ means that there are additional sources besides the natural sources, and $EF<1$ means that the

local source can be diluted by other materials such as carbonates, for instance.²⁵

The results obtained are shown in Table 5. The sediment samples from Serra do Navio showed that $EF<1$, suggesting that the Hg concentration is diluted. The EF for the two samples collected upstream Garimpo do Chicão presented a value similar to Serra do Navio samples ($EF=0.25$).

For the Vila Nova river basin EF values ranged from 1.3 to 7.9, indicating an anthropogenic contribution of Hg in the sediments from this region.

Table 6 shows the Hg levels in sediments, from different gold mining areas in Brazil. It is clear that the background level at Serra do Navio region is higher than several investigated areas considered contaminated, being 10 times higher than values found for sediments from rivers considered not contaminated in Amazonia ($20 \mu\text{g}\cdot\text{kg}^{-1}$).⁵

Table 5. Enrichment factor (*EF*) for sediment samples

Sediments from Serra do Navio						
SDPP0101		SDAP0101		SDAP002	SDAP003	SDAP004
SILT	SAND	SILT	SAND	SILT	SILT	SILT
0.34	0.21	0.21	0.29	N.D.	0.19	0.23

Sediments from Vila Nova river basin

SDVN004	SDVN006	SDVN001A		SDVN001B		SDVN001C		SDVN007
SILT	SILT	SILT	SAND	SILT	SAND	SILT	SAND	SILT
0.29	0.25	3.9	7.9	1.3	2.1	2.6	1.9	1.94

Hg (crust) = 0.08 mg·kg⁻¹.Al (crust) = 8.2%.²⁹

Table 6. Hg levels in sediments from different Brazilian regions

Location	Hg, µg·kg ⁻¹	Reference
Poconé – Mato Grosso	50–180	LACERDA (1991)
Rio Madeira, norte de Porto Velho	50–280	LACERDA (1987)
Rio Mutum do Paraná, Rondônia	210–19800	PFEIFFER (1989)
Rio Tapajós, Pará	3–143	PADBERG (1990)
Bacia do Cumaru – Pará	300–9000	RAMOS (1990)
Rio Madeira, Humaitá – Amazonas	<10–50	MARTINELLI (1988)
Bacia de Crixás, Goiás	270–12750	ANDRADE (1988)
Poconé, Pantanal, Brazil	130–255	GUIMARÃES (1999)
Rivers considered not contaminated in Amazonia	<20	PFEIFFER (1989)
Serra do Navio – Igarapé Pedra Preta	210–460	This work
Vila Nova river basin	240–2980	This work

Table 7. Hg levels in soils from different Brazilian regions

Location	Hg, µg·kg ⁻¹	Reference
Poconé – Mato Grosso	20–30	LACERDA (1991)
Alta Floresta – Mato Grosso	50–4100	RODRIGUES (1995)
Rio Madeira	50–2620	PFEIFFER (1991)
Soils from forest	30–180	PFEIFFER (1991)
Negro river basin	up to 212	FORSBERG (1999)
Serra do Navio	141–431	FOSTIER (1999)
Igarapé Pedra Preta	94–380	This work
Vila Nova river basin	179–26700	This work

GUIMARÃES et al.²⁶ studied Hg in sediments around Poconé Gold mining area, Pantanal, Brazil. They found in sediment cores that Hg was higher in surface layers (130–255 ng·g⁻¹ d.w.) in Poconé (the oldest gold mining area near the Pantanal) and locations downstream, while bottom layers ranged from 17–75 ng·g⁻¹, suggesting some mobilisation of Hg from gold mining fields.

Soils

Table 4 shows the results obtained for mercury concentrations in surface soils and in soil profiles.

Comparing mercury levels in the areas studied, it is observed that mercury concentrations in Igarapé Pedra Preta basin are lower than in ‘garimpo do Chicão’, a contaminated area, where mercury levels reached 27 mg·kg⁻¹ at the surface.

Soil samples from Serra do Navio have presented Hg levels around 0.3 mg·kg⁻¹ such as for sediments. No meaningful differences were noticed between Serra do Navio and ‘garimpo do Vicente’.

In all sampling, no significative relationship has been found between the different depths and the content of mercury. It seems that mercury distribution is

independent of grain size. A correlation between Hg and Fe levels in soil samples was not observed. (Serra do Navio $r_{xy}=0.16$, $n=13$ and Vila Nova $r_{xy}=0.11$, $n=10$).

Table 7 shows a comparison between Hg in soils from different Brazilian regions with gold mining activities.

FORSBERG et al.²⁷ at Negro river basin (Brazilian Amazon), also found mercury levels in soils exceptionally high (up to $212 \mu\text{g}\cdot\text{kg}^{-1}$). Depth integrated mercury stocks were many times higher than those expected from anthropogenic sources and thus considered predominantly of natural origin.

FOSTIER et al.²⁸ determined the total mercury concentrations in soils from a forested and a neighboring deforested area from Serra do Navio region. They found that Hg concentrations in the 0-10 cm samples ranged from 141 to $431 \mu\text{g}\cdot\text{kg}^{-1}$ following a downhill gradient. Considering soil profiles, Hg concentrations decreased with depth to less than $100 \mu\text{g}\cdot\text{kg}^{-1}$. In the deforested area, Hg ranged from 57 to $103 \mu\text{g}\cdot\text{kg}^{-1}$ in the 0-10 cm layer.

Conclusions

The RNAA method using the Parr bomb mixed acid digestion system has proven to be an accurate method for mercury leaching in soil and sediment samples. The detection limits of the analytical procedure were adequate, reaching values of $54 \mu\text{g}\cdot\text{kg}^{-1}$ for soils and $14 \mu\text{g}\cdot\text{kg}^{-1}$ for sediments when 200 mg of samples were analyzed.

The results achieved by RNAA method were compared with those obtained by CV AAS and most of them were in agreement. The results obtained for reference materials analysis were also good, proving that the RNAA is a very reliable method for mercury analysis.

Our results showed that the soil and sediment samples collected at Vila Nova river basin presented a very high level of mercury contamination. The levels of Hg in the samples from Serra do Navio region, an area considered without direct effect of mercury contamination, were about $0.3 \text{ mg}\cdot\text{kg}^{-1}$, value considered as too high if it is compared to other non contaminated areas in Brazil.

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References

1. L. D. LACERDA, W. SALOMONS, *Mercury from Gold and Silver Mining: A Chemical Time Bomb?*, Springer-Verlag, Berlin, 1998, p. 146.
2. A. C. BARBOSA, A. A. P. BOISCHIO, G. A. EAST, I. FERRARI, A. GONÇALVES, P. R. M. SILVA, T. M. E DA CRUZ, *Water, Air Soil Pollut.*, 80 (1995) 109.
3. E. D. BIDONE, Z. C. CASTILHOS, T. J. S. SANTOS, T. M. C. SOUZA, L. D. LACERDA, *Bull. Envir. Contam. Toxicol.*, 59 (1997) 194.
4. E. D. BIDONE, Z. C. CASTILHOS, T. J. S. SANTOS, T. M. C. SOUZA, L. D. LACERDA, *Water, Air Soil Pollut.*, 97 (1997) 9.
5. W. C. PFEIFFER, L. D. LACERDA, O. MALM, C. M. M. SOUZA, E. G. SILVEIRA, W. R. BASTOS, *Sci. Tot. Environ.*, 87/88 (1989) 233.
6. W. C. PFEIFFER, L. D. LACERDA, O. MALM, C. M. M. SOUZA, E. G. SILVEIRA, W. R. BASTOS, *Forest Ecol. Managem.*, 38 (1991) 239.
7. S. RODRIGUES FILHO, J. E. L. MADDOCK, *Proc. Intern. Conf. on Heavy Metals in the Environment*, Hamburg, Vol. 2, 1995, p. 303.
8. L. D. LACERDA, W. C. PFEIFFER, O. MALM, C. M. M. SOUZA, W. R. BASTOS, E. G. SILVEIRA, *I. Congresso Brasileiro Geochimica*, Vol. 2, 1987, p. 165.
9. L. D. LACERDA, W. C. PFEIFFER, W. R. BASTOS, *Ciência e Cultura*, 43 (1991) No. 4, 317.
10. S. PADBERG, *Química Nova*, 15 (1992) 155.
11. J. F. F. RAMOS, M. Q. COSTA, *Riscos e Consequências do uso do Mercúrio*, R.J.: S. HACON, L. D. LACERDA, D. CARVALHO, W. C. PFEIFFER (Eds), Universidade Federal do Rio de Janeiro, 1990, p. 70.
12. L. A. MARTINELLI, J. R. FERREIRA, B. R. FORSBERG, *R. L. Victoria, Ambio*, 17 (1988) 252.
13. J. C. ANDRADE, M. I. M. S. BUENO, P. V. SOARES, A. CHOUDHURI, *An. Acad. Bras. Cienc.*, 60 (1988) 294.
14. L. D. LACERDA, W. SALOMONS, W. C. PFEIFFER, W. R. BASTOS, *Biogeochemistry*, 14 (1991) 91.
15. B. R. FORSBERG, M. C. S. FORSBERG, C. R. PADOVANI, E. SARGENTINI, O. MALM, in: *Proc. Intern. Workshop on Environmental Mercury Pollution and its Health Effects in Amazon River Basin*, Rio de Janeiro, Brazil, 1994, p. 33.
16. C. GONÇALVES, D. I. T. FÁVARO, S. M. B. OLIVEIRA, R. BOULET, M. B. A. VASCONCELLOS, M. SAIKI, *J. Radioanal. Nucl. Chem.*, 235 (1988) 267.
17. O. MALM, W. C. PFEIFFER, C. M. M. SOUZA, R. REUTHER, *Ambio*, 1911 (1990) 15.
18. A. H. FOSTIER, J. R. FERREIRA, M. O. ANDRADE, *Química Nova*, 18 (1992) No. 5, 425.
19. L. A. CURRIE, *Anal. Chem.*, 40 (1968) 586.
20. N. S. FERREIRA, M. M. VEIGA, *Environtech'95*, R. J., Brazil, 1995, p. 53.
21. M. M. VEIGA, F. R. C. FERNANDES (Organizers), *Poconé: Um campo de estudos do impacto ambiental do garimpo*. Centro de Tecnologia Mineral, Conselho Nacional de Desenvolvimento Científico e Tecnológico, Rio de Janeiro, 1991.

22. S. RODRIGUES FILHO, J. E. L. MADDOCK, Proc. Intern. Conf. on Heavy Metals in the Environment, Hamburg, Alemanha, Vol. 2, 1995, p. 303.
23. M. RAVINCHANDRAM, M. BASKARAN, P. H. SANTSCHI, T. S. BIANCHI, Environ. Sci. Tec., 29 (1995) No. 6, 1495.
24. G. MULLER, Umschau, 79 (1971) 778.
25. H. E. BELKIN, H. M. SPARCK, Environ. Geol., 22 (1993) 106.
26. J. R. D. GUIMARÃES, O. MALM, M. MEILI, Proc. 5th Intern. Conf. on Mercury as a Global Pollutant, Rio de Janeiro, Brazil, Book of Abstracts, 1999, p. 154.
27. B. R. FORSBERG, W. F. JARDIM, V. K. ZEIDEMANN, P. S. FADINI, A. CARNEIRO, C. R. PADOVANI, M. C. SILVA-FORSBERG, M. ROULET, M. LUCOTTE, E. M. NAKAZANO, A. E. MARTINS, E. C. CHAGAS, Proc. 5th Intern. Conf. on Mercury as a Global Pollutant, Rio de Janeiro, Brazil, Book of Abstracts, 1999, p. 153.
28. A. H. FOSTIER, S. M. B. OLIVEIRA, J. R. D. GUIMARÃES, M. C. FORTI, A. J. MELFI, R. BOULET, D. I. T. FÁVARO, F. J. KRUG, Proc. 5th Intern. Conf. on Mercury as a Global Pollutant, Rio de Janeiro, Brazil, Book of Abstracts, 1999, p. 557.
29. S. R. TAYLOR, S. M. MCLENNAN, *The Continental Crust: Its Composition and Evolution*, Blackwell Scientific, Palo Alto, Ca, 1985.