



ELSEVIER

The Science of the Total Environment 213 (1998) 203–211

**the Science of the
Total Environment**

An International Journal for Scientific Research
into the Environment and its Relationship with Man

Distribution and partition of total mercury in waters of the Tapajós River Basin, Brazilian Amazon¹

M. Roulet^{a,*}, M. Lucotte^a, R. Canuel^a, I. Rheault^a, S. Tran^a,
Y.G. De Freitas Gog^b, N. Farella^a, R. Souza do Vale^b, C.J. Sousa Passos^b,
E. De Jesus da Silva^b, D. Mergler^c, M. Amorim^d

^aChaire de recherche en environnement H-Q / CRSNG / UQAM, C.P. 8888, Suc. Centre Ville, Montréal, Québec, Canada H3C 3P8

^bLaboratorio de Biologia Ambiental, Santarém-UFPA campus, Santarém, Brazil

^cCIMBIOSE, UQAM, Montréal, Québec, Canada H3C 3P8

^dUFPA, Belém, Brazil

Abstract

Filtered water and particulate burdens of Hg (0.43–2.81 ng/l and 0.28–13.13 ng/l, respectively) in the Tapajós River (Brazilian Amazon) are one order of magnitude lower than previously reported concentrations in Amazonian waters. Hg content in the water column is influenced by the amount of particulate matter and is independent from upstream goldmining activities. The particulate load of Hg in the river is attributable to sedimentation patterns in relation to physiography of the river. We contend that the particulate Hg in the river and its tributaries is strongly influenced by fine particles eroded from pertubated soils in the river catchment. © 1998 Elsevier Science B.V.

Keywords: Filtered water; Particulate burdens; Tapajós River

1. Introduction

In the downstream region of the Tapajós River, numerous studies have reported the presence of

mercury (Hg) contamination in diverse fish species (Akagi et al., 1995; Malm et al., 1995a,b). The daily consumption of these fishes in human communities of the river results in a chronic exposure to this contaminant to such an extent that neuro-physiological alterations have developed (Lebel et al., 1996, 1997, 1998). Health effects observed have commonly been attributed to Hg wastes produced from goldmining camps upstream from the study area (Akagi et al., 1995; Malm et al., 1995a,b). However, the alleged link between

* Corresponding author. Tel.: +1 514 9873000 ext. 4080; fax: +1 514 9873000 ext. 3635.

¹The present investigation is part of an ongoing study, the CARUSO project (CRDI-UFPA-UQAM), initiated to determine the sources, fate and health effects of the presence of MeHg in the area of the Lower Tapajós.

goldmining waste dispersion and bioaccumulation in fishes lacks any scientific evidence and relies exclusively on an assumed influence of this well known source point. There are no data that prove unambiguously that long distance transport of this heavy metal from goldmining camps has a direct geochemical influence on Hg burdens in the Tapajós' water column. Recently, Roulet et al. (1996a,b) have shown that ferralitic soils from this region accumulate naturally considerable quantities of Hg and that erosion of these soils, following deforestation and cultivation, promotes the weathering of Hg accumulated in this compartment. These authors suggested that such a weathering process may influence the Hg burden in the aquatic system of any perturbed catchment area.

In this context, the objectives of the present study is the observation of Hg distribution in the water column of the Tapajós River along a 350-km transect, starting 50 km downstream from goldmining camps to more than 400 km. This study focuses on the geochemical processes that

govern the Hg burden and partition in the river waters in relation to its dynamic. This allowed us to evaluate the influence zone of the mining activities and the importance of soil erosion on particulate loads on the Hg burdens in the water column.

2. Materials and methods

The Tapajós River is one of the major tributaries of the Amazon River. This clear water river is located in the state of Pará (Brazil) in the Lower Amazon (Fig. 1). We have sampled 30 stations in surface waters (1 m deep) of this river system along a 350-km long transect between São Luis do Tapajós (50 km downstream from mining camps) and Santarém (400 km downstream). Sampling was conducted during both wet (March to April 1995, AM95a) and dry seasons (October to November 1995, AM95b). The portion of the river studied can be divided in two distinct physiographic zones (Fig. 1, see #1 and #2). The upper zone (rio, #1) is constituted by a river–floodplain

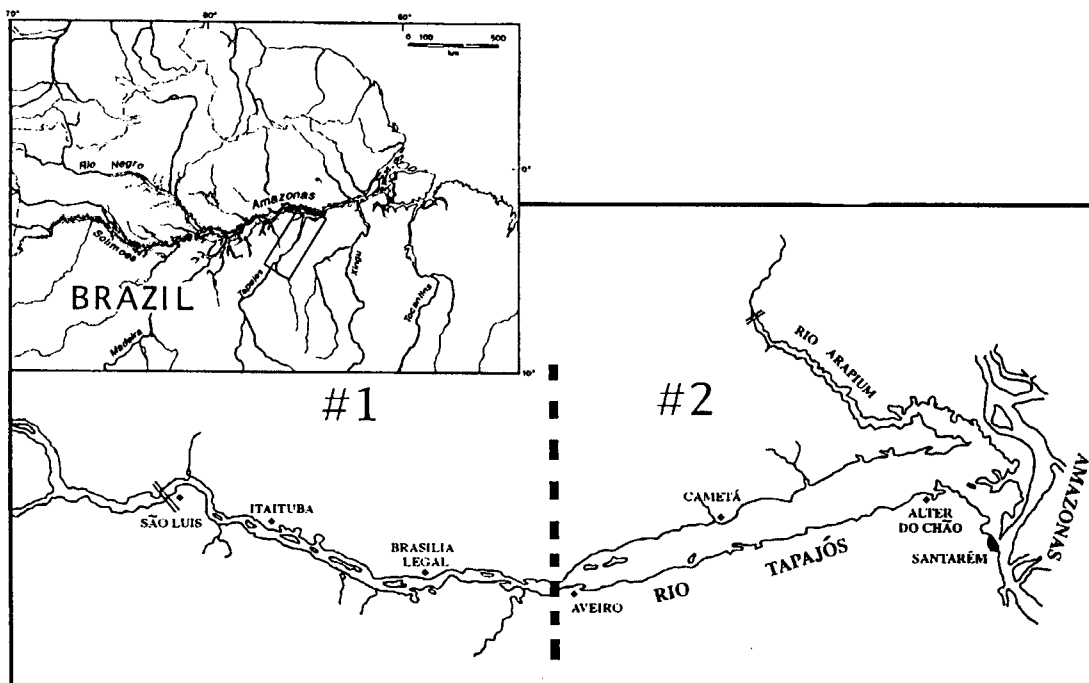


Fig. 1. Map of the lower Tapajós Basin.

system in which the river is 2–4 km wide with a strong current. The lower part (ria, #2), from Aveiro to the confluence with the Amazon River, is a mouthbay–lake system 8–12 km wide with a slow current (Sioli, 1984).

The filtered fraction was sampled in triplicate using a manual peristaltic pump and a millipore online filter–holder assembled with a 0.2- μm glass fiber filter EPM2000 following the clean hands–dirty hands protocol (Montgomery et al., 1995).

Particulate matter was sampled in two fractions for each stations. The fine particulate matter (FPM) fraction was collected by filtering a known volume of pre-filtered water ($< 63 \mu\text{m}$) on 15–20 pre-weighed and pre-combusted (300°C) glass fiber filters (0.7 μm , filter Gelman AE) using an acid-clean vacuum filtration system. The coarse particulate matter (CPM) fraction was collected using a 63- μm mesh plankton net. All CPM samples were observed with binoculars to identify the different constituents of this fraction.

Analyses of filtered total Hg (HgD) in wet season's samples, were conducted both onboard the ship in the field laboratory and in our laboratory in Montréal. After confirmation that samples were not affected by the transport, all the dry season's samples were brought back and analysed in Montréal. Determination of HgD was conducted by cold vapour atomic fluorescence spectrometry (CVAFS) following modifications to the technique developed by Bloom and Fitzgerald (1988). More details on this specific method are given by Montgomery et al. (1995) and Louchouart et al. (1993). Gaseous digestion of glass fiber filters was used to extract Hg associated to FPM (HgFP). The digestion was conducted in a glass vial with a teflonated hermetic cap. HNO_3 (0.5 ml) and 50 μl of HCl were added to one filter and heated in an oven at 120°C for 6 h. Following this step, 5 ml of NANOpure water and 50 μl of HCl were added to allow the injection of 1–2 ml of solution directly into the CVAFS reactor. All filters were previously oven-dried (45°C) and weighed. For each filter it was possible to determine both the concentration per mass of matter (HgFP concentration in suspended matter in nanograms per gram, ng/g) and the concentra-

tion per volume of water (HgFP burden in water in nanograms per litre, ng/l).

Digestion of 5–15 mg of CPM in 10 ml of a 10:1 mixture of HNO_3/HCl allowed the direct injection of 1 ml of diluted solution (with NANOpure water) for analysis by CVAFS of Hg associated to the coarse fraction, HgCP (Mucci et al., 1995).

Additionally, filters and CPM were used for carbon (C) and nitrogen (N) analyses using a Carlo-Erba elemental detector and for reactive iron oxy-hydroxides quantification using an extraction with buffer citrate–dithionite–bicarbonate (Fe_{cdb}) followed by Atomic Absorption analysis (Lucotte and d'Anglejan, 1985).

3. Results

3.1. Filtered Hg burdens

The burdens of HgD obtained in this study ($< 1.7 \text{ ng/l}$ and $< 1.9 \text{ ng/l}$ for the wet and dry seasons, respectively; Fig. 2a) are an order of magnitude lower than recently reported values for Amazonian rivers close to other mining centers, 10–20 ng/l (Nriagu et al., 1992). They are similar, however, to waters influenced by non-point inputs of Hg (Gill and Bruland, 1990; Hurley et al., 1995; Montgomery et al., 1995; Watras et al., 1995a,b).

Along the transect, no decreasing gradient is observed away from the goldmining zone (50 km upstream from the beginning of the transect) down to the confluence with the Amazon River (400 km downstream). HgD concentrations during the dry season are slightly more elevated than those from the wet season. Igarapés (creeks, sampled during the dry season), from catchment areas without goldmining activities, show HgD concentrations of a similar order of magnitude (0.5–2.8 ng/l) than those from the transect (Fig. 2a, Table 1).

3.2. Composition of FPM

For each season, the FPM is homogeneous in terms of Hg, iron oxy-hydroxides (Fe_{cdb}) and organic matter (%C) concentrations, as well as in

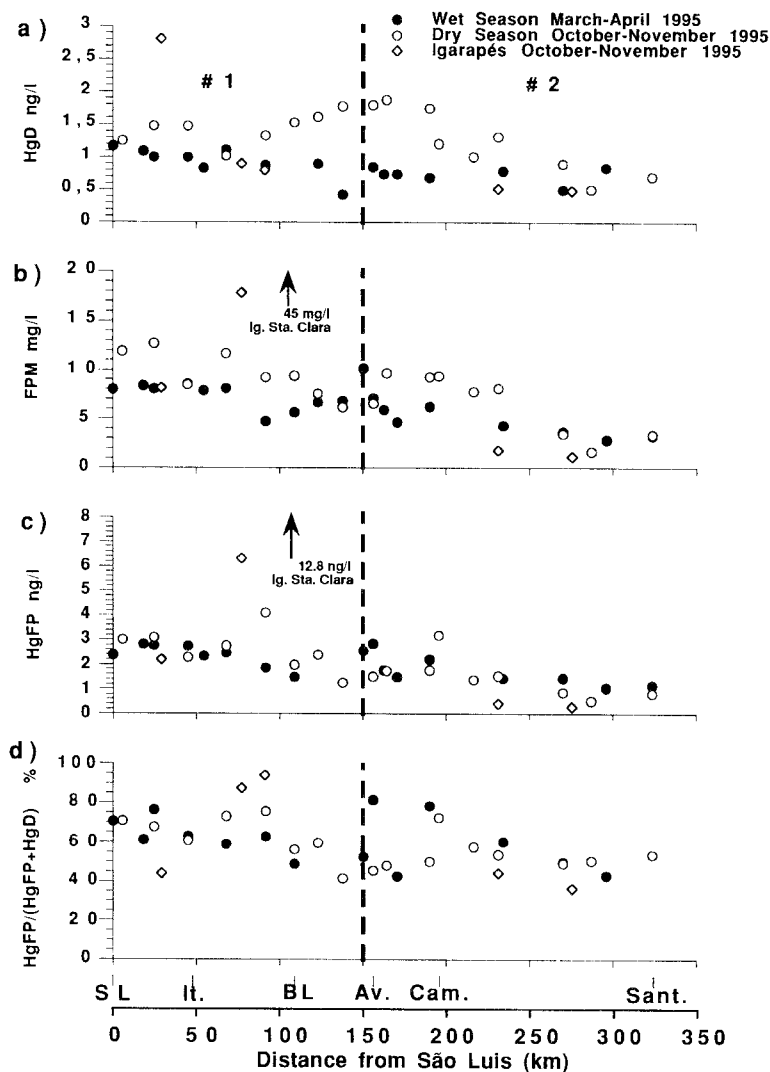


Fig. 2. Burdens of Hg in water and particulate suspension load in the Tapajós River and tributaries. SL, São Luis do Tapajós; It., Itaituba; BL, Brasília Legal; Av., Aveiro; Cam., Cameté; Sant., Santarém.

the nature of organic matter (C/N; Fig. 3) suggesting that the FPM is qualitatively homogeneous along the transect in the rio and in the igarapés. HgFP and Fe_{cdb} concentrations are more elevated during the wet season than during the dry season (Fig. 3 and Table 1).

3.3. Composition of CPM

A sharp step in Hg, iron oxy-hydroxides (Fe_{cdb}) and organic matter (%C) concentrations, as well

as in the nature of organic matter (C/N) is observed between the river–floodplain system (#1) and the mouthbay–lake system (#2; Fig. 4). This step is the result of a shift in the quality of CPM corresponding to the transition from terrigenous matter (#1) to purely authigenic plankton material (#2). Similarly, during the dry season, the decrease in both C/N ratios and Fe_{cdb} concentrations in the rio suggests an increased influence of planktonic material in the water column.

Table 1
Concentrations and burdens of Hg in surface water of aquatic ecosystems from the Tapajós Basin

	HgD (ng/l)		FPM (mg/l)		HgFP (ng/l)		HgFP (ng/g)	
	AM95a	AM95b	AM95a	AM95b	AM95a	AM95b	AM95a	AM95b
Rio Tapajós								
Zone #1 rio <i>n</i> = 14	1.09	1.38	7.6	9.4	2.44	2.48	319	274
Zone #2 ria <i>n</i> = 12	0.72	1.23	4.6	7.1	1.56	1.57	332	239
Igarapé da Rainha		2.81		8.2		2.2		253
Igarapé do lago do Roque		0.9		17.8		6.32		355
Igarapé Santa Clara		0.8		45.7		12.82		281
Igarapé Camara		0.52		1.8		0.41		226
Rio Arapium		0.49		1.2		0.28		243
Lago Sujo		1.58		50.6		8.19		154
Lago Piranga								
Center of lake	1.26	0.89	5.5	5.9	1.66	1.19	303	193
Macrophyte mats (capims)	0.84		5.4		2.18		411	
Flooded forest (igapo)	1.31		9.2		3.06		350	
Lago Enseada Grande								
Center of lake	1.57	0.62	3.9	21.7	1.16	4.02	332	172
Macrophyte mats (capims)	1.5		7.9		2.36		327	
Flooded forest (igapo)	2.58		5.5		2.19		400	
Laguna de Cameta	0.64	2.1	5.4	84.5	1.53	13.13	299	139
Rio Amazonas								
Lago Pacoval	1.55				19.02			
Rio Amazonas	1.31	2.52	67.2	46.1	8.7	4.99	124	110
Mixing zone Tapajós- Amazon	2.38		20.6		3.09		140	

3.4. Fine particulate burdens

The significant gradient in FPM burden (milligrams per litre, mg/l) observed along the transects is directly related to the physiography of the Lower Tapajós River (see Sioli, 1984) from the rio (#1, turbid) to the ria (#2, decantation due to the reduction in current speed; Fig. 1b). This corresponds to the development of a large sedimenta-

tion zone downstream from Aveiro, where the river widens rapidly. Moreover, since Hg concentrations in this fraction is homogeneous, the abatement in FPM burden is responsible for an equivalent decreasing gradient in Hg burden in the water column (Fig. 2c). The partition of particulate Hg burden (Fig. 2d) shows that the majority of the Hg present in the water column of the Tapajós River is associated to the FPM fraction (40–80% of the total Hg burden).

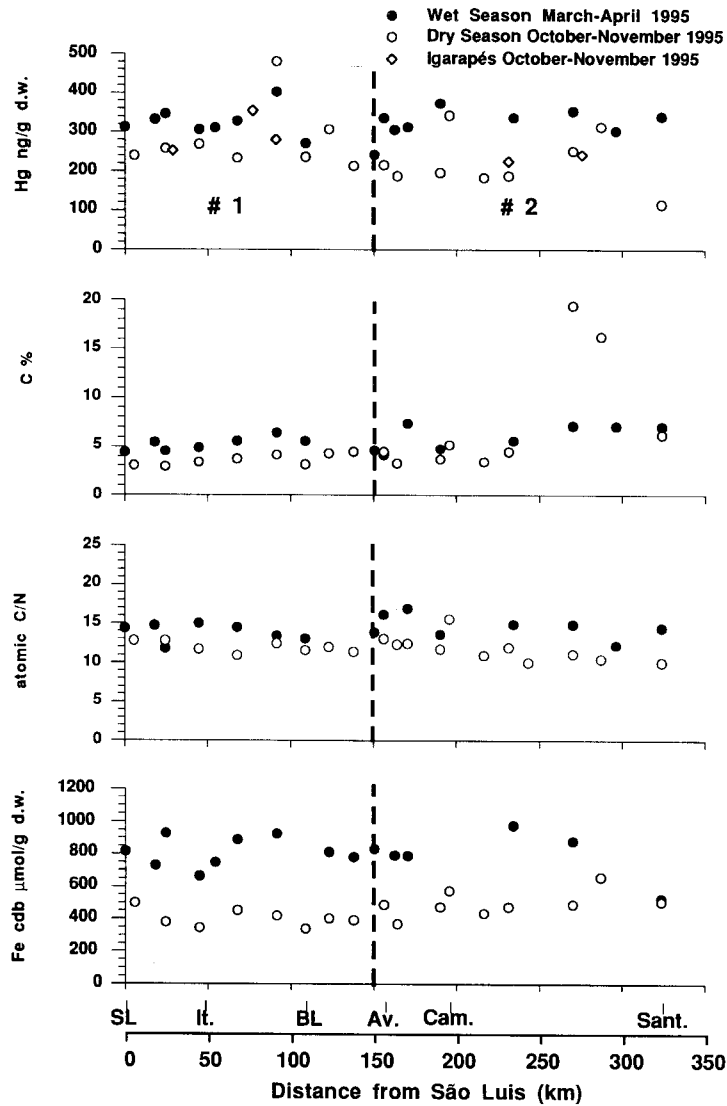


Fig. 3. Concentrations of Hg, C, Fe_{cdb} and atomic C/N ratios of the fine particulate matter fraction along the Tapajós River and tributaries. SL, São Luis do Tapajós; It., Itaituba; BL, Brasilia Legal; Av., Aveiro; Cam., Cametá; Sant., Santarém.

4. Discussion

HgD burdens are low and uniform throughout the Tapajós River. Hg concentrations in the fine particulate fraction are homogeneous in both the river and igarapés. Hg associated to coarse particles reflects two distinct ecological ecosystems: (#1) a fast flowing and turbid rio with a dominant terrigenous source of suspended material; and

(#2) a lentic decanted ria dominated by autochthonic planktonic organisms. Along the transect of the river, the absence of any significant gradient in HgD burdens and HgFP concentrations indicates that the presence of the goldmining zone 50 km upstream does not lead to an enrichment in Hg in either the filtered or the particulate fraction. In the present study of the Lower Tapajós aquatic system, we did not detect any long dis-

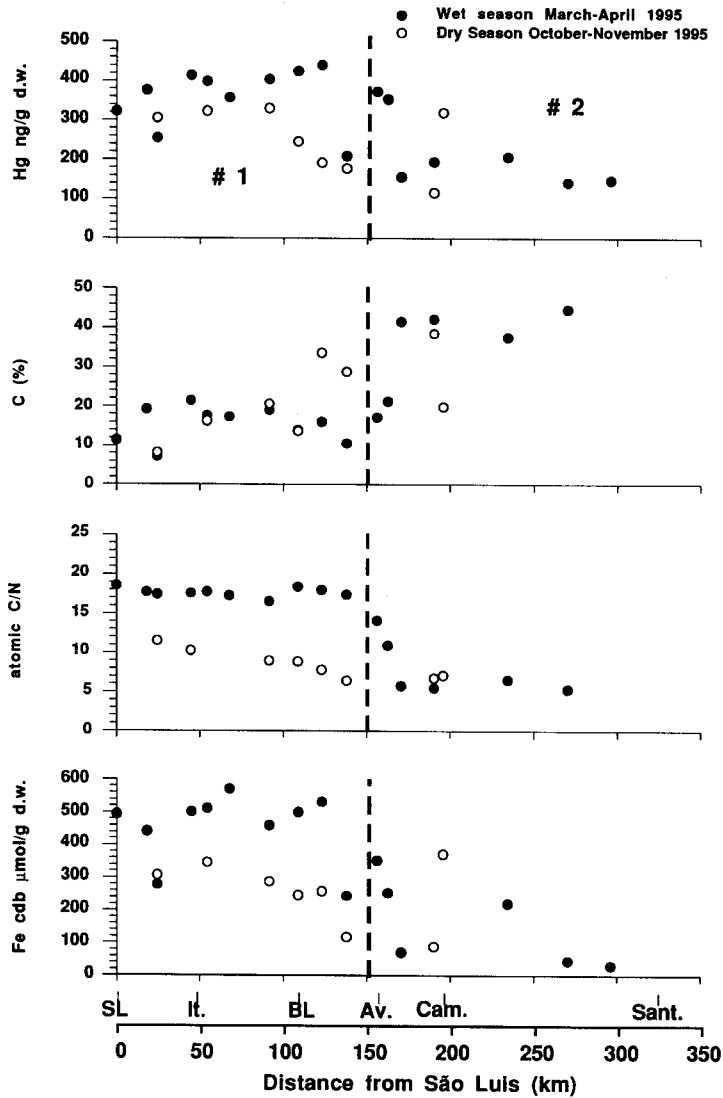


Fig. 4. Concentrations of Hg, C, Fe_{cdb} and atomic C/N ratios of the coarse particulate matter fraction along the Tapajós River. SL, São Luis do Tapajós; It., Itaituba; BL, Brasilia Legal; Av., Aveiro; Cam., Cametá; Sant., Santarém.

tance influence of released Hg contaminated wastes resulting from upstream mining activities.

Because the majority of the Hg present in the water column of the Tapajós River is associated to the fine particulate fraction, total Hg burdens are governed by the quantity of suspended material in the water column. Elevated burdens were observed in several aquatic environments resulting from high particulate loads (see Table 1). During the dry season, shallow water aquatic sys-

tems (floodplain lakes and lagoons) have high particulate Hg loads resulting from resuspension events of bottom sediments. Similarly, the high suspended load of the Amazon River is responsible for a high burden of Hg. However, although the waters from the Amazon contain more Hg than those from the Tapajós, its burden is diluted in the mixing-zone at the confluence of the two rivers downstream of Santarém by the less concentrated waters of the Tapajós. Some igarapés

without goldmining activities show higher loads of Hg than that of the Tapajós itself. All these Hg loaded aquatic systems are far removed from goldmining sources of Hg but contain more of this heavy metal than the rivers close to the mining centers. In small igarapés and within the rio, particulate Hg is suspected to be strongly influenced by the fine particles eroded from soils of the river catchment (Roulet et al., 1996a).

The differences observed between the wet and dry seasons show that HgD is more concentrated during periods of low water volumes. In contrast, both the FPM and the CPM show higher concentrations in Hg and Fe_{cdB} during the wet season indicating that during the season of active goldmining particulate matter is less concentrated in Hg. The increased particulate Hg concentrations during the heavy rain-season seem to result from an intense leaching of fine soil particles enriched in both iron oxy-hydroxides and Hg from the catchment area (cf. Roulet et al., 1996a,b). High water volumes correspond equally to a reduced burden in FPM indicating that, in the lower Tapajós River, the high water discharge during the wet season dilutes the suspended particulate matter.

5. Conclusions

Numerous recent publications about Hg contamination by goldminers in the Amazon (Nriagu et al., 1992; Cleary et al., 1994; Akagi et al., 1995; Malm et al., 1995a,b) have used the universally assumed hypothesis that an increase of Hg in aquatic systems conduct to an increase of Hg concentration in fishes. Using the same assumption, intoxication by Hg of riverine villagers through fish ingestion in the lower Tapajós region (Lebel et al., 1997) cannot solely be attributed to the dispersion of Hg from the upstream goldmining centers. The release of Hg used by these mining activities does not seem to influence the Hg burdens in the water column of the river on the long distance scale (more than 50 km downstream). In the studied aquatic ecosystems, elevated Hg burdens in the water column seem instead to be attributable to high loads of fine particles in suspension. In the Tapajós River,

particulate loads of Hg seem to be strongly influenced by the presence of eroded soil particles enriched in iron oxides and Hg (Roulet et al., 1996a,b). Erosion of soils particles could result from any disturbances of soils in the catchment area like extraction of gold, construction of roads, logging, cattle ranching and cultivation. In view of the importance of the colonization of the river banks along the Tapajós River (more than 50% of the banks along the transect), erosion of fine clayey particles from deforested ferrallitic soils (Roulet et al., 1996a,b) could strongly explain the increase in Hg concentrations in the aquatic system (waters and sediments). This process could be applied to any perturbed catchment area in Amazonian regions.

Acknowledgements

This research was supported mainly by Canada's International Development and Research Center (IDRC) as part of the CARUSO project (grant #96-1052-01/001300-01 and scholarship to the first author). We also acknowledge the Universidade Federal do Pará (UFPA) and the UFPA-Santarém Campus for additional support and help for the realisation of this project.

References

- Akagi H, Malm O, Kinjo Y, et al. Methylmercury pollution in Amazon Brazil. *Sci Total Environ* 1995;175:85–95.
- Bloom N, Fitzgerald WF. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold-vapor atomic fluorescence detection. *Anal Chim Acta* 1988;208:151–161.
- Cleary D, Thornton I, Brown N, Kazantziz G, Delves T, Worthington S. Mercury in Brazil. *Nature* 1994;369: 613–614.
- Gill GA, Bruland KW. Mercury speciation in surface freshwater systems in California and other areas. *Environ Sci Technol* 1990;24:1392–1400.
- Hurley JP, Benoit JM, Babiartz CL, et al. Influences of watershed characteristics on mercury levels in Wisconsin Rivers. *Environ Sci Technol* 1995;29:1867–1875.
- Lebel J, Mergler M, Lucotte M, et al. Evidence of early nervous system dysfunction in Amazonian populations exposed to low-level methyl mercury. *Neurotoxicology* 1996;17:157–168.
- Lebel J, Roulet M, Mergler D, Lucotte M, Laribe F. Fish diet

- and mercury exposure in a riparian Amazonian population. *Water Air Soil Pollut* 1997;97:31–44.
- Lebel J, Mergler D, Branches FJP, et al. Neurotoxic effect of low-level methylmercury contamination in the Amazon Basin. *Environ Res* 1998;in press.
- Louchouart P, Lucotte M, Mucci A, Pichet P. Geochemistry of mercury in two hydroelectric reservoirs in Québec, Canada. *Can J Fish Aquat Sci* 1993;50:269–281.
- Lucotte M, d'Anglejan B. A comparison of several methods for the determination of iron hydroxides and associated orthophosphates in estuarine particulate matter. *Chem Geol* 1985;48:257–264.
- Malm O, Castro MB, Bastos WR, et al. An assessment of Hg pollution in different goldmining areas, Amazon, Brazil. *Sci Total Environ* 1995a;175:127–140.
- Malm O, Branches FPJ, Akagi H, et al. Mercury and methylmercury in fish and human hair from the Tapajós Basin. *Sci Total Environ* 1995b;175:141–151.
- Montgomery S, Mucci A, Lucotte M, Pichet P. Total dissolved mercury in the water column of several natural and artificial systems of northern Quebec (Canada). *Can J Fish Aquat Sci* 1995;52:2483–2492.
- Mucci A, Lucotte M, Montgomery S, Plourde Y, Pichet P, Van Tra H. Mercury remobilization in a hydroelectric reservoir of northern Quebec, La Grande-2: results of a soil resuspension experiment. *Can J Fish Aquat Sci* 1995;52:2507–2517.
- Nriagu JO, Pfeiffer WC, Malm O, Souza CMM, Mierle G. Mercury pollution in Brazil. *Nature* 1992;356:389.
- Roulet M, Lucotte M, Reault I, et al. Mercury in Amazonian soils: accumulation and release. In: Botrell SH, editor. *Proceedings of the 4th International Symposium on the Geochemistry of the Earth's Surface*, 22–28 July 1996, Ilkley, Yorkshire, England, 1996a:453–457.
- Roulet M, Lucotte M, Farella N, et al. Effects of recent human colonization on the presence of mercury in Amazonian ecosystems. *Water Air Soil Pollut*, 1996b:submitted.
- Watras CJ, Morrison KA, Host JS, Bloom NS. Concentration of mercury species in relationship to other site-specific factors in surface waters of northern Wisconsin lakes. *Limnol Oceanogr* 1995a;40:556–565.
- Watras CJ, Morrison KA, Host JS, Bloom NS. Mercury in remote Rocky Mountain lakes of Glacier National Park, Montana, in comparison with other temperate North American regions. *Can J Fish Aquat Sci* 1995b;52:1220–1228.
- Sioli H. *The Amazon-limnology and landscape ecology of a mighty tropical river and its basin*. Dordrecht: Dr. W Junk Publishers, 1984.