

## Spatio-temporal geochemistry of mercury in waters of the Tapajós and Amazon rivers, Brazil

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### *Abstract*

Spatial and temporal variations of mercury (Hg) concentrations were monitored in the surface waters from the lower portion of the Tapajós River, the Arapiuns River, its principal tributary, and the Amazon River at its confluence with the Tapajós. In the rivers, Hg concentrations in the water column are governed by the concentration of suspended particles. Hg in the filtered water showed very little seasonal variation with low concentrations in the lower Tapajós ( $<1.8 \text{ ng L}^{-1}$ ), Arapiuns ( $<0.8 \text{ ng L}^{-1}$ ), and Amazon ( $<2.8 \text{ ng L}^{-1}$ ). Concentrations of fine particulate Hg ( $0.6\text{--}29.7 \text{ ng L}^{-1}$ ) represent 40%–90% of the total volumetric concentration of Hg. In relation to their oxyhydroxide contents, suspended particles are not richer in Hg than nearby soils where oxyhydroxides control the accumulation of Hg. The study shows that the dominant stock of Hg in the aquatic ecosystems of this region is derived from erosion of natural soils in the catchment rather than from anthropogenic pollution. The input of natural Hg coming from soils into the aquatic ecosystems may have increased over historical levels in the region. This increase of total Hg in aquatic ecosystems could potentially account for high levels of methylmercury recently reported in fish and humans in the lower Tapajós River area, but the link between the different processes that promote high levels of methylmercury exposure for the human community remains to be proved.

Numerous recent studies (Bidone et al. 1997; Lebel et al. 1997; Malm et al. 1997) have documented exceedingly elevated levels of mercury in fish of the Tapajós River, one of the principal tributaries of the Amazon River. Exposure to methylmercury (MeHg) through fish consumption by the

populations living along the river has resulted in early signs of sensory and motor deficiencies (Lebel et al. 1998). The Hg contamination measured in fish of the Tapajós was initially attributed to the use of Hg in upstream gold-mining centers. With relatively high levels of Hg in the soils of the valley, the pedologic cover constitutes a considerable reservoir of naturally accumulated Hg (Roulet et al. 1998b). In

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

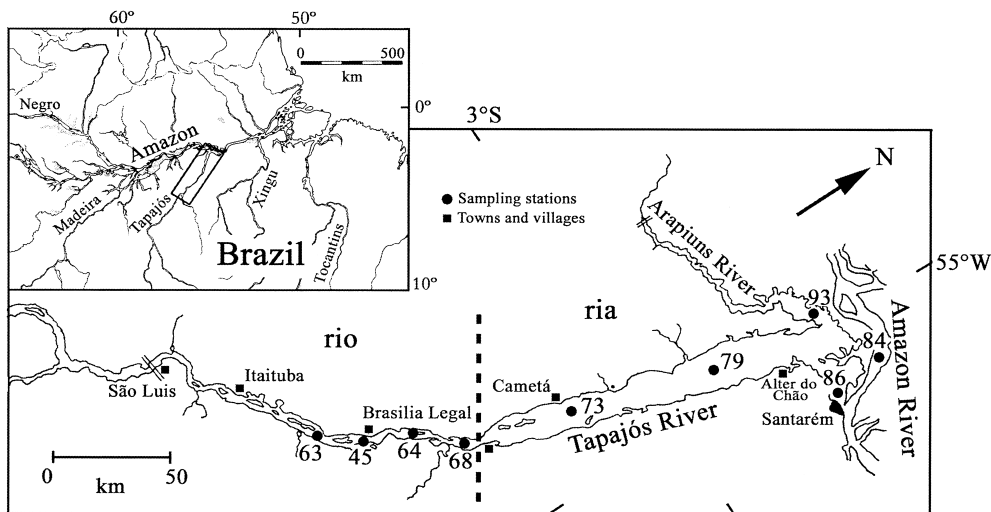


Fig. 1. Map of the study region and sampling sites.

these soils, the cumulative Hg deposition from gold mining activities represents <3% of the burden of Hg accumulated in the first 20 cm (Roulet et al. 1999). The Hg waste from these activities has no effect on Hg concentrations measured in the water column 50 km downstream from gold-mining centers (Roulet et al. 1998a). The soils represent a potentially large source of Hg relative to the amounts being released by mining activities. Roulet et al. (1998b) proposed that the erosion of fine soil particles is responsible for an

increase in Hg contamination of aquatic ecosystems along the Tapajós River valley.

The main objective of this study is to evaluate the role of suspended sediments and soil erosion as a potential source for Hg in three Amazonian riverine systems. We observed spatial and temporal variation of Hg concentrations in surface waters from the downstream portion of the Tapajós River, the Arapiuns River, its principal tributary, and the Amazon River at its confluence with the Tapajós. Three size fractions were considered: filtered water, fine particulate matter (FPM), and coarse particulate matter (CPM). These fractions were monitored during four different seasons to determine Hg concentrations and their relation to organic matter (carbon and nitrogen) and mineral fractions (iron and aluminum oxyhydroxides). Hg levels normalized to their oxyhydroxide and carbon contents were compared with soils and bottom sediments to trace the origin of particulate Hg. This allowed us to evaluate the seasonal and geographical variation in the sources and the behavior of Hg in the water column.

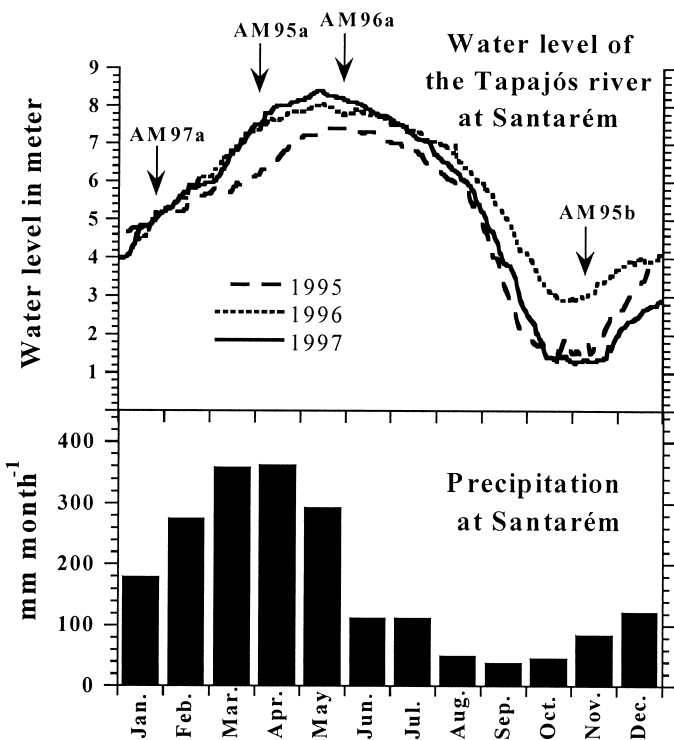


Fig. 2. Annual variation in Tapajós River water levels and mean precipitation at Santarém (1931–1960). (Capitania do porto de Santarém, 1997; Inemet, in Salati and Marques 1984) Sampling periods are indicated.

## Material and methods

**Study area**—The Tapajós River basin is located in the lower region of the central Amazon (Fig. 1). One of the principal tributaries of the Amazon River, the Tapajós is a clear water river that drains, on its upper reach, the Precambrian shield and, on its lower part, the central plateau of the Cretaceous Alter-do-Chão formation (Putzer 1984). In the region of Santarém, the maximum water-level variation is 5 m (Fig. 2). The annual mean (1931–1960) precipitation in Santarém (02°25'S, 54°42'W) is 2,096 mm, and the annual mean temperature is 26°C (Inemet 1979, in Salati and Marques 1984). The climate is equatorial, with a marked dry season.

The section of the Tapajós River studied is composed of two distinct aquatic systems corresponding to two successive physiographic zones in the lower part of the river (Fig. 1). The section upstream from Aveiro (*rio*) is formed by a river-

flood plain system, the river being relatively narrow (2–4 km wide) with a strong central advection current. Immediately downstream from Aveiro, the Tapajós suddenly widens and the current slows, resulting in a large sedimentation zone dotted with numerous islands separated by channels (Sioli 1984). The area downstream from Aveiro, until it joins with the Amazon, is a river lake 8–12 km wide with a weak current (*ria*, “mouth-bay lake”). Two sites on the Amazon River near Santarém, and on the Arapiuns River were also sampled (Fig. 1).

**Sampling methods**—Four field trips for water column sampling were conducted in 1995, 1996, and 1997, corresponding to the lowest water levels at the end of the dry season (AM95b); the onset of heavy rains corresponding to early rising water levels (AM97a), late rising water levels (AM95a), and the maximum of high water levels (AM96a) (Fig. 2).

The water column was sampled following protocols previously described in Roulet et al. (1998a) and Montgomery et al. (1995). Briefly, three different size fractions were collected at each water column site (Fig. 1): filtered water ( $<0.2 \mu\text{m}$ ), FPM ( $0.7 < x < 63 \mu\text{m}$ ), and CPM ( $x > 63 \mu\text{m}$ ). Following the clean hands–dirty hands protocol (Montgomery et al. 1995), filtered water was sampled in triplicate by use of a manual peristaltic pump and an in-line filter holder equipped with a glass fiber filter ( $0.2 \mu\text{m}$  pore size, EPM2000). The FPM fraction was collected by prefiltering water on a  $63 \mu\text{m}$  nitex mesh and capturing the remaining particles on combusted ( $300^\circ\text{C}$ ) and preweighed glass fiber filters ( $0.7 \mu\text{m}$ , Gelman AE). The CPM fraction was sampled by use of a plankton net equipped with a  $63 \mu\text{m}$  nitex mesh. All of the CPM samples were qualitatively classified after sampling with the aid of a microscope. Plankton refers to material without detectable visual traces of organomineral debris. Four classes were defined. The phytoplankton class contains  $>95\%$  by sample volume of vegetal plankton, whereas the zooplankton class was characterized as making up  $>95\%$  of animal plankton. The organomineral class is represented by samples where plankton is not detectable by microscopic inspection. The last class represents the organomineral and plankton mixed in various proportions.

**Laboratory analyses**—All of the CPM samples were freeze dried, and the FPM filters were dried in an oven at  $45^\circ\text{C}$ . The Hg analyses were performed by cold vapor atomic fluorescence spectrometry, following a modification of the method developed by Bloom and Fitzgerald (1988). The technique is described in greater detail in Montgomery et al. (1995) and Pichet et al. (1999).

Hg in the filtered water samples, operationally called dissolved Hg (HgD), was measured by direct injection of a 4-ml subsample after a 30-min photochemical (ultraviolet light) digestion in the presence of potassium persulfate.

Hg associated with fine particles was determined by the gaseous digestion of the Gelman AE filters in glass tubes hermetically sealed with screw caps lined with teflon. One whole filter was placed in a tube, 0.5 ml of  $\text{HNO}_3$  and 50 ml of HCl were added, and the tube was sealed and then placed for 6 h in an oven at  $120^\circ\text{C}$ . Since the filters were

Table I. Notation.

Hg	Total mercury
HgD	Total mercury in filtered water ( $<0.2 \mu\text{m}$ ) in $\text{ng L}^{-1}$
HgFPM <sub>m</sub>	Content of total mercury per mass of FPM in $\text{ng g}^{-1}$ of dry matter
HgFPM <sub>v</sub>	Concentration of total mercury per volume of water in $\text{ng L}^{-1}$
HgCPM <sub>m</sub>	Content of total mercury per mass of CPM in $\text{ng g}^{-1}$ of dry matter
Al <sub>cdb</sub>	Aluminum extracted by the cdb buffer in $\mu\text{mol g}^{-1}$ of dry matter
Fe <sub>cdb</sub>	Iron extracted by the cdb buffer in $\mu\text{mol g}^{-1}$ of dry matter
C	Carbone in % of dry matter
N	Nitrogen in % of dry matter
FPM	Fine particulate matter ( $0.7 < x < 63 \mu\text{m}$ )
CPM	Coarse particulate matter ( $>63 \mu\text{m}$ )
C/N <sub>atom</sub>	Atomic C/N ratios = $(\text{C}/12)/(\text{N}/14)$
Hg/Fe <sub>cdb</sub>	Atomic Hg/Fe <sub>cdb</sub> ratios = $1,000 \times [(\text{Hg}/200.59)/\text{Fe}_{\text{cdb}}]$
Hg/Al <sub>cdb</sub>	Atomic Hg/Al <sub>cdb</sub> ratios = $1,000 \times [(\text{Hg}/200.59)/\text{Al}_{\text{cdb}}]$
Hg/C	Atomic Hg/C ratios = $(\text{Hg}/200.59)/(\text{C}/12)$
Al/(Fe+Al) <sub>cdb</sub>	Atomic Al <sub>cdb</sub> /(Fe <sub>cdb</sub> + Al <sub>cdb</sub> ) ratios

preweighed, we were able to determine Hg content per weight of particulate on the filter (HgFPM<sub>m</sub>) and Hg concentration per volume of water filtered (HgFPM<sub>v</sub>).

For Hg content of the coarse particulate fraction (Hg-CPM), 5–15 mg of dried sample were digested at  $120^\circ\text{C}$  in open glass tubes with a 10 ml mixture of 1:10  $\text{HNO}_3/\text{HCl}$ .

Organic carbon and nitrogen were determined by use of a Carlo-Erba elemental analyzer. The iron and aluminum oxyhydroxides were measured through chemical extraction using a citrate-dithionite-bicarbonate buffer (cdb). The solution extracted by the cdb was then analyzed by atomic absorption for aluminum and iron (Fe<sub>cdb</sub> and Al<sub>cdb</sub>) determination. A list of acronyms used in the text is available in Table 1.

## Results

**Spatiotemporal variations of Hg concentrations in the water column**—Along the Tapajós River, concentrations of FPM and HgFPM<sub>v</sub> decrease when the sedimentation zone is reached (Fig. 3). The decrease continues progressively over the length of the *ria*. These observations correspond to the progressive decantation of fine particles determined by limnological conditions (Roulet et al. 1998a). The seasonal variations of FPM and HgFPM<sub>v</sub> (Fig. 3 and Table 2) show a significant increase during the early rising water period (AM97a). This period corresponds to the beginning of the rainy season (Fig. 2). The low volume of water in the Tapajós River during this period (onset of flooding, water level of +4 m in Santarém) and the increasing flow of water in the basin results in elevated concentration of FPM ( $4\text{--}16 \text{ mg L}^{-1}$ ) and, subsequently, an increased concentration of particulate Hg in the water ( $1.1\text{--}5.7 \text{ ng L}^{-1}$ ). During the rainy season, the volume of water in the river increases and flooding progresses (up to +8 m). At the maximum of the high

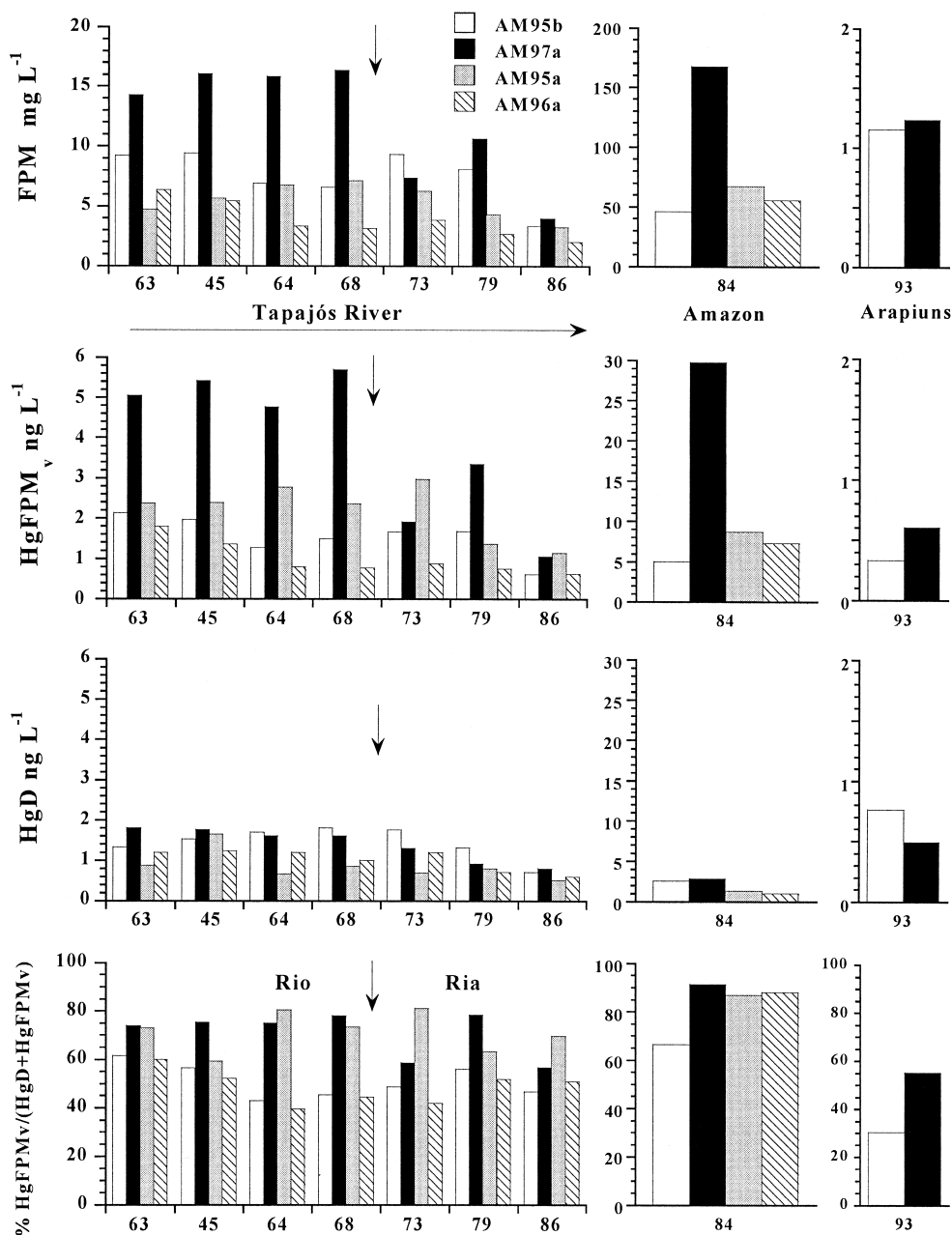


Fig. 3. Spatiotemporal variation in fine particle load and volumetric concentration of Hg in surface waters. The Tapajós stations are in order from upstream to downstream, and the bars in the diagrams are in order from low water to high water. The arrow indicates the location of the sedimentation zone. AM95b, lowest water levels at the end of the dry season; AM97a, onset of heavy rains corresponding to early rising water levels; AM95a, late rising water levels; and AM96a, maximum of high water levels.

water period (AM96a), corresponding to the end of the rainy season, lower particulate concentrations (2–6 mg L<sup>-1</sup>) are followed by decreased concentrations of particulate Hg (0.6–1.8 ng L<sup>-1</sup>). During the dry season (AM95b), although the water level of the river is at its lowest (+3 m) and the current at its slowest, the FPM concentration remains elevated (3–9 mg L<sup>-1</sup>).

The concentrations of FPM are 10–40 times greater in the

Amazon (46–167 mg L<sup>-1</sup>, mixture of white waters from the Andes, and clear and black waters from the principal upstream tributaries) than in the Tapajós (clear water from lowlands; Konhauser et al. 1994). As a result of its elevated particle concentration, water from the Amazon River contains up to 30 ng L<sup>-1</sup> of particulate Hg and is four to seven times more concentrated in Hg than the Tapajós River.

The main tributary of the Tapajós River, the Arapiuns Riv-

Table 2. Mean (SD [range]) quantities of fine particles and concentrations of Hg in waters of the Tapajós, Arapiuns, and Amazon Rivers. Hg partition in water.

	<i>n</i>	FPM (mg L <sup>-1</sup> )	HgFPM <sub>v</sub> (ng L <sup>-1</sup> )	HgD (ng L <sup>-1</sup> )	HgFPM <sub>v</sub> + HgD (ng L <sup>-1</sup> )	% HgFPM <sub>v</sub>
Tapajós						
AM95b: lowest water levels	7	7.2 ± 2.2 (3.4–9.4)	1.5 ± 0.5 (0.6–2.1)	1.2 ± 0.4 (0.7–1.8)	3.0 ± 0.8 (1.3–3.5)	51 ± 7 (43–62)
AM97a: early rising water levels	7	7.5 ± 4.9 (3.9–16.4)	3.9 ± 1.8 (1.0–5.7)	1.4 ± 0.4 (0.8–1.8)	5.3 ± 2.2 (1.8–7.3)	75 ± 9 (57–78)
AM95b: late rising water levels	7	12.1 ± 1.4 (3.3–7.1)	2.2 ± 0.7 (1.1–2.9)	1.4 ± 0.4 (0.5–1.6)	3.1 ± 0.8 (1.6–4.0)	71 ± 8 (59–81)
AM96a: high water levels	7	5.4 ± 1.5 (2.0–6.4)	1.0 ± 0.4 (0.6–1.8)	0.9 ± 0.3 (0.6–1.2)	2.0 ± 0.6 (1.2–3.0)	49 ± 7 (40–60)
Amazon*	4	83 ± 56 (46–167)	12.7 ± 11.5 (5.0–29.7)	1.9 ± 0.9 (1.0–2.8)	15 ± 12 (7.5–32.5)	83 ± 11 (66–91)
Arapiuns†	2	1.19 ± 0.06 (1.15–1.23)	0.5 ± 0.2 (0.3–0.6)	0.6 ± 0.2 (0.5–0.8)	1.1	43 ± 18 (30–55)

\* All periods confounded.

† Calculation with two periods.

er (only sampled during the lowest water level, AM95b, and early rising water, AM97a, periods), is a very clear water river. Here we found the lowest FPM concentrations (1.2–1.3 mg L<sup>-1</sup>) and, in turn, the lowest HgFPM<sub>v</sub> concentrations (0.3–0.6 ng L<sup>-1</sup>).

Compared with HgFPM<sub>v</sub>, HgD showed very little seasonal variation and remained at relatively low concentrations in the lower Tapajós (<1.8 ng L<sup>-1</sup>), Arapiuns (<0.8 ng L<sup>-1</sup>), and Amazon (<2.8 ng L<sup>-1</sup>) rivers (Fig. 3). Consequently, concentrations of fine particulate Hg represent 40%–90% of the total concentration of Hg (HgFPM<sub>v</sub> + HgD) in the water column of the Tapajós and Amazon rivers. The concentration of fine suspended particles, therefore, has a significant influence on the total concentration of Hg in the water column of the Tapajós and Amazon rivers. In the Arapiuns, the role of particles is less important (30%–55%).

Regardless of the season, the FPM concentration seems to control the total amount of Hg measured in the water column (Fig. 4). The Amazon is clearly distinguished from the Tapajós by its high particulate concentration and, consequently, particle-associated Hg. The trends of total Hg concentrations in the Arapiuns are similar to those in the Tapajós. The lowest total Hg concentration measured was found in this very clear Tapajós tributary (HgD + HgFPM<sub>v</sub> = 1.1 ng L<sup>-1</sup>).

*Geochemistry of Hg associated with particulate matter*—Geochemistry of fine particulate matter: A more or less progressive increase in C content of FPM was observed along the length of the Tapajós River (Fig. 5), particularly at the end of the rainy season, during the late increasing and maximum water level periods (AM95a, 4.1%–7.2% and AM96a, 4.1%–8.7% respectively). The FPM of the *ria* are richer in C than those of the *rio*, without a corresponding variation in C/N<sub>atom</sub>. As was noted for C, the highest Fe<sub>cdB</sub> and Al<sub>cdB</sub> contents were also observed during late rising water and maximum water levels (510–790 μmol g<sup>-1</sup> and 220–650 μmol g<sup>-1</sup>, respectively). An increase in Al<sub>cdB</sub> along the *ria* was clearly observed when the maximum water level was attained. For other seasons, a tendency toward higher values, beginning in the middle of the *ria*, was observed. The spatial variation in Fe<sub>cdB</sub> contents is less significant than in the case of Al<sub>cdB</sub>. The Al<sub>cdB</sub> and Fe<sub>cdB</sub> concentrations in FPM show a significant covariation with C concentrations along the length of the Tapajós (Fig. 6).

The temporal variations in HgFPM<sub>m</sub> are different from those observed for C, Al<sub>cdB</sub>, and Fe<sub>cdB</sub>. For each season, the amplitude of the variation in HgFPM<sub>m</sub> contents is low (ΔHg is within 61–122 ng g<sup>-1</sup>). The highest Hg contents were observed during early rising water levels (AM97a, 237–299 ng g<sup>-1</sup>) and during the late rising water levels (AM95a, 303–425 ng g<sup>-1</sup>). The lowest Hg contents were measured during low water levels (AM95b, 167–237 ng g<sup>-1</sup>). No spatial variation in HgFPM<sub>m</sub> contents was evident along this section of the Tapajós.

The FPM from the Amazon is poor in C (0.5–1.6%), Fe<sub>cdB</sub> (270–390 μmol g<sup>-1</sup>) and Al<sub>cdB</sub> (<130 μmol g<sup>-1</sup>), compared with that of the Tapajós. The seasonal variation in Fe<sub>cdB</sub> contents is negligible. As was noted for C, Al<sub>cdB</sub>, and Fe<sub>cdB</sub>, the Hg contents of FPM (HgFPM<sub>m</sub>) measured in the Amazon

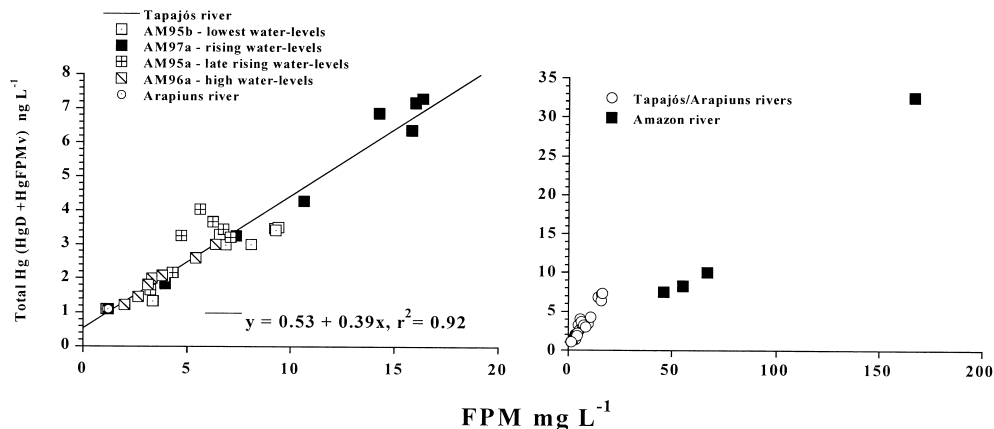


Fig. 4. Relationship between total concentration of Hg (dissolved + fine particulate) and the quantity of fine particles in surface waters.

(<190 ng g<sup>-1</sup>) are the lowest and show little seasonal variation.

The FPM of the Arapiuns is richer in C (21.1%–26.1%), Fe<sub>cdB</sub> (750–890 μmol g<sup>-1</sup>), and Al<sub>cdB</sub> (690–1700 μmol g<sup>-1</sup>) than the Tapajós. HgFPM<sub>m</sub> levels were among the highest (288–457 ng g<sup>-1</sup>) but are of the same order of magnitude as those of the Tapajós.

The affinity of a given compound for the particulate phase is described by the distribution coefficient,  $K_d$ , defined as:  $K_d = C_p/C_f$ , where  $C_p$  is the particulate Hg content (Hg-FPM<sub>m</sub>) in ng kg<sup>-1</sup> and  $C_f$  is the HgD in ng L<sup>-1</sup>. Higher  $K_d$ s suggest a stronger affinity for the particulate phase. In the water of the rivers, log  $K_d$ s for Hg range from 4.6 to 5.9. The lowest  $K_d$  values were calculated for the Amazon River (mean 4.9) and the highest for the Arapiuns River (mean 5.5). Regressions of log  $K_d$  against log values of FPM concentrations and C, Al<sub>cdB</sub>, and Fe<sub>cdB</sub> contents are shown in Fig. 7. These values correspond to other studies in the St. Lawrence River (mean 5.5; Quémerais et al. 1998) and in Wisconsin rivers (mean 4.9; Babiarez et al. 1998). A negative regression with FPM suggests a greater affinity of suspended particulate matter for Hg at low particle concentrations. This could also be due to the influence of the “particle concentration effect,” according to which the concentration of colloids in the filter-passing fraction increases as concentrations of particulate matter increase (Benoit et al. 1994). Positive regressions are noted for C, Fe<sub>cdB</sub>, and Al<sub>cdB</sub>, indicating that an increase of their contents increases the affinity of particles for Hg in the water column.

Geochemistry of the coarse particulate matter: All of the samples of CPM were sorted in the field into four classes: zooplankton, phytoplankton, organomineral material, and an organomineral/plankton mix. The averages calculated for these four classes are presented in Table 3. The C/N<sub>atom</sub> of the zooplankton (<5.8) clearly distinguishes this fraction from the other C sources. The phytoplankton is less easily distinguished from the others by C/N<sub>atom</sub>. In the Tapajós, it is always <9, permitting its distinction from coarse plant debris and the fine terrigenous mineral fraction. In the Arapiuns, two types of phytoplankton were identified and cor-

respond to different C and C/N<sub>atom</sub> values, thereby explaining the considerable variation observed for these two parameters. The presence of phytoplankton in the Arapiuns River, with C/N<sub>atom</sub> ratios as high as 14, hinders the use of this parameter for interpreting sources of organic matter associated with particles. In all cases, phytoplankton was found to contain very little Hg, Fe<sub>cdB</sub>, and Al<sub>cdB</sub>.

Along the Tapajós, there is a transition from a lotic system (*rio*), with a current capable of transporting coarse material such as quartz, organic materials, plant debris, and clay clusters, to a lentic system (*ria*), with a very weak current, little turbidity, and essentially biological coarse material consisting of zooplankton and phytoplankton (Irion 1984; Roulet et al. 1998a). These changes are particularly well illustrated by C/N<sub>atom</sub>, C (CCPM), and HgCPM contents of the CPM (Fig. 8). The water upstream from Aveiro contains CPM characterized by higher C/N<sub>atom</sub> levels, C contents of ~10%–20%, and elevated levels of Hg (200–500 ng g<sup>-1</sup>). In the *ria*, distinctly lower C/N<sub>atom</sub> ratios (<7) accompanying elevated C concentrations (35%–45%) indicate the presence of plankton. The CPM yields the lowest Hg contents (50–200 ng g<sup>-1</sup>).

During the lowest water level and the maximum water level periods, it is important to note the presence of plankton in the transition zone upstream from Aveiro, as indicated by the progressive increase of C levels accompanied by a decrease in those of C/N<sub>atom</sub> and Hg. The presence of plankton in the *rio* is probably related to the weaker current and the lower turbidity; both conditions ecologically favourable for the development of plankton observed during low water and at highest water level periods. During the other periods, the CPM is essentially made up of allochthonous organomineral material (C/N<sub>atom</sub> > 11). In the Arapiuns, elevated C levels with low Hg, Fe<sub>cdB</sub>, and Al<sub>cdB</sub> contents indicate, as in the Tapajós *ria*, the presence of plankton. This plankton is principally composed of phytoplankton.

In the Amazon River, the seasonal variations in the Hg and C contents of the CPM are greater than those of the Tapajós River. Higher levels of C (18.7%) and Hg (900 ng g<sup>-1</sup>) of the CPM were measured during the early rising water period (AM97a). During this period, CPM was found to con-

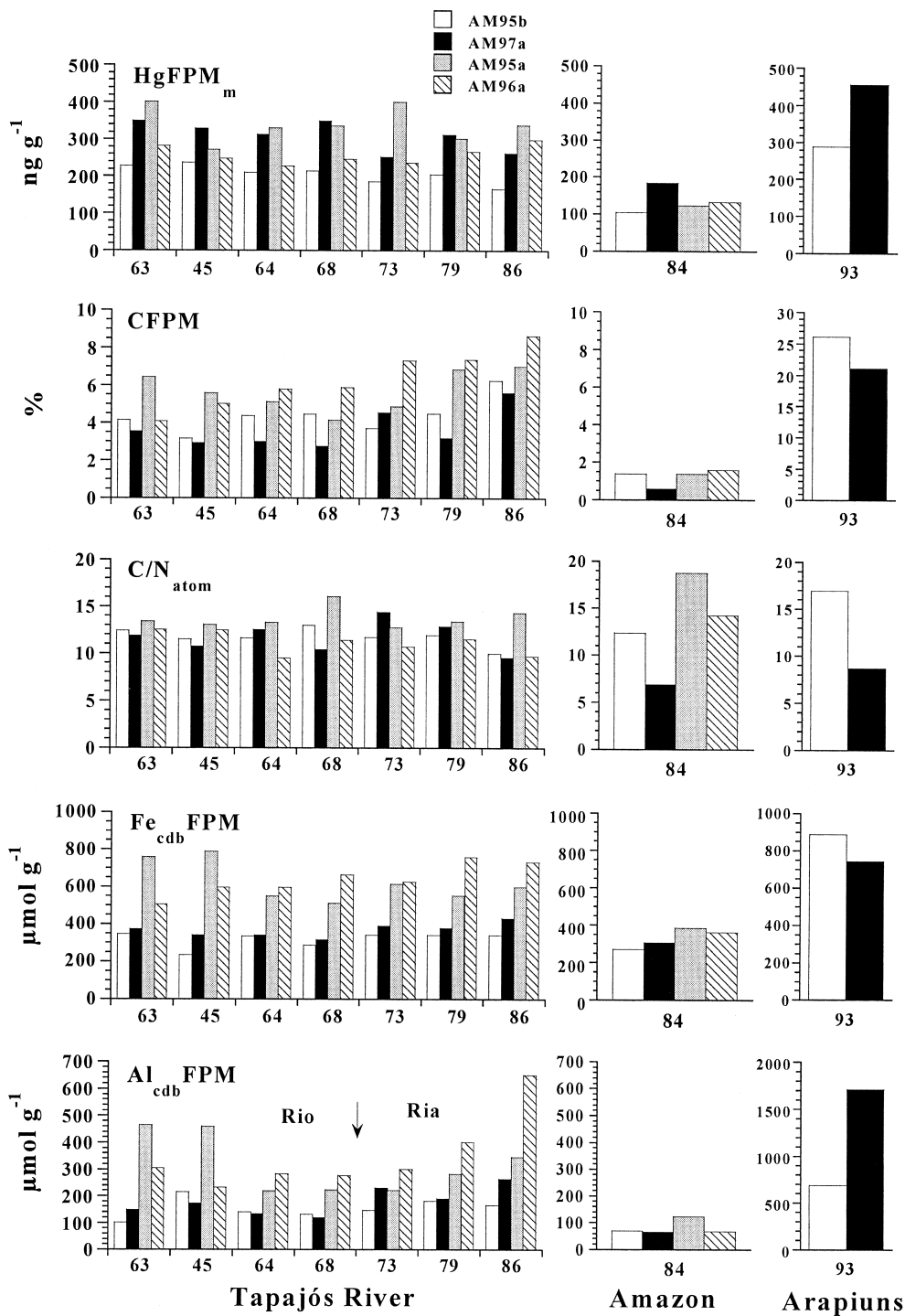


Fig. 5. Spatiotemporal variation in concentrations (per weight basis) of Hg, C, Fe<sub>cdb</sub>, Al<sub>cdb</sub>, and C/N<sub>atom</sub> in fine particles. AM95b, lowest water levels at the end of the dry season; AM97a, onset of heavy rains corresponding to early rising water levels; AM95a, late rising water levels; and AM96a, maximum of high water levels.

tain 27 times more C and 20 times more Hg than CPM sampled at low water, the latter being very low in Hg (46 ng g<sup>-1</sup>) and C (0.7%). Elevated C/N<sub>atom</sub> (>20) indicates that the high C content of the CPM is not related to the presence of organic matter of planktonic origin but may be attributed

to the presence of humus from surface soils (Hedges et al. 1986). The Hg contents of CPM appear elevated in relation to those of oxyhydroxides and seem to correlate to C content (regression:  $y = 32.2 + 47.4x$ ,  $r^2 = 0.95$ ,  $P < 0.001$ ,  $n = 4$ ) without any accompanying Al<sub>cdb</sub> or Fe<sub>cdb</sub> enrichment. The

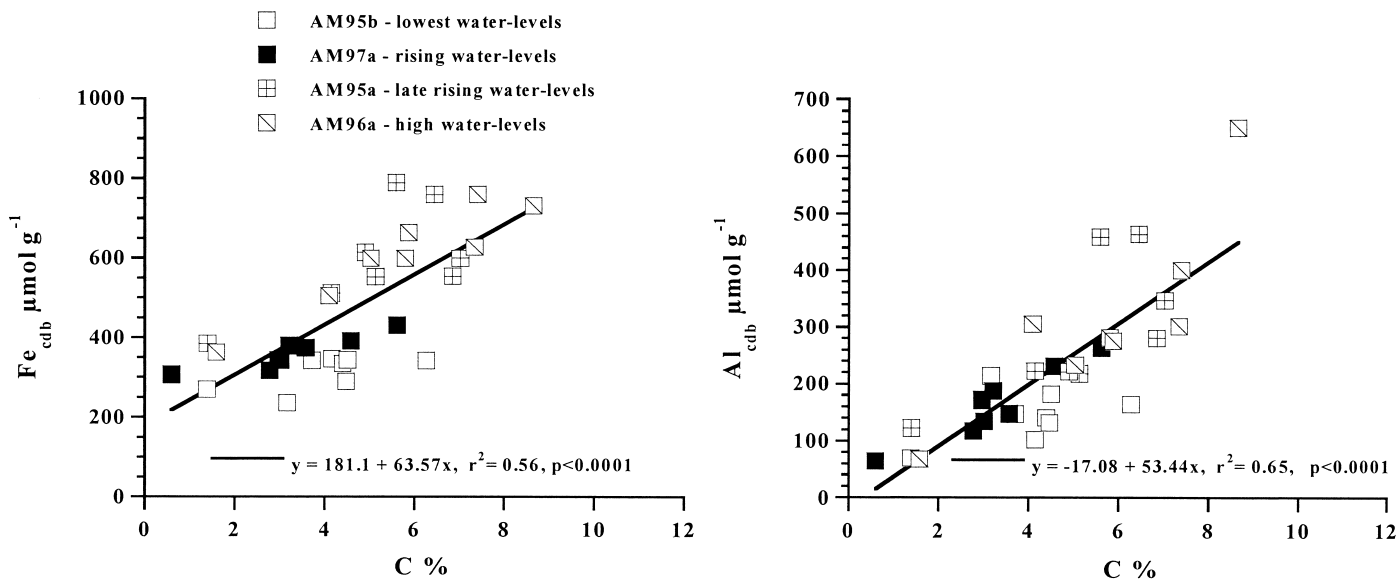


Fig. 6. Relationship between concentrations (per weight basis) of  $\text{Fe}_{\text{cdb}}$ ,  $\text{Al}_{\text{cdb}}$ , and C in fine particles (FPM).

low number of samples ( $n = 4$ ), however, makes a clear conclusion difficult.

## Discussion

*Apparent controls on Hg levels in the rivers*—In river systems, Hg concentrations are controlled by a number of complex reactions and transport processes within the watershed (Hurley et al. 1995). Natural Hg levels in river waters vary by water type, and the behavior of the metal, which,

once discharged, may vary greatly depending on the quantity and quality of particulate, colloidal, and dissolved matter (Babiarz et al. 1998). In the Tapajós and Amazon rivers, data show that Hg in the water column is primarily associated with suspended particles, suggesting that factors controlling the transport of suspended material also control concentrations of Hg in water. Total concentrations of Hg in water increase during rising water periods principally because FPM concentrations increase. This increase corresponds to high precipitation with a small volume of water in the river

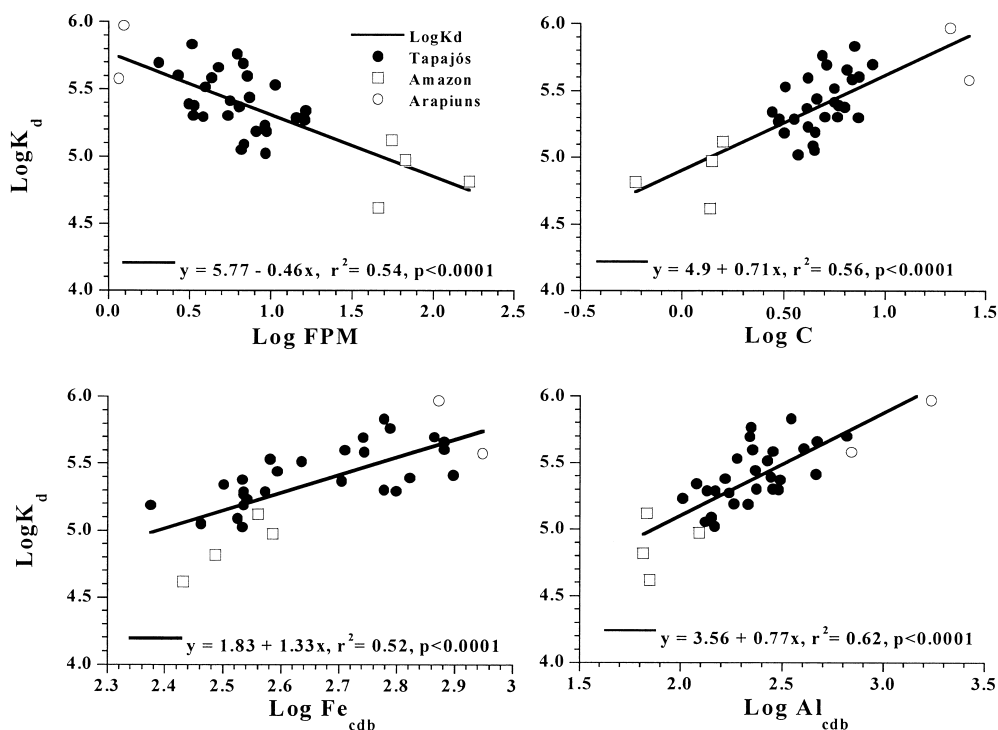


Fig. 7. Relationship between  $\log K_d$  for Hg and the log values of FPM,  $\text{Fe}_{\text{cdb}}$ , and  $\text{Al}_{\text{cdb}}$ .

Table 3. Mean values (SD [range]) of the different geochemical parameters in fine and coarse particles from the Tapajós, Arapiuns, and Amazon Rivers.

	<i>n</i>	Hg (ng g <sup>-1</sup> )	C (%)	N (%)	Atomic C/N	Fe <sub>carb</sub> (μmol g <sup>-1</sup> )	Al <sub>carb</sub> (μmol g <sup>-1</sup> )
FPM							
Tapajós river	28	285 ± 68 (167–425)	5.0 ± 1.5 (2.8–8.7)	0.5 ± 0.2 (0.3–1.0)	12.1 ± 1.6 (9.5–16.1)	489 ± 164 (247–790)	250 ± 124 (102–651)
Arapiuns river*	2	373 ± 120 (288–457)	23.6 ± 3.6 (16.1–21.1)	2.3 ± 0.7 (1.8–2.8)	12.8 ± 5.8 (8.7–16.9)	815 ± 101 (744–887)	1,201 ± 724 (689–1713)
Amazon river	4	136 ± 34 (105–184)	1.2 ± 0.4 (0.6–1.6)	0.11 ± 0.02 (0.09–0.13)	13.1 ± 4.9 (6.9–18.8)	331 ± 52 (270–385)	82 ± 28 (65–123)
CPM							
Phytoplankton							
Tapajós river	4	70 ± 30 (38–116)	42.2 ± 3.4 (38.6–45.7)	7.2 ± 1.6 (5.2–8.6)	6.7 ± 1.1 (6.2–8.7)	57 ± 44 (7–89)	17 ± 11 (10–32)
Arapiuns river*	7	54 ± 11 (38–66)	37.1 ± 5.7 (28.7–43.9)	4.4 ± 2.4 (2.7–9.1)	10.2 ± 2.9 (5.6–14.7)	55 ± 12 (41–65)	41 ± 8 (35–46)
Zooplankton							
Tapajós river	14	142 ± 29 (83–194)	43.9 ± 2.5 (38.9–46.1)	9.9 ± 1.3 (7.8–11.9)	5.2 ± 0.4 (4.5–5.8)	50 ± 29 (20–89)	32 ± 25 (4–63)
Organomineral							
Tapajós river	16	351 ± 91 (209–534)	17.9 ± 4.3 (10.6–26.1)	1.8 ± 0.7 (0.7–3.3)	12.9 ± 3.8 (7.1–18.4)	342 ± 103 (243–532)	52 ± 22 (21–111)
Amazon river	7	450 ± 321 (48–921)	10.2 ± 6.6 (0.7–18.7)	0.8 ± 0.6 (0.05–2.1)	19.0 ± 5.8 (11.8–25.8)	240 ± 77 (110–312)	24 ± 7 (13–30)
Mixture							
Tapajós river	6	213 ± 84 (141–375)	27.6 ± 5.3 (21.3–33.7)	4.2 ± 1.2 (2.3–5.2)	8.0 ± 1.7 (6.5–10.9)	210 ± 80 (118–258)	80 ± 69 (32–128)
SOLS†							
Humus (litter and organic horizon)	69	115 ± 42 (58–236)	37.1 ± 11.7 (11–51.4)	1.9 ± 0.6 (0.6–3.3)	23.0 ± 4.7 (15.1–36.9)	80 ± 52 (20–188)	54 ± 29 (15–145)
Fine fraction <63 μ (mineral horizons)	20	176–360	1.0–9.6	0.05–0.56	13.5–22.4	250–620	87–292

\* Mean of only two periods.

† After Roulet et al. (1998a).

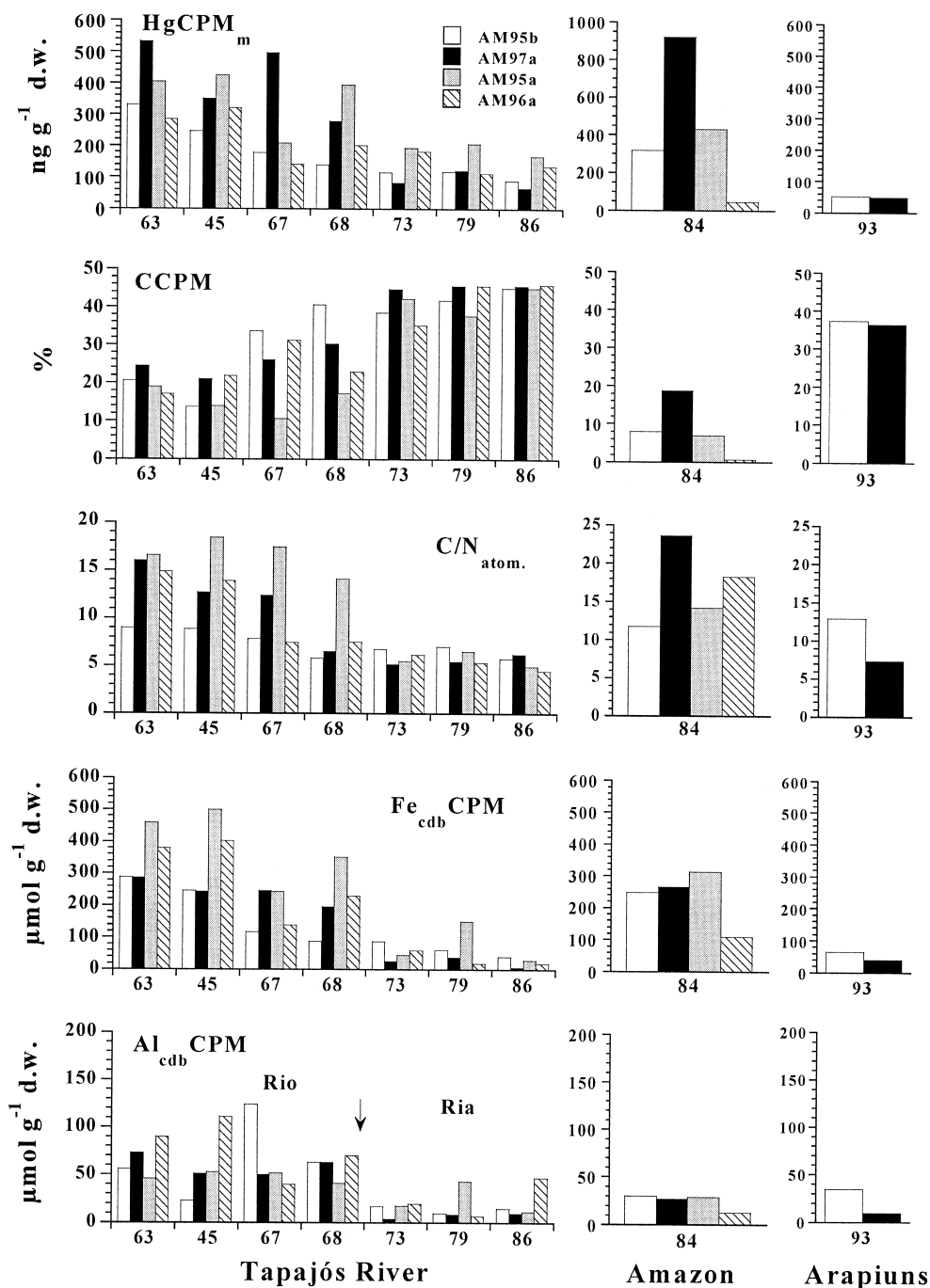


Fig. 8. Spatiotemporal variation of concentrations (per weight basis) of Hg, C, Fe<sub>cdb</sub>, Al<sub>cdb</sub>, and C/N<sub>atom</sub> in CPM. AM95b, lowest water levels at the end of the dry season; AM97a, onset of heavy rains corresponding to early rising water levels; AM95a, late rising water levels; and AM96a, maximum of high water levels.

at the beginning of the rainy season. The concentration of fine mineral particles diminishes during the period of flooding (increasing water level) and when the maximum water level is attained. The elevated precipitation and hence river volume results in a dilution effect relative to the concentration of particles in the water column. The correlation of total Hg with particulate matter concentrations in rivers has also been documented by Babiarez and Andren (1995) and Ba-

biarez et al. (1998) for several rivers in Wisconsin and by Balogh et al. (1997, 1998) for the Minnesota and Mississippi rivers in the United States.

The partition of Hg in the water column and the particle enrichment of Hg seem to be influenced by the specific geochemistry and the nature of the association with organic matter and oxyhydroxides. The cdb buffer extracts, for the most part, all nonsiliceous forms of Fe, the amorphous forms of

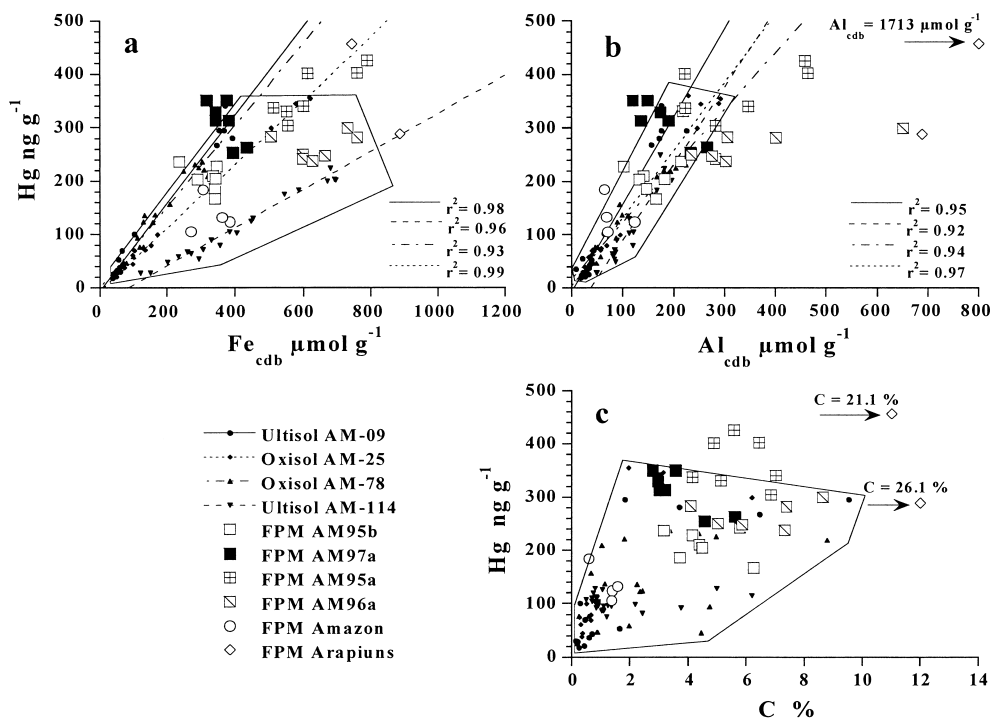


Fig. 9. Relationship between concentrations (per weight basis) of Hg,  $\text{Fe}_{\text{cdb}}$ ,  $\text{Al}_{\text{cdb}}$ , and C in FPM of the Tapajós River. Note: Soil data from Roulet et al. (1998a). The coarse and fine fractions of each soil are not differentiated.

Al, as well as Fe and Al complexed by organic matter (Parfitt and Childs 1988; Ross and Wang 1993). Crystallized and amorphous Fe and Al have a tremendous complexation capacity for organic matter and most notably for large, hydrophobic organic molecules that constitute colloidal organic matter (Jonsson 1997). In central Amazonia, organic colloidal matter transports an important part of Fe and Al and other metals in dissolved fractions ( $<0.45 \mu\text{m}$ ) (Eyrolle et al. 1996) and coagulated with mineral particles (Chauvel et al. 1996). In the Tapajós River,  $\text{Fe}_{\text{cdb}}$  and  $\text{Al}_{\text{cdb}}$  contents of FPM are related to the C content (Fig. 6). Oxyhydroxides have been shown to be responsible for the adsorption of Hg in the mineral horizon of the Tapajós basin soils (Roulet et al. 1998b). This suggests that in particulate material, oxyhydroxides are the principal adsorbents of Hg as for other trace metals (Gibbs 1977). Hg contents do not directly parallel  $\text{Fe}_{\text{cdb}}$ ,  $\text{Al}_{\text{cdb}}$ , and C contents in FPM, but an increase of the latter seems to increase the affinity of FPM for the Hg in the water column. Hg geochemistry of particles seems to be more influenced by Fe and Al contents in particles than by organic matter (Fig. 9). This behavior could be explained by a surface complexation model of Hg within the mineral particulate matter, not only with oxyhydroxides but also with the organic colloidal phase (Quémerais et al. 1998).

The increase of C contents of FPM along the *ria* is inconsistent with an enrichment in autochthonous organic debris. The  $\text{C}/\text{N}_{\text{atom}}$  values are stable and the elevated  $\text{Fe}_{\text{cdb}}$ ,  $\text{Al}_{\text{cdb}}$ , and Hg contents do not suggest the presence of fine plankton debris. Since the cdb effectively extracts Al associated with organic matter (Parfitts and Childs 1988), the higher concentrations of  $\text{Al}_{\text{cdb}}$  and C in FPM at the end of

the rainy season, particularly in the *ria*, can be explained by an increase in colloidal C coagulation in the lentic systems, favored by a longer residence time of allochthonous mineral matter (Chauvel et al. 1996). This process may influence the particle sorption of Hg, but it does not result in significant Hg enrichment of the FPM from the Tapajós River, where the contribution of C remains relatively low ( $<9\%$ ). It would explain the geochemistry of the FPM from the Arapiuns, with high C ( $>20\%$ ) and  $\text{Al}_{\text{cdb}}$  ( $>800 \mu\text{mol g}^{-1}$ ) contents. The elevated Hg content of FPM in the Arapiuns compared to those in the Tapajós could be the result of the affinity of this organic matter for Hg and Al.

*Sources of the river-borne Hg*—Normalization and comparison with soil and sediment (evidence from relationships with Fe, Al, and C): If soil erosion is the assumed source of particulate matter in the Tapajós River, one would expect similar or lower contents of Hg in particles, compared with soils. In the soils of the lower Tapajós basin, a relationship between the levels of Hg and  $\text{Fe}_{\text{cdb}}$  and especially  $\text{Al}_{\text{cdb}}$  has been documented (Roulet et al. 1998b).  $\text{Fe}_{\text{cdb}}$  and  $\text{Al}_{\text{cdb}}$  can be used to normalize and trace Hg coming from the erosion of the soil particles in the drainage basin of the Tapajós River. Figure 9a,b illustrates the association between Hg,  $\text{Fe}_{\text{cdb}}$ , and  $\text{Al}_{\text{cdb}}$  in FPM in comparison with that previously obtained from the granulometric fraction of different soils from the Tapajós basin (Roulet et al. 1998b). Variations in the relationship between Hg and  $\text{Fe}_{\text{cdb}}$  contents among soils are linked to the importance of  $\text{Al}_{\text{cdb}}$  in the apparent sorption of Hg by Fe oxyhydroxides.  $\text{Hg}/\text{Fe}_{\text{cdb}}$  ratios show a positive

Table 4. Atomic Hg/Fe<sub>cdB</sub>, Hg/Al<sub>cdB</sub>, and Hg/C ratios (range) in FPM, CPM, soils, and sediments from the lower Tapajós Valley.

Compartment	Hg/Fe <sub>cdB</sub> × 10 <sup>6</sup>	Hg/Al <sub>cdB</sub> × 10 <sup>6</sup>	Hg/C × 10	Al/(Fe + Al) <sub>cdB</sub>
<i>Soils</i>				
Mean mineral horizon*				
Ultisol AM-09	3.22 (2.11–4.75)	6.73 (4.51–10.79)	49.9 (15–204)	0.32 (0.25–0.37)
Ultisol AM-114	1.40 (1.11–1.96)	8.89 (5.03–13.81)	64.3 (14.6–128)	0.14 (0.06–0.20)
Oxisol AM-25	3.50 (2.78–5.21)	7.09 (5.22–10.49)	81.5 (33.7–196)	0.34 (0.32–0.36)
Oxisol AM-78	3.75 (3.31–4.11)	6.01 (4.64–8.76)	51.9 (11.4–148)	0.39 (0.31–0.47)
Organic horizons	4.6–8.9	5.9–34.5	1.9–7.9	0.30–0.48
<i>Sediments</i>				
Tapajós	2.54 (0.79–9.12)	9.9 (3.45–27.72)	28.9 (9.1–59.8)	0.21 (0.13–0.34)
Arapuans AM-94	1.58 (1.06–1.78)	4.62 (3.44–5.02)	14.2 (1.7–16.4)	0.25 (0.22–0.27)
Amazon AM-102	2.14 (0.69–4.29)	15.31 (5.79–26.12)	24.9 (16.3–45.4)	0.12 (0.08–0.25)
<i>Suspended particles</i>				
<i>FPM</i>				
Mean Tapajós	3.14 (1.85–5.52)	6.67 (2.29–14.71)	37.5 (15.9–75.8)	0.33 (0.23–0.47)
AM95b: lowest water levels	3.28 (2.43–4.99)	6.95 (5.05–11.13)	29.5 (15.9–44.7)	0.23 (0.23–0.47)
AM97a: rising water levels	4.27 (3.04–5.52)	9.47 (4.96–14.71)	54.8 (28.1–75.8)	0.32 (0.27–0.38)
AM95b: late rising water levels	2.92 (2.64–3.28)	6.19 (4.32–9.06)	39.2 (26.5–49.1)	0.33 (0.26–0.37)
AM96a: high water levels	2.07 (1.85–2.78)	4.05 (2.29–4.98)	26.3 (19.4–41.3)	0.34 (0.28–0.47)
Mean Arapuians	2.34 (1.62–3.06)	1.71 (1.33–2.08)	9.8 (6.6–12.9)	0.57 (0.43–0.70)
Mean Amazon	2.08 (1.60–2.99)	9.06 (5.01–14.11)	83.6 (45.5–186.6)	0.19 (0.16–0.24)
<i>CPM†</i>				
Mean Tapajós	5.66 (3.97–10.09)	39.9 (14.42–75.97)	11.9 (8.76–18.1)	0.14 (0.05–0.22)
AM95b: lowest water levels	5.13 (4.29–5.73)	48.80 (29.97–75.97)	10.8 (9.6–14.3)	0.11 (0.05–0.16)
AM97a: rising water levels	8.85 (7.18–10.09)	40.04 (34.21–49.45)	11.5 (9.9–13.0)	0.18 (0.17–0.20)
AM95b: late rising water levels	4.52 (4.13–5.58)	37.79 (20.64–47.90)	14.6 (11.8–18.1)	0.09 (0.091–0.096)
AM96a: high water levels	3.97	14.42	9.36	0.22
Mean Amazon	6.66 (6.4–6.9)	63.72 (53.01–74.44)	32.9 (23.9–41.8)	0.10 (0.09–0.11)

\* Mineral horizons.

† Organomineral matter, as defined in the text.

and linear relationship with Al/(Fe+Al)<sub>cdB</sub> in these soils (Roulet et al. 1998b).

The FPM relationships, Hg versus Fe<sub>cdB</sub> and Al<sub>cdB</sub> show greater variations than in the soils and present different seasonal patterns. Most of the FPM data plots within the same region as that defined by the fine Hg-rich soil fractions (upper part of the curve defined by soil fraction data in Fig. 9a,b; see also Table 3). As was noted for the soils (Roulet et al. 1998a), no relationship was observed between Hg and C in the Tapajós FPM (Fig. 9c). Mean Hg/Al<sub>cdB</sub>, Hg/Fe<sub>cdB</sub>, Hg/C, and Al/(Fe+Al)<sub>cdB</sub> atomic ratios are compiled in Table 4, together with the ratios obtained for soils and sediments (Roulet et al. 1998a, 2000a). Soils and FPM have similar Hg contents in relation to oxyhydroxides. Bottom sediments have lower Hg/Fe<sub>cdB</sub> ratios and lower Al/(Fe+Al)<sub>cdB</sub> ratios than soils and FPM. This may illustrate a loss of Hg due to geochemical processes that occur between particle transport and early diagenesis at the bottom of lakes (Roulet et al. 2000a).

Coarse organomineral matter in suspension (CPM, having no plankton) has higher contents of C and Hg (12%–20% and 300–550 ng g<sup>-1</sup>) and Fe<sub>cdB</sub> and Al<sub>cdB</sub> contents that are lower than those of fine soil matter and FPM (Table 3). Hg/Al<sub>cdB</sub>, Hg/Fe<sub>cdB</sub>, and Hg/C atomic ratios of the CPM show intermediate values between mineral and organic soil horizons (Table 4). Some of the C/N<sub>atom</sub> are too low to exclusively indicate freshly degraded soil organic material (hu-

mus, Table 3). Coagulation of colloidal organic matter on particle surfaces could explain the higher C and Hg concentrations. A similar observation was made for the FPM of the Arapuians, but the relatively low levels of Fe<sub>cdB</sub> and Al<sub>cdB</sub> compared with C are not entirely compatible with this hypothesis. The presence of plankton debris cannot be completely excluded but, as indicated by the C/N<sub>atom</sub> ratios, it does not appear to dominate the quantity of organic matter. The enrichment of C in coarse particles from the Tapajós, as compared with the fine ones, is likely the result of a mixing of the first two sources of organic matter with a certain affinity for Hg. Coagulation of colloids increases the size of suspended organomineral particles (Milligan and Loring 1997) and terrestrial plant debris is generally associated with this fraction in Amazonian rivers (Hedges et al. 1986).

Effect of land use and land cover on Hg transport processes: Far from point sources, watershed export processes can control the release of atmospherically, geologically, and land use-derived Hg to a river system. Revolatilization, sorption, and leaching through soils are key mechanisms in rivers. The watershed type can exert a strong influence on Hg transport. For instance, in agriculturally dominated watersheds, Hg is mainly associated with particulate phases, whereas in wetland-dominated watersheds filtered phases dominate (Hurley et al. 1995; Babiarsz et al. 1998; Balogh et al. 1998). In natural undisturbed watersheds, increases in

particulate matter can be observed during the rising water because of channel down-cutting. In rivers, turbulence due to wind action or dredging results in resuspension of bottom sediments and can be an important source of Hg. In colonized areas, point source discharges of particulate matter must also be considered to fully understand the seasonal cycling of Hg.

In the upper Tapajós basin, gold-mining activities have considerably decreased since 1990–1992. Colonization and slash and burn for establishing new agricultural land have continued in the lower part and elsewhere along trans-Amazonian routes (Walker et al. 1997). The direct environmental impacts of these human activities are deforestation and river siltation.

Gold miners require abundant water supplies to operate. Those working on the river resuspend tons of sediment daily, and primary gold mining introduces comparable amounts of soil into nearby streams. Although affecting smaller areas, gold mines are probably more intense soil erosion factors than deforestation for agriculture. In the Amapá State, Guimarães et al. (1999) and Fostier et al. (2000) observed an increased transport of Hg due to erosion caused by mining activities on the soil. Mining is responsible for increased transport of particulate matter to the water column and results in an increased concentration and sedimentation of FPM enriched in oxyhydroxides and Hg in flood-plain lakes (Guimarães et al. 1999). In the Tapajós basin, some small clear-water tributaries acquired the aspect of typical white-water rivers after the onset of gold-mining activities. K. Telmer et al. (unpubl.) have recently confirmed that the Hg contamination in the Crepuri River, a medium-sized, clear-water tributary of the Tapajós supporting important gold-mining activities, is dominantly caused by the enhanced physical erosion of mining operations and not directly by new discharges of anthropogenic Hg. The confluence of the Crepuri River with the Tapajós River is located in the upper part of the river, 250 km upstream from Itaituba (Fig. 1). Downriver, Roulet et al. (1998b) have also observed that small tributaries without gold-mining activities can contain greater quantities of Hg in the water than the Tapajós River. In these rivers, a stronger concentration of particles is due to increased erosion following deforestation for agriculture. For example, the Tapajós River has undergone a radical change in its transparency during the last three decades of intense colonization (Roulet et al. 2000a). Analyses of sediment cores from floodplain lakes and the *ria* of the Tapajós River show an increase of Hg concentration in recent sediments. This increase is the result of a relative enrichment of the sedimentary deposit in fine particulate matter rich in aluminosilicates, oxyhydroxides, and Hg, coming from the soil and transported by the river (Roulet et al. 2000a). The source of the increase in fine particulate Hg is mainly the erosion of deforested natural soils in this part of the drainage basin. The increase coincides with the important colonization of the basin since the 1960s.

*Previously reported levels and other nonpolluted systems*—The results presented here for four different periods of the year confirm previously reported data for the Tapajós (Roulet et al. 1998a). Furthermore, these data, as do data for

the Madeira River (Lechler et al. 2000; Maurice-Bourgoin et al. 2000) and the Negro River (Fadini and Jardim in press; Maurice-Bourgoin et al. in press), indicate that the Hg concentrations first reported for Amazonian waters (*see* Pfeiffer et al. 1989, 1991 in Table 5) were overestimated as a result of contamination during sampling or sample manipulation. The Hg concentrations in river waters are in the region of  $\text{ng L}^{-1}$ . The HgD concentrations in Amazonian rivers are of the same order of magnitude as those generally measured in other rivers not affected by point source pollution.

Recent data on Hg geochemistry in Amazonian waters are consistent with the division of water type into white-, clear-, and black-water rivers (Table 5). The contents of Hg and C in particles from the Amazon white waters are lower than clear waters like those from the Tapajós River, probably as a result of dilution by other abundant mineral elements coming from the Andean portion of the drainage basin (Irion 1984; Konhauser et al. 1994). Particulate matter in the Amazon River is generally fine-grained marine and volcanic rock fragments from the Andes, silt and clay from the intensely weathered low lands, and organic particulates (Richey et al. 1986). In the Madeira River, high concentrations of Hg in water can be explained by the high particulate concentration in this white-water river (similar to what was noted for the Amazon River). Hg contents of particles in white waters are lower than those in the other water types, but Hg concentrations are high because of elevated particulate concentrations in the water. Black waters seem to show high Hg content and concentrations in particulate matter because of the importance of coagulation of colloidal organic matter (Maurice-Bourgoin et al. in press) and results from the intense podzolization of the soil cover in the Negro River basin (Roulet et al. 1998b; Zeidemann 1998).

In Amazonian rivers, higher Hg concentrations in water were noted in disturbed watersheds where anthropogenic perturbations (colonization, mining, slash and burn agriculture, and highways) increase erosion and transport of particles to aquatic ecosystems (Guimaraes et al. 1999; K. Telmer et al. unpubl.; Fostier et al. 2000; Maurice-Bourgoin et al. 2000). This is also the case for Hg concentrations in the water column from watersheds colonized and exploited for many decades in North America (e.g., those of Wisconsin and Minnesota rivers). In these rivers, Hg is controlled by the high supply of eroded particles from agricultural land and Hg contents of particles are also similar to soil Hg contents from the watershed (Hurley et al. 1995; Balogh et al. 1997, 1998). However, Hg contents in the soils from these river basins are strongly influenced by anthropogenic Hg coming from industrial and domestic sources that have released Hg within the Northern hemisphere since the industrial revolution (Jackson 1997).

## Conclusions

In the water of lower Tapajós River, Hg is associated with suspended particles rather than occurring in dissolved form. The Hg enrichment in the particles is similar to the soils of the basin where Hg is primarily of natural origin (Roulet et al. 1999). The study shows that the dominant stock of Hg

Table 5. Mercury concentrations in river waters.

Locations	Unfiltered or total Hg (ng L <sup>-1</sup> )	Dissolved or filtered Hg (ng L <sup>-1</sup> )	Particulate Hg		Notes and comments	References
			ng L <sup>-1</sup>	ng g <sup>-1</sup> d.w.		
Worldwide background in rivers	0.1–3.5					Nriagu (1990); Mason et al. (1994)
Whitewater rivers						
Solimões River, Amazonas, Brazil	5.97		45–140		Amazon River upstream its confluence with Negro River	Maurice-Bourguoin et al. (1999b)
Madeira River and tributaries	<100–8,600				From Bolivian border to Porto Velho, gold mining area	Pfeiffer et al. (1989)
Madeira River	200–5,100				From Bolivian border to Porto Velho, gold mining area	Pfeiffer et al. (1991)
Madeira River, Rond./Amaz, Brazil	1.2–20*	0.3–8.0			From Porto Velho to the confluence with Amazon river	Lechler et al. (2000)
Madeira River, Amazonas, Brazil	7.0–10.9	5.5–10.4	0.4–1.3	10–210	Amazon plain to its confluence with the Amazon River transect	Maurice-Bourguoin et al. (2000)
Madeira River, Amazonas, Brazil	19–33*	10–17	6–18			Nriagu et al. (1992)
Amazon River, Pará, Brazil	7.5–32.5	1.0–2.8	5.0–29.7	105–184‡	Upstream from the Tapajós river confluence	This study
Clear-water rivers						
Tapajós River, Pará, Brazil	1.8–7.3	0.5–1.8	0.6–5.7	167–425‡	350-km transect beginning 50 km from gold mines, partly deforested catchment	Roulet et al. (1998b) and this study
Tributaries of the Tapajós river	0.8–13.6	0.5–2.8	0.3–12.8	154–355‡	Without goldmining activities, partly deforested catchment	Roulet et al. (1998b) and this study
Crepuri River, Pará, Brazil			42	78§	Tapajós tributary with important goldmining activities	Telmer et al. (1999)
Tapajós River, Pará, Brazil			6.5	217§	Tapajós River downstream the confluence of the Crepuri	Telmer et al. (1999)
Small forest stream, Amapá, Brazil	2.6*				Undistributed forest catchment, 100 km remote from gold mines	Fostier et al. (2000)
Small forest stream, Amapá, Brazil	8.5*				Deforested area: mines	Fostier et al. (2000)
Black-water rivers						
Negro River, Amazonas, Brazil	4.5*, ¶				Undistributed forest catchment without gold mines	Fadini and Jardim (1999)
Negro River, Amazonas, Brazil	18.2	7.1	11.1	2,074	Surface water, confluence with the Solimões River	Maurice-Bourguoin et al. (1999b)
Andean glacial water rivers						
Zongo River, Bolivia	2.2–2.6	1.9–2.4		121–145	Head water, Andean tributary of the Beni River	Maurice-Bourguoin et al. (2000)
African Rift Valley streams						
Lake Naivasha watershed, Kenya	1.8–12.1				Watersheds with agricultural activities	Bonzongo et al. (1996)
Wisconsin rivers						
Wisconsin, U.S.A.	0.93–21*	0.28–15.8			Wetland and forest watershed	Hurley et al. (1995)
	0.74–18.1*	0.49–6.06			Agricultural and forest watershed	Hurley et al. (1995)
	0.69–6.69*	0.54–2.58			Agriculture-only water shed	Hurley et al. (1995)
	1.04–42.7*	0.79–24.2			Urban watershed	Hurley et al. (1995)
	0.7–8.9*			140–150†	Spring and autumn, mean of 16 rivers	Babiarz and Andren (1995)

Table 5. Continued.

Locations	Unfiltered or total Hg (ng L <sup>-1</sup> )	Dissolved or filtered Hg (ng L <sup>-1</sup> )	Particulate Hg		References
			(ng L <sup>-1</sup> )	ng g <sup>-1</sup> d.w.	
Minnesota rivers					
Minnesota river, Minnesota, U.S.A.	1–35*	0.4¶	44†	Diffuse/point source of Hg, agricultural watershed	Balogh et al. (1997, 1998)
Mississippi river, Minnesota, U.S.A.	0.6–4	0.8¶	100†	Headwater LDI, agricultural and forested watershed	Balogh et al. 1998
Forest stream					
Northern Vermont, U.S.A.	1.1–23* ‡	0.5–2.6		Deciduous forest catchment	Scherbatskey et al. (1998)
Nevada rivers					
Carson river, U.S.A.	3–325 *	2.4–40		Ancient Ag and Au mining area, resuspension of Hg-rich sediment	Wayne et al. (1996)
Appalachian Piedmont rivers					
Southern U.S.A. (Alabama, Georgia and North Carolina)	0.13–13.0*			Ancient Au mining area	Mastrine et al. (1999)
Antartica					
Glacial streams	0.54–0.96				Vandal et al. (1998)

\* Unfiltered.

† Slope of linear regression Total Hg = f(TSP mg L<sup>-1</sup>)

‡ Single anomalous maximal value was excluded according to authors' comments.

§ Fine particulate matter (<63 mm).

|| Calculated as particulated Hg (ng L<sup>-1</sup>)/TSP (mg L<sup>-1</sup>).

¶ Mean.

in the aquatic ecosystems of this region is derived from erosion of natural soils in the catchment rather than from anthropogenic pollution. These results in combination with evidence that rates of erosion have been enhanced by anthropogenic deforestation in the catchment (Roulet et al. 1998b, 2000a), suggest that the input of natural Hg coming into the aquatic ecosystems may have increased over historical levels.

Recent reports refer to the occurrence of high levels of MeHg in fish and people with neurological disorders in the lower Tapajós River region (Lebel et al. 1997; Malm et al. 1997). Inorganic Hg from any source needs to be methylated in the aquatic environment prior to being bioaccumulated and biomagnified in the food-chain in the form of MeHg. Favorable methylation conditions were observed in the Tapajós floodplain (Guimarães et al. 2000; Roulet et al. 2000b). The increased input of total Hg coming from erosion could potentially account for high levels of MeHg recently reported in fish, but the link between the different processes that promote high levels of MeHg exposure for the human community remains to be proven. Two hypotheses can be suggested to explain the high level of MeHg reported in fish and humans: (1) increased sediment input to aquatic ecosystems because of chronic and long-term disturbance in the terrestrial landscape has crossed a threshold and somehow resulted in more production and/or bioaccumulation of MeHg in aquatic food chains; and (2) significant levels of MeHg have always been present in aquatic organisms of this region (derived from methylation of natural Hg coming from soil) but were never reported because no one was looking for it before the Amazonian gold rush in the 1980s.

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