

METHYLMERCURY PRODUCTION AND ACCUMULATION IN SEDIMENTS AND SOILS OF AN AMAZONIAN FLOODPLAIN – EFFECT OF SEASONAL INUNDATION*

M. ROULET^{1*}, J.-R. D. GUIMARÃES² and M. LUCOTTE¹

¹ *Chaire de Recherche en Environnement H-Q/CRSNG/UQAM, University du Québec à Montréal, Montréal, Québec, Canada;* ² *Laboratório de Radioisótopos, Inst. de Biofísica da UFRJ, Rio de Janeiro, Brazil*

(* author for correspondence, e-mail: r34664@er.uqam.ca; fax: +1 514 9873635)

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Abstract. This study investigated the spatial and seasonal variations of MeHg concentrations and burdens of different sediments and soils of the Tapajós river floodplain, one of the major clear-water tributaries of the Amazon. The small floodplain of the Tapajós is typical of Amazonian floodplain ecosystems. The studied lakes are bordered by inundated forest (igapó), while floating macrophyte mats (*Paspalum* sp.) develop at the margin of lakes during the flooded season. During the flood, we observed very low MeHg concentrations in the open water lake sediments ($<0.5 \text{ ng g}^{-1} \text{ d.w}$ or $<0.5 \mu\text{g m}^{-2} \text{ cm}^{-1} \text{ d.w.}$) as compared to the semi-aquatic sediments of the macrophyte zone ($0.2\text{--}1.4 \text{ ng g}^{-1} \text{ d.w}$ or $1\text{--}3 \mu\text{g m}^{-2} \text{ cm}^{-1} \text{ d.w.}$) and the igapó semi-terrestrial soils ($0.2\text{--}3 \text{ ng g}^{-1} \text{ d.w}$ or $2\text{--}12 \mu\text{g m}^{-2} \text{ cm}^{-1} \text{ d.w.}$). The litter horizon from the igapó soils showed the highest value of MeHg ($4\text{--}8 \text{ ng g}^{-1} \text{ d.w.}$) representing $0.2\text{--}2 \mu\text{g m}^{-2} \text{ cm}^{-1} \text{ d.w.}$ at the sediment/water interface during the aquatic phase. The inundation had no effect on the concentrations and burdens of MeHg in the sediment of the central part of the lake. The inundation had a clear effect on the methylation of Hg at the surface of semi-aquatic shoreline sediments (macrophyte zone) and semi-terrestrial forest soils, where MeHg concentrations and burdens appeared to be 3 times greater following inundation. In all cores, total Hg concentrations follow those of Fe and Al oxy-hydroxides, whereas the MeHg concentrations are linked to organic matter quality and quantity. It is suggested that organic matter and inundation control MeHg production and accumulation at the benthic interface. These results confirm previous observations, in the same study area, of net ^{203}Hg methylation potentials. The fresh and labile organic matter in the litter of the igapó forest appears as the most important factor leading to significant enrichment of MeHg in these particular terrestrial/aquatic sedimentary environments.

Keywords: Amazonia, floodplain, igapó, methylmercury, seasonal inundation

1. Introduction

Recent advances have been made in the understanding of the origins and dispersion of mercury (Hg) in the Amazon (Forsberg *et al.*, 1994; Lechler *et al.*, 1997; Roulet *et al.*, 1996, 1998a, 1999a; Silva-Forsberg *et al.*, 1998). In the lower Tapajós valley

* The 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.



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it was demonstrated that Hg of natural origin accumulates in soils and is released by weathering and following erosion of terrestrial surfaces (Roulet *et al.*, 1996, 1998b). Increased erosion following colonisation of the Tapajós basin seems responsible for the increased transport and deposition of particulate total Hg (Hg_{tot}) in the aquatic environment, as measured in the water column (Roulet *et al.*, 1998a, 1999b) and sediments (Roulet *et al.*, 2000) of the Tapajós river.

Few studies have considered methylmercury (MeHg) geochemistry in Amazonian floodplain environments (Guimarães *et al.*, 1995, 1998a, b, 2000). The presence and production of MeHg determines the toxic potential of increased anthropogenic inputs of Hg to aquatic systems, since Hg bioaccumulation in fish and its toxic effect in riverine human populations is due to the methylated form of this metal (Cleary *et al.*, 1994; Akagi *et al.*, 1995; Malm *et al.*, 1995, 1997; Lebel *et al.*, 1997, 1998). The relative contribution of human perturbations in the watershed that contributed to an increased production and flux of MeHg to humans through the food chain remains to be evaluated. The first step of this evaluation is the identification of MeHg production sites in Amazonian aquatic environments.

Floodplains along large rivers are one of the most important types of wetlands in the tropics, and are especially prevalent along the great rivers of the Amazon Basin (Melack and Fisher, 1990). Within the floodplain, is a mosaic of open water (lake and canals), flooded forest (igapó or várzea) and floating meadow of macrophytes (capims) that changes in area and proportions as the water level rises and falls each year (Melack, 1984). The floodplain along the Amazon main stem in Brazil occupies 92 400 km², of which 11% is covered with lakes, and the total area of floodplains along the major Amazon tributaries within Brazil reaches 62 000 km² (Sippel *et al.*, 1992). In addition to the importance of floodplains in supporting fisheries (Goulding, 1980; Welcomme, 1979) and in providing relatively fertile soils for agriculture (Junk *et al.*, 1989), the floodplain is important in the regulation of water balance and biogeochemical cycles (Richey *et al.*, 1991; Junk, 1997).

The seasonal inundation in Amazonian floodplains corresponds to an enrichment of nutrients that stimulate the productivity of these terrestrial/aquatic ecosystems. This flood-pulse (Junk, 1997) is also responsible for an increased production of biodegradation products such as CO₂, CH₄ and H₂S (Junk, 1985; Devol *et al.*, 1988; Richey *et al.*, 1988). The biogeochemical cycles of a floodplain depend on the decomposition of the organic matter of the macrophyte meadows and flooded forest leaves that control the release of organic compounds and nutrients. Organic detritus is also an important factor in the food webs of Amazonian river floodplains (Furch and Junk, 1997). Numerous studies in nordic environments have clearly demonstrated that flooding forest soils are responsible for an increased production and accumulation of MeHg in organic rich layers (Porvari and Verta, 1995; Kelly *et al.*, 1997; Bégin, 1998; Heyes *et al.*, 1998). The decomposition of fresh plant tissue under anoxic conditions increases the MeHg production and impoundment promotes this process (Heyes *et al.*, 1998). Recent work on net MeHg production estimated by in-situ incubations with ²⁰³Hg have shown that during the aquatic

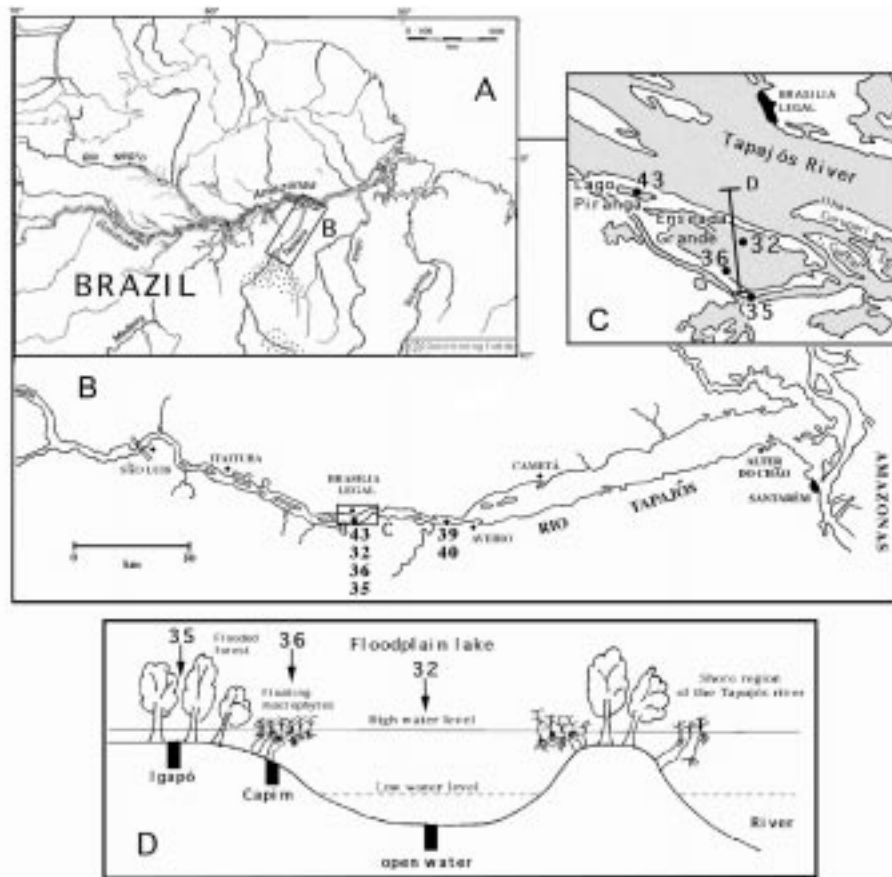


Figure 1. Map of the study area and sampling sites.

phase, the surface of the igapó forest soils produces 10 times more MeHg than open water sediment (Guimarães *et al.*, 1998b, 2000).

This study proposes to identify the main Hg methylation sites in Amazonian floodplain sedimentary environments and observe the effect of seasonal inundation (flood-pulse) on the biogeochemistry of MeHg and Hg in floodplain soils and sediments. The coupling of Hg and MeHg cycles is discussed in relation to organic and mineral matter geochemistry.

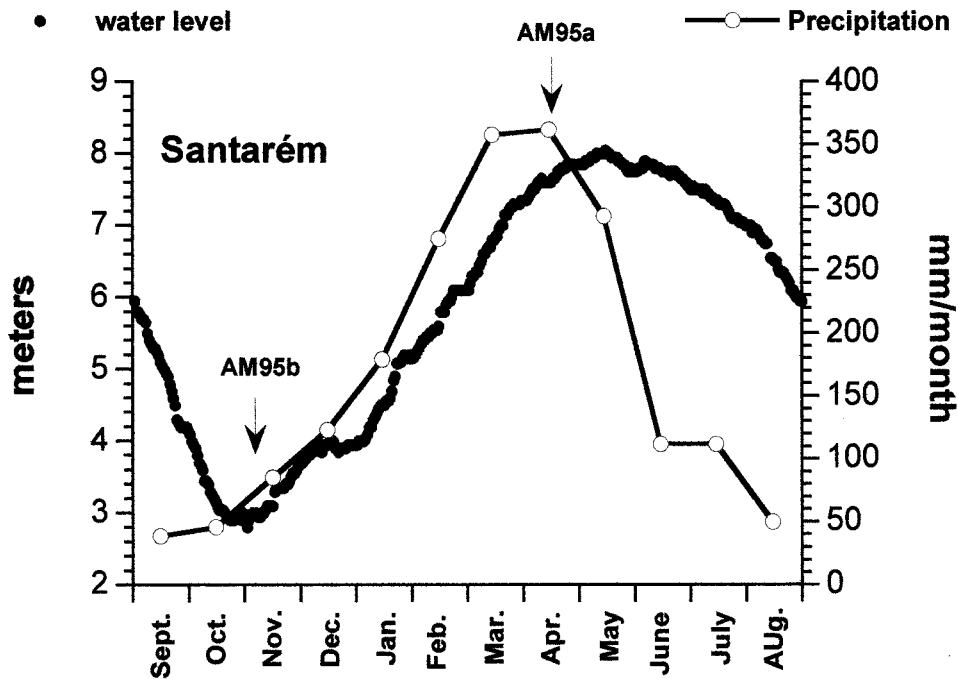


Figure 2. Annual variation of water level of Tapajós River and precipitation at Santarém. (Capitania do porto de Santarém, 1997; Inemet, in Salati and Marques, 1984). Sampling periods are indicated.

2. Material and Methods

2.1. STUDY SITE AND MATERIAL

The Tapajós river drains the more elevated Brazilian shield region and the Alterdo-Chão formation in its lower part. According to Sippel *et al.* (1992), the Tapajós River has floodplains that occur as numerous discontinuous units, separated by points of higher ground that extend to the margin of the river channel, total inundation area reaches 550 km². This clear water floodplain is relatively small but shows some ecological similarity with Amazonian white water várzea and differs from the igapós of the rio Negro. Characterised by the presence of floating macrophyte meadows on the shores and by the sedimentation of fine organo-mineral particles from the water, the floodplain forest in our study area is not rich in sclerophyl species. It is called igapó in the region but is more similar to várzea forest developed on clayey sediments of white-water rivers. The term igapó is more appropriate for the sclerophyl forest developed on sand along the shores of the mouth-bay lake of the Tapajós (Figure 1) (cf. Prance, 1979; Sioli, 1984).

The Tapajós river shows a seasonal monomodale inundation corresponding to an increasing water level that follows rain intensity (Figure 2). Receding begins at the end of the wet season (May–June) and continues until the end of the dry

season (December). The wet season sampling (April 1995) in the present study corresponds to the aquatic phase for forest soil and shoreline sediment. In the Enseada Grande floodplain, the forest sites were already inundated for three months at the time of sampling (Figure 1). The forest and shoreline sites were respectively submerged by 1.6 and 3 m of water. They were completely dry during the terrestrial phase (November 1995), as the water table was not attained at the maximum sampling depth of the cores (30 cm). Depth at the Enseada Grande lake center varied from 1.5 m (November 1995) to 6 m (April 1995). Seasonal variation was followed by sampling a transect from the lake center to the shore at the Enseada Grande Lake (32-36-35) in November and April 1995. Another transect at Ilha de Jutuarana cacal (39-40) and a core from open water sites of the Piranga Lake (43) were collected during April 1995 (Figure 1).

Open water sediments were permanently flooded (Figure 1). They are clayey and homogeneous sediments with no vertical differentiation (horizon G). The shoreline sediments of the macrophyte zone capims sediments are flooded 5 to 7 months yr^{-1} . The surface of these semi-aquatic sediments shows a mixture of homogeneous felt-like plant residues (humic sediment, layer Ah) in a clayey matrix similar to the lake center (open water) sediments (G). Igapó soils are semi-terrestrial forest soils (flooded 4 to 6 months yr^{-1}). These soils are alluvial, with little or no profile development. They are characterized by well developed litter (L) and humic soil layers (Ahh horizon) under clayey mineral soils formed by sediment (G) in restricted drainage conditions.

2.2. SAMPLING METHODOLOGY

Soils and sediments were sampled manually by inserting a 15-cm diameter PVC tube to a maximum depth of 30 cm. During the inundation phase the cores were sampled by scuba-diving. During the dry season another set of cores were taken at the same locations.

Before the core extrusion, redox potentials (Eh) were measured with small Pt electrodes inserted at different depths in the intact core. The cores were sectioned at one cm intervals and the resulting 1 cm thick slices were weighed for subsequent calculation of real bulk densities at each cm interval. Litter and humic soil layers on the top of the soil cores were manually sorted (with clean gloves) into leaf, wood fractions and humus (unidentified small debris). Geochemical analyses were performed on the humus fraction.

Field samples were homogenized, subsampled, stored in clean polyethylene pre-weighed vials and then immediately frozen until later freeze-drying. Laboratory analyses were conducted in the laboratory at UQAM in Montréal.

2.3. LABORATORY ANALYSIS

For Hg_{tot} analysis, 0.1 to 0.2 g of dry matter were digested in a 10:1 mixture of concentrated nitric acid and 6 N hydrochloric acid (HCl) during 6 hr at 120 °C. Hg

was determined by cold-vapour atomic fluorescence spectrometry (CVAFS) using a modification of the method of Bloom and Fitzgerald (1988) (Louchouart *et al.*, 1993; Montgomery *et al.*, 1995; Grondin *et al.*, 1995).

For the MeHg analysis, 0.2 to 0.5 g of dry soil or sediment were digested in a solution of 25% CuSO₄ in 6 N HCl. This digestion allows the release of MeHgCl to the acid solution, from which it is removed by three consecutive extractions with 2 mL of toluene. Extracts were evaporated to a final volume of 0.1 to 0.5 mL and 50 μ L of the concentrated extracts were injected in a chromatographic column made of a mixture of 10% (wP/wP) of FFAP (Free Fatty Acid Phase) in a 80–100 mesh Supelco Chromosorb W-AW. MeHg is eluted at 140 °C, and transported by an Argon gas flow (60 mL min⁻¹). MeHg is decomposed to Hg⁰ in a heated quartz wool tube (500 °C) and finally detected by atomic fluorescence spectrometry. This method was developed by Gage (1961) and adapted in our laboratory (Ma, 1995). This method allows 95.5% MeHg recovery efficiency.

The carbon (C_{org}) and nitrogen (N) contents were measured using a Carlo Erba elemental analyser. Iron and aluminium oxy-hydroxides were extracted using the citrate-dithionite-bicarbonate buffer method (Lucotte and d'Anglejan, 1985). Fe_{cdb} and Al_{cdb} were determined on the same cdb extract following elemental analysis by atomic absorption spectrometry.

Dry densities and burdens (Q) of the different elements were determined by Grondin *et al.* (1995) and Roulet *et al.* (1998b). Cumulative burdens (ΣQ) were calculated by the integration of Q with depth.

3. Results

3.1. FLOODPLAIN TRANSECTS

In the cores collected in the Enseada Grande lake and Jutuarana canal during the inundation period (Figure 1), sediment of the open water (lake and canal centers) contained low levels of MeHg (<0.5 ng g⁻¹ d.w.) representing always less than 1% of the Hg_{tot} (Figure 3 and Table I). They also showed no variation of MeHg contents with depth.

At the margin of the lake Enseada Grande, capim sediments under macrophyte mats contained up to one order of magnitude more MeHg than the open water sediment at the center of the lake. The higher MeHg concentrations corresponded to the mixture of macrophyte remains and organo-mineral sediment at the surface (humic layer).

The higher MeHg concentrations were observed in the litter and organic layers (3–8 ng g⁻¹ d.w., 2–5% of the Hg) of inundated forest soils. Maximum level of MeHg in the Enseada Grande forest soil correspond to the base of the litter layer and the surface of the organic horizon composed by humus of freshly degraded organic material. Litter and organic layers contained 15 to 100 times more

TABLE I
Mean Hg and MeHg concentration and burden, and cumulative burden in soils and sediments of the floodplain

		Hg (ng g ⁻¹)	Q Hg (μg m ⁻² cm ⁻¹)	Σ Q Hg (μg m ⁻²)	MeHg (ng g ⁻¹)	MeHg (%)	Q MeHg (μg m ⁻² cm ⁻¹)	Σ Q MeHg (μg m ⁻²)
Wet season/aquatic phase								
Enseada Igapo litter layer		160	42	167	5.91	3.72	1.51	6.03
Jutuarana Igapo litter layer		139	37	74	6.00	4.37	1.50	3.00
<i>Surface sediment/soil (0–5 cm)</i>								
Lago Piranga	Lake	237	697	2933	0.49	0.24	1.18	2.86
Enseada Grande	Lake	192	597	2987	0.08	0.08	0.23	1.12
	Capim	203	803	4013	0.97	0.44	2.77	13.31
	Igapó	190	1154	5769	2.24	1.11	9.84	32.93
Ilha Jutuarana	Paraná	171	408	2026	0.40	0.20	0.83	3.98
	Igapó	112	304	1520	0.55	0.45	1.05	3.40
Dry season/terrestrial phase								
Enseada Igapo forest litter		185	84	168	3.50	1.93	1.55	3.10
<i>Surface sediment/soil (0–5 cm)</i>								
Lago Piranga	Lake	237	686	3486	0.43	0.20	1.34	4.29
Enseada Grande	Lake a	149	467	2132	0.05	0.03	0.15	0.81
	Lake b	147	722	3609	0.08	0.06	0.40	1.99
	Capim	162	477	2622	0.30	0.18	0.86	4.16
	Igapó	209	1020	5057	0.59	0.26	2.17	13.11

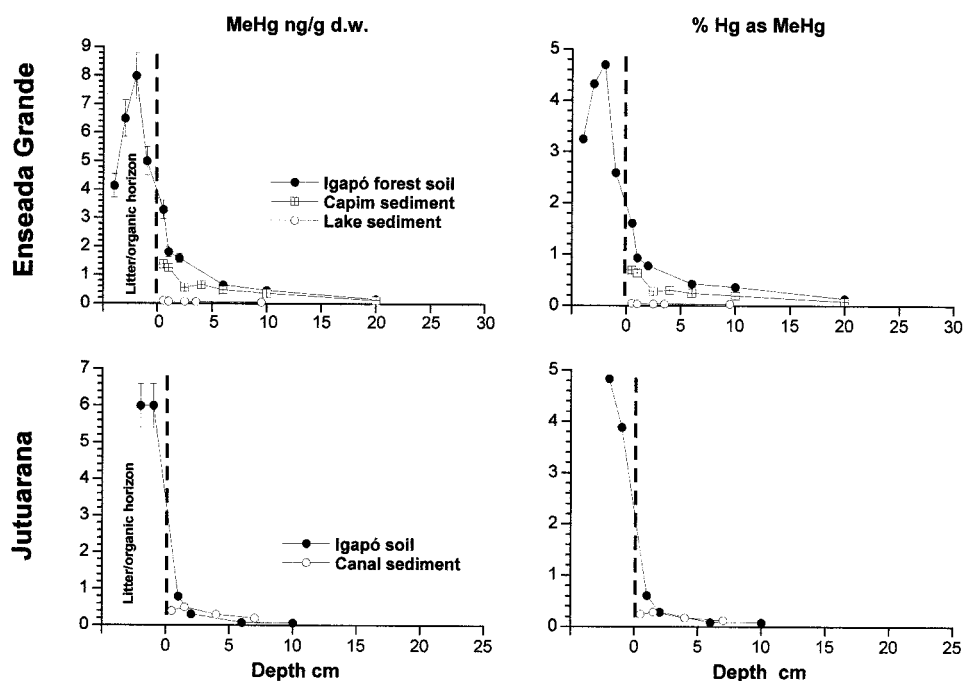


Figure 3. Profiles of MeHg concentration (ng g^{-1} dry weight) and fraction of MeHg to total Hg (%) in soils and sediments of the floodplain during the aquatic phase (AM95a).

MeHg than the open-water sediment surface of the Jutuarana canal (paraná) and the Enseada Grande lake.

The difference between the MeHg levels could be directly linked to the C_{org} enrichment of the sediments and soils. During the flood both MeHg concentration and proportion of MeHg to Hg (%MeHg) in the different cores of the Tapajós floodplain increase with the C_{org} enrichment (Figure 4). At the bottom of the floodplain, MeHg occurrence seemed to be favoured by the accumulation of fresh and labile organic matter at the surface of the semi-aquatic sediment and semi-terrestrial soil (shoreline sediments from the capims zone and igapó forest).

In comparison with other studies (Table II), levels of MeHg measured in the igapó litter layers are among the highest measured in sediment, >1% (Table II). Relative to many lakes and wetlands, %MeHg in estuarine and marine sediment is generally low (<0.5%). In reservoirs, the %MeHg is highest in the flooded soil organic horizon and decreases sharply in the mineral horizons (Bégin, 1998; Roulet and Lucotte, 1995), similar to igapó forest soils.

3.2. SEASONAL VARIATION

Depth profiles of MeHg concentrations and burdens for the Enseada Grande transect are illustrated in Figure 5. The seasonal variation of the water level (4.5 m)

TABLE II
Hg and MeHg concentration and fraction of MeHg to total Hg (%) in different type of sediments and inundated soils

	Hg (ng g ⁻¹ d.w.)	MeHg (ng Hg g ⁻¹ d.w.)	% MeHg	References
Atlantic and Gulf Coasts of Florida, U.S.A.	1–219	<0.001–0.49	<0.01–6.1	Kannan <i>et al.</i> , 1998
South China Sea, Malaysia	20–127	0.01–0.053	0.02–0.27	Kannan and Falandysz, 1998
Patuxent estuary, U.S.A.	60–160	0.1–0.7	0.1–0.5	Benoit <i>et al.</i> , 1998
Scheldt estuary, Belgium	144–1192	0.80–5.70	0.54–0.98 ^a	Muaya <i>et al.</i> , 1997
Northern Everglades, Florida, U.S.A.	60–400	<0.1–5	0.2–2	Gilmour <i>et al.</i> , 1998
Elbe River and Hambourg Harbor, Germany	2000–59000	50–2700	2–10	Wilken and Hintelmann, 1991
Onondaga Lake, U.S.A.	1008–49000	3.7–10.6	0.2–0.5	Hurley <i>et al.</i> , 1995
Clear Lake, California, U.S.A.	500–8300	0.2–15	0.007–0.32	Suchanek <i>et al.</i> , 1998
Fox River, Wisconsin, U.S.A.	970 ^a	6.8 ^a	0.7 ^a	Hurley <i>et al.</i> , 1998
Finish forest lake	134–277	<0.3–8	<0.1–6	Verta and Matilainen, 1995
Polish freshwater sediment	2.3–32	0.032–0.57	1.0–1.83	Kannan and Falandysz, 1998
Northern Québec, réservoir flooded soils				Bégin, 1998
Peat			1–15	
Podzol (organic horizon)			5–40	
Podzol (minearl horizon)			<1	
French Guiana inundated soil				Roulet and Lucotte, 1995
Litter and organic horizon	103–172	2.7–29.3	2.4–19.3	
Surface mineral horizon	152–197	0.6–2.5	0.3–1.6	

^a Mean value.

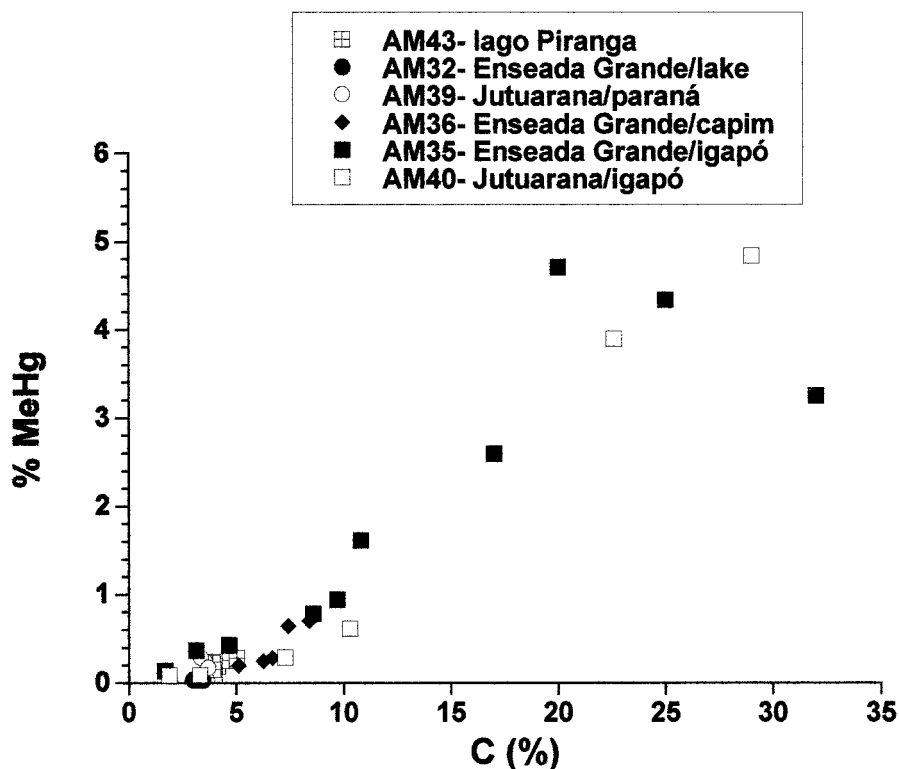


Figure 4. Relationship between fraction of MeHg to total Hg (%) and C_{org} content in soils and sediments during the aquatic phase (AM95a).

appeared to have no influence on the concentrations and burdens of MeHg in lake center sediments. Seasonal influences were more marked in the shoreline capim sediments and forest soils where the concentrations of MeHg were more elevated during the aquatic phase. The inundation promoted a 3-fold increase of MeHg burdens in the first 5 cm of igapó soils as well as in the shoreline capims sediments (Figure 5 and Table I). This increase suggests a net accumulation and/or production of MeHg in the litter and humic layers.

In the forest soils, the litter and organic layers showed the highest concentrations of MeHg but the maximal variation of MeHg burden (Q MeHg) took place in the more dense sub-surface humic horizon. Variation of the quantity of MeHg accumulated in the litter was in fact more dependent on variation in the thickness of the litter layer. Following Table I, seasonal inundation in the Enseada Grande floodplain appears to be responsible for a net accumulation of $19.8 \mu\text{g m}^{-2}$ in the igapó forest soil and $9.1 \mu\text{g m}^{-2}$ in the capim sediment.

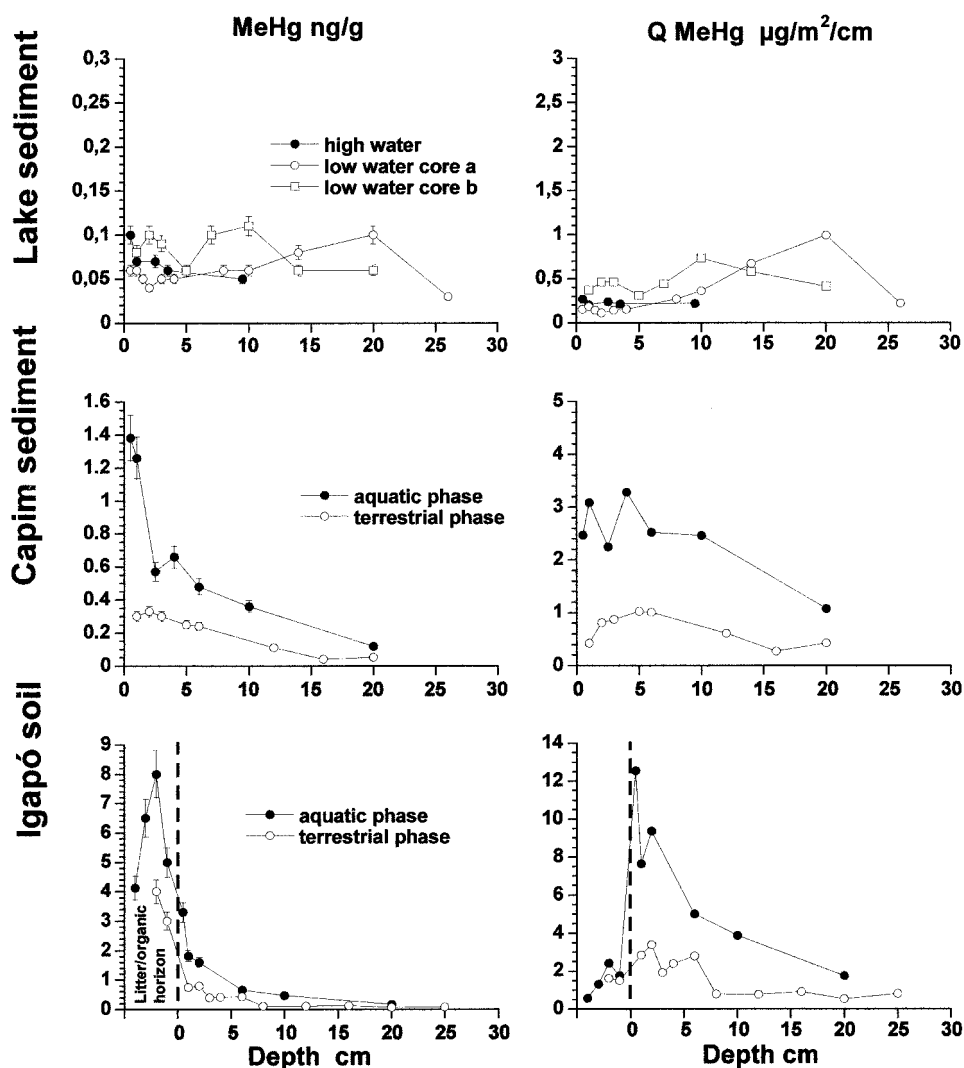


Figure 5. Profiles of MeHg concentration and burden in soils and sediments during the aquatic phase (AM95a) and terrestrial phase (AM95b) along the lago Enseada Grande transect.

3.3. GEOCHEMISTRY OF FLOODPLAIN SEDIMENTS AND SOILS

Depth profiles of Hg, Fe_{cdb} , Al_{cdb} , C_{org} and C/N atomic ratios ($\text{C}/\text{N}_{\text{atom}}$) (Figures 6 and 7) were relatively stable during the extreme variation of the geochemical conditions introduced by the seasonal flooding. Eh profiles were variable and did not show any relationship to the oxy-hydroxides or Hg accumulation patterns. In the aquatic sediments, the interfaces were always oxic, and the lower layers were reduced, but this seemed to have no influence on the MeHg concentration measured with depth along the cores (see Figure 5). Small differences in Hg, C_{org} , $\text{C}/\text{N}_{\text{atom}}$,

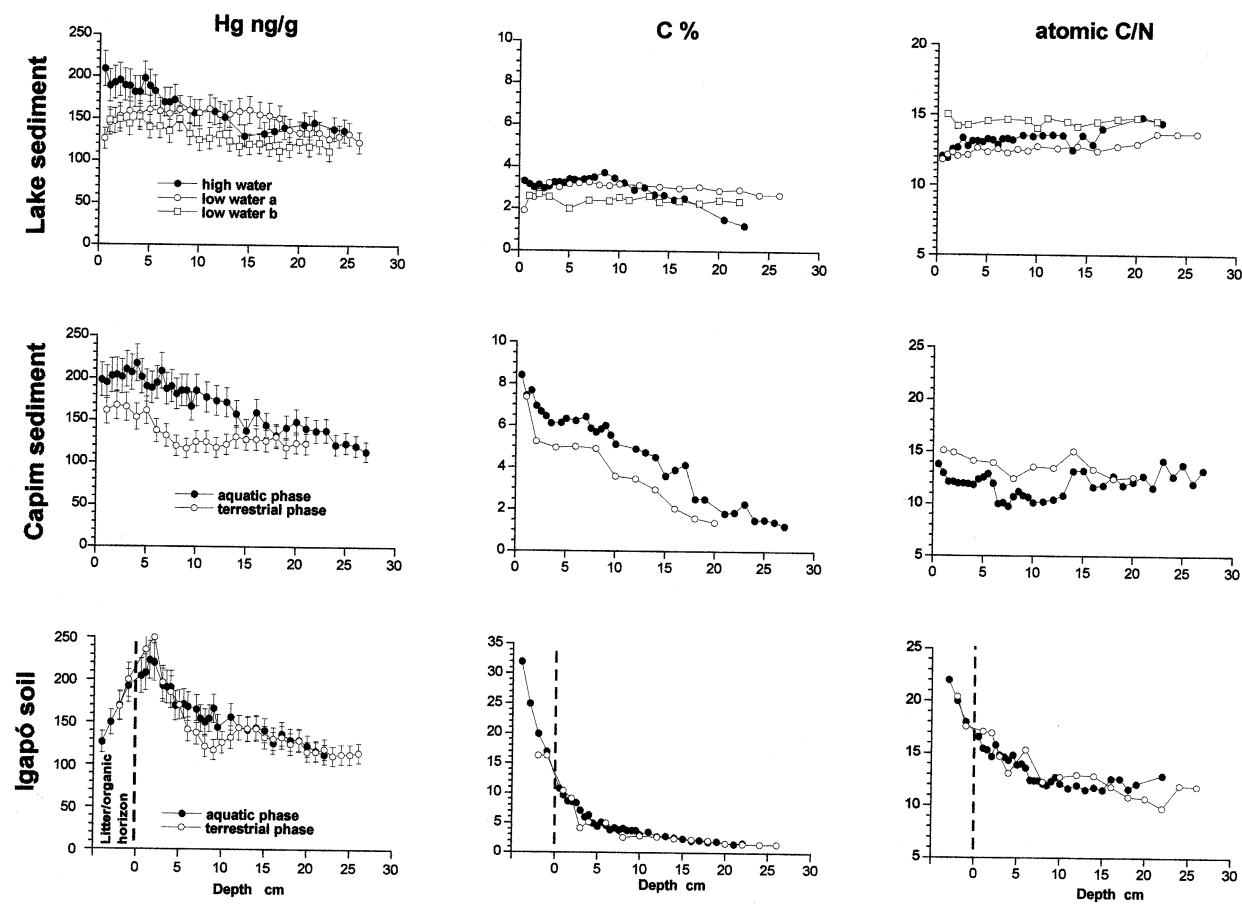


Figure 6. Profiles of Hg and C_{org} concentration and C/N_{atom} ratio in soils and sediments during the aquatic phase (AM95a) and terrestrial phase (AM95b), Enseada Grande floodplain.

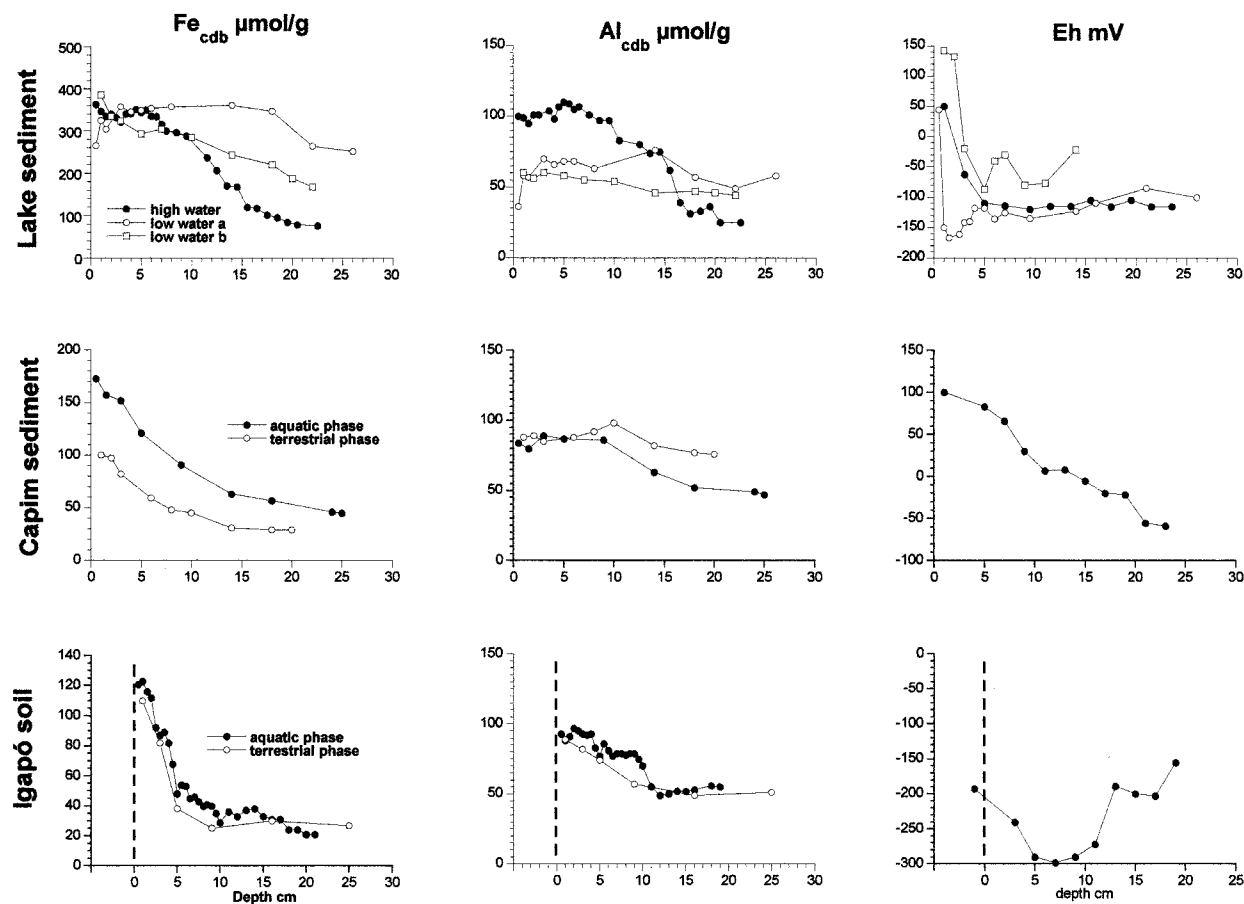


Figure 7. Profiles of Fe_{cdb} and Al_{cdb} concentration and redox potential in soils and sediments during the aquatic phase (AM95a) and terrestrial phase (AM95b), Enseada Grande floodplain.

Fe_{cdb} and Al_{cdb} could be observed in the sediments at the center and shoreline of the lake (capim sediments) but the cores taken during the two different seasons in the open water and shoreline zone were not exactly at the same locations and the variations in the elemental concentrations could be due to the inter-site variations. The cores in the igapó forest soil were sampled exactly at the same place and the profiles of Hg, C_{org} , C/N_{atom} , Fe_{cdb} and Al_{cdb} concentrations did not show any variation with inundation. The only difference was that the litter and the organic horizon were more developed during the aquatic phase than during the aquatic phase. These soils were strongly reduced during the flood and had the lowest concentrations of Fe_{cdb} and Al_{cdb} of all the substrates (Figure 7). The C/N_{atom} in sediments and mineral horizon of the soils show similar levels and no profile variation with depth. In contrast, an increase level of C/N_{atom} was noted in the litter and organic horizon of the forest soil where higher MeHg concentrations were measured (Figure 5).

The geochemistry of Fe and Al oxy-hydroxides seems to control Hg accumulation in soils and sediments (Figure 8). The cdb extraction is specific for Fe oxy-hydroxides and correspond to crystalline and amorphous forms (Jonsson, 1997). Al_{cdb} represents amorphous Al, as well as Al substituted for Fe in Fe oxy-hydroxides. The cdb method also seems to be able to extract Al and Fe associated with organic matter (Parfitt and Childs, 1988; Ross and Wang, 1993). Relationships between Hg and Fe_{cdb} were different in lake sediments in comparison to shoreline sediments and igapó soils, but the relationships between Hg and Al_{cdb} were similar for all profiles. Al extracted by cdb appears to be have a greater influence of the Hg sorption in comparison to Fe_{cdb} . This particularity correspond to the observation made in the *terra firme* oxisols from the Tapajós Valley (Roulet *et al.*, 1998b) where the substitution of Al in the Fe crystal is supposed to increase the sorption capacity of Fe oxy-hydroxides. The latter observation could explain in part the relationship between Hg/Fe_{cdb} and $Al/(Fe+Al)_{cdb}$ (Roulet *et al.*, 1998b) meaning that there is an increase adsorption of Hg by Fe oxy-hydroxides when the proportion of Al in the Fe crystal become more important. Although, we cannot excluded an increased influence of Al associated to C_{org} in igapó soils and shoreline sediments because their surface are richer in organic matter than the lake sediment. In the humic and mineral layers of the soils, Hg, Fe_{cdb} , and Al_{cdb} profiles followed the increase of C_{org} at the surface suggesting a retention of these compounds by the accumulation of organic matter at the surface of the igapó soils, as was observed in hydromorphic soils of the French Guyana forest (Roulet and Lucotte, 1995)

4. Discussion

Differences in MeHg concentrations between lake sediments, shoreline sediments and igapó forest soils are in good agreement with the differences observed in the net methylation potentials measured by ^{203}Hg incubations in sediment and soil samples

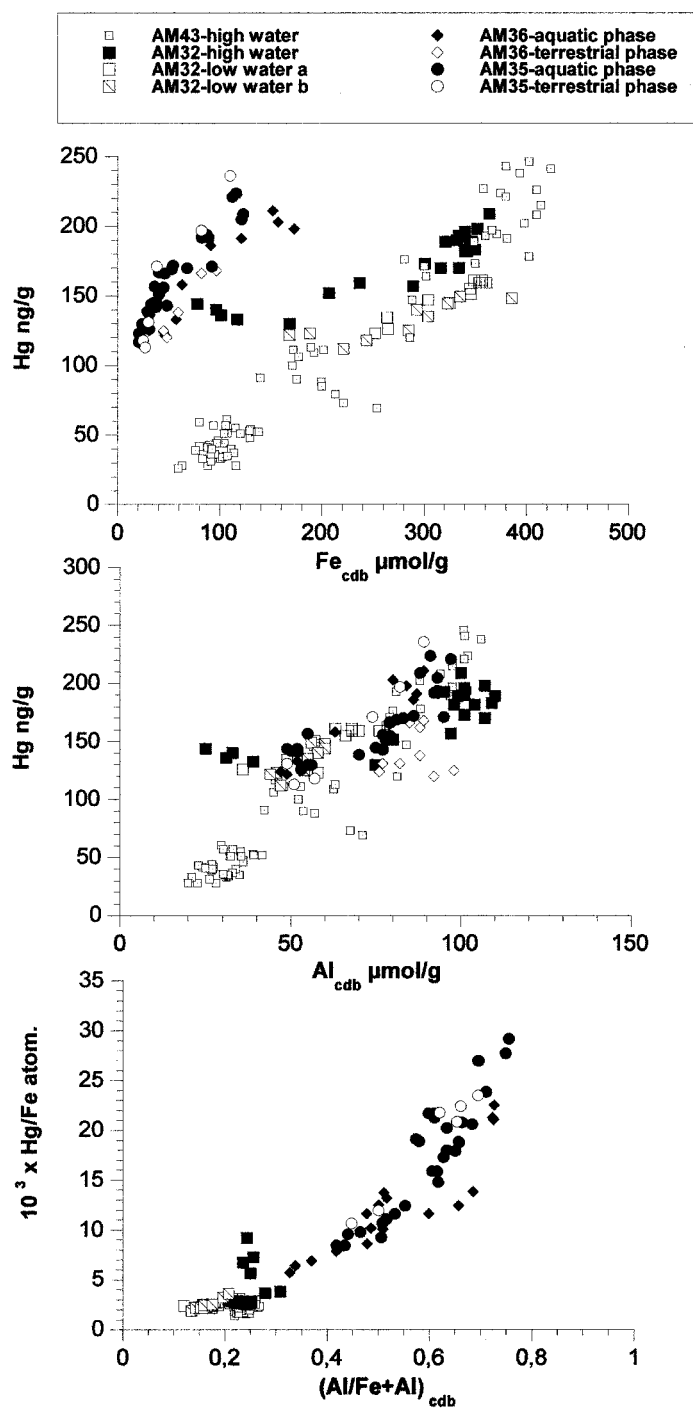


Figure 8. Relationships between Hg and oxy-hydroxides in the soils and sediments of the lago Piranga and lago Enseada Grande floodplain.

from the Enseada Grande floodplain (Guimarães *et al.*, 2000). Higher MeHg formation rates were found at the surface at all sites, and it was about one order of magnitude more important in the littoral macrophyte zone and the flooded forest than in the center of the lake. In the macrophyte zone, Hg methylation was mainly associated with the thin humic layer. In the flooded forest higher methylation was found in the flocculent material settled over the litter layer. In the present study higher concentrations and accumulation of MeHg were observed below the litter layer, at the surface of organic horizon. The accumulation of MeHg seems to be due to a better retention of MeHg in this layer by this freshly humified organic matter.

Hg levels seem to be controlled by the Fe and Al oxy-hydroxides geochemistry and correspond to the observations made on soils, suspended matter and lake sediments of the Tapajós river valley (Roulet *et al.*, 1998b, 1999b, 2000). MeHg biogeochemistry is apparently not controlled by Hg geochemistry in the floodplain. MeHg production and accumulation in floodplain sediments and soils seems to be favoured by the incorporation and degradation of fresh organic matter of forest and macrophyte litter at the surface. The fresh and labile organic matter in the litter of the igapó forest appears to be the most important factor leading to significant enrichment of MeHg in these particular terrestrial/aquatic sedimentary environments.

The decay of organic matter under reducing conditions is believed to create favourable conditions for MeHg production and accumulation (Ramlal *et al.*, 1987; Heyes *et al.*, 1998). Seasonal flooding controls the environmental conditions favourable to MeHg production and accumulation in the organic rich layers of soil (igapó) and littoral sediments (macrophyte zone). Net accumulation of MeHg in the igapó soil and capim sediments suggests that the production of MeHg is favoured during inundation, as compared to MeHg consumption. This process is comparable to the effect observed on submerged forest soils in reservoirs where the accumulation of MeHg over time is favoured in the organic rich surface horizons (Bégin, 1998).

Decomposition of herbaceous plants and forest leaves of the forest and macrophytes during the aquatic phase is very rapid, as these materials lose 80–90% of their weight in 4 to 6 months (Howard-Williams and Junk, 1976; Irmiler and Furch, 1980; Furch *et al.*, 1989; Furch and Junk, 1997). Dry weight loss is 2 to 4 times slower on land than in water. The differences between decomposition on land and in water can be attributed in part to different leaching rates. The loss starts when the material is inundated and increases with the frequency and duration of contact with water. Weight loss is explained by leaching of easily soluble organic substances and considerable amounts of nutrients (Furch and Junk, 1997). The large amount of organic material accumulated is an important pool of bioelements that are released during decomposition and modify the chemical conditions of the environment. The biogeochemical cycles of the floodplain depend on the amount of the organic material and its fate. (Furch and Junk, 1997). Incorporation of new

sediments corresponding to the inundation phase and coming from the Tapajós River has been observed at the surface of the litter. The result is a mixture of recent sediment and organic matter from the forest at the surface of the soils where Hg coming from the river and/or vegetation could be methylated. Thus the semi-terrestrial soils and semi-aquatic sediments could also be an important source of MeHg for the adjacent aquatic ecosystems during the aquatic phase.

Because of the relatively low uptake by herbivorous animals, most of the plant material produced on the floodplain enters the detrital food-web. The inundation also significantly increases the surface of benthic substrate for aquatic invertebrates (Walker *et al.*, 1991; Furch and Junk, 1997). In the absence of a complete hypoxia, litter of flooded soils is colonised by numerous aquatic invertebrate organisms where leaves are used as a substratum and for shelter but not as a food item (Furch and Junk, 1997). Grazing on epiphyton, detritus and fungi or filtering phytoplankton from the water may be a more important feeding strategy (Irmiler and Junk, 1982; Henderson and Walker, 1986). Meyer (1991) observed diverse involvement of the soil fauna in litter decomposition during the terrestrial phase. Soil fauna leads to a stronger incorporation of organic matter into the upper mineral soil layers of floodplain forest soils. Invertebrates have been identified as an important link in the transfer of MeHg to fish from permanently inundated soils of northern reservoirs (Tremblay *et al.*, 1996, Tremblay and Lucotte, 1997). A comparison between these two systems could easily be made and the possibility of this pathway of MeHg transfer across the aquatic/terrestrial food web deserves further investigation.

4.1. CONCLUSION

The most important methylation sites in sediment and soils of the Tapajós river floodplain are the litter and organic horizon of the flooded forest soils. MeHg accumulation and production in the Tapajós floodplain sediments and soils is linked to the inundation of fresh organic matter mixed with organo-mineral sediment particles at the surface of igapó soils and littoral sediments (capim). Inundation seems to promote the production and accumulation of MeHg. This process could greatly increase the quantity of MeHg available to Amazonian benthic aquatic and terrestrial food chains. We now need to evaluate the importance of Hg coming from the watershed that is readily methylated and transferred to organisms.

Floodplains are a common aquatic/terrestrial environment in the Amazon basin. They assure supply, protection and food of the majority of fish species during the flood (Goulding, 1980). The large number of detritivorous animals, including many Amazon fish species, suggest that detritus is an essential factor in the food webs of Amazonian river floodplains (Furch and Junk, 1997). Further studies are needed to evaluate the fate of the MeHg produced in the floodplain with respect to the food-web structure of these particular aquatic/terrestrial environments.

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