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The role of organic matter on the adsorption of mercury in sediments from Amazon lakes, Brazil

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Abstract Gold has been exploited intensively in the Brazilian Amazon during the past 20 years, and the elemental mercury (Hg) used in amalgamating the gold has caused abnormal Hg concentrations in waterways. Since 1986 particular attention has been given to the Madeira River because it is the largest tributary of the Amazon River and gold mining was officially allowed on a 350-km sector of the river. In this paper, samples of sediments from nine lakes located in the Madeira River basin, Rondônia State, Brazil, were analysed for mercury and organic matter. The average Hg content ranged between 33 and 157 ppb, which is about 8–40 times higher than the average value corresponding to 4.4 ppb for rocks occurring in the area (regional background). Significant correlation was found between the Hg content and organic matter in the sediments, indicating its importance on the retention of this heavy metal.

Key words Amazon lakes; Madeira River basin; mercury; organic matter; physical weathering; sediments

INTRODUCTION

In aquatic systems, heavy metals (including mercury) and other elements are mainly transported in the solid phase, either sorbed onto particle surfaces and coatings, or incorporated into mineral grains. Thus, 90–99% of the total metal load in rivers is transported in the particulate phase, depending on the geochemical behaviour of the metal and the nature of the physical and chemical environment (Miller, 1997).

Special attention has been paid to mercury inputs at the Madeira River in the Amazon by many investigators (Pfeiffer *et al.*, 1989; Malm *et al.*, 1990; Lacerda, 1995; Maurice-Bourgoin *et al.*, 2000). It is one of the largest tributaries of the Amazon River, and gold mining was officially allowed and practiced as far as the Andean headwaters, which caused the release of metallic mercury into the atmosphere and waterways. Gold mining activities on the Madeira River extended from the Bolivian headwaters, on the Beni River, to the city of Porto Velho, capital of Rondônia state, Brazil. Although it is practically absent at present, mercury (Hg) continues to be evaluated in the aquatic system by local authorities and environmentalists because of the possibility of human contamination (Cleary *et al.*, 1994). Contamination of the aquatic food chain of the Madeira River tributaries has been demonstrated by Maurice-Bourgoin *et al.* (2000), who report that 86% of the piscivorous fish collected in the

Beni River exhibit high mercury concentrations at values exceeding, by almost four times, the WHO (1976) safety limit.

Several parameters affect the mobility and dispersion of Hg and other heavy metals and elements throughout the aquatic environment, where adsorption has been recognized to be a key parameter. In this paper, samples of sediments from nine lakes located in the Madeira River basin, Rondônia State, were analysed for mercury and organic matter, with the objective of investigating whether retention of this metal is occurring under the present conditions taking place there, because sediments are often recognized as important sinks for metals.

AREA OF INVESTIGATION

The Madeira River is one of the largest tributaries of the Amazon River, extending from Bolívia and crossing the city of Porto Velho, capital of Rondônia State in Brazil, which is the most populated site (population approximately 300 000, according to the 1999 census) along it. The Aw-tropical rainy climate (Köppen classification) characterizes Rondônia state, i.e. the relative air humidity ranges from 74.2 to 90.8% and air temperature from 20.7 to 32.2ºC. The wet season (average rainfall = 250 mm month^{-1}) occurs between October and April, whereas the dry season (average rainfall = 20 mm month^{-1}) is between May and September.

This study considers data for Hg concentration in three types of materials: (a) sediments collected by Silveira (1998) at 17 points along 25 km of the Madeira River between the Teotônio and Santo Antônio waterfalls, upstream from Porto Velho (area of about 260 km^2) (Fig. 1); this sector of the river is not suitable for navigation, and fieldwork was performed from a small boat during the dry season in a 2-week period in August 1996. Approximately 500 g of sediment was collected from each sampling point with a bottom dredge that slowly trawled upstream and transferred samples to a half-filled, thick polyethylene bag. (b) Six rock samples collected at Teotônio and Santo Antônio waterfalls; they are coarse-grained igneous rocks corresponding to granites, syenites, and monzonites already characterized in terms of petrographic, geochemical, and geochronological aspects (Payolla, 1994). (c) Core sediments (20–80 cm deep) collected at nine lakes between the Jamari and Ji-Paraná rivers, that are tributaries of Madeira River; this area is situated between 8° and 9°S and between 62° and 64°W (Fig. 2). The fieldwork was undertaken during October 1999 and February 2000, also utilizing a small boat that crossed several *igarapés* for reaching the lakes. The lakes exhibited variable dimensions (5–10 m deep, 600–7000 m long, and 300–1200 m wide), with clear and black waters, depending on the dissolved organic matter content. A 1-m long acrylic tube (10 cm in diameter) adapted to an iron outliner was driven into the sediments preferentially at the middle of each lake, each core profile being cut in 5-cm thick slices that also were transferred to polyethylene bags.

EXPERIMENTAL

All bags containing the sediments were stored in iceboxes and transported to the laboratory. The material was dried at 60°C, crushed, quartered, sieved for separation of

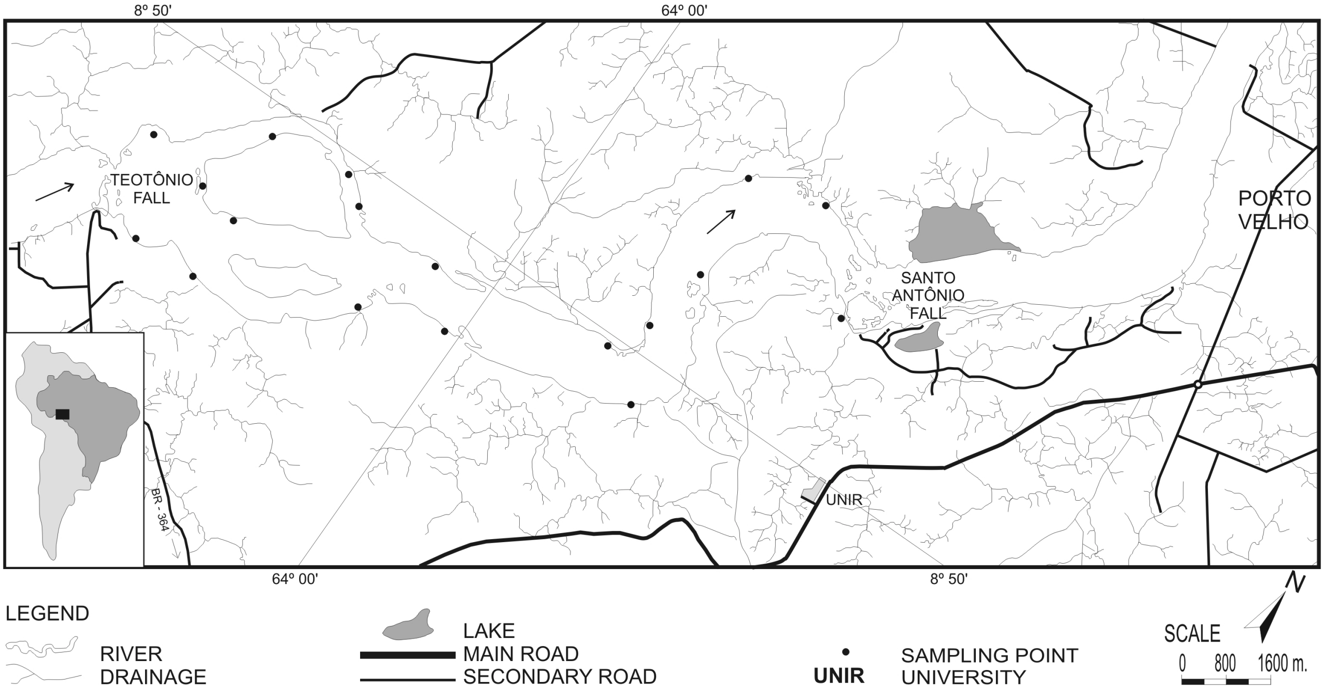

Fig. 1 Location of the sediment sampling sites for Hg analysis at the Madeira River between Teotônio and Santo Antônio waterfalls (Silveira, 1998).

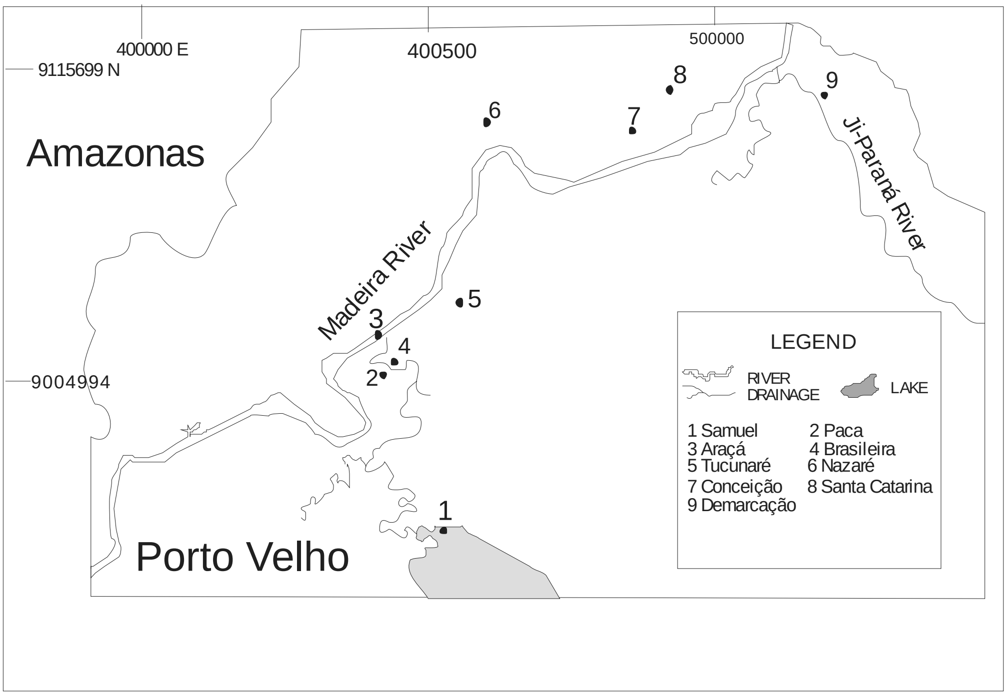

Fig. 2 Location of the lake sediment sampling sites for Hg analysis at the Madeira River basin, Rondônia state, Brazil.

the <200 mesh (<74 µm) size fraction, and divided into different aliquots for analysis of the total Hg content, organic matter and loss on ignition (LOI).

The experimental procedures applied to standards were also utilized for the sediment samples in order to acquire Hg concentration data. Digestion of the samples and Hg extraction steps were used, as described by Malm *et al.* (1989). About 0.5 g of each sample was used, 1 ml of Milli Q water plus 2 ml of aqua regia were added, and heated to 50°C for 5 min. After cooling, 10 ml of Milli Q water plus 4 ml of 5% potassium permanganate were added and heated to 55°C for 30 min. The excess $KMnO_4$ was neutralized with 12% hydroxylamine hydrochlorate. Each aliquot representing the sample was divided into three sub-aliquots.

The analyses of total Hg concentrations were carried out using atomic absorption spectrophotometry with cold vapour generation. The equipment used was a Perkin Elmer model FIMS-400 atomic absorption spectrophotometer, containing a cylindrical cell with quartz window, a Hg lamp (253.7 nm), a specific detector for absorption on the Hg wavelength, a system of flow injection analysis, and a cold vapour generator system. The parameters of calibration utilized in this equipment consisted on an Ar flow of 50 ml min^{-1}, a 3% HCl flow between 9 and 11 ml min^{-1}, and a 0.2–0.5% $NaBH_4$ + NaOH flow between 5 and 7 ml min^{-1}. The concentrations of the analytical solutions for obtaining the calibration curve of the equipment varied between 2 and 40 μg L^{-1}, and were prepared from a 2 μg mL^{-1} stock preserved with 5% HNO_3 and 0.01% $K_2Cr_2O_7$.

The organic matter content was evaluated by spectrophotometry (Hach, 1992) held in a solution obtained after adding potassium dichromate and sulphuric acid to 1 g powdered aliquot not submitted to digestion; organic carbon was oxidized to carbon dioxide with a parallel reduction of hexavalent chromium to trivalent chromium and an accompanying colour change from orange to green read at 610 nm (Hach, 1992).

Another (indirect) evaluation of the organic matter content in the sediment samples was determined by measuring weight loss in subsamples after burning at selected temperatures. Since the samples are from freshwater, the majority of “loss-on-ignition” (LOI) refers to organic carbon oxidizing to CO_2. In general, these results are typically accurate to 1–2% for sediment with over 10% organic matter, where, in high clay sediment, water of hydration may be lost during the ignition, resulting in additional error. Additional steps to subtract out weight loss due to the oxidation of sulphur to SO_2 were not used, as this procedure is often applied to samples from saline environments. The procedure utilized was to weigh the crucible using the mass balance; place a few grams of moist subsample in the crucible and measure the combined mass; dry the sample in the oven at 100°C; re-weigh the crucible + subsample (the difference yields the water content); set the muffle furnace temperature to 450°C and leave the crucible in it for 8 h; remove crucible from furnace and allow to cool briefly; re-weigh crucible + subsample (the difference from the dry state yields the organic content).

RESULTS AND DISCUSSION

All chemical data for Hg, organic matter and LOI contents in sediment lakes analysed in this paper are given in Tables 1–3. The average Hg content in the lake sediments ranged between 33 and 157 ppb, which is similar to the range of 21–136 ppb found by Silveira (1998) for the bottom sediments between Teotônio and Santo Antônio waterfalls (Table 4).

Table 1 Hg content (in ppb) of lake sediments from the Madeira River basin, Rondônia State, Brazil.

Depth Range (cm)	Samuel	Paca	Araçá	Brasileira	Tucunaré	Nazaré	Conceição	Santa Catarina	Demarcação
0–5	126.2	128.8	58.5	76.5	48.8	33.8	56.6	49.7	164.9
5–10	162.9	145.3	55.2	78.8	44.7	34.0	48.4	57.6	110.3
10–15	171.4	148.4	46.8	113.8	45.4	23.7	47.3	82.4	92.9
15–20	168.2	58.2	42.6	120.0	39.6	30.9	50.8	83.4	84.2
20–25		175.5	42.5	118.6	34.0	41.3	49.6	74.2	99.6
25–30			47.4	115.4	39.3		80.6	74.3	100.3
30–35			44.2	114.6	36.5		62.4	72.4	97.8
35–40			37.2	127.0	36.7		66.9	82.2	
40–45			34.0	153.2	38.1		66.1	77.0	
45–50			33.8	131.7	49.0		65.6	95.0	
50–55			35.8	119.6	38.1				
55–60			36.5		39.0				
60–65			33.8		40.2				
65–70			39.7						
70–75			50.2						
75–80			49.5						
Mean	157.2	131.2	43.0	115.4	40.7	32.8	59.4	74.8	107.2

Table 2 Organic matter content (in %) of lake sediments from the Madeira River basin, Rondônia State, Brazil.

Depth range (cm)	Samuel	Paca	Araçá	Brasileira	Tucunaré	Nazaré	Conceição	Santa Catarina	Demarcação
0–5	17.8	9.7	4.0	6.0	3.9	3.7	9.1	5.0	10.1
5–10	18.0	8.6	3.1	4.9	3.5	1.9	6.1	8.6	6.5
10–15	18.7	9.8	7.1	5.6	3.8	3.8	7.1	3.9	6.1
15–20	17.8	9.3	6.9	4.0	5.5	3.9	8.0	5.0	6.9
20–25		9.4	4.0	8.2	3.6	4.0	6.7	6.8	6.9
25–30			7.1	4.8	4.0		7.0	12.8	7.8
30–35			5.0	5.0	3.0		7.8	5.9	8.8
35–40			4.8	4.0	2.0		7.7	4.6	
40–45			20.5	4.7	3.6		8.8	5.7	
45–50			2.0	3.8	3.0		9.1	2.7	
50–55			4.0	4.0	3.6				
55–60			2.0		2.8				
60–65			5.0		4.6				
65–70			7.1						
70–75			4.2						
75–80			4.2						
Mean	18.1	9.4	5.7	5.0	3.6	3.5	7.7	6.1	7.6

The Hg concentration in the rocks analysed by Silveira (1998) varied between 3.3 and 7.2 ppb (average = 4.4 ppb) (Table 5). Jovanovic & Reed (1968) and Jonasson & Boyle (1979) reported total Hg contents for several rock types, for example, between 7 and 250 ppb for ultrabasics, between 5 and 84 ppb for basics, and between 30 and 90

Table 3 Loss on ignition (LOI) content (in %) of lake sediments from the Madeira River basin, Rondônia State, Brazil.

Depth range (cm)	Samuel	Paca	Araçá	Brasileira	Tucunaré	Nazaré	Conceição	Santa Catarina	Demarcação
0–5	16.1	13.9	9.6	10.5	6.8	6.9	11.6	8.0	14.4
5–10	15.1	14.0	9.0	10.5	7.0	6.9	9.9	7.6	11.7
10–15	14.8	14.7	8.5	12.3	6.6	6.6	11.3	7.5	11.0
15–20	14.5	7.4	8.2	11.1	6.1	6.8	10.6	7.2	11.1
20–25		16.0	7.8	11.0	6.1	7.1	10.8	7.0	11.3
25–30			7.9	11.7	6.5		11.1	7.3	11.3
30–35			7.7	11.6	5.8		11.4	7.4	11.5
35–40			6.6	11.6	6.2		12.0	7.5	
40–45			6.3	11.7	6.2		12.2	7.2	
45–50			6.6	11.8	6.0		12.9	7.3	
50–55			6.7	11.5	6.4				
55–60			7.5		6.3				
60–65			7.7		5.6				
65–70			7.7						
70–75			7.4						
75–80			7.2						
Mean	15.1	13.2	7.6	11.4	6.3	6.9	11.4	7.4	11.8

Table 4 The total Hg content data reported by Silveira (1998) for sediments collected at the Madeira River (Fig. 1).

Sample no.	Hg (ppb)	Sample no.	Hg (ppb)	Sample no.	Hg (ppb)
1	52.0	7	40.2	13	48.1
2	36.5	8	45.6	14	58.3
3	40.8	9	39.1	15	20.9
4	135.7	10	48.0	16	44.4
5	51.8	11	60.4	17	45.4
6	54.3	12	57.6		

Table 5 The total Hg content data reported by Silveira (1998) for rocks collected at Teotônio and Santo Antônio waterfalls (Fig. 1).

Sample no.	Site of sampling	Hg (ppb)	Remark
1	Teotônio	7.2	fayalite-chlinopyroxene-amphibole alkali-feldspar syenite
2	Teotônio	3.7	chlinopyroxene-amphibole alkali-feldspar granite
3	Teotônio	4.0	fayalite-chlinopyroxene-amphibole quartz-syenite
4	Santo Antônio	3.6	biotite monzogranite
5	Santo Antônio	4.5	biotite monzogranite
6	Santo Antônio	3.3	biotite monzogranite

ppb for quartzites and amphibolites. The mean total Hg concentration in the rocks from Teotônio and Santo Antônio waterfalls is lower than such reported values for metamorphic rocks, and also lower than the values within the range of 7–200 ppb reported by Lindqvist *et al.* (1984) for acid rocks. Thus, the Hg content values in rock samples from Teotônio and Santo Antônio waterfalls may be considered appropriate for defining the regional background, as they represent analyses of samples free from inputs of anthropogenic Hg due to the processing of alluvial gold ores.

Fine sediments play a significant role in the transport and fate of mercury in tropical aquatic systems in the Amazon region, and the data in Tables 1 and 4 shows that the Hg concentration in sediment lakes and Madeira River is much lower than the range of 65–1675 ppm reported by Pfeiffer *et al.* (1989) for sediments collected at Teotônio waterfalls during the peak gold mining activities, as they involved the use of a large number of mechanical dredges operating simultaneously. However, the Hg content values for sediments in Tables 1 and 4 are about 8–40 times higher than the average value corresponding to 4.4 ppb for rocks occurring in the area (regional background, Table 5). Intense weathering processes affecting the crystalline rocks cropping out in the studied area have been partially responsible for the generation of fine sediments transported by water and deposited in the Madeira River, and, consequently, it would be expected that similar Hg concentrations in the rocks and sediments occur there. Because this was not the case, it is plausible to suggest that the influence of Hg anthropogenic emissions that occurred in the past, during the gold mining activities on the Madeira River, still remain at the present day when such activities have substantially reduced and are practically absent now.

The pH and Eh data reported by Bonotto & Silveira (2003) for waters from the Madeira River between Teotônio and Santo Antônio waterfalls allowed the identification of transitional field, tending to be reducing in character. The Eh-pH diagram for metallic Hg, the sulphide cinnabar and the oxide montroydite in a system containing $\Sigma S = 10^{-3}$ mol. L^{-1} at 25°C and 1 atm (Faure, 1991) indicates that mercury may be present as the metallic Hg° inert form in the area. Significant correlation (r = 0.78) was found between the average Hg content and organic matter in the lake sediments, as shown in Fig. 3. Since the loss on ignition (LOI) (Table 3) expresses the organic matter + adsorbed water + water in crystal lattices and fluid inclusions + CO_2 of carbonates + SO_2 of sulphides, it is a parameter related to organic matter, thus, justifying the significant relationship (r = 0.90) between the average Hg content and LOI in the lake sediments (Fig. 3).

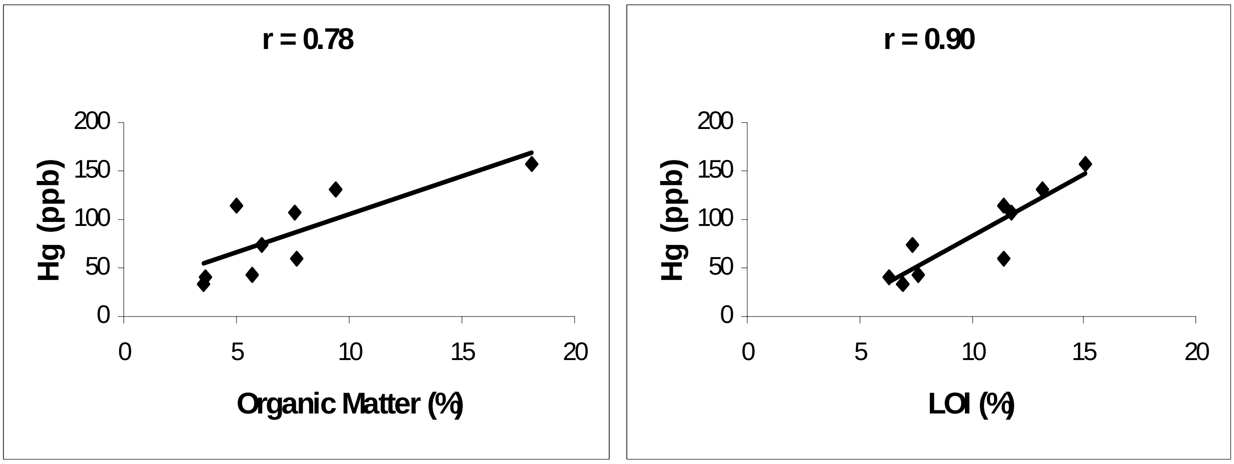

Fig. 3 The relationships among Hg, organic matter, and loss on ignition (LOI) contents for lake sediment from Madeira River basin, Rondônia state, Brazil.

Beyond modifying the bulk density and porosity of soils and sediments, organic matter also influences their specific surface (area per mass, often expressed in $m^2 g^{-1}$), since 1% of organic matter in porous matrices may cause an increase of the specific surface by about 7 m^2 (Kiehl, 1977). Consequently, other parameters are also affected significantly, for instance, the cation exchange capacity, the cation adsorption, and the percentage of water retention in soils/sediments, which, in general, increase with increasing specific surface area. Thus, the results of this study clearly identify the role of organic matter on the adsorption of mercury in lake sediments from the Madeira River basin, where Hg organic compounds are certainly being formed. This may be a subject of major concern as several species of fish ingest organic matter, Hg and microorganisms associated with the sediments at the bottom of lakes and margins of rivers. The sediments act as important sinks for Hg in Amazon lakes, yielding important information relevant to the hydrological resources in the area with implications for food-chain contamination.

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