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Methylmercury formation in the anoxic waters of the Petit-Saut reservoir (French Guiana) and its spreading in the adjacent Sinnamary River

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Abstract. The present work was carried out on the hydroelectric reservoir Petit-Saut on the Sinnamary river in French Guiana. Measurements were performed during the wet and dry seasons along a longitudinal gradient, from upstream of the reservoir in two inflow rivers, to the Sinnamary estuary downstream of the dam. Gold extraction has led to a marked increase in suspended matter and total mercury (HgT) in one of the rivers. Dissolved monomethylmercury (MMHg) measured in surface waters were similar for both rivers: 0.03-0.05 ng l^{-1} (1.0-1.7% of the dissolved HgT). These results indicate similar methylation efficiency and/or transfer of MMHg into the dissolved fraction of the water column, independently of the amounts of inorganic mercury transported. Dissolved MMHg concentrations in surface waters of the reservoir were similar to those in the rivers, but were more than 10 times higher in deep anoxic waters, up to 0.6 ng l^{-1} (20 % of dissolved HgT). The MMHg concentration profiles in the water column suggest that methylation occurs mainly in anoxic waters and sediments in relation with the activity of sulfate reducing bacteria. Dissolved MMHg concentrations measured in the Sinnamary at the base of the dam were still high (0.5 – 0.6 ng l^{-1} ; 20 to 35% of the dissolved HgT).

1. INTRODUCTION

This study is a part of the ongoing multidisciplinary programme, "Mercury in French Guiana". The objective of the current work was to determine the sources and speciation of mercury in water basins affected by input of mercury originating from gold mining [1]. Recent studies of the origin and distribution of mercury in the Amazon basin indicate that the main sources of contamination are the release of particulate Hg as a result of widespread erosion of soils naturally rich in mercury and local inputs of elemental Hg (Hg^0) from gold mining activities. The present work was carried out on the hydroelectric reservoir Petit-Saut on the Sinnamary river. This reservoir was filled in 1994, without destruction of the primary equatorial forest in the area covered by the waters, which led to a very slowly evolving anoxia in the water column. The oxycline is now at –5 m, for a maximal depth of 35 m. As sulfate reducing bacteria are thought to be the principal methylating agents in aquatic systems, the bottom waters of the reservoir were thought to represent an excellent site for mercury methylation.

2. FIELD SITE AND METHODS

2.1 Study site: Petit Saut Reservoir

The Petit Saut reservoir is located 50 km off the city of Kourou on the Sinnamary river. The reservoir covers 80 km of the river course. Impounding started in January 1994 and was completed in July 1995. Maximal depth of the Petit Saut reservoir is 35 m and the water level varies between 35 and 31.5 m depending on exploitation of the hydroelectric station. During impounding, approximately 350 km^2 of uncleared tropical forest were flooded. Within the dammed water-body the decomposition of submerged vegetation still takes place, with slow degradation kinetics. Possible localized sources of mercury contamination in Petit Saut reservoir include the upstream Saint-Elie gold-mining area, flowing into the reservoir through the Leblond river, and the impounded "Adieu Vat" former mining sites, located near the Roche Genipa sampling site (Fig. 1).

Sampling and measurements were performed in June 1999 (wet season) and December 1999 (end of dry season) along a longitudinal gradient, from upstream of the Petit-Saut reservoir (Coursibo and

Leblond rivers) to the Sinnamary river and the estuary downstream of the dam. The main vertical profile measurements were carried out at Roche Genipa station (N 4°56'474", W53°02'468"), located in the middle of the reservoir (Fig. 1).

2.2 Sampling and analytical methods

Sub-surface water samples were collected directly by hand in 2-l Teflon bottles. Water samples for the vertical profiles were collected using an ultra-clean Teflon pumping system or with a teflon-coated Niskin bottle. All Teflon and plastic ware was washed and stored according to the ultraclean procedure [2]. Filtered water samples (<0.7 µm) for dissolved total mercury (HgT) were transferred into Teflon bottles (FEP) and acidified with concentrated HCl. Filtered water for monomethylmercury (MMHg) and filters were stored at -18°C before analysis. Analyses of HgT were performed by reduction with $SnCl_2$, double gold amalgamation and detection by atomic fluorescence spectrometry (AFS). Dissolved HgT was determined after BrCl oxidation according to the EPA method [3]. Concentrations of particulate HgT were measured after acid mineralization in Teflon (PFA) reactors. Concentrations of dissolved MMHg were determined after double extraction using dichloromethane, followed by aqueous phase ethylation, isothermal gas chromatography, and detection by AFS [4]. Method accuracy and precision were checked by analysis of duplicate matrix spikes according to the EPA method [3] and the use of available reference materials (sediments: MESS-2 from the National Research Council of Canada and IAEA-356).

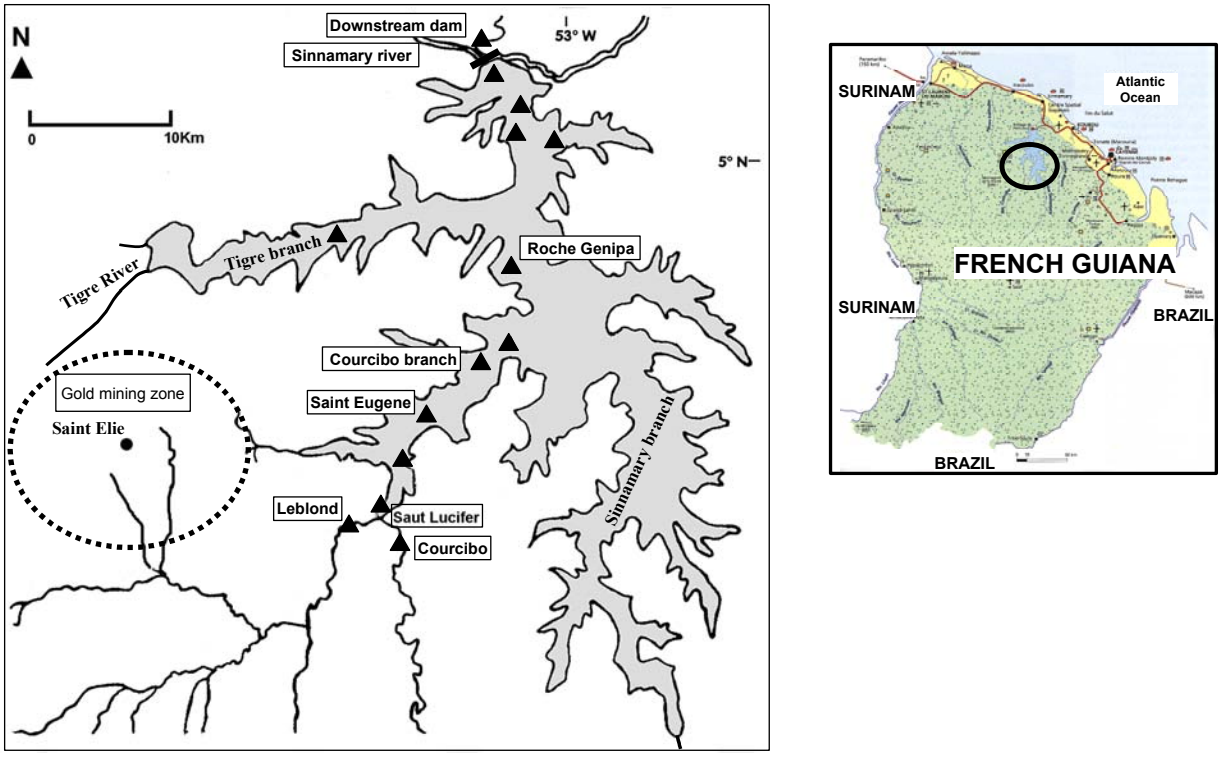

Figure 1. Localization of the study area and sampling sites along the Petit-Saut hydroelectric reservoir in French Guiana.

3. RESULTS AND DISCUSSION

Concentrations of dissolved and particulate Hg measured along the Sinnamary basin are summarized in Table 1 and show comparable values to published data for the Tapajos river and the Amazon river in Brazil [5].

Gold extraction has led to a marked increase in suspended matter (SM) in the Leblond river as compared to the Courcibo river, with mean values 7 and 4-fold higher during dry and wet seasons respectively (Table 1). Total mercury (HgT) concentrations in unfiltered water samples were 16 and 5 times higher in the Leblond river (dry and wet season respectively), with more than 80% in the particulate fraction. Our results also show marked differences of HgT concentrations in suspended particles

expressed in ng g^{-1} (x6.5 and x2 during dry and wet seasons, respectively). These differences could be due to direct mercury input from gold-mining activities and selective soil erosion at mining sites, involving discharge into the river of mercury-enriched particles different from those originating from natural watershed erosion.

In comparison, dissolved MMHg concentrations measured in surface waters were very close for both rivers with an average of 0.05 ng l^{-1} for Leblond and 0.03 ng l^{-1} for Courcibo, corresponding to 1 and 1.7% of dissolved HgT concentration, respectively. These results indicate similar methylation efficiency and/or transfer of MMHg into the dissolved fraction of the water column, independently of the amounts of inorganic mercury transported by the rivers.

The concentrations of dissolved HgT in surface waters of the reservoir were found to be of the same order of magnitude as the global average for unpolluted waters and were less than 4 ng l^{-1} (Table 1). In both seasons, concentrations of SM, dissolved and particulate HgT decreased along a longitudinal gradient from upstream stations (Saut Lucifer, Coursibo branch, see Fig.1) towards the dam and revealed an enrichment of HgT due to gold mining in the upstream Saint-Elie area that affects the Leblond river. Dissolved HgT in surface waters averaged 3.6 ng l^{-1} upstream and was less than 0.7 ng l^{-1} near the dam. According to the particulate load of the waters, the particulate mercury, which represented about 80% of the total mercury upstream, decreased very rapidly and was lower than 45% near the dam. Total Hg in suspended particulates also diminished in surface waters from upstream stations towards the dam (460-590 ng g^{-1} at Saut Lucifer and only 50-133 ng g^{-1} near the dam).

In contrast, dissolved MMHg concentrations in surface waters were similar all along the longitudinal gradient upstream and within the reservoir (0.01 to 0.05 ng l^{-1}, average: 0.02 ± 0.01 ng l^{-1}) representing on average 1.8 % of the HgT and comparable to what was found in the two upstream rivers (Table 1). This relatively low proportion of MMHg is typical for unpolluted surface freshwaters.

Table 1. Suspended particulate matter (SM) and mercury concentrations in the water column

	SM (mg l^{-1})	HgT (ng l^{-1})	HgT *dissolved* (ng l^{-1})	HgT *particulate* (ng l^{-1})	HgT *particulate* (ng g^{-1})	MMHg *dissolved* (ng l^{-1})
Leblond river	ds: 18.7 ± 0.9 ws: 36.7 ± 1.8	ds: 34.9 ± 5.4 ws: 25.4 ± 2.0	ds: 8.2 ± 1.2 ws: 2.9 ± 0.4	ds: 26.7 ± 5.3 ws: 22.5 ± 2.0	ds: 1431 ± 286 ws: 613 ± 55	ds: 0.061 ± 0.010 ws: 0.041 ± 0.008
Courcibo river	ds: 2.6 ± 0.1 ws: 9.8 ± 0.5	ds: 2.1 ± 0.2 ws: 5.4 ± 0.5	ds: 1.5 ± 0.2 ws: 2.4 ± 0.4	ds: 0.6 ± 0.1 ws: 3.0 ± 0.3	ds: 219 ± 44 ws: 308 ± 28	ds: 0.032 ± 0.008 ws: 0.026 ± 0.006
Petit Saut reservoir surface waters	ds: (4.9 – 8.6) ws: (5.2 – 22)	ds: (0.7 – 6.8) ws: (1.1 – 14.0)	ds: (0.6-3.9) ws: (0.7-3.3)	ds: (0.3 – 2.9) ws: (0.5 – 11.6)	ds: (34-593) ws: (59-528)	ds: 0.023 ± 0.011 ws: 0.025 ± 0.014
Roche Genipa bottom waters (below 10m)	ds: 0.6 ± 0.2 ws: 4.7 ± 2.3	ds: 3.9 ± 0.5 ws: 4.6 ± 0.7	ds: 3.6 ± 0.5 ws: 2.3 ± 0.3	ds: 0.3 ± 0.1 ws: 2.3 ± 0.6	ds: 583 ± 175 ws: 548 ± 141	ds: 0.56 ± 0.15 ws: 0.38 ± 0.08
Sinnamary - downstream dam station	ds: 4.7 ± 0.3 ws: 5.4 ± 0.3	ds: 2.4 ± 0.7 ws: 3.4 ± 0.4	ds: 1.8 ± 0.7 ws: 2.4 ± 0.4	ds: 0.6 ± 0.1 ws: 1.0 ± 0.1	ds: 125 ± 6 ws: 176 ± 16	ds: 0.56 ± 0.10 ws: 0.49 ± 0.08

HgT = inorganic Hg (Hg° + Hg(II)) + MMHg ; MMHg: monomethylmercury ;
ds: dry season, – ws: wet season ; mean values ± SD or (range).

At the Roche Genipa station, the shape of the vertical concentration profiles obtained on the 35 m deep water column showed a steep increase of dissolved HgT as well as dissolved MMHg with depth which corresponds to the diminution of oxygen (Fig. 2). Dissolved MMHg concentrations were more than 10 times higher in bottom waters (below 10m) compared to surface concentrations, with highest concentrations up to 0.6 ng l^{-1} with a corresponding percentage of MMHg compared to HgT of 20 %.

The observed difference in dissolved HgT concentrations in oxic and anoxic parts of the reservoir indicates that the principal source of mercury in the water column are soils flooded by the dam impounding as also shown for temperate water reservoirs [6, 7]. Forest soils in French Guiana contain relatively high Hg concentrations compared to other Amazonian soils [8]. During the dry season, mercury

released from sediments may accumulate in the bottom layer of the reservoir because of relatively low mixing processes [7].

The MMHg concentration profiles in the water column suggest that methylation occurs mainly in anoxic waters, below 10 m depth, and in surface sediments in the Petit Saut reservoir, in relation with the activity of sulfate reducing bacteria. Indeed, during the wet season, the dissolved MMHg profile shows a similar vertical distribution as sulphides. The water layer where MMHg and S(-II) concentrations rapidly increase with depth is located between 10 and 20m [7].

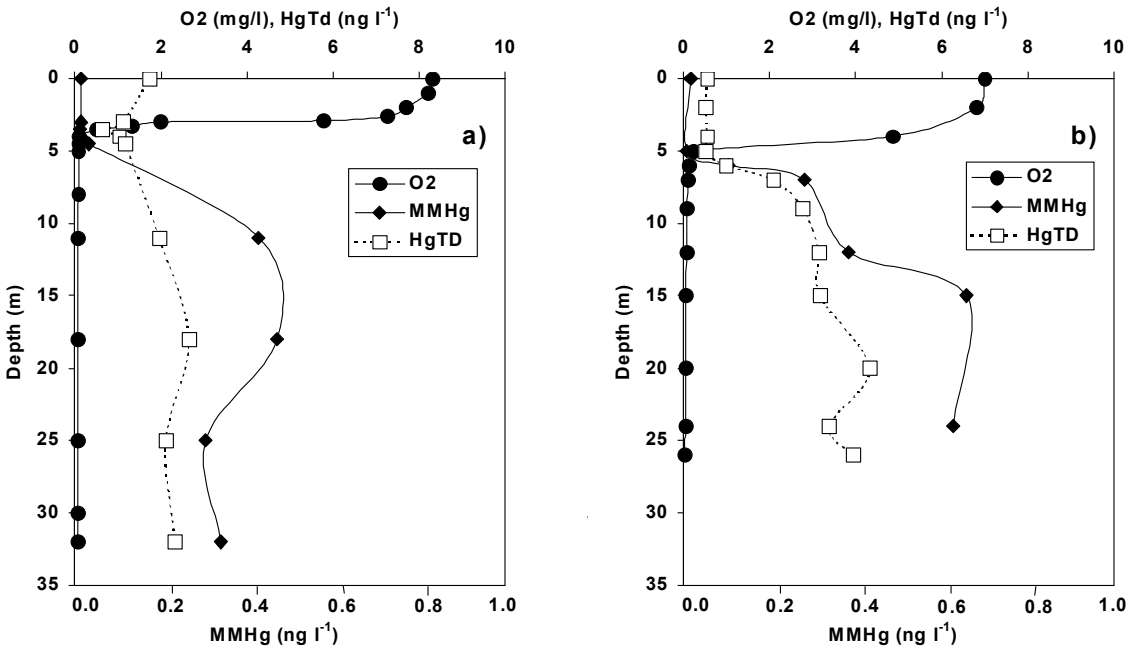

Figure 2. Vertical profiles of mercury concentrations at Roche Genipa station : a) wet season ; b) dry season.

Dissolved MMHg concentrations measured in the waters flowing through the turbine at the base of the dam and in the Sinnamary river downstream of the dam were still very high (0.5 – 0.6 ng l^{-1}) and constituted 20 to 35% of the dissolved HgT (Table 1). Concentration of dissolved HgT averaged about 2 ng l^{-1} in the Sinnamary river downstream of the dam and varied between 1 and 2.8 ng l^{-1} downstream.

In the estuarine waters, preliminary results showed that dissolved HgT concentrations were lower than 0.5 ng l^{-1} for a salinity of 24.4 PSU and the MMHg represented about 1% of the HgT, a fraction similar to what is usually found in this type of environment.

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