Elemental Mercury in the Atmosphere of a Tropical Amazonian Forest (French Guiana)

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Gaseous atmospheric mercury was investigated at two sites of a tropical Amazonian forest (French Guiana) in the Petit Inini River basin and the Petit Saut Lake in June, 1998. Gaseous atmospheric mercury was identified as elemental mercury (Hg^0). Diurnal variation of atmospheric Hg^0 in both studied aquatic environments were significantly correlated with air temperature and anticorrelated with relative humidity. Average Hg^0 concentrations were higher above the Petit Inini River (75 pmol m^{-3}/15.0 ng m^{-3}) than the Petit Saut Lake (14 pmol m^{-3}/2.8 ng m^{-3}). Background Hg^0 concentrations in the Petit Inini River basin were higher (27 pmol m^{-3}/5.4 ng m^{-3}) than those observed in remote environments. These data suggest that gold mining activity (i.e., Petit Inini River basin) may influence mercury mobilization in tropical forest ecosystems and that atmospheric transfer is a major pathway for mercury cycling in these environments.

Introduction

Mercury (Hg) contamination in the Amazon ecosystem has been investigated since the early nineties (*1*, *2*). This sudden interest in Hg pollution and cycling follows the development of gold mining exploitation in the different Amazonian countries since the mid-seventies (*1*, *3–5*). The use of elemental mercury (Hg^0) to amalgamate and extract gold from river sediments or ore deposits by independent and mostly illegal gold miners ("garimpeiros") has led to the release of an important fraction of this pollutant into the environment (*6*, *7*). The low-cost procedures used by these small exploitations discharge between 1 and 2 kg of Hg per kg of extracted gold, either by volatilization resulting from the amalgam burning or by direct loss into the sediments or soils (*5*, *6*). Additionally, impact on human population has been observed in major gold exploitation areas of Brazil (*3*, *8*, *9*). High mercury concentrations were measured in urine or blood samples from gold miners and gold traders or fish-eating local populations, respectively (*3*, *8*). The fish-eating population are specially affected by Hg contamination because they ingest the harmful methylmercury (MeHg) which accumulates and reaches toxic levels. Malm et al. (*8*)

found high concentrations of Hg ($>50\ \mu g\ g^{-1}$, mostly as MeHg) in hair samples of populations living in the Tapajós River basin. In Amazonian river basins, where gold mining expands, carnivorous fishes exhibit high Hg concentrations ($>0.5\ \mu g\ g^{-1}$), 10 times greater than noncarnivorous species (*6*). Bioaccumulation of MeHg within the aquatic food chain seems therefore to be the major pathway for Hg contamination.

A major issue for the assessment of Hg contamination from gold mining activities is to understand how Hg can be spread over a whole river basin and affect aquatic organisms. Although Hg can be transported by rivers over long distance, this metal is suspected to be principally emitted to the atmosphere as Hg^0 from gold extraction/purification processes in roasting devices (*5*, *6*). For Brazil, 77.9 t yr^{-1} of Hg has been estimated to be released to the atmosphere from gold mining, representing 67.3% of that country's anthropogenic emissions (*7*). In the case of French Guiana, 3 t yr^{-1} of Hg are believed to be emitted to the atmosphere as a result of gold mining activities (*10*). In the Amazonian atmosphere, gaseous Hg lifetime is expected to be shorter than in temperate environments (ca. 1 yr, *11*), because this rainforest ecosystem is emitting large amount of reactive gases and aerosols (*12*) which are able to enhance Hg^0 oxidation rate and therefore precipitation washout. Nevertheless, the scarce Hg speciation studies in the Amazonian environment do not permit understanding how Hg is transported, methylated, and finally transferred to aquatic organisms.

In this paper, we present the first gaseous Hg speciation measurements in the atmosphere and waters from a tropical Amazonian forest ecosystem. Diurnal variability and average site concentrations of gaseous Hg have been investigated in two remote areas in French Guiana suspected to be directly or indirectly affected by gold mining activities.

Experimental Section

Air and water samples were collected at two distinct areas of the French Guiana, as shown in Figure 1, during a wet season (two weeks in June, 1998). Two sampling sites were studied in the Petit Inini river basin (200 km SW of Cayenne; latitude 3°45′ N/longitude 53°33′ W), which has been prospected for the last 100 years, but with a large development of illegal exploitations since the eighties. Air samples were collected at both sites: the Dorlin Camp Hill (DCH), in an open deforested area (altitude 250 m), and downhill from the Dorlin camp in the margin of the Petit Inini River (PIR) and beneath the forest canopy (altitude 130 m). The second sampling area is in the Petit Saut Lake (PSL; 50 km SW of Kourou; latitude 5°05′ N/longitude 53°03′ W), a large artificial lake covering a former tropical forest valley (310 km²) that was formed 5 years ago due to the construction of a hydroelectric power plant dam. The lake is situated on the Sinnamary river basin which is also an area of past and present gold exploitations (upstream of the lake). Air samples were collected on a floating platform positioned in the central part of the lake (altitude 30 m), 20 km upstream of the dam of Petit Saut. It is important to mention that no rainfall occurred during the atmospheric sampling periods.

Sampling and storage equipment was made of Teflon, PVDF, PE, or PP, washed with detergent, soaked several days with 10% nitric acid, rinsed with milli-Q Millipore water and stored in double-zipped plastic bags. The sampling techniques and analytical methodologies used in this work are described below and are detailed elsewhere (*13–16*).

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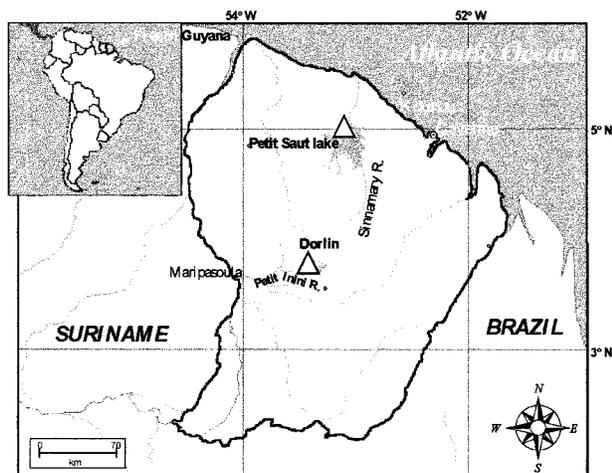†On leave from the Department of Geochemistry, University Federal Fluminense, Niteroi, Brazil.

FIGURE 1. Location of sampling sites in French Guiana (South America).

Air samples were collected at 1.5 m height above the ground (soil or water). The air inlet was made of a filtration cartridge (Millipore) with a quartz microfiber filter (Whatmann) to separate aerosols from the air stream (pore size 0.1 μm). Air was pumped for 1 h with a vacuum membrane pump (KNF) through a Teflon tubing line (i.d. 1.6 mm; maximum length 5 m) to the gaseous Hg trapping device. Potential back diffusion contamination from the pump was avoided by placing an activated charcoal cartridge (Supelco) between the pump and the Hg trap. Air-pumping flow rate ranged from 0.5 to 1 L min^{-1}, which was continuously controlled during every 1 h sampling period by a calibrated gas flowmeter. Most of the samples were collected on single gold-coated quartz sand (Brooks) traps (borosilicate tube, o.d. 8 mm, length 120 mm). Dual sampling was also performed for the speciation study on both gold-coated traps and cryogenic traps. For cryogenic trapping, the air stream passed through a moisture trap, held at -20 °C, and subsequently through silanized glass wool (U-borosilicate tube, o.d. 8 mm, length 200 mm) maintained at -180 °C in a Dewar containing boiling liquid nitrogen. After collection, gold-coated and cryogenic traps were sealed with gas chromatographic end-caps (Alltech) and stored until analysis in a hermetically sealed plastic box filled with activated charcoal and in a transportable cryogenic container filled with liquid nitrogen (L'Air Liquide), respectively.

Water samples were collected and immediately transported in an opaque refrigerated box to the site where the equipment was installed. Analyses were always performed within less than 2 h of the sampling. Dissolved gaseous Hg was trapped by purging 1 L of surface water, with pure helium (L'Air Liquide) at 1 L min^{-1} during 1 h (16). The gas stream was dried through a moisture trap, and gaseous Hg species were trapped either in a gold-coated or cryogenic trap in the same manner as for the air samples. Water samples were also acidified to 1% ultrapure nitric acid (Prochilab) for determination of total reducible Hg content, after direct hydride generation-cryofocusing gas chromatography and atomic absorption spectrometry (17).

Gold-coated and cryogenic traps were subsequently desorbed in the laboratory at 500 and 300 °C, respectively, under pure He carrier gas into a cryogenic gas chromatographic device connected to an ICP/MS (ELAN 6000, Perkin-Elmer-Sciex). The gaseous species are then cryofocused on the GC column to be subsequently separated and detected by choosing appropriate Hg stable isotopes (i.e., ^{200}Hg and ^{202}Hg) (15). Cryogenic traps were therefore used to investigate the speciation of gaseous Hg compounds in several atmospheric and aqueous samples (15, 16). Theoretically, a
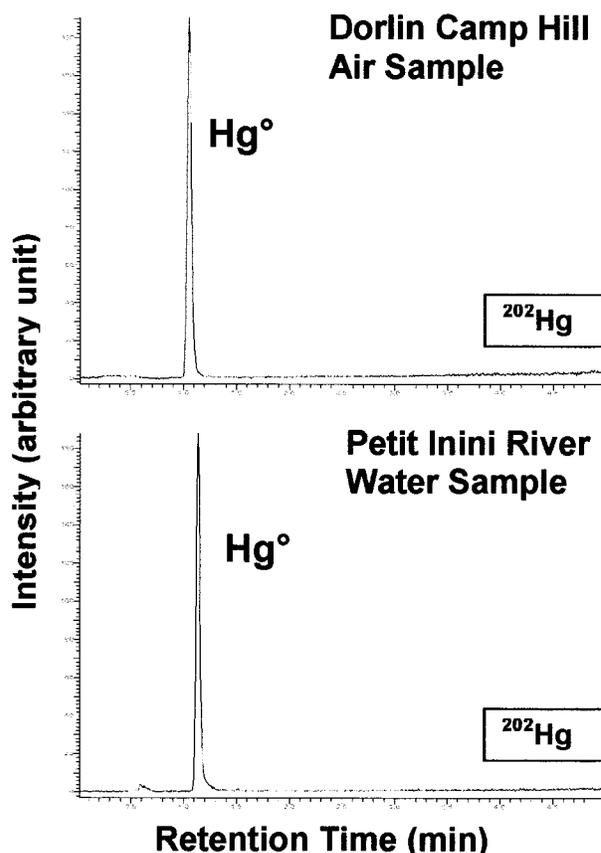

FIGURE 2. Chromatograms of gaseous mercury speciation of air and water samples from Dorlin Camp Hill and Petit Inini River, respectively. Analyses were performed by cryofocusing gas chromatography, followed by inductively coupled plasma mass spectrometry detection (15,16).

number of organic and inorganic gaseous forms of mercury can be detected by this method, but only standards of Hg^0, dimethylmercury, and diethylmercury were tested. Nonetheless, the chromatograms in Figure 2 indicate that the unique form present in air and water samples is Hg^0. Quantitative data were based on gold-coated trapped samples.

For both trapping methods, several traps were used for blank field measurements following the same process as for sample traps. Average measured values of the blanks were subtracted from the sample measured values of the samples, and the standard deviation of the blank values allowed us to estimate the field detection limit for the method to be 150 fmol, which represents 3 pmol m^{-3} (600 pg m^{-3}) in air samples and 150 pmol m^{-3} (30 ng m^{-3}) in water samples.

Atmospheric relative humidity, air temperature, and direct UV−visible sunlight radiation were also measured at the air-sampling inlet using a data logging thermohygrometer (Hanna Instruments) and an UV−visible photocell (Applied Photophysics).

Results and Discussion

Speciation of Atmospheric Mercury. Speciation analysis of volatile Hg compounds by cryotrapping air and purged water samples indicate that the only species identified is Hg^0 (Figure 2). The intercomparison between cryogenic trapping and gold amalgamation for atmospheric samples has been performed on four duplicates at the DCH site. Although cryogenic trapping quantification suffered from ice clogging due to high moisture content, the cryogenic trapping and gold amalgamation sampling methods show rather good
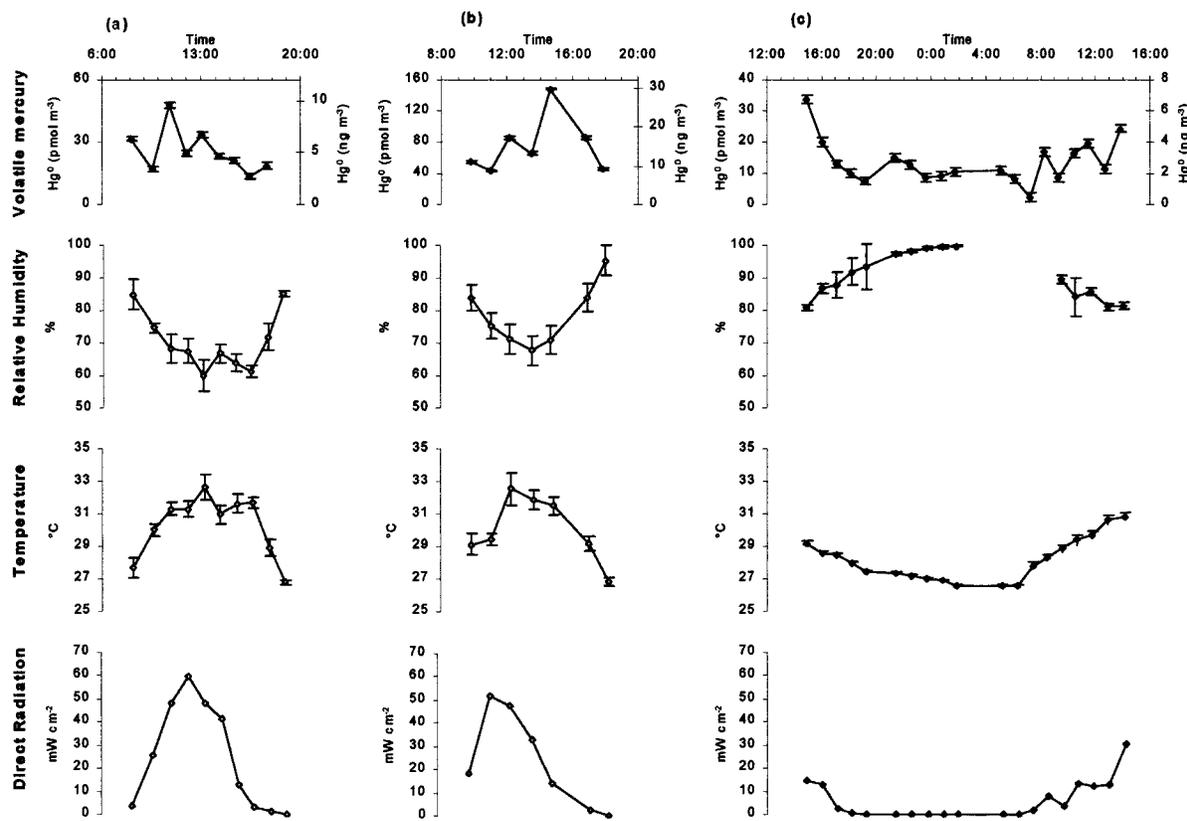
FIGURE 3. Time series measurements of atmospheric elemental mercury concentrations at (a) Dorlin Camp Hill, (b) Petit Inini River, and (c) Petit Saut Lake, together with air temparature, relative humidity, and vertical sunlight UV—visible radiation. Time = UTC − 6 h.

TABLE 1. Linear Regression Equations for Elemental Mercury (Hg⁰) vs Air Relative Humidity (RH) and Temperature (Tp) for the Various Atmospheric Sampling Sites in French Guiana (June, 1998)

regression	site	n	r^2	slope	intercept
Hg⁰ vs RH	DCH	14	0.001	0.15	71.94
	PIR	7	0.210	−0.62	87.64
	PSL	19	0.457	−3.32	101.00
Hg⁰ vs Tp	DCH	14	0.003	0.08	29.31
	PIR	7	0.299	0.15	27.62
	PSL	19	0.303	0.52	26.77

agreement with 26 ± 10 pmol m^{-3} (5.0 ± 2.0 ng m^{-3}) and 29 ± 2 pmol m^{-3} (5.8 ± 0.4 ng m^{-3}; $n = 4$), respectively. Higher average concentrations obtained with gold amalgamation probably illustrate the occurrence of inorganic or reactive gaseous Hg species which are suspected to be formed under such meteorological conditions (*18*). However, the difference between both methods was not statistically significant. We can therefore assume that gaseous Hg in the atmosphere was essentially in the form of Hg⁰.

Diurnal Variabilty of Atmospheric Hg⁰. Atmospheric concentrations of Hg⁰ were investigated during a 2-day time period at DCH and PIR and one complete diurnal cycle at PSL. The results obtained are displayed on time series plots in Figure 3, along with atmospheric relative humidity (RH), air temperature (Tp), and direct UV—visible sunlight radiation (UVR). The variability of Hg⁰ concentrations in all three sites seems to correlate with the meteorological parameters recorded, exhibiting a maximum concentration at noon (between 12:00 a.m. and 2:00 p.m.) and a minimum concentration in the evening and at night. Regressions between Hg⁰ and RH, Hg⁰ and Tp are shown in Table 1. No regression analysis was performed with UVR because they were not corresponding to total incident radiation and were

recorded only every 15 min (each minute for RH and Tp). Good correlations were obtained with RH and Tp for both PIR and PSL sampling sites. On the other hand, no correlation was observed for both parameters at DCH site. These results indicate that atmospheric samples collected at DCH are more homogeneous and represent atmospheric Hg⁰ concentrations of a well mixed atmosphere rather than mercury coming from soil evasion. The two sampling sites above aquatic environments have both wider ranges of RH and Tp throughout the day which lead to increase atmospheric Hg⁰ variations. As surrounding environments such as surface waters and soils and vegetation are probably potential source of Hg⁰ to the atmosphere, meteorological conditions are therefore playing a major role in the volatilization of Hg⁰. Previous studies have demonstrated that temperature, sunlight, and air movement were significant parameters for surface exchanges of gaseous Hg with the atmosphere (*19–24*). Our results indicate that they apparently play a similar role in the tropical rainforest.

Distribution and Potential Sources of Atmospheric Hg⁰. Table 2 shows the average concentrations of Hg⁰ (± standard deviation) in the atmosphere at the three different sites investigated in French Guiana: Dorlin Camp Hill (DCH), Petit Inini River (PIR) and Petit Saut Lake (PSL). Additionally, Hg⁰ concentrations measured in surface waters of the PIR and PSL are indicated.

PSL Hg⁰ concentrations in the atmosphere are similar to values observed in most background sites at various latitudes (*25*). Average concentrations recorded at DCH and PIR are significantly higher than those obtained at PSL (Table 2). This indicates that Hg⁰ measured in the DCH and PIR could originate partly from natural sources (*26, 27*) but also from anthropogenic local sources (gold mining). DCH samples, collected in a higher and clearer point, represent the well-mixed layers over the rain forest canopy and could be considered as background concentration for the Petit Inini

TABLE 2. Average Elemental Mercury Concentrations in the Atmosphere (Height: 1.5 m) and Surface Waters of French Guiana (June, 1998)

sample site	Hg^0-atmosphere pmol m^{-3} (ng m^{-3})	Hg^0-water[a] pmol m^{-3} (ng m^{-3})
Dorlin Camp Hill (DCH) 16-18/06/98	27 ± 8 (5.4 ± 1.6) ($n = 14$)	n.s.
Petit Inini River (PIR) 17/06/98	75 ± 36 (15.0 ± 7.2) ($n = 7$)	2859 ± 90 (573.5 ± 18.1) ($n = 2$)
Petit Saut Lake (PSL) 24-25/06/98	14 ± 7 (2.8 ± 1.4) ($n = 19$)	979 ± 50 (196.4 ± 10.0) ($n = 2$)
background levels (ref)	5−20 (1.0−4.0) (22)	10−1000 (2.0−200.6) (25)

[a] n.s.: no sample.

basin during the sampling period (June, 1998). On the other hand, higher concentrations at PIR could result from a sort of "greenhouse" effect retaining beneath the canopy the Hg^0 which is released by the river water or by the dense vegetation. The role of tropical vegetation in the volatilization of Hg is unknown and difficult to investigate. The atmosphere beneath the canopy is probably not well mixed with the overlaying troposphere, and the accumulation of Hg^0 from surface exchange processes may occur in this compartment (26).

Hg^0 concentrations in surface waters are about 3 times higher at PIR than at PSL (Table 2) and demonstrate that the Hg load at PIR is probably more important than at PSL. Natural biological and chemical pathways of Hg^0 production in surface waters (28−30) suggest that PSL site (sunlight, water temperature 31 °C) is more favorable for Hg^0 formation than PIR site (shaded, water temperature 25 °C). However, total reducible Hg concentrations (by sodium borohydride method, see ref 17) were also found to be higher at PIR than at PSL, exhibiting 680 and 480 pmol L^{-1} (136.4 and 96.3 ng L^{-1}), respectively. PIR seems therefore directly affected by gold exploitations that release their slurries upstream from the sampling point. In Brazilian gold mining areas, Roulet et al. (31) found that ferralitic soils enriched with Hg were a major source of Hg to the aquatic environment via erosion or resuspension processes. At both sites PSL and PIR, surface waters were found highly supersaturated with Hg^0 compared to the atmosphere with average saturation of 2937 and 1372%, respectively. Consequently, assuming an average water−air transfer coefficient for Hg^0 of 0.5 m d^{-1} (typical for low turbulent surface water), Hg volatilization fluxes from both PSL and PIR surface waters are 473 and 1325 pmol m^{-2} d^{-1} (95.0 and 266 ng m^{-2} d^{-1}), respectively. These fluxes are much higher than those measured in various lakes or marine environments (25) and indicate that aquatic environments, such as rivers, lakes, or flooded areas, in tropical rain forests are probably important sources for atmospheric Hg. Considering a simple mass balance model used by Mason et al. (28) for Hg^0 formation and volatilization in surface waters, and neglecting Hg^0 oxidation (30), we estimated that first-order Hg(II) reduction rate into Hg^0 would be approximately 20 and 40% day^{-1} for PSL and PIR, respectively. The potential Hg(II) reduction capacity of these environments seems therefore extremely high and represents a major pathway for the dynamic recycling of Hg from gold mining areas, enhancing the atmospheric transfer in the Amazonian ecosystem.

The Hg sources responsible for the relatively high Hg^0 concentrations measured in Petit Inini River basin could be attributed to direct Hg^0 emission from amalgam combustion or mine tailing and indirect Hg^0 formation from reducible Hg released by atmospheric washout, soil weathering, or mining activity. Atmospheric Hg cycling in the tropical rain forest is probably more dynamic and critical than in previously investigated temperate environments and requires further investigations.

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