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Photochemical Dissolved Gaseous Mercury (DGM) Formation/Consumption in the Negro River Basin, Brazilian Amazon

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Consumo/formação de mercúrio dissolvido gasoso (MDG) foi medido durante campanhas na Bacia do Rio Negro, Amazônia, Brasil. Foram realizadas medidas diuturnas em águas brancas e pretas. Em águas brancas, pH próximo a 7 e baixa concentração de carbono orgânico dissolvido (DOC), a saturação de MDG prevalece no período iluminado, similar a outras regiões do planeta. Esta geração de MDG foi atribuída à redução fotoinduzida do Hg^{2+}. Por sua vez, em águas pretas, caracterizada pelo pH próximo a 5 e alto valor de DOC (até 20 mg L^{-1}), a concentração de MDG permanece abaixo do limite de detecção no período iluminado, o que pode estar associado a oxidação fotoinduzida do Hg^0. Experimentos fotoquímicos *in situ* corroboram a influência da radiação solar no consumo/formação do MDG. A comparação da saturação do MDG é apresentada para águas pretas e brancas.

Dissolved gaseous mercury (DGM) formation/consumption was measured during several scientific excursions in the Negro River basin, Amazon, Brazil. Measurements were carried out following diel patterns in both white and black water bodies. In white waters, with pH values around 7 and low dissolved organic carbon (DOC) concentration, mercury saturation prevails during the sunlit period, similar to behavior observed elsewhere. This was attributed to DGM generated by a photoinduced mechanism of Hg^{2+} reduction. On the other hand, in black waters, with pH around 5 and high DOC values (up to 20 mg L^{-1}), DGM concentration stays below the detection limit during sunlit periods, which was associated to photoinduced Hg^0 oxidation. Photochemical experiments carried out *in situ* corroborate the influence of sunlight on DGM formation/consumption. A comparison of diel DGM saturation is presented for both black and white water bodies.

Keywords: dissolved gaseous mercury (DGM), dissolved organic carbon (DOC), black water, photolysis.

Introduction

Dissolved gaseous mercury (DGM) includes all gaseous species of mercury such as dimethylmercury and the elemental form (Hg^0), the latter being responsible for more than 90% of this pool of species.[1] In water bodies, DGM undergoes bidirectional fluxes at the water/air interface, in a mechanism that helps to regulate the mercury pool in these compartments.[2] Mercury flux across this interface involves both kinetic and thermodynamic aspects, which may be evaluated with the help of Fick's law and Henry's law, respectively.[3] Both approaches have been widely applied to both continental and oceanic environments.[4,5]

Vandal *et al.*,[4] for instance, investigated several temperate lakes in the United States and observed that, in general, these water bodies are supersaturated with respect to DGM, reaching the highest concentration in summer and decreasing as a function of pH. Costa and Liss,[5] during their study on the generation of DGM in sea water, pointed out that photoinduced reduction of mercury mediated by humic substances could be responsible for the diel variation, as the DGM fluxes were higher during the day when compared to the nocturnal period. According to Schroeder *et al.*,[6] DGM formation/consumption in Lake Eagle, in Canada, followed not only a seasonal but also a diel pattern, with higher values observed during sunlit periods. To explain such behaviors, the authors quoted an early work of Cooper and Lean,[7] who observed a variation

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in the H_2O_2 concentration in lake waters as a compound that could be the principal one responsible for the redox chemistry of aqueous mercury species.

In a broad sense, DGM formation in water bodies follows a general pattern that can be summarized[4,6,8-14] as: (*i*) DGM formation is higher during sunlit periods, (*ii*) DGM formation is seasonal, with a peak in summer, (*iii*) photoinduced reactions are the principal one responsible for DGM formation/consumption, (*iv*) dissolved organic matter contributes to the DGM formation/consumption.

In the case of the Negro River basin, DGM formation/consumption were firstly investigated by Fadini and Jardim,[15] who pointed out the existence of a very distinctive behavior for black waters, where the authors observed photoinduced Hg^0 oxidation. Recently, Lalonde *et al.*[16] also showed photoinduced Hg^0 oxidation for St. Lawrence Estuary, where reaction rates were evaluated at different wavelengths.

Understanding the redox chemistry of mercury in Negro River basin waters is of paramount importance, due to the fact that the region presents high levels of this metal, as pointed out by Fadini and Jardim.[17] As the metal residence time in the aquatic system increases, the chances of biomagnification also rise, thus increasing the mercury concentration in fish, the major protein source in the region.[18,19] Riparian population along the Negro River tends to present very high levels of mercury in the hair, as shown by Forsberg *et al.*[20] The present study helps to understand the transport of mercury across the water/air interface.

Experimental

Study area

The Negro River basin spreads over an area of 690 × 10^3 km^2, corresponding to 14% of the Brazilian Amazon. This ecosystem is very abundant in water, showing two major types of aquatic bodies, with very distinctive chemical properties, originally classified as black and white waters.[21] Representatives of each of these bodies are Aracá Lake (white water, S01°14´, W61°50´), Branco River (white water, S01°14´, W61°50´), Caurés River (black water, S01°79´, W62°19´) and Iara Lake (black water, S01°20´, W62°03´), some of whose physical-chemical parameters are presented in Table 1. Iara Lake can be considered different from other lakes because it is branch of a main stream of the Negro River, but comparable to lentic aquatic systems. During the dry season, when the field campaigns were carried out, the water column varied from 2 to 4 m approximately, but reaches up to 12 m in the rainy season. Aracá Lake is an isolated and small aquatic system, some meters off Branco River's right bank, and has less sediment in its waters. Although constituted by white waters, Branco River seems more susceptible to waters properties changing due to large drainage area compared to Aracá Lake. Branco River's waters showed a great variation in total mercury concentration (Hg_{total}) depending on field campaign. For instance, during 2002, Hg_{total} was 4.6 ng L^{-1}, and in the next year, 2003, Hg_{total} was 0.8 ng L^{-1} (Table 1), the lowest value observed in the campaigns. In general, it is not uncommon this variation in mercury concentration in the Negro River Basin due to its peculiar and complex hydrology. DGM results presented in this paper were obtained in two different campaigns in this basin (dry seasons of 2002 and 2003).

Water sampling

Sub-surface (10 cm) water samples were collected using 1.5 L polyethylene terephthalate (PET) bottles, commercially available from mineral water suppliers. After sampling, the bottles were immediately transported to the laboratory installed in the boat for DGM analysis. Fadini and Jardim[22] validated the use of PET bottles for water sampling of the Negro River area by comparison with the traditional Teflon bottles, taking into consideration both sampling and storage of low concentration mercury samples. Laboratory preparation of PET bottles consists of discharging the original mineral water, washing several times with MilliQ water, drying in a class 100 fume hood, rinsing with 100 mL of high purity 0.1 mol L^{-1} HCl and, finally, wrapping in three layers of plastic bags

Table 1. Water properties of the aquatic systems investigated in this work.

Lake	Sort Amazon water	time (h)	Date	T ^{0}C	pH	Cond.[a] (µS/cm)	Dissolved Oxygen (mg O_2 L^{-1})	DOC (mg C L^{-1})	Hg_{total} (ng L^{-1})
Aracá Lake	White	12:00	01/02/02	31.4	6.49	7.8	3.60	7.3	7.4 ± 0.6
Branco River	White	13:00	01/19/03	30.0	7.20	28	5.3	3.5	0.8 ± 0.2
Iara Lake	Black	12:00	01/28/03	31.6	4.75	10.6	4.84	16	2.7 ± 0.5
Caurés River	Black	16:00	01/25/03	29.3	5.00	12	5.9	12.1	3.1 ± 0.5

[a] conductivity.

until sampling. Samples were collected and handled using ultra-clean techniques, including shoulder-length polyethylene gloves, taking account of precautions similar to the ones used for measurement in open sea water.[23,24] The determination of pH, conductivity and temperature was carried out *in situ* using an Orion field instrument. Dissolved organic carbon (DOC) was determined using a Shimadzu 5000 TOC analyser, after preserving the samples with phosphoric acid (pH *ca.* 2) and keeping them under refrigeration until they were analyzed in the Environmental Chemistry Laboratory, UNICAMP, Campinas.

Determination of DGM in the surface waters

DGM was determined by purging 1.0 L of the water that had just been collected for 30 min using an argon flow of 500 mL min^{-1}. The mercury released was amalgamated in a gold-coated column, thermally desorbed by heating, and detected on board using a Brooks Rand™ Cold Vapor Fluorescent Atomic Spectrometer (CVFAS).[17,25,26] The analytical curve was constructed using mercury saturated vapor, as recommended by Dumarey *et al.*[27]

Analytical working curves for Hg^0 were made *in situ* before DGM measurement for each gold coated column. The quantification limit was 45 fmol L^{-1}, defined as 10 times the standard deviation of the blank obtained in the procedure. Procedural blanks were made for the same water sample after DGM measurements, using the same purge and trap procedures described above. Successive blank measurements were reproducible, which indicate measurement conditions were appropriate to remove all DGM from the water sample. Triplicate analyses of water samples were carried out to determine the coefficient of variation, which ranged between 8.1 to 16.8%. Between measurements, vapor saturated elemental mercury standards were injected using a gas-tight syringe into the gold-coated column to check recovery.

During these campaigns, DGM measurements were carried out at two different sites: Aracá Lake (white water) and Iara (black water).

Determination of the total mercury in the atmosphere

The quantification of mercury in the atmosphere was obtained by pumping air through a quartz gold-coated column, situated about 1 m over the water surface using a battery-operated air pump, continuously monitored by a flowmeter. A known volume of air, typically 90 to 180 L, was collected employing a flow rate between 300 and 500 mL min^{-1}, corresponding to a sampling time of 5 to 10 h. Atmospheric mercury concentrations were obtained in triplicate for the diurnal and the nocturnal periods. The mercury trapped in the quartz gold-coated column was thermally desorbed and analyzed by cold vapor atomic fluorescence spectrometry (CVAFS). Analytical curves were constructed by injecting different volumes of saturated mercury vapor into the system.[27]

Photochemical experiments

During the campaigns of January 2002 and 2003, photochemical experiments were carried out using both white water samples from the Branco River and black water samples from the Caurés River and Iara Lake, aiming to evaluate the role of solar irradiation on DGM formation/consumption in these aquatic systems. Five different water surface samples (1.5 L) were collected in PET bottles in the morning with no headspace, and received a spike of 100 ng L^{-1} of Hg^{2+}. This spike took place due to the fact that the natural DGM concentration was too low. One bottle was kept in the dark by wrapping it in aluminum foil, while the other four bottles were exposed to sunlight. All bottles were incubated *in situ*, 5 cm below the water surface. At specified intervals (including at zero hour, e.g., just after the spike), one of the sunlit bottles was removed from the incubation place and analyzed for DGM according to the procedure described above. The bottle kept in the dark was analyzed at the end of each experiment. Solar intensity was measured using a 365 nm Cole Parmer Radiometer. All experiments were carried out in triplicate.

Saturation index (SI) for DGM

It is possible to calculate the saturation index for DGM (SI)[28] in the aqueous phase using the equation 1:

$$SI = 100 \text{ x } \frac{C_{\text{water measured}}}{C_{\text{water equilibrium}}} \qquad (1)$$

where $C_{\text{water/measured}}$ is the measured DGM in the water, and $C_{\text{water/equilibrium}}$ is the expected concentration calculated according to Henry's Law constant (equation 2), where C_{atm} is total mercury concentration in atmosphere; Henry's Law constant is obtained using the linear relationship between elemental mercury solubility and temperature, according to equation 3,[29] where T is the absolute water temperature.

$$H = C_{\text{atm}} / C_{\text{water equilibrium}} \qquad (2)$$

$$Log\ H = -1002 \text{ x } (1/T) + 2.886 \qquad (3)$$

Results and Discussion

Total mercury in the atmosphere

Total mercury concentration in the atmosphere (pmol m^{-3}) for different rivers and lakes along to Negro River basin showed a mean value of 6.8 ± 3.2 (n = 26), with a range of 2.9 to 13.1 pmol m^{-3}. The mean value is in accordance with that found by Fadini and Jardim,[17] which is approximately three times higher than the value estimated from the last century, 2.5 pmol.m^{-3}.[30] Particularly for the aquatic systems studied in this work, atmospheric total mercury concentrations were measured in triplicate. These values for Aracá Lake in 2002 and 2003 were 7.8 ± 1.4 and 7.1 ± 2.0 pmol m^{-3} respectively, and 5.0 ± 1.5 pmol m^{-3} for Iara Lake in 2003.

White waters

Values of SI were calculated in campaigns carried out for Aracá Lake in January 2002 and 2003 (Table 2), where a well-behaved diel pattern was observed, with day time values ranging from 245 to 2299%. During the nocturnal period, SI decreased below the quantification limit. Solar intensities for both campaigns reached their maximum values at 12 h, 2.17 mW cm^{-1} and 3.10 mW cm^{-1}, respectively. Despite the fact that mercury water chemistry is closely related to solar light, significant correlation was not obtained between DGM production and instantaneous solar intensity, as measured in the experiments. When compared to values obtained for other aquatic systems elsewhere on the planet,[28] SI values obtained for these Amazonian water bodies are comparable.

Field photochemical experiments were carried out during the campaigns and the results obtained for the Branco River are presented in Figure 1. DGM values in a sunlit water samples in the 2002 campaign increased from 25,000 fmol to 40,000 fmol after 6 h of incubation, while the dark sample showed approximately the same DGM value after 6.5 h. Therefore, it is observed that when samples spiked with 100 ng L^{-1} of Hg^{2+} are incubated under solar light, they show a much higher DGM concentration than the ones kept in the dark. Similar behavior was observed for photochemical experiments carried out in January 2003.

Higher SI in the aqueous phase during the day were observed by other authors.[4,11-13,31-34] Particularly for white water bodies in the Negro River basin, marked by neutral and alkaline conditions, Fadini and Jardim[15] suggested that H_2O_2 is able to reduce mercury ($H_2O_2 + 2OH^- + Hg^{2+} = O_2 + 2H_2O + Hg^0$). Fadini[35] showed experimentally that samples from the Rio Branco spiked with H_2O_2 had an increase in DGM formation. Therefore, the author emphasized the importance of considering a photoinduced reductive mechanism for Hg^{2+}. It is worth mentioning that, in both white and black waters, H_2O_2 background concentrations ranged from 50 to 300 nmol L^{-1}, similar to other aquatic systems elsewhere.[36]

Table 2. Saturation Index (SI) for DGM at Aracá Lake observed during the dry seasons of 2002 and 2003.

Campaign	time (h)	Solar Intensity mW cm^{-1}	T (^{0}C)	H^a	C^b $_{water/measured}$ (fmol, n=3)	C^c $_{water/equilibrium}$ (fmol)	SI^d
January 2002	17:00	0.81	30.1	0.363	500 ± 40	21.8	2299
	21: 30	-	29.9	0.361	< QL^e	ND^f	ND
	7:00	0.32	28.5	0.349	181 ± 20	22.6	799
	12:00	2.17	31.4	0.375	81 ± 10	21.1	385
	16:00	0.13	30.1	0.363	152 ± 15	21.8	699
	18:30	-	29.6	0.359	54 ± 5	22.0	245
	22:00	-	28.8	0.351	< QL	ND	ND
	2:00	-	28.2	0.346	< QL	ND	ND
January 2003	01:00	-	28.4	0.348	< QL	ND	ND
	06:00	0.06	28.0	0.344	< QL	ND	ND
	12:00	3.10	32.0	0.381	125 ± 10	18.4	680
	15:00	2.67	31.0	0.371	215 ± 21	18.8	1141
	18:00	0.20	29.4	0.357	79 ± 7	19.6	403
	06:00	0.03	28.3	0.347	< QL	ND	ND

$C_{atm/measured}$ = 7.9 pmol m^{-3} and 7.0 pmol m^{-3} for 2002 and 2003, respectively . [a]H is the Henry´s Law constant. [b]$C_{water/measured}$ is the dissolved gaseous mercury concentration measured in the water column. [c]C $_{water/equilibrium}$ is the dissolved gaseous mercury concentration in the water column expected at equilibrium in both phases (atmosphere and water column) at a given temperature. [d]SI is the percentage of DGM saturation, [e]QL is the quantification limit, [f]ND is non-determined.

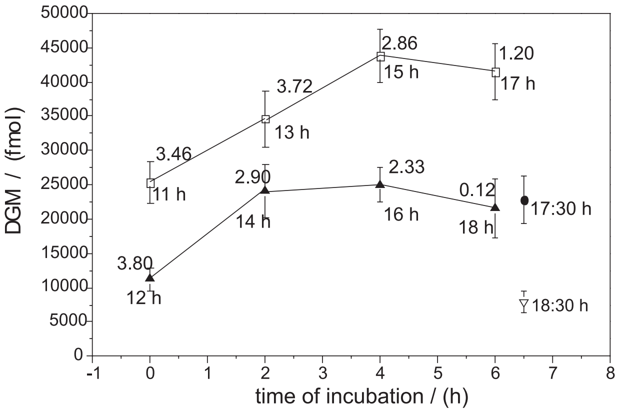

Figure 1. Photochemical results obtained with Branco River surface waters (January 2002 and January 2003). For each point solar radiation intensity (mW cm^{-1}, 365 nm) and time of sampling is shown. The values represent the mean ± SD based on three replicates. ●: 2002, dark; □: 2002, solar radiation; ▲: 2003, solar radiation; ▽: 2003, dark.

Besides H_2O_2, it should be mentioned that humic and fulvic acids are able to reduce aqueous ions of transition metals such as Hg^{2+} and Fe^{3+}, and the literature has reported the production of elemental mercury in the presence of humic material in both sunlit and dark systems.[31,37-41]

Black waters

When SI values were measured in black water bodies, a different diel behavior compared to the ones observed for white waters was obtained, wherein high nocturnal percentages were detected. As presented in Table 3, SI values varied between 710 and 1312% for Iara Lake. In contrast, during day time, SI values dropped below detectable values.

On the other hand, Figure 2 shows the results obtained from photochemical experiments with water collected in Iara Lake and Caurés Rivers, both representatives of black waters. In Iara Lake, DGM concentration decreases from an initial value of 12,000 fmol to 4,000 fmol after 6 h of incubation under sunlight. Similar behavior is observed for the Caurés River, where the DGM values varied from 7,000 fmol to approximately 3,500 fmol. Dark samples presented DGM concentrations higher than the sunlit samples after 7 h, which reinforces the importance of light in DGM consumption.

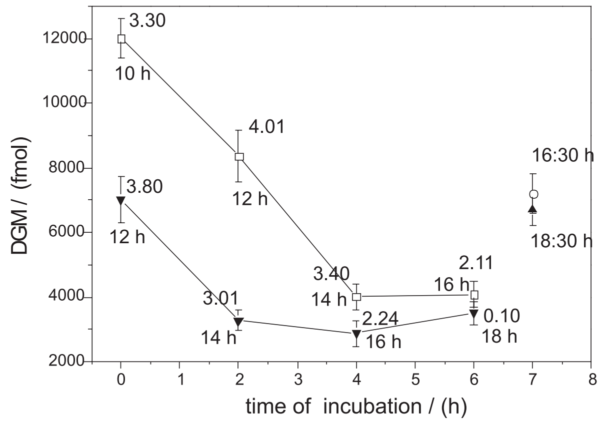

Figure 2. Photochemical results obtained for the Caurés River (January 2003) and the Iara Lake (January 2003). For each point solar radiation intensity (mW cm^{-1}, 365 nm) and time of sampling is shown. The values represent the mean ± SD based on three replicates. □: 2003 Iara Lake – solar radiation, ▲: 2003 Iara Lake - dark, ▼: 2003 Caurés River – solar radiation, ○: 2003 Caurés River - dark.

This peculiar behavior of SI observed for Amazonian black water bodies was pointed out by Fadini and Jardim,[15] who suggested the existence of an oxidative mechanism of Hg^0 to Hg^{2+} by photogenerated H_2O_2 ($H_2O_2 + 2H^+ + Hg^0 = 2H_2O + Hg^{2+}$), similar to the one pointed out by Brosset[42] and Schroeder *et al.*[6] In this case, H_2O_2 contribute to Hg^0 oxidation since the pH in black waters is more acid than in white waters, around 4. Therefore, H_2O_2 could have a double role in mercury redox as a function of the pH value. However, there is no conclusive evidence that this is the effective mechanism operating in these Amazonian water bodies in this work, being only an insight. In addition, other publications report oxidation of Hg^0 in natural waters.[16, 43] In general, these authors suggest that Hg^0 oxidation is possible in natural water by photoinduced reactions involving

Table 3. Saturation Index (SI) for DGM observed at Iara Lake during the dry season of January 2003.

time (h)	Solar Intensity mW cm^{-1}	Temperature (^{0}C)	H	$C_{water/measured}$ (fmol, n=3)	$C_{water/equilibrium}$ (fmol)	SI
12:00	4.05	32.0	0.381	< QL[a]	ND[b]	ND
14:00	3.80	32.0	0.381	< QL	ND	ND
16:00	2.57	29.9	0.361	< QL	ND	ND
19:00	-	30.0	0.362	181 ± 18	13.8	1312
20:00	-	30.0	0.362	98 ± 11	13.8	710
22:00	-	29.8	0.360	125 ± 12	13.9	901
24:00	-	29.2	0.355	< 45	ND	ND

$C_{atm/measured}$ = 5 pmol m^{-3}. [a]QL is the quantification limit. [b]ND is non-determined.

hydroxyl radical ($^\bullet OH$) or superoxide radical ($^\bullet O_2^-$), which may be produced in the aqueous phase by numerous other mechanisms, such as hydroxyl radical ($^\bullet OH$) production via Fenton reactions, by photolysis of nitrate and nitrite, as well as by direct photolysis of organic matter.

The possibility of a transient species such as the hydroxyl radical ($^\bullet OH$) generated by the photoinduced reaction of dissolved organic matter acting as a mercury oxidant cannot be ruled out.[44-47] On the other hand, Southwoth and Voelker,[48] for example, demonstrated that the photoinduced reaction between Fe^{2+} and H_2O_2 can form hydroxyl radical ($^\bullet OH$) in acidic waters in the presence of fulvic acid. According to the authors, complexation of Fe^{3+} by organic matter increases Fe^{2+} photoproduction rates, creating favorable conditions for the photo-Fenton reaction ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^\bullet OH$). Considering the chemical composition of most black water bodies of the Negro River basin, this mechanism seems be possible, due to the low pH and high concentrations of DOC, rich in humic and fulvic substances, with H_2O_2 background levels in the range of 300 nmol L^{-1}.[36] Besides this, to corroborate this suggestion, in a recent study, the authors have observed Fe^{2+} photoproduction in black waters from Negro River basin. However, according to Garcia *et al.*,[49] the role of organics in the mercury redox mechanism is matter of controversy, maybe because the amounts of DOC rather than its properties have been considered. But these authors indicated that DGM production is more relevant in clear waters than in those rich in humic substances.

Finally, it is necessary to mention that the incubation experiments carried out in this work using PET bottles, a material presenting a transparency cutoff at 330 nm,[50] means that under the field experimental conditions UV-A radiation prevailed. The agreement between the results obtained in the incubation experiment compared to the ones obtained in the direct measurement of DGM concentrations in natural freshwater corroborates the existence of two different photoinduced mechanisms. Clearly, further investigation about UV-B radiation on aqueous mercury cycling and toxicity will be necessary.[51]

Conclusions

White water bodies have shown to be saturated with respect to DGM during the day probably due to photoinduced mercury reduction while, during the night, this concentration tends to drop, in a behavior similar to that observed in many other water bodies. The authors emphasized the importance of considering a photoinduced reductive mechanism for Hg^{2+}. On the other hand, for black waters, low DGM concentrations were observed during the day, very likely due to photooxidation associated to the acidic waters and high levels of DOC. Therefore, Hg^{2+} may be more available for methylation and, consequently, bioaccumulation and biomagnification are expected in the biota. So, within the same watershed, water bodies sharing the same climatic conditions tend to behave in opposite ways concerning DGM formation/consumption, due to the unique chemical characteristics of the black waters compared to the white waters.

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