



Mercury degassing from forested and open field soils in Rondônia, Western Amazon, Brazil

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ABSTRACT

A Teflon[®] dynamic flux chamber was used to characterize Gaseous Elemental Mercury (GEM) flux from forested and open field soils in a highly changing environment in Rondônia State, western Amazon. We simultaneously analyzed meteorological parameters at the soil level relating GEM fluxes to soil temperature, air humidity, soil moisture, solar radiation, and speed and wind direction. We also examined variations of atmospheric GEM concentration. GEM fluxes during the day and night in the open field site were significantly different ($17 \pm 14 \text{ ng m}^{-2} \text{ h}^{-1}$ and $0.9 \pm 1.9 \text{ ng m}^{-2} \text{ h}^{-1}$, for day and night, respectively), but were similar within the forest site ($4.8 \pm 1.4 \text{ ng m}^{-2} \text{ h}^{-1}$ and $4.4 \pm 1.8 \text{ ng m}^{-2} \text{ h}^{-1}$ for day and night periods, respectively). A comparison between 24-h periods averages in the two sites showed much larger emission from the open field site. GEM fluxes at the open field site were positively correlated with soil moisture, solar irradiation and soil temperature and inversely correlated with air humidity. At the forest site GEM fluxes showed no correlation with meteorological variables. At the open field site GEM concentrations significantly correlated with GEM flux, at least during the day. At night in the open field site and during the day and night at the forest site no correlation was found between GEM fluxes and GEM concentrations in the ambient air. Higher emissions from the open field site support earlier studies showing larger Hg remobilization following forest conversion to pasture.

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1. Introduction

The gold rush in the Brazilian Amazon and its associated Hg emissions has nearly ended by the late 1990, after releasing about 4000 tons of Hg to the environment during the 25-year gold rush (Bastos et al., 2006). Notwithstanding the cessation of activities, recent studies on the fate of Hg in the Amazon have shown the maintenance of elevated Hg concentrations in fish and in the riverine human population (hair, blood and maternal milk) in areas under the previous influence of artisan gold mining (Gonçalves and Gonçalves, 2004; Bastos et al., 2006). Other studies outside gold prospecting areas have also shown Hg concentrations in fish and human hair samples similar to those found in gold mining areas. This is the case of the Negro River basin (Silva-Forsberg et al., 1999) and the Tucuruí reservoir, where no prospecting area was ever reported, but from where fish and local human groups presented relatively high Hg concentrations (Aula et al., 1995).

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Gonçalves and Gonçalves (2004) summarized results from Brazilian research projects published in the 1980s and 1990s, in the Tocantins and Xingu river basins, these authors also reported high methylmercury concentrations in human hair and high total mercury in the blood and urine of local populations. Bastos et al. (2006), based on literature data on the Hg distribution in soils, waters, sediments, biota and humans living in the Amazon Basin, showed evidences that human exposure to Hg contamination is not directly related to the Hg emission to a specific area, but rather to the complex biogeochemistry processes at the ecosystem level controlling Hg mobility and bioavailability.

Forest soils are considered significant sinks of Hg in the biosphere, with residence time of several thousand years (Grigal et al., 1994). Amazonian soils have also been suggested as important Hg reservoirs (de Oliveira et al., 2001). However, changes in land use can drastically reduce Hg residence time to days or months, as is typical of regions where pasture areas are created by forest slash and burning, increasing erosion and transport as well as the importance of air–soil exchanges to the Hg biogeochemical cycle (Lacerda et al., 2004; Magarelli and Fostier, 2005; Xin and Gustin, 2007). The increasing conversion of natural forest ecosystems to agricultural purposes can be responsible for

maintaining high concentrations of Hg being mobilized in the Amazon environment. Through a grasshopper effect, when Hg is mobilized and further deposited in soils and again mobilized following forest conversion, remobilization can result in Hg contamination of extensive areas (Lacerda et al., 2004; Almeida et al., 2005). Preliminary results obtained in Rondônia, Western Amazon, showed the effect of deforestation on Hg degassing may be significant with pasture soils showing degassing rates of $46.5 \pm 10.7 \text{ ng m}^{-2} \text{ h}^{-1}$, about six times higher than in forest soils ($8.4 \pm 1.2 \text{ ng m}^{-2} \text{ h}^{-1}$) (Almeida et al., 2008).

Measurement of Hg soil–air exchanges are generally achieved by the use of dynamic flux chambers. The first studies were performed using stainless steel chambers (Xiao et al., 1991). Although simple in project and easily operated, stainless steel chambers were condemned by presenting elevated blank values and were eventually substituted by Teflon-made chambers, which resulted in extremely low blank values (Carpi and Lindberg, 1998). Experimental studies performed on natural and contaminated soils using Teflon chambers have demonstrated the strong dependence of Hg emission from surface soil on meteorological parameters, therefore, making mandatory the simultaneous determination of meteorological parameters for interpreting Hg emission from soils (Gustin et al., 1997, 2002; Poissant and Casimir, 1998; Lindberg et al., 1998; Scholtz et al., 2003).

In this study we used a Teflon[®] dynamic flux chamber to characterize Gaseous Elemental Mercury (GEM) flux from forested and open field soils from a highly changing environment in Rondônia State, where nearly 70% of the primary forest has been converted mostly to pasture and agriculture. We simultaneously analyzed meteorological parameters at the soil level relating GEM fluxes to soil temperature, air humidity, soil moisture, solar radiation, and speed and wind direction. We also examined the variations of atmospheric GEM concentration.

2. Materials and methods

2.1. Study area

The study was carried on at the Rondônia University-UNIR Campus ($7^{\circ}58'$ and $13^{\circ}43'$ S; $66^{\circ}48'$ and $59^{\circ}50'$ West) about 20 km from

Rondônia state capital Porto Velho, western Amazon (Fig. 1). The region's climate is predominantly tropical, humid and hot year round, with insignificant annual thermal variability, but notable diurnal thermal variations, especially during winter (June–September). Rondônia State has an Aw weather type (Koppen classification) with annual rainfall varying from 1.400 to 2.300 mm and a short but well-defined dry season from June to September, when most forest burning occurs. The mean annual maximum and minimum temperatures range from 24.4 to 25.5 °C and 18.8 to 20.3 °C, respectively, and the dominant native forest vegetation is open humid upland tropical forest (Bastos et al., 2006).

At the UNIR Campus, two sampling points were monitored through two 24 h periods; the first in an open grassland area lacking any arboreal vegetation, the second located inside a preserved primary forest stand. About 1 km from the Campus area the Porto Velho municipal landfill is located.

2.2. Analytical method

GEM concentrations were determined by a dual amalgamation system with a Tekran 2500 CVAFS detector. The analytical cartridge was calibrated with the established method by saturated Hg vapor injection (Dukarey et al., 1985). The analytical calibration curve was used to calculate the detection limit according to Miller and Miller (1993). The detection limit was $0.02 \pm 0.01 \text{ ng}$ ($n = 3$), corresponding to quantification limits varying from 0.2 to 0.4 ng Hg m^{-3} , for sampling volumes varying between 0.1 and 0.05 m^3 . These limits are well below the reported background TGM concentrations measured in many different parts of the world (Pirrone, 2001; Temme et al., 2007) including the Amazon region (Marins et al., 2000; Magarelli and Fostier, 2005). Details on calibration procedures and quality assurance of the GEM determination method are available in Almeida et al. (2008).

2.3. Dynamic flux chamber

The chamber is a hollow Teflon cylinder with 30 cm of external diameter, 28 cm internal diameter and 15 cm of height (9.2 L internal volume), closed in one of the extremities. In the laterals, at 2 cm from the soil surface eight equally spaced orifices of 1 cm in

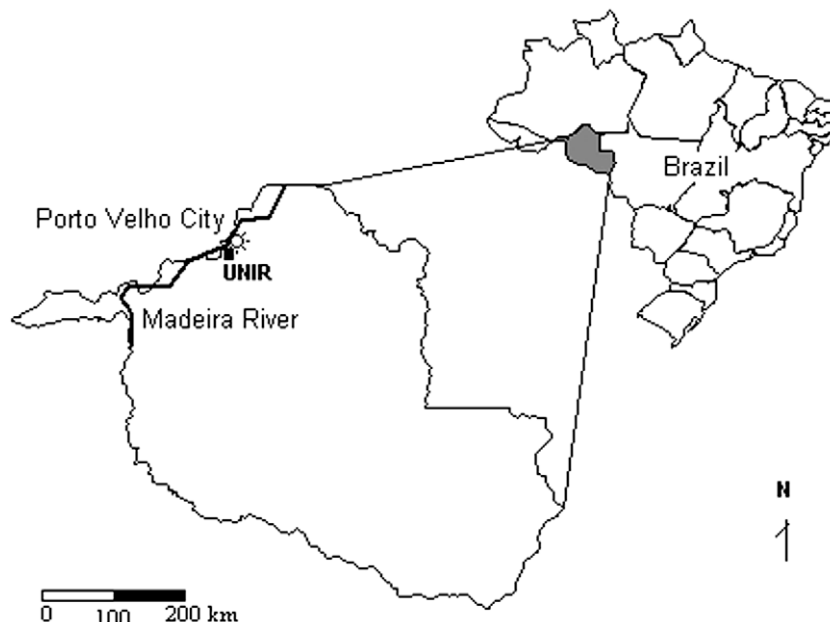


Fig. 1. Study site at Rondônia Federal University (UNIR) Campus near Porto Velho, Rondônia State, Western Amazon.

diameter were made for the air inlet. In the top of the chamber an orifice was connected to two exits, one of ½ in. and another one of ¾ in. In the larger exit a regulated suction pump with flow rate of 20 L min⁻¹ was connected, whereas the smaller exit (½ in.) was connected to a gold cartridge for trapping outlet GEM (GEM_o). In the external part of the chamber, next to the air inlet, another gold cartridge was placed to trap GEM in the surrounding air, inlet GEM (GEM_i).

The cartridges were always kept warm (~60 °C) during the sampling phase to prevent water vapor condensation in the gold surface (Almeida et al., 2008). MILLEX-FG 50 filters attached to the inlet of the cartridges were used to eliminate particulate material and thus prevent contamination. These filters also help preventing against humidity since they are hydrophobic.

Two computerized air pumps (URG-3000-02BA) were utilized for sampling. One pump was dedicated to control the sampling flow of the two cartridges (GEM_o and GEM_i) in 1.5 L min⁻¹ each. A build-in pump timer set the sampling periods to 30 min, with intervals of 5 or 10 min for exchange of the cartridges. Small differences between the cartridges due to different resistances may have caused variations of sampling volume, but the air volume passing through each cartridge was accurately measured by a flow meter (AALBORG GFM 171) together with a volume totalizer (AALBORG TOT1-10). Another pump, never turned off during the sampling period, was regulated to 20 L min⁻¹. This pump was responsible for the renewal of the air in the interior of the chamber. The chamber has an internal volume of 9.2 L and renewal air flow was 21.5 L min⁻¹ (20 L min⁻¹ of flushing flow plus 1.5 L min⁻¹ of the sampling trap flow). The total time for complete renewal of the air inside the chamber was only 25.7 s.

The GEM flux was calculated using the following equation:

$$F = \frac{(GEM_o - GEM_i)}{A} \times Q \quad (1)$$

where F is the GEM flux (ng m⁻² h⁻¹), A is the enclosed emission area (m²), Q is the flushing flow rate (L min⁻¹), GEM_o and GEM_i are the steady state GEM concentration (ng m⁻³) in the outlet and inlet of the chamber, respectively.

The variability of the chamber blank was determined to evaluate any possible influence of the chamber cleaning and to calculate the detection limit of the GEM flux measurements. The chamber blanks measurements were made in different days during the field campaign. Detection limit was calculated as equal to three times the standard deviation of chamber blanks. For the measurements of the chamber's blank, it was placed on a clean Teflon surface and the air was pulled through the chamber as during a normal sampling. The chamber blank average was 0.5 ± 0.4 ng m⁻² h⁻¹ ($n = 7$) and the detection limit calculated was 1.3 ng m⁻² h⁻¹. The blank value was not subtracted from the GEM fluxes, but GEM fluxes below 1.3 ng m⁻² h⁻¹ were computed on the calculated average and were not evaluated as positive fluxes.

2.4. Estimate of variation

Each flux or concentration measurement was a single measurement in a given moment, i.e. without repetition or duplicate. Estimates of error were used to illustrate the uncertainty of each measurement. The error in the measurement of GEM concentration was estimated for each cartridge by 16 repetitions at a constant concentration. Through the coefficient of variation of the cartridge (7.3%), the standard deviation for each measurement of GEM concentration was estimated. Besides the error in the measurement of GEM concentration, the errors of the measurements of the physical geometry of the chamber and the estimated error in the flow measurement were considered when calculating the GEM flux. This error was attributed to measuring the chamber with a 1.0 mm scale

ruler. Thus we have assumed 0.2 mm as error to this measurement, which resulted in a final flow measurement error of 0.2 m³ h⁻¹.

2.5. Meteorological data collection

Meteorological data (air and soil temperature, air humidity, soil moisture, solar radiation and wind speed and direction) were collected every 5 min by a Global Water® weather station equipped with a GL400-7-1 data logger. At every 35 or 40 min averages of meteorological data were made for open field or forest area, respectively.

3. Results and discussion

3.1. UNIR Campus open field site

The dynamic flux chamber was installed in an open field located less than 400 m from the primary forest stand at the University of Rondônia Campus. Soil in the open field site is a Red-Yellow Latosol with relatively low Hg concentration (57 ± 3 ng g⁻¹; $n = 3$), but high concentrations of extractable (citrate-bicarbonate-dithionite) iron (Fe_{cbd} = 6.0 ± 0.1% w/w; $n = 3$) and aluminum (Al_{cbd} = 0.80 ± 0.01% w/w; $n = 3$). Soil organic matter was 10.8 ± 3.0% w/w; $n = 3$. These parameters are involved in the Hg accumulation in Amazon soils and may affect Hg degassing rates from (de Oliveira et al., 2001). However, their concentrations measured in the open field site are not significantly different from forested latosols soils analyzed elsewhere in the Amazon.

The GEM flux distribution and GEM concentrations (GEM_o and GEM_i) at the open field site are shown in Fig. 2. The averages of the meteorological variables as well as the GEM flux and GEM concentrations during day and night periods at the open field site are summarized in Table 1A. The GEM flux varied from -2 to 58 ng m⁻² h⁻¹ with an overall average of 9.2 ± 13 ng m⁻² h⁻¹. Day and night GEM fluxes averages were 17 ± 14 ng m⁻² h⁻¹ ($n = 22$) and 0.9 ± 1.9 ng m⁻² h⁻¹ ($n = 20$), respectively. Night period was defined as when solar radiation was smaller than 3.0 W m⁻². Day and night GEM fluxes were statistically different (t -test, $p < 0.001$), and the night GEM flux average (18:00–06:00 h) was not statistically different from zero (t -test, single sample, critical p -level = 0.053). Actually however, the average of the first five night samplings, between 18:00 and 21:15 h, was 3.3 ± 0.6 ng m⁻² h⁻¹, whereas the average of the remainder fifteen night samplings, between 21:15 and 06:00 h, were 0.1 ± 0.1 ng m⁻² h⁻¹, this average was also not different from zero (t -test, single sample, critical p -level = 0.87), but with higher confidence. The relatively higher GEM flux in the first five night samplings may result from the still higher soil temperature during this period (28–30 °C) resulting from soil heat accumulated during day, relative to the remaining of the night period (27–28 °C). Of the fifteen night sampling GEM fluxes, five were negative, i.e. considered as elemental Hg deposition. Xin and Gustin (2007) showed that light/dark conditions and air GEM concentrations were the most important factors influencing soil GEM flux at low air GEM concentrations, and that natural background soil may be a source or sink of atmospheric GEM.

Magarelli and Fostier (2005) at the Negro River Basin, Central Amazon, estimated GEM flux in open field sites of 2.8 ± 2.1 ng m⁻² h⁻¹, with notable variation between day and night. An overall soil GEM flux of 0.9 ± 0.2 ng m⁻² h⁻¹ for background (Hg soil concentration < 100 ng g⁻¹) was obtained at eleven locations across the United States by Ericksen et al. (2006). Gustin et al. (2006) synthesized in situ GEM flux measurements previously reported for others studies that focused on soils with low Hg concentrations, they reported a range of concentrations varying

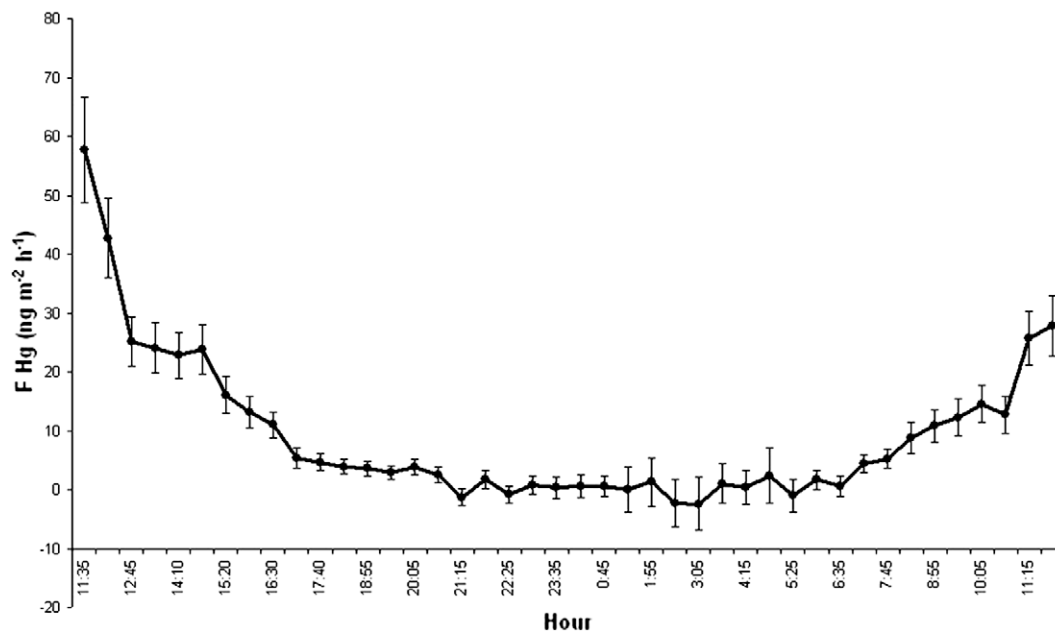


Fig. 2. The GEM flux (●) ($\text{ng m}^{-2} \text{h}^{-1}$) distribution in the open field site, at the UNIR Campus near Porto Velho, Rondônia State, Western Amazon.

Table 1

Averages of the meteorological variables, GEM flux and GEM concentrations during the day and the night at open field site (A) and forested site (B).

	T_{air}	H_{air}	I	T_{soil}	M_{soil}	S	F	GEM_i	GEM_o
A									
Day	30 ± 3	75 ± 18	534 ± 336	30 ± 2	22 ± 1	0.1 ± 0.1	17 ± 14	1.5 ± 0.3	2.2 ± 1.0
Night	25 ± 1	104 ± 6	1 ± 1	28 ± 1	20 ± 1	0.1 ± 0.1	1 ± 2	1.8 ± 1.0	2.0 ± 1.0
24 h	28 ± 4	89 ± 20	280 ± 361	29 ± 2	21 ± 1	0.1 ± 0.1	9 ± 13	1.6 ± 0.8	2.1 ± 1.0
B									
Day	27 ± 2	97 ± 10	31 ± 25	24 ± 1	14 ± 1	n.m.	5 ± 1	0.8 ± 0.2	1.0 ± 0.1
Night	24 ± 1	107 ± 3	2 ± 0.1	25 ± 1	14 ± 1	n.m.	4 ± 2	0.8 ± 0.1	1.0 ± 0.1
24 h	26 ± 2	102 ± 9	17 ± 23	24 ± 1	14 ± 1	n.m.	5 ± 2	0.8 ± 0.1	1.0 ± 0.1

T_{air} – air temperature ($^{\circ}\text{C}$); H_{air} – air humidity (%); I – irradiation (W m^{-2}); T_{soil} – soil temperature ($^{\circ}\text{C}$); M_{soil} – moisture (%); S – wind speed (m s^{-1}); F – GEM flux ($\text{ng m}^{-2} \text{h}^{-1}$); GEM_i – GEM air concentration at the inlet of chamber (ng m^{-3}); GEM_o – GEM air concentration at the outlet of chamber (ng m^{-3}).

between $-51 \text{ ng m}^{-2} \text{h}^{-1}$ at desert alluvium in fall, to $45 \text{ ng m}^{-2} \text{h}^{-1}$ in an open agriculture field in summer. The chamber geometry however may have influenced some of these values. Chamber geometry should guarantee a sufficient air renewal time to make possible air saturation, but not long enough to make difficult the distinction between inlet and outlet GEM concentrations. The renewal time of our chamber has shown consistent and reproducible values (Almeida et al., 2008) and the range of values found under our experimental conditions fall within the reported range of the above mentioned studies.

Table 2 shows the relationships between GEM fluxes and GEM concentrations with the meteorological parameters during daylight, night and overall 24-h cycle. During the day and the entire 24 h cycle considered, the GEM flux presented stronger correlation with soil moisture. The correlation of the GEM flux with soil moisture was already reported by other researchers (Gustin et al., 1997; Zhang and Lindberg, 1999; Song and Van Heyst, 2005; Gustin and Stamenkovic, 2005). These authors suggest that the penetration of rain water in the soil physically displaces interstitial soil air containing Hg^0 and produces a spike in the GEM flux. However rain events did not occur during our sampling period. The soil moisture was high at the beginning of the period due to rain occurrence in the previous day, and a soft increase occurred in the dawn because

of dew deposition. The correlation between GEM flux and soil moisture did not appear at night probably because of the small variation of the soil moisture and the very low GEM fluxes at night.

Solar radiation has been also shown as a significant meteorological parameter influencing GEM flux (Gustin et al., 2006). Some researchers argue that ultraviolet (UV) radiation would be responsible for the photo-reduction of the Hg^{2+} forming a reservoir of Hg^0 at the soil surface (Zhang and Lindberg, 1999; Gustin et al., 2002). Solar radiation can also cause the increase of soil temperature, leading to expansion of gases in the soil and emission to the atmosphere. For this reason they recommend the construction of chambers with UV transparent material. However, these processes can also occur in the neighborhoods of the chamber and the Hg^0 would spread out throughout the surface soil layer. Thus the lesser the soil area covered by the chamber the smaller the impact caused by the chamber itself. Opaque chambers have been recently used in some studies (Poissant and Casimir, 1998; Poissant et al., 2004) and recurring dial cycles of Hg emissions were consistently observed in dry soils held at constant temperature in the dark in the laboratory (Zhang et al., 2008). These studies have hypothesized that some unidentified ambient air parameter might be responsible for the observed dial cycles of soil Hg emission. In the present work GEM fluxes were strongly correlated with solar

Table 2
Relationship between fluxes and GEM concentrations with the meteorological parameters during the day, night and overall 24-h cycle at the open field site.

Parameter	T_{air}	H_{air}	I	T_{soil}	M_{soil}	S	GEM_{air}	$\text{GEM}_{\text{chamber}}$
<i>Day (n = 22)</i>								
F ($\text{ng m}^{-2} \text{h}^{-1}$)	0.57	-0.58	0.70*	0.48	0.88*	0.13	0.53	0.88*
GEM_{air} (ng m^{-3})	0.21	-0.24	0.55	0.04	0.43	0.33	1	0.81*
$\text{GEM}_{\text{chamber}}$ (ng m^{-3})	0.53	-0.54	0.75*	0.40	0.67*	0.28	0.81*	1
<i>Night (n = 20)</i>								
F ($\text{ng m}^{-2} \text{h}^{-1}$)	0.60	-0.60	-0.18	0.62	-0.18	-0.62	-0.49	-0.43
GEM_{air} (ng m^{-3})	-0.82*	0.57	-0.15	-0.82*	0.80	0.59	1	1.00*
$\text{GEM}_{\text{chamber}}$ (ng m^{-3})	-0.81*	0.55	-0.14	-0.81*	0.76*	0.56	1.00*	1
<i>Overall 24 h (n = 42)</i>								
F ($\text{ng m}^{-2} \text{h}^{-1}$)	0.73*	-0.74*	0.82*	0.63*	0.90*	0.13	-0.02	0.58*
GEM_{air} (ng m^{-3})	-0.26	0.21	-0.02	-0.33	0.09	0.26	1	0.78*
$\text{GEM}_{\text{chamber}}$ (ng m^{-3})	0.26	-0.31	0.51*	0.15	0.57*	0.33	0.78*	1

T_{air} – air temperature ($^{\circ}\text{C}$); H_{air} – air humidity (%); I – irradiation (W m^{-2}); T_{soil} – soil temperature ($^{\circ}\text{C}$); M_{soil} – moisture (%); S – wind speed (m s^{-1}); F – GEM flux ($\text{ng m}^{-2} \text{h}^{-1}$); GEM_{air} – GEM air concentration at the inlet of chamber (ng m^{-3}); $\text{GEM}_{\text{chamber}}$ – GEM concentration at the outlet of chamber (ng m^{-3}).

* $p < 0.001$.

radiation during 24 h cycle ($r = 0.82$, $p < 0.001$), and during the day ($r = 0.70$, $p < 0.001$), notwithstanding the use of an opaque chamber.

In the night period, the absence of solar radiation makes GEM flux variation too small or near zero. In this period, relative air humidity increased to about 100% and the temperature was relatively low. This facilitates condensation and dew deposition. The decrease in temperature forms a dense cold air layer on the soil surface (high pressure) making difficult GEM flux to the atmosphere. The mercury deposition through the dew can be significant (Malcolm and Keeler, 2002), but is not detected by the measurement obtained with the chamber. Therefore, at night GEM flux was close to zero or virtually negative (deposition).

The GEM flux was strongly influenced by soil humidity, solar radiation, and air and soil temperatures. The air humidity presented strong negative correlation with the GEM flux. The relationships between air humidity and air and soil temperatures were also inverted, meaning that air temperature quite possibly controls air humidity and soil temperature. In addition, soil temperature control GEM flux.

3.2. UNIR forested site

The chamber was installed inside of a primary forest stand inside the campus of UNIR, at approximately 200 m from the laboratory. The meteorological station was mounted next to the chamber. Only the sensors of air and soil temperatures, air humidity, soil moisture and solar radiation were installed.

In the forest the Red-Yellow Latosols (Oxisol) presented higher mercury concentration ($83 \pm 19 \text{ ng g}^{-1}$) compared to the open field area, as observed by other studies in the Amazon region (Lacerda et al., 2004; Almeida et al., 2005; Bastos et al., 2006). The concentrations of extractable (citrate–bicarbonate–dithionite) Fe_{cbd} and Al_{cbd} were $6.5 \pm 1\%$ (w/w) and $1.0 \pm 0.1\%$ (w/w), respectively. The average organic matter content was $10.5 \pm 4.2\%$ (w/w). Concentrations of major soil parameters in the forested site are similar to the open field site, with the exception of Hg concentrations, and are also similar to other latosols soils in the Amazon region. Notwithstanding their importance on Hg immobilization in Amazon soils reported by other authors, at least in the present experiment soil composition is not related to the differences in degassing rates observed between the two sites.

Fig. 3 shows the distribution of GEM flux and GEM concentrations in the forested site at UNIR. The average values of meteorological variables, as well as the GEM flux and concentrations

during day and night at the forested site, can be visualized in Table 1B. As can be observed, the GEM flux in the forested site ($4.6 \pm 1.6 \text{ ng m}^{-2} \text{h}^{-1}$) did not show any variation (t -test, critical p -level = 0.40) between day ($4.8 \pm 1.4 \text{ ng m}^{-2} \text{h}^{-1}$) and night ($4.4 \pm 1.8 \text{ ng m}^{-2} \text{h}^{-1}$). Day average was lower (t -test, critical p -level = 0.03) than the daylight flux observed in the adjacent open field area ($9.2 \pm 13.0 \text{ ng m}^{-2} \text{h}^{-1}$). On the other hand the average night flux in the forest area was much higher (t -test, critical p -level = 0.000000001) than the nocturnal flux ($0.9 \pm 1.9 \text{ ng m}^{-2} \text{h}^{-1}$) at the open field area. Soil humidity at the open field site reaches maximum values (>100%) during the night, whereas in the forested site soil humidity in the night remain similar to day values with maximum humidity of less the 20%. It is possible that higher humidity together with a decrease in air temperature would hamper Hg evasion at the open field site. Carpi and Lindberg (1998) also using a flux chamber, found GEM emissions in a forest soil varying between 2 and $7 \text{ ng m}^{-2} \text{h}^{-1}$, with peaks of 10 – $14 \text{ ng m}^{-2} \text{h}^{-1}$, whereas in adjacent bare areas, the flux found was significantly higher, varying from 20 to $55 \text{ ng m}^{-2} \text{h}^{-1}$. Other researchers working in forested areas have already suggested that GEM emission could be highly increased in bare soil directly exposed to sunlight (Xiao et al., 1991; Kim and Lindberg, 1995; Kim et al., 1995; Lindberg et al., 1998). Magarelli and Fostier (2005) observed low GEM fluxes with positive values during the day (maximum: $0.6 \text{ ng m}^{-2} \text{h}^{-1}$) and null or negative fluxes (minimum: $-0.5 \text{ ng m}^{-2} \text{h}^{-1}$) during the night. The authors suggested, however, that the negative flux could be due to TGM absorption on the water film that is formed on the walls of their sampling device during the night as a result of water condensation and not an absorption of Hg by the soil.

3.3. Air GEM concentrations

The average and distribution of air GEM concentrations for open field site are shown in Table 1A. The averages of air GEM concentrations for the open field site were $1.6 \pm 0.8 \text{ ng m}^{-3}$ for a 24 h period and $1.5 \pm 0.3 \text{ ng m}^{-3}$ and $1.8 \pm 1.0 \text{ ng m}^{-3}$ for day and night periods, respectively. Apparently there is no difference between the day and night averages (t -test, critical p -level = 0.14). But, if we exclude the anomalous values occurred in the period between 1:20 h until 5:25 h, the night average decreases to $1.1 \pm 0.2 \text{ ng m}^{-3}$ and becomes significantly lower than the daylight average GEM air concentration average (t -test, critical p -level = 0.002).

The significant correlation between air GEM concentration and the flux during the day in the open field site (Table 2) indicates that

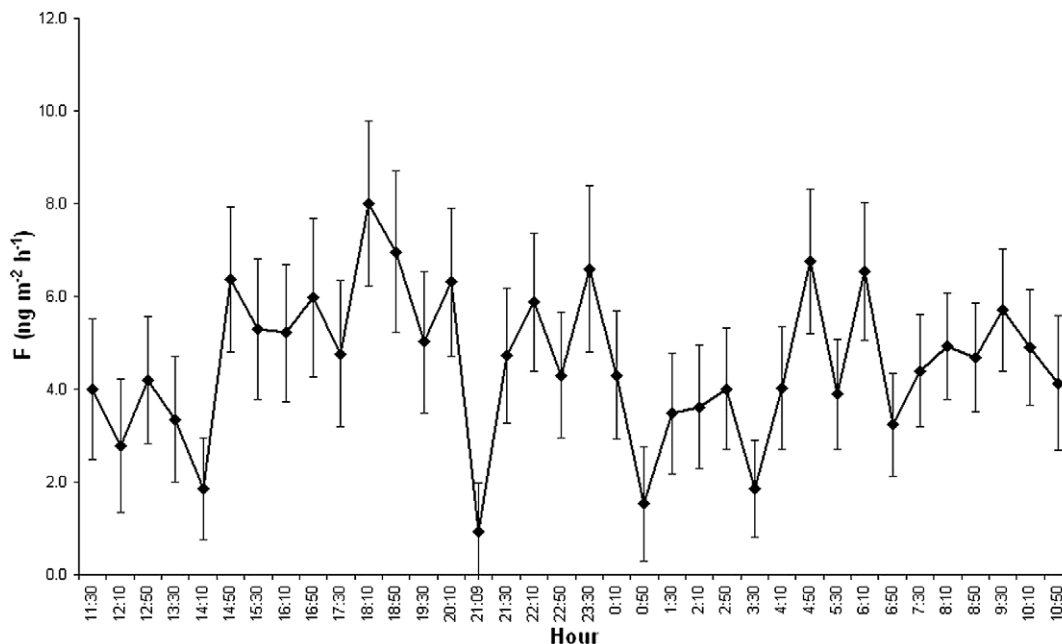


Fig. 3. The GEM flux (●) ($\text{ng m}^{-2} \text{h}^{-1}$) distribution in the forested site at the UNIR Campus near Porto Velho, Rondônia State, Western Amazon.

GEM flux can be an important factor controlling air GEM concentration in the local atmosphere. At night, air GEM concentration did not correlate with GEM flux that was frequently closed to zero and constant. On the other hand, air GEM concentration in the period between 1:20 h until 5:25 h quickly increased, but no increase in the local soil GEM flux was observed. Examining the air GEM concentrations in detail we verified that in this period the highest GEM concentrations of all the 24-h cycle were registered. The hypothesis to explain this increase in air GEM concentration was the existence of an external source. In order to test the hypothesis, a polar graph of the air GEM concentrations against the wind direction was plotted (Fig. 4). The graph presents the highest air GEM concentrations grouped in one direction ($\sim 222^\circ$) to the southwest. At about 1 km in this direction the municipal landfill of Porto Velho city is located, strongly suggesting that the landfill was responsible for this increase in the GEM concentrations.

GEM concentrations inside the forest ($0.8 \pm 0.2 \text{ ng m}^{-3}$) was significantly lower (*t*-test, *p*-level < 0.000001) than in open field site ($1.6 \pm 0.8 \text{ ng m}^{-3}$) and no significant difference occurred (*t*-test, critical *p*-level = 0.36) between day and night. It seems reasonable that the forest canopy may act as sink to GEM emissions from soils, sequestering GEM from the canopy atmosphere. Silva Filho et al. (2006) suggested, based on the dominating role of leaf litter fall in the deposition of Hg from the canopy of tropical forests, that tropical rainforest's canopies can absorb significant amounts of atmospheric Hg, including emissions from soils.

In conclusion, our results confirm the key role played by soil use changes in the mobilization of Hg as suggested by some other studies carried on in the Amazon region. Conversion of natural forest to pastures or open field areas, largely increased Hg degassing, mostly during daylight, and resulted in higher ambient air Hg concentrations. Although some deposition and re-absorption of Hg to open field soils may have occurred during the night, it was not sufficient to balance the amount lost during the day. On the other hand, Hg emission inside the forest, although being relatively high most of the time, seems to be re-absorbed by the forest and does not result in higher ambient air Hg concentrations. The overall results of this study may partially explain the relatively higher Hg content re-

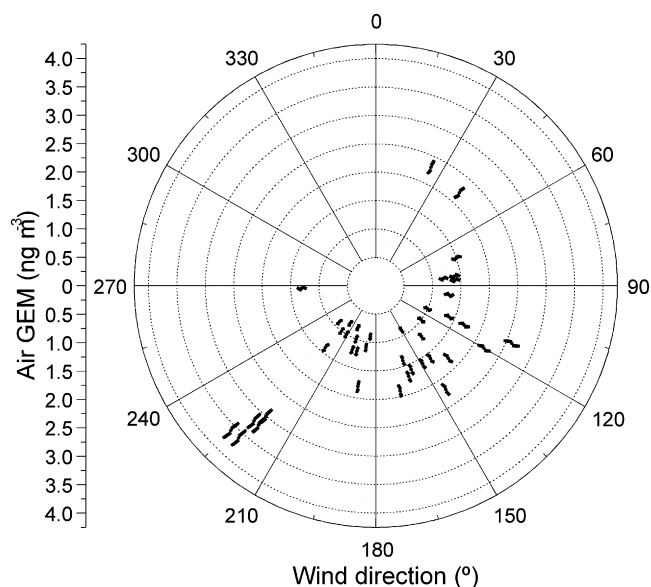


Fig. 4. Polar graph of the air GEM concentrations against the wind direction at the open field site at the UNIR Campus near Porto Velho, Rondônia State, Western Amazon.

ported by various authors in forest soils of the Amazon region, and is also in agreement with the reported grasshopper effect of spreading Hg contamination in the Amazon region. However, the limited geographical and temporal scale of the measurements hampers its generalization for the larger Amazon region, particularly when considering the large diversity of natural environments found in the region.

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