

Methodology Optimization and Application for Measurement of Gaseous Elemental Mercury in the Amazon Atmosphere

Marcelo D. Almeida,^{*,a,b} Rozane V. Marins,^a Heloisa H. M. Paraquetti^{a,b} and Luiz D. Lacerda^{a,b}

^aInstituto de Ciências do Mar, Universidade Federal do Ceará, Av. Abolição 3207, 60165-081 Fortaleza- CE, Brazil

^bDepartamento de Geoquímica, Universidade Federal Fluminense, Campus do Valonguinho, 24020-007 Niterói-RJ, Brazil

O objetivo desse trabalho foi otimizar uma metodologia semi-automática utilizando cartuchos comerciais preenchidos com ouro puro (Tekran Inc.) para a quantificação de mercúrio gasoso elementar em atmosfera tropical. O limite de detecção foi $0,020 \pm 0,006$ ng de Hg. Isso corresponde a limites de detecção variando entre 0,2 e 0,4 ng m⁻³, para volumes de amostragem entre 0,1 e 0,05 m³. A similaridade entre os 9 cartuchos foi avaliada. A avaliação do efeito da vazão de amostragem entre 0,4 e 2,0 L min⁻¹ não representou diferença. A capacidade máxima de retenção dos cartuchos (breakthrough) não foi alcançada nos experimentos com vazão de 1 ou 2 L min⁻¹, concentração de Hg de 25 ng m⁻³ e volume máximo de 150 L. A condensação de água na superfície do ouro mostrou ser um problema, mas isso foi solucionado com o aquecimento do cartucho de amostragem a 60 °C.

The aim of this study was to optimize a semi-automatic methodology using commercial pure gold cartridges (Tekran Inc.) to quantify gaseous elemental mercury (GEM) in the Amazon atmosphere. The detection limit was 0.020 ± 0.006 ng Hg. This corresponds to detection limits varying from 0.2 to 0.4 ng Hg m⁻³, for field sample volumes ranging between 0.1 and 0.05 m³. The similarity between the 9 tested cartridges was evaluated. Under sampling flow rates varying between 0.4 and 2.0 L min⁻¹ no difference among cartridges was observed. The maximum retention capacity of the cartridge (breakthrough) was not reached in experiments with flow rates of 1 or 2 L min⁻¹, and with Hg concentration of 25 ng m⁻³ and maximum air volume of 150 L. Water condensation on the gold surface showed to be a problem, but that was solved by heating the sample cartridge at 60 °C during sampling.

Keywords: gaseous elemental mercury (GEM), atmospheric mercury, Amazon atmosphere, methodology optimization

Introduction

There are many available methods for atmospheric mercury sampling and measurement in the atmosphere. The procedure chosen depends on the resolution time, the mercury concentration and ambient interferents.¹ Notwithstanding, to determine trace mercury concentrations in gaseous matrixes, such as in natural air, a pre-concentration phase is essential. Pre-concentration can be achieved by various forms, the most common are: absorption in liquid, such as a permanganate solution;² solid adsorption, such as onto coal^{3,4} and amalgamation with metal surfaces, such as silver, gold or platinum.^{5,6}

After pre-concentration, detection techniques frequently used are cold vapor atomic absorption spectrometry (CVAAS) and cold vapor atomic fluorescence spectrometry (CVAFS). Both techniques detect mercury vapor (Hg⁰). CVAFS is considered the preferred method due to its sensitivity, specificity and better linearity. Nowadays, the most used system (sampling and detection) is gold amalgamation onto small cartridges and CVAFS detection of the gaseous elemental mercury (GEM). The sampling and analysis of atmospheric mercury are made frequently only for total gaseous mercury (TGM), an operationally defined fraction that includes Hg species that pass through 0.45 µm pore diameter filters or some other simple filtration device, such as quartz wool plugs, and is collected onto the gold. TGM is composed mainly of the GEM with minor contents of other Hg species, particularly HgCl₂,

*e-mail: marcelo_dominguez@hotmail.com

CH_3HgCl and $(\text{CH}_3)_2\text{Hg}$. In remote regions, where the concentrations of particulate mercury are generally very low, TGM corresponds to over 99% of the total mercury concentration in air.^{7,8}

Most used automate instruments currently available to quantify TGM concentrations in atmospheric air are: the PSA-Sir Galahad II System,⁹ Tekran Inc., model 2537A,¹⁰ NIC-SP-3D¹¹ and the Gardis mercury analyzer.¹² All these equipments worked with pre-concentration by gold amalgamation. The two first equipments use detection by CVAFS while the others use CVAAS. Another instrument that uses CVAAS detection is the RA915+ by Lumex,¹³ but this does not use pre-concentration. Detection is possible because the RA915+ uses a 10-meter multipath optical cell and simultaneous Zeeman background correction. This combination eliminates interferences and provides the highest sensitivity in real-time, but the detection limit (about 2 ng m^{-3}) is in general too high for studies in remotes areas. Pre-concentration systems can reach much lower detection limits, which are crucial to natural atmospheric mercury determinations. The annual average surface concentrations of TGM simulated with the global AER/EPRI chemical transport model showed range of 1.2 to 1.6 ng m^{-3} for remote areas.¹⁴ On the other hand, pre-concentration systems have longer response time, sometimes making difficult to evaluate short-term changes in mercury concentrations.

Gold cartridges are capable to sample TGM but AFS or AAS detectors can only detect GEM. Schroeder and Jackson¹⁵ proposed an analytical system able to detect all "mercury species of environmental interest" (operationally defined as TGM). The key step of this analytical system is the application of a pyrolysis tube heated at $900 \text{ }^\circ\text{C}$ between the sampling cartridge and the analytical cartridge. Pyrolytic decomposition releases GEM that can be readily determined by AFS or AAS. Currently the systems do not use pyrolytic decomposition for TGM determination but automatic instruments, such as the Tekran Inc., 2537A, is described as a TGM analyzer.¹⁰ There is a debate as to whether it measures TGM or just GEM. However many researchers have used this measurement as TGM.¹⁶⁻²⁰ In this work the sampling and analytical cartridges were quickly heated at $900 \text{ }^\circ\text{C}$ during the desorption phase. However, some preliminary tests (data under preparation) have suggested that reactive gaseous mercury (RGM), which mostly includes HgCl_2 , CH_3HgCl and $(\text{CH}_3)_2\text{Hg}$, crosses the cartridge before the pyrolytic temperature is reached. Thus mercury concentrations in this work are better described as GEM.

Although some studies have reported on Hg concentrations in the Amazon atmosphere, the sampling, pre-concentration and detection procedures used until now

were not fully tested for the natural interferents, such as humidity, present in ambient air, in particular in tropical regions. Only few studies has tested for the effect of humidity on gold-coated, quartz, cartridges.^{21,22} Therefore the aim of this study was to optimize a semi-automatic methodology using pure gold cartridges (Tekran Inc., N. 35-26500-00) to quantify gaseous elemental mercury (GEM) in the Amazon atmosphere. The effect of the high relative humidity and the sampling air volume were investigated in laboratory experiments. Pure gold cartridges were tested for the GEM sampling and detection under a standard elemental mercury atmosphere under typical environmental conditions and different collection flows. Finally, GEM measurements were actually made in the filed at Rondônia University campus located near to Porto Velho city, state of Rondônia, Western Amazon.

Experimental

The method is based on gold cartridge amalgamation and subsequent analysis using CVAFS. Sampling cartridges are routinely used in the field for collection of GEM. Once in the laboratory, the cartridges were thermally desorbed to release the collected GEM. The analysis were made using a double amalgamation system connected to a fluorescence detector.²³ In this procedure the sampling cartridge is installed in series with an analytical cartridge in the carrier flow (Argon) that carries the GEM to the fluorescence detector. The argon flow is regulated by a build-in mass flow control in the Tekran Inc., 2500. The heating for the release of the amalgamated GEM is obtained with a Ni-Cr resistance by feeding a variac (17 Vac, 10 amps) for 30 s reaching a maximum temperature of $900 \text{ }^\circ\text{C}$. In the first stage the GEM is thermally desorbed from the first cartridge (sampling cartridge) and is carried through a Teflon pipe at the second cartridge (analytical cartridge). The analytical cartridge is then quickly (30 s) heated to $900 \text{ }^\circ\text{C}$ and the GEM is carried to the detector by 80 mL min^{-1} argon flow. The system was assembled with the fluorescence detector, a Tekran Inc., model 2500, connected to a computer through a RS-232c multimeter interface (Minipa Ms-60). The data were captured and analyzed by an especially designed program (programming language C# NET 1.1) for this function. The program detects and calculates peak area and maximum and minimum values. The opening and closing of the solenoid valve that controls the argon flow, as well as the heating and cooling of cartridges, were controlled by a programmable timer (Chronrol XT). Figure 1 illustrates the double amalgamation system used for GEM analysis, structuralized for system calibration. By changing the port of injection by the sampling cartridge the system is mounted for sampling cartridges analysis.

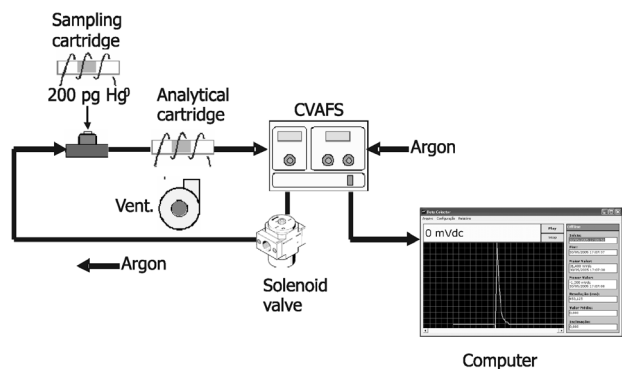


Figure 1. Calibration and analytical systems used in the present study.

System calibration

The GEM concentration analytical detection system was calibrated by saturated mercury vapor injection method.⁶ The saturated mercury vapor was supplied by a chamber containing 5 mL of mercury. The chamber is kept under ambient atmospheric pressure by a small orifice that has access to ambient conditions through a capillary. The chamber is placed in a container with water and the temperature is monitored. The vapor pressure of mercury as a function of temperature is well documented. The amount of mercury contained per unit volume at a given temperature is a well known function that is available on the following numerical formulation.²⁴

$$\text{Conc. Hg}^0 = \left(\frac{A}{T}\right) \times 10^{-\left(-B + \left(\frac{C}{T}\right)\right)}$$

where Conc. Hg⁰, mercury concentration (pg μL⁻¹); T, temperature (K); A, 3216522.61; B, 8.134459741; C, 3240.871534.

Thus, different saturated mercury vapor micro-volumes are removed through one septum using a gas-tight Teflon micro-syringe (Hamilton® 81030). The analytical system was calibrated by injection of known amounts of gaseous elemental mercury in the argon flow carried to the analytical cartridge and, after heating, to the detector (Figure 1). The calibration curves were built on a mass basis and final concentrations were calculated using the field volume data. The instrument was daily calibrated with a five point linear standard curve (*r* value > 0.995).

Field sampling cartridge

The air sampling used pure gold cartridges (Tekran Inc., 35-26500-00). These cartridges consist of quartz pipes (4 millimeters of internal diameter, 6 millimeters of external diameter and a length of 13 cm) with approximately one centimeter filled with small pure gold balls. These cartridges are closed with Teflon plugs that are removed only at the sampling moment.

The sampling was made by connecting the sampling cartridge to a computerized sampling pump URG-3000-02BA regulated for 1.5 L min⁻¹ and a 0.45 μm Millipore filter (MILLEX – FG 50) to prevent against inlet water drops and particulate matter. All cartridges were submitted to heating at 900 °C prior to utilization for eliminating any traces of Hg. The cartridges were only taken to the field when zero reading was obtained.

Standard mercury vapor atmosphere

For the accomplishment of the tests of the efficiency of the 9 cartridges under the sampling conditions it was necessary to use a constant Hg⁰ concentration source. The first test was accomplished by using an equipment with a permeation tube (VICI Metronics Dynacalibrator®). However, the equipment produced too high mercury concentrations. The solution to the problem was to use a Teflon® sampling bag for the dilution of known mercury concentrations.

Standard mercury atmosphere simulations were made by the dilution of saturated mercury vapor in a Teflon® sampling bag of 350 L volume. The air used to prepare the standards was pumped through an active carbon filter, which virtually absorbs all Hg eventually present. To reach the desired diluted gaseous mercury concentrations, we controlled the Hg-free air total volume with a flowmeter-totalizer (GFM171 of AALBORG) and injected known volumes of saturated mercury vapor with a micro-syringe (Hamilton® 81030).

Cartridges test system

The cartridge test system is the system used for all tests. The system is composed of an air source with known Hg concentration (sampling bag) and cartridges in parallel for comparison of different temperatures and humidity or simply duplicate measurements, and cartridges in series to test the overflow. The sampling unit was assembled with a computerized pump (URG-3000-02BA) and flowmeter with totalizer (GFM171 of AALBORG) together with switching and flow regulator valves. The sampling cartridges were connected to the sampling unit and to sampling bag with standard mercury atmosphere simulations. The scheme is shown in Figure 2. All the tests were made with that configuration.

Statistical analyses

To avoid assuming a given statistical distribution of the obtained values, the nonparametric Kruskal-Wallis

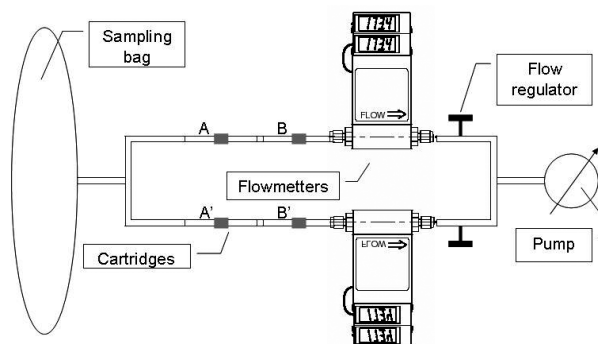


Figure 2. Schematic representation of system used to test cartridges.

ANOVA, Median Test, Sign test and Wilcoxon matched pairs test were used to test for differences between two data sets. The statistical significance was tested at a p-level of 0.05 or 0.01. The Statistica 7.0 by StatSoft was used for the statistical tests.²⁵

Results and Discussion

Limit of detection of the method for GEM measurement

There are several ways to calculate detection limits. A quick way is simply to divide three times the standard deviation of the field blank by the calibration curve slope and additionally divide this result by the sampling air volume.²⁶ The field blank consists of sampling cartridges that are taken to the field but are not submitted to sampling. The field blank did not returned detectable values during the entire sampling period. Thus the analytical calibration curve was used to calculate the detection limit according to Miller and Miller.²⁷ Under the described operational conditions, the detection limit was 0.020 ± 0.006 ng Hg ($n = 3$). This corresponds to detection limits varying from 0.2 to 0.4 ng Hg m⁻³, for sampling volumes varying between 0.1 and 0.05 m³, which are well below the reported background TGM concentrations measured in many different parts of the world. For example, background TGM concentration for Western Europe is around 1.5 ng Hg m⁻³.²⁸ Over the Atlantic Ocean, TGM concentrations vary from 1.02 to 2.31 ng m⁻³, with the highest concentrations found in the northern hemisphere.^{18,19} In the Amazon region very few data on TGM in the atmosphere distant from mine areas are available. However, Amouroux *et al.*²⁹ measured an average TGM concentration of 2.8 ± 1.4 ng m⁻³ for a 24 h-cycle in lake Petit Saut, in French Guyana. Fadini and Jardim³⁰ reported a median value of 1.3 ng m⁻³ in the Negro River basin. Artaxo *et al.*³¹ reported concentrations ranging from 0.5-2 ng m⁻³ in air samples collected from

an airplane over the Amazon. With such concentrations, the employment of a minimum sample volume of about 0.05 m³ is probably sufficient for detection.

Similarity between cartridges

To work with different sample cartridges it is necessary to test if all the 9 cartridges used showed the same collecting efficiency. To make this test all 9 cartridges were submitted to a known gaseous mercury concentration. The mounted system for this test is presented in Figure 2. Each cartridge was tested 16 times. Figure 3 shows the Box whisker plot with average, standard error and standard deviation of the concentrations recovered by each cartridge. The Kruskal-Wallis ANOVA by Ranks, Median Test and subsequent Multiple Comparisons p values were used to compare ($p < 0.05$; $n=16$) the mercury concentrations of the nine cartridges. Only a cartridge differed from the others by presenting extremely low recovery and was not used in the following tests.

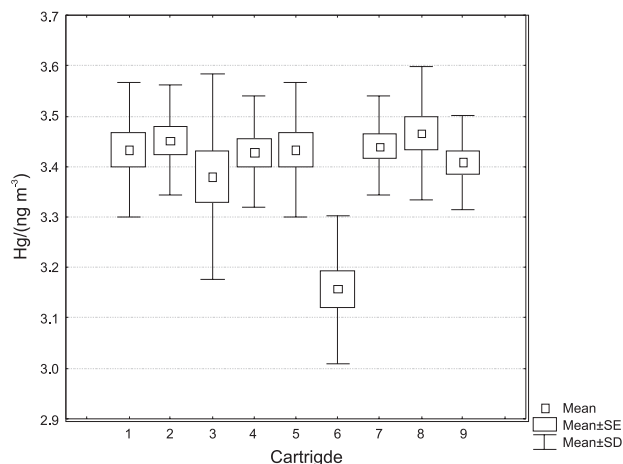


Figure 3. Box and whisker plot showing the GEM concentration recovery of each cartridge used in this study.

Sampling flow evaluation

Automated methods typically use a sampling flow varying from 1 to 1.5 L min⁻¹.^{9,10,12} Thus, a short sampling time (5 or 10 min) confers enough volume for mercury detection. Manual methods generally use air flows of approximately 0.5 L min⁻¹.³² Lower sampling flows can be interesting for large sampling intervals but are not efficient for short sampling periods. Thus a range of air flows between 0.4 and 2.0 L min⁻¹ with sampling volume of 10 L was used to analyze a constant GEM concentration (Figure 4). The Kruskal-Wallis ANOVA by Ranks, Median Test and subsequent Multiple Comparisons p values were used to compare the air flow rate. Although the highest air

flows seem to have a lower recovery, the test did not show any significant difference ($p < 0.05$; $n = 6$) within the group of cartridges.

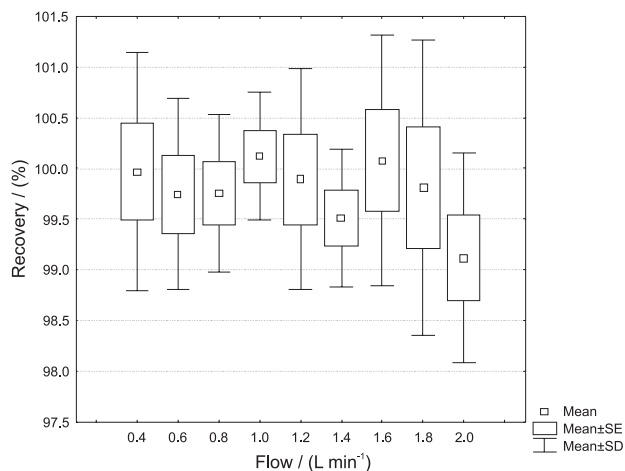


Figure 4. Box and whisker plot of the GEM recovery (%) under different sampling flows.

Cartridges breakthrough evaluation

Breakthrough (overflow) is defined as 5% of the collected mercury amount in the first cartridge that is found in the second cartridge when assembled in series.³³ The sampling time and the air volumes must be enough to make possible trustworthy mercury concentration analysis. However, volumes can not be large enough to cause breakthrough. The cartridges in general possess very large surface areas. Theoretically, gold has the capacity to absorb $1 \mu\text{g Hg}^0 \text{ cm}^{-2}$. Therefore, a cartridge of approximately 20 cm^2 of gold area would be able to absorb $20 \mu\text{g}$ of mercury.²⁴ However, an increase of the flow can quickly result in cartridge overflow. The breakthrough of pure gold cartridge of a constant concentration of GEM was studied as a function of sampling flow rate (1 L min^{-1} and 2 L min^{-1}) and volume sampled. In both tests, the GEM concentration in sampled air was *ca.* 25 ng Hg m^{-3} .

For the breakthrough test, two cartridges were placed in series and known volumes of air were passed through them. Figure 2 shows the general system configuration to test for breakthrough volume. With this arrangement, mercury breakthrough is detected with a significant mercury amount in the second cartridge. In the first test a flow of 1 L min^{-1} was used and a maximum sample volume of 150 L (2 h and 30 min). Only 1 pg of Hg^0 (a value below the detection limit and therefore showing large uncertainty) was detected in the second cartridge after the sampling of 120 L . After 2 h and 10 min or 130 L , 16 pg of Hg^0 (or only 0.5% of the total Hg mass added to the system) were detected in the second cartridge. Following periodical additions of larger

air volumes, the mercury mass in the second cartridge grew approximately in the rate of 0.28 pg per additional liter of air (Figure 5a). The experiment was repeated using a flow of 2 L min^{-1} . The volume varied from 10 up to 150 L . After 75 L the collected Hg mass in the second cartridge started to increase in a rate of 0.34 pg per additional liter of air (Figure 5b).

Breakthrough of the cartridge was not reached in any of the experiments, with less than 1% of the Hg passing to the second cartridge. However ambient factors such as humidity can affect the collection and therefore the nominal breakthrough of the cartridge.

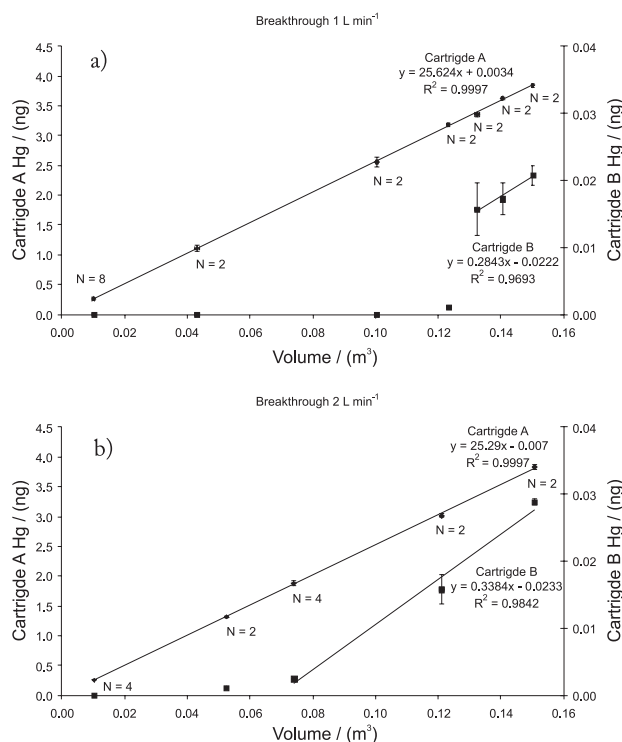


Figure 5. Scatter plot of mercury mass versus sampling volume at 1 and 2 L min^{-1} flow (a and b respectively) for breakthrough assessment.

Cartridge passivation by humidity

Under the determined conditions, the cartridge breakthrough can occur in smaller sampling volumes of that recommended in the laboratory tests. This is generally due to the presence of trace constituents in air that obstruct the gold surface. Possible contaminants are polycyclic aromatic hydrocarbons, water vapor, organic compounds and inorganic species formed through atmospheric reactions (for example: $(\text{NH}_4)_2\text{SO}_4$). Marins *et al.*²¹ showed that humidity is a key factor in the determination of mercury breakthrough. Under humidity above of 80% the collecting capacity of gold-covered annular denuders, used by those authors, can decrease to

about ten times. Humidity is only a problem when water condenses on the denuder surface clogging the gold, which can easily be avoided by heating the denuders during sampling.

The breakthrough of a constant concentration of GEM (4.7 ng Hg m^{-3}) through the gold cartridge as a function of sampling parameters including temperature and humidity was investigated. To test for the effect of humidity on cartridge efficiency, two cartridges were placed in parallel collecting the same standard mercury atmosphere. One of the cartridges was kept cooled at approximately $10 \text{ }^\circ\text{C}$ and the other in ambient temperature (about $30 \text{ }^\circ\text{C}$). At ambient temperature the relative humidity was approximately 70%, but in the cooled cartridge the relative humidity reached 100%, easily causing condensation. Before mercury determination in the cartridge, a dryer stage was performed. This stage consists in heating the cartridge at $60 \text{ }^\circ\text{C}$ for 10 min under a dry argon flow without any mercury loss. Sign Test and Wilcoxon Matched Pairs Test were used to compare the two dependent samples ($n = 14$ pairs). The tests indicate difference ($p < 0.01$) between the pairs. The recovery in the cooled cartridge ($71.1 \pm 23.3\%$) was smaller than in the cartridge under ambient temperature ($99.9 \pm 2.50\%$).

Humidity can also be a problem during the detection phase. Extreme humidity in the optical pathway causes a gradual loss of sensitivity and the variation of the baseline.²¹ In fact the baseline increases when the humidity enters into the cell. Therefore it is recommended to keep the cartridge warm during sampling. However extreme heating can cause problems in the sampling. Aeschliman and Norton³⁴ compared sampling efficiency as a function of temperature and reported that the amount of captured Hg^0 at $200 \text{ }^\circ\text{C}$ was approximately 80% of the Hg^0 captured at ambient temperature, and this percentage diminished quickly when temperature increased to $300 \text{ }^\circ\text{C}$. At this temperature only 3% of the Hg^0 was successfully captured.

To test if heating the cartridge to $60 \text{ }^\circ\text{C}$ would affect sampling efficiency a similar system to that in Figure 2, was built with two pairs of cartridges mounted in parallel. A cartridge of the first pair (A') was kept warm at $60 \text{ }^\circ\text{C}$ while cartridge A and the other pair (B and B') were kept at ambient temperature. The sampling flow was 2 L min^{-1} and the volume ranged from 10 to 150 L, with GEM concentrations of approximately 30 ng m^{-3} . After 75 L of sampling, the mercury content in the second cartridge pair (B and B') was similar roughly increasing at a rate of about 0.4 pg L^{-1} , indicating that heating at $60 \text{ }^\circ\text{C}$ not only avoided water condensation but also has no effect on GEM capture efficiency (Figure 6).

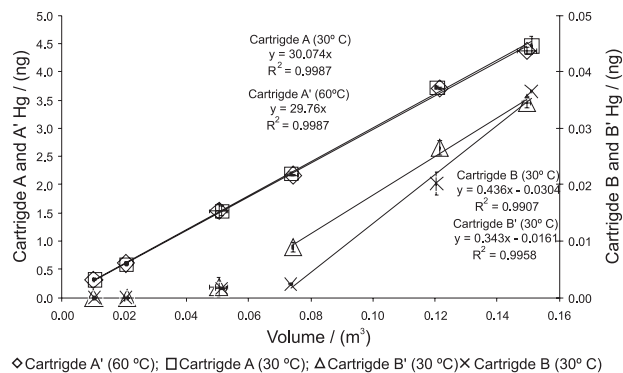


Figure 6. Scatter plot of mercury mass versus sampling volume at 2 L min^{-1} flow for breakthrough assessment with one cartridge kept warm at $60 \text{ }^\circ\text{C}$.

Gaseous elemental mercury measurements in the Amazon atmosphere

After optimization, GEM measurements were carried on in Porto Velho City, State of Rondônia, Western Amazon. Two cycles of 24 h, one in a deforested, grassland area and the other in the forest, were monitored. In the deforested area measurements were taken every 35 min, with 30 min for pre-concentration and 5 min for changing the cartridge. In the forest each measurement was taken every 40 min, with 30 min for pre-concentration and 10 min to change the cartridge. The laboratory nearness made possible high time resolution, which is very important for the observation of the relationship between GEM concentration and meteorological parameters (Humidity and temperature were measured *in situ* by the sensor WE600 and WE700 connected to a datalogger GL400 of Global Water).

The sampling cartridges were kept heated at $60 \text{ }^\circ\text{C}$ during the sampling to eliminate condensation and passivation of the gold surface. The sampling flow was 1.5 L min^{-1} and the total volume of each pre-concentration step was approximately 45 L.

The average GEM concentration obtained in the forest was $0.8 \pm 0.2 \text{ ng m}^{-3}$ ($n = 19$) and $0.8 \pm 0.1 \text{ ng m}^{-3}$ ($n = 17$) during day and night respectively. Whereas in the deforested area the average obtained was $1.5 \pm 0.3 \text{ ng m}^{-3}$ ($n = 22$) and $1.8 \pm 1.0 \text{ ng m}^{-3}$ ($n = 20$) during day and night, respectively. The average of the 24 h-cycle was $0.8 \pm 0.1 \text{ ng m}^{-3}$ ($n = 36$) with air humidity $100 \pm 8.8\%$ and $1.6 \pm 0.8 \text{ ng m}^{-3}$ ($n = 42$) with air humidity $89 \pm 20\%$, for forest and deforested area, respectively. The sampling volume and flow rate used (about 45 L and 1.5 L min^{-1}) were sufficient to detect the GEM.

These concentrations were very low when compared with other measured values reported a decade ago in the Amazon, when total mercury concentrations in the atmosphere of urban areas in Alta Floresta, Southern

Amazon, ranged from 10 to 5,800 ng m⁻³, and with indoor gold dealer's shops atmosphere ranging from 141 up to 40,600 ng m⁻³.³⁵ In the urban area of Poconé City, Marins and co-workers^{36,37} reported concentrations ranging from < 140 up to 1,900 ng m⁻³ close to gold dealers shops. Lodenius and Malm³⁸ found mercury concentration ranging from < 140 to 500 ng m⁻³ close to the Teotônio Waterfalls and from < 20 up to 660 ng m⁻³ in urban areas far from mining areas. They have also reported total Hg concentrations ranging from 450 to 7,500 ng m⁻³ in urban areas close to gold-Hg amalgam smelting sites in the Porto Velho-RO, and up to 60,000 µg m⁻³ when smelting occurred in the field without using retorts. These higher measurements however, included sometimes total Hg species present in air, including particulate-Hg, since all used air bubbling through an oxidizing permanganate solution, which also results in extremely high detection limits. Also all these results were obtained during the peak of gold mining and therefore higher of Hg emission to Amazon atmosphere. More recently, studies using gold amalgamation pre-concentration techniques similar to ours have produced similar results to those from Porto Velho presented here. Magarelli and Fostier,³⁹ reported average atmospheric TGM concentrations in the Negro River basin, northern Amazon, of 1.4 ± 0.9 ng m⁻³ and 0.4 ± 0.2 ng m⁻³ for forest and deforested sites, respectively. These values although similar to those obtained in the present work showed higher Hg concentrations in forest rather than in deforested areas. Amouroux *et al.*²⁹ also reported TGM concentrations of 2.8 ± 1.4 ng m⁻³ in a forest area of French Guiana, whereas Fadini and Jardim³⁰ reported average TGM concentrations in air samples from forest areas at the Negro River basin of 1.3 ng m⁻³.

Conclusions

The detection limit of the proposed procedure was 0.020 ± 0.006 Hg ng as GEM. This corresponds to detection limits varying from 0.2 to 0.4 ng Hg m⁻³, for field sample volumes between 0.1 and 0.05 m³. Sampling flow rates between 0.4 and 2.0 L min⁻¹ did not show any difference in cartridge performance, but the highest flow rate seems to results in a poorer recovery, although not statistically significant. Sampling flow rate of 1.5 L min⁻¹ was chosen optimal since enables fast sampling and showed no effect on cartridge performance. Cartridge breakthrough was not reached in any of the experiments, with less than 1% of the total Hg mass passing to the second cartridge with flow rates of 1 or 2 L min⁻¹, GEM concentration of up to 25 ng m⁻³ and maximum air volume of 150 L. Water condensation on the gold surface showed to be a problem, but it was solved by keeping the sampling cartridge heated to 60 °C.

This heating procedure showed no effect on GEM capture by the cartridges.

GEM measurements were made in Porto Velho City, Western Amazon, and the average of the 24 h-cycle was 0.8 ± 0.1 ng m⁻³ (n = 36) and 1.6 ± 0.8 ng m⁻³ (n = 42) for forest and deforested areas, respectively. Sampling volume and flow rates of about 45 L and 1.5 L min⁻¹ respectively, showed to be sufficient to detect the GEM present in the Amazon atmosphere, whereas heating the cartridge during sampling avoided water vapor condensation.

Acknowledgments

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