Sampling techniques for the assessment of anthropogenic vapour and particulate mercury in the Brazilian Amazon atmosphere

Rozane V. Marins,†[a] Jailson B. de Andrade,*[b] Pedro A. de P. Pereira,[b] Elizabeth C. Paiva[a] and Heloisa H. M. Paraquetti‡[a]

[a]Centro de Tecnologia Mineral, CETEM/CNPq, Rua 4, Quadra D, Ilha do Fundão, Rio de Janeiro, RJ, 21941-590, Brazil
[b]Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Salvador, BA, 40170-290, Brazil. E-mail: jailsong@ufba.br

A system, based on annular gold-coated denuders, was optimized and used in the atmospheric sampling of mercury in urban and rural sites of the Alta Floresta, a region in the Brazilian Amazon. Results showed that vapour phase mercury (Hg_v) is dominant in samples collected in both sites. However, particulate mercury (Hg) may sometimes be significant at the urban site, with values representing up to 77% of the total Hg collected during sampling, but may also be insignificant at the same site, depending on the gold commercialization activity and, probably, on the meteorological conditions during the sampling period. The presence of mercury in both the vapour and particulate phases in the atmosphere of the urban site can explain the high mercury concentrations found in urban dust reported for some cities in the Amazon, and also the relatively high Hg concentrations found in soils adjacent to the urban centre of Alta Floresta. It appears that the urban dust of "garimpo" areas in the Amazon can act as an efficient adsorber of Hg_v emitted by gold dealer operations during the purification process. Mercury emissions from gold dealer shops in the Amazon have been considered as a human health risk through the inhalation of Hg vapour. However, although true for indoor sites, the significant contribution of particulate phase Hg shown in this study in outdoor urban sites calls for a re-evaluation of the risk assessment estimates performed up to now in urban centres in the Amazon.

Introduction

Mercury emissions to the Amazon atmosphere resulting from gold mining reach 50–70 tonnes per year, and may represent 1–6% of the global anthropogenic Hg emissions into the atmosphere. Elemental mercury vapour is released into the atmosphere during roasting of Au : Hg amalgam and vaporized during the different processes of gold extraction, and also during the purification of gold for commercialization in gold dealer shops located in urban areas. This latter kind of emission is a serious public health problem in many towns in the Amazon region.[1]

Marins and Tonietto[2] suggested that mercury emitted from the process of gold purification includes not only metallic mercury vapour but also other mercury species. This conclusion was based on the results obtained in a comparative study using three different sampling techniques for mercury in air in urban areas. These results also showed that methodologies with insufficient sensitivity could be responsible for the inaccuracy of most data on mercury concentration in the Amazon atmosphere.

Once emitted to the atmosphere, metals can be transported in the gaseous (or vapour phase), or in a solid form within or condensed onto aerosols of varying sizes. The transport of particulate phase Hg is generally the most significant. Transport of metals in the vapour phase depends much more on the chemical properties and emission sources of the metal concerned.[3] However, the transport of metalloids, such as mercury, can be important in the vapour phase.

Diffusion denuders have been used since the 1980s in the monitoring of gaseous atmospheric pollutants. Diffusion-based sampling has proven to be a reliable approach for the measurement of a gas in the presence of an aerosol, because the diffusion coefficient of a gas molecule is, in general, about four orders of magnitude larger than the smallest aerosol with a significant mass contribution to the atmosphere.[4]

The first diffusion-based collectors were single-channel denuders. However, Possanzini et al.[5] showed that annular denuders gave a better performance.

The low atmospheric concentrations of mercury suggest that annular denuders may be useful in the evaluation of mercury contamination in gold mining areas, because they can collect large air volumes per unit time,[4] and because it is possible to automate the sampling system to the final detection, by cycles of sorption and desorption of mercury from the denuders. In addition, this type of collector prevents reactions between reactive gases and the filters used in traditional samplers.[5,6]

Losses or gains of mercury can occur when new fluxes of air, more diluted or more concentrated in mercury, pass through the filters, or due to variations in the relative humidity (RH) of the air or in the concentrations of other gases, such as ozone.[7,8] In the Amazon region, the extraction and commercialization of gold is a rudimentary activity, and the mercury content in gold can be very different from site to site, resulting in different mercury emissions from hour to hour during a working day in gold dealer shops. Second, gold mining areas are often impacted by the burning of forests and biogenic emissions from vegetation, with associated gases and particles. Finally, the RH in this region can range from 20% to 99% during a single day.

The efficiency of the denuder system for mercury collection depends on several parameters, including the sampling flow rate, sampling time, coating thickness of the denuder walls and external variables such as the RH and temperature. One type

that has been used for mercury sampling is the annular denuder impregnated with gold. Mercury compounds, in the gaseous phase, are collected on gold,[9] or fine films of gold (50–200 Å), deposited over an inert material, such as quartz or B_4C, producing small blank values. In addition, the mercury sampled can be analysed by desorption at 650 °C in an optimized flow of "mercury free" gas.[10]

This work presents, as its main objective, the optimization of mercury sampling with a denuder system based on a gold-coated commercial model, by evaluating the effects of temperature, RH and different air flow rates on its performance. Secondly, the applicability of the method was checked by determining vapour and particulate mercury in the atmosphere of a Brazilian Amazon region affected by gold mining operations, namely Alta Floresta, in the state of Mato Grosso. Results for vapour and particulate Hg are presented for this site and discussed.

Experimental methods

Evaluation of the denuders

Gold-coated annular denuders (URG-2000-30CA, No. 30; URG Co., Chappel Hill, NC, USA) were tested and optimized for mercury sampling under a standard atmosphere of Hg^0 at different humidity conditions and air flow rates. The Hg^0 standard atmosphere was generated by a Dynacalibrator model 450-58-YS (VICI Metronics, Santa Clara, CA, USA), which contained an enclosed mercury permeation tube. Under conditions of 30 °C and the dilution factor that was set for the experiments, the Hg^0 concentration produced was determined to be, after 21 measurements, 12.76 ± 0.42 µg Hg m^{-3} of air. In these tests, the mass of mercury released by the Dynacalibrator was collected, as a known volume of standard air, directly in a gold trap through amalgamation. The Hg^0 was then desorbed by heating the trap and determined by cold vapour atomic absorption spectrometry (CVAAS).

The denuder efficiency for mercury sampling and the influence of the RH were determined according to the scheme shown in Fig. 1. The clean air was passed through a water bath, before entering the permeation chamber and making up the dilution. The RH generated in this way was then determined with an RH sensor device (PACER, model DH 300, Pacer Industries Inc., WI, USA) put immediately after the trap and before the rotameter and the vacuum pump. The sensor response was checked against solutions of K_2SO_4 (RH = 97%) and LiCl (RH = 12%), as recommended by the equipment's manual.

The gold trap or permanganate solution, placed after the denuder, was checked every 15 min, or less when necessary, for Hg, in order to control the beginning of metal release by the sampler. The mercury adsorbed onto the denuders under different test conditions was desorbed in a furnace at 700 °C by passage of "Hg free" air throughout. The air fluxes were then trapped onto an impinger containing an acid permanganate solution. This permanganate trap, after optimization, presented recovery efficiences of the order of 99%, confirming other references.[11–13]
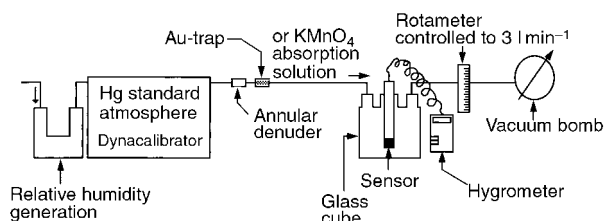
Mercurial compounds in the permanganate trap were

Fig. 1 Calibration system for mercury annular denuders.

reduced to Hg^0 by $SnCl_2$ in acid solution and then liberated by bubbling with "Hg free" air. The mercury released was preconcentrated into an Au trap stage and then determined by CVAAS, as described above. The absolute detection limit for this system was around 1.0 ng of Hg.[14]

Field measurements

After optimization of the sampling conditions, the gold-coated denuders were used in field measurements. The collection apparatus using denuders was set along with a filter cartridge. All parts of the collection system were made of quartz, Teflon or Teflon-coated material.

Two sites were studied in the field measurements: a rural area in the neighbourhood of a primary forest and the urban centre of Alta Floresta, indoors and outdoors of a gold delivery shop. These measurements were performed at different times of day and on different days, but at the same sites in the urban and rural areas. During sampling, measurements of the RH, temperature and wind direction and velocity were carried out at 1.5–2.0 m from the soil surface, the height of the sampler devices.

The measurements were performed in three different ways, aiming to observe differences in the results among different collection devices. The first device was a denuder/filter system, to sample vapour and particulate mercury, respectively, with an air flow rate of 3.0 L min^{-1}. The second device was an absorption solution of acidic potassium permanganate, to collect total mercury, at the same air flow rate. The third device was a simple filter system, to collect only particulate mercury, here named total particulate mercury, at different air flow rates to optimize the sampling time and to permit comparisons among the different sampling systems and procedures.

Several different types of filter can be used to collect particulate mercury.[15] In this work, all filters used were glass fibre filters (Gelman type A/E, Gelman Sciences, Ann Arbor, MI, USA), pre-baked at 200 °C over 12 h, to eliminate any possible mercury contamination.

Results and discussion

The first observation made with the mercury annular denuders was that it was necessary to decontaminate them before use, because of common high blank values. Also, repeated use made them more efficient, as shown in Fig. 2. After the third desorption cycle, results for the mass of mercury retained became stable. A possible explanation of this seems to be that, when Hg desorbs from the denuder surface, it leaves a larger sorptive surface on the gold coating. The lifespan of the denuders had not been reached after 20 cycles, although we used a temperature of 700 °C to desorb the mercury in each cycle.

During the evaluation of the breakthrough, it was observed that air flow rates higher than 3.0 L min^{-1} resulted in a rapid
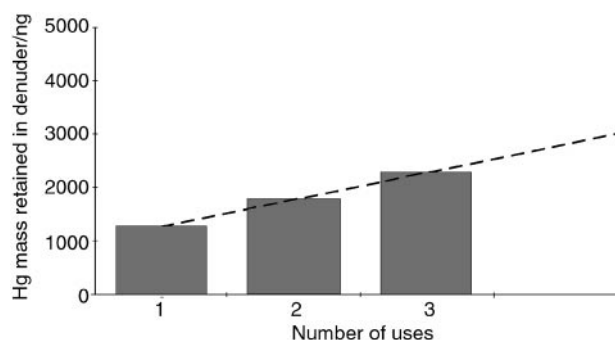

Fig. 2 Mass of mercury retained in annular denuders after three repeated uses.
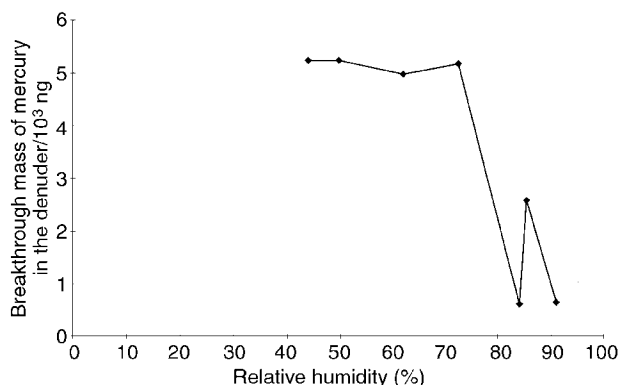
Fig. 3 Effect of relative humidity on the retained mass of mercury in annular denuders.

fall in Hg retention. Therefore, all tests were carried out using this flow rate. Under these conditions, the average mass of mercury retained, before breakthrough was reached, was around $5.0 \pm 0.2\ \mu g$.

RH was a key factor influencing the proper functioning of the system. Fig. 3 shows the effect of RH on the breakthrough masses of mercury in the denuder. At values between 45% and 70%, retained masses were high and constant. However, at higher humidities, they decreased nearly tenfold. This suggests that water vapour may be competing with mercury for exchange sites on the gold coating.

Since the air humidity in the Amazon region can typically vary from about 60% to 98% in diurnal intervals, the operational standards established in this optimization exercise were considered to be vital to a proper sampling procedure, making it essential to measure the air humidity during sampling.

The concentrations and phase distribution of mercury in the sampling campaign in Alta Floresta are shown in Table 1. The highest mercury concentrations were found inside the gold dealer shop, followed by samples collected at the urban area. The former were up to two orders of magnitude higher than values measured at the rural site. Concentrations measured in the urban area of Alta Floresta are in the same range as those reported elsewhere[11,12] for total mercury in other gold mining cities located in the Amazon. Although mercury concentrations measured at the rural site are much lower than those at the urban sites, they are still higher than that reported for pristine forest areas.[16–19]

Mercury in the vapour phase predominates in the atmosphere of the sampled sites. However, the relative importance of this phase to the total mercury content is different between the urban and rural areas. Today, it is generally agreed that 95–100% of the total mercury in air is in the gaseous phase, as elemental mercury, with perhaps some very minor amount of divalent mercury, with methylmercury (MeHg) being the most

likely candidate.[20] The remaining mercury, the airborne particulate mercury, is important for long-range transport and mercury deposition processes and patterns.[21]

At the rural site, nearly 3 km from the downtown area, mercury in the vapour phase represented 69–100%, averaging 92%, of the total mercury concentration measured in the atmosphere. At the urban site, the relative importance of mercury vapour ranges between 23% and 100%, averaging 66%, of the total mercury concentration measured. Inside the gold dealer shop, mercury vapour nearly corresponds to all the mercury present in the atmosphere, in the range 92–99%, which shows that the evaluation of its phase distribution may contribute to an appropriate selection of protective gear for the operators of the shops.

Mercury in the vapour phase ranged from 10 to 945 ng Hg m^{-3} at the urban site. Since these samples were collected very close to the gold dealer shop, they may reflect the amount of gold being commercialized during the sampling period, which ranged from 300 g to about 4600 g.

Also noteworthy is that the RH did not exceed 70%.

A comparison between the total mercury concentrations measured in a KMnO$_4$ solution and the total mercury measured as the sum of vapour and particulate Hg collected with the denuder system showed similar values for the rural site 1A. At the urban site, changes in the KMnO$_4$ solution occurred, probably due to the high temperatures achieved during sampling (up to 43 °C) rendering impossible the use of these solutions.

Similarly, Hg concentrations measured by sampling directly through a filter compared well with the particulate mercury measured with the denuder system for rural sites 1A and 1C and urban site 2. During sampling at the urban site 2C, however, the filter concentration was only 8 ng Hg m^{-3} compared with 33 ng Hg m^{-3} with the denuder system. This last sampling of particulate Hg, however, was performed under relatively high air flows (20 L min^{-1}), and this may have resulted in the lower efficiency of the filters for such a reactive species as mercury; more comparative samples are necessary to confirm this observation.

Larger particles containing mercury have high deposition velocities and, consequently, a lower residence time in the atmosphere, and are probably the cause of high mercury concentrations in the soil dust of urban areas in the Amazon.[11,22,23] Resuspension of soil dust may also significantly affect the transport and deposition pattern of Hg after emission. The wind suspension of continental dust is one of the well-documented processes responsible for the introduction into the atmosphere of several constituents.[22]

Only mercury associated with aerosol-sized particles <1.0 μm, such as, in general, trace metals, are transported into the atmosphere,[24] have lower deposition velocities, and therefore have longer atmospheric residence times, making possible transfer over longer distances from the source of the

Table 1 Mercury concentrations in the atmosphere of Alta Floresta, sampled at rural and urban sites and inside a gold dealer shop

Sampling site	Hg vapour/ng m^{-3}	Particulate Hg/ng m^{-3}	Total Hg/ng m^{-3}	Total particulate Hg^a/ng m^{-3}
Rural site 1	185	<LOD^b	—^{c}	—
Rural site 1A	41	<LOD	49	<LOD
Rural site 1B	27	<LOD	—	—
Rural site 1C	33	15	84	<LOD
Urban site 2	550	81	—	74
Urban site 2A	319	14	—	—
Urban site 2B	945	<LOD	—	—
Urban site 2C	10	33	—	8
Indoor gold dealer shop	2372	44	—	—
Indoor gold dealer shop	141	13	—	—

^{a}Sampled without denuders. ^{b}LOD, limit of detection. ^{c}Sampling not carried out.

gold delivery shops. The amount of atmospheric particles that can transport mercury over longer distances is still unknown. However, this paper represents the first contribution to an assessment of the distribution of mercury concentrations between vapour and particulate phases in rural and urban atmospheres of an Amazon region. The decrease in importance of mercury in the particulate phase in rural areas suggests that most of this form is deposited close to the source (<10 km). According to Lindqvist,[25] approximately 50% of the anthropogenic mercury emissions are deposited 1000–2000 km from the source. However, recent estimates show that the global background is increasing by 1% per year. Therefore, resuspension of Hg-rich particles from urban sites may be a significant source of mercury to the atmosphere, albeit non-predictable and intermittent but always active.

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