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Atmospheric Mercury Concentrations in the Basin of the Amazon, Brazil

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Abstract

A wide regional mercury pollution in Amazon, Brazil is closely associated with goldmining that has been carried out in the basin of tributaries of the Amazon since the eighteenth century. Possible involvement has been discussed on atmospheric circulation in distributing the volatile pollutant. We developed a portable air sampler for the collection of mercury compounds and determined atmospheric mercury concentrations at several sites in Brazil including the basin of the Amazon tributaries. The mean concentration of total mercury was between 9.1 and 14.0 ng/m^3 in the basin of the Uatumã River located in the tropical rain forest far from goldmining sites and from urbanized area. These mercury levels exceeded the background level previously reported in rural area and, furthermore, were higher than concentrations observed in Rio de Janeiro and in Manaus that were compatible with the reference values for urban area. Mercury concentrations were also determined in gold refineries in the basin of the Tapajos River, and detected at a significant but not a health deteriorating level. Although only preliminary data were available, the present observations were in favor of the hypothesis that mercury is distributed widely by long distant transport by the atmospheric circulation after released at gold mining sites.

Key words: Mercury, Air contamination, Amazon, A portable air sampler, Global environment

Introduction

Since widespread mercury pollution was reported in the Brazilian Amazon[1], many investigations have been carried out because of its public health impact[2, 3]. Mercury has been found to be accumulated mostly as methylmercury in fishes in tributaries of the Amazon, and also detected at high concentrations in hair, blood and urine of inhabitants who consumed fish diet frequently[4, 5]. Akagi et al.[4] found methylmercury deposition reaching 68.1 ppm in the hair of fishermen residing in the basin of the Tapajos, one of the main tributaries of the Amazon, approaching to threshold for methylmercury poisoning. The mercury pollution is closely associated with goldmining that has been carried out since the eighteenth century in Amazon[2, 3]. Two thousand or more gold mining sites existed in the tropical rain forest of the Amazon in 1980's, which was the most enthusiastic period. In the first step of the mining procedure in this region, gold amalgam was made by addition of plentiful mercury to alluvial gold that was extracted from bottom sediments. Crude gold was then obtained by heating the amalgam with a burner and evaporating the mercury content. It has been assumed that an enormous amount of mercury flowed into and contaminated rivers during the process. It was estimated that 55% of the metal mercury lost in the mining site was discharged into atmosphere[6]. The atmosphere is considered to play an important role in global transport of the volatile pollutant[7]. Metallic mercury vapor can be oxidized to ionic divalent mercury (Hg^{2+}) and the inorganic mercury undergoes conversion to organic mercury compounds in the environment. In the present study, a carrying type air sampler was developed for collecting atmospheric mercury compounds in the field survey. We determined mercury concentrations in the air of several sites in Brazil including the basins of the Amazon tributaries: the Uatumã and the Tapajos River to investigate possible involvement of the atmospheric circulation in the wide regional mercury pollution in Amazon.

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Materials and Methods

A portable air sampler for collecting atmospheric mercury compounds

The air sampler and outline of total mercury collection system are shown in Figs.1 and 2, respectively. A buffer tank of a volume of 250ml was included in the apparatus for stabilizing air flow. The external size of the sampler was 217×304×118mm and weight was about 3kg excluding collection columns and batteries. Four collection columns were fitted in a cassette made of transparent polyvinyl chloride. In addition to a cassette connected to an aspirator, five reserve cassettes could be stored in the apparatus. The power supply of the aspiration pump was eight alkaline dry batteries (SUM-3, 12 V as a total) and two lines were available.

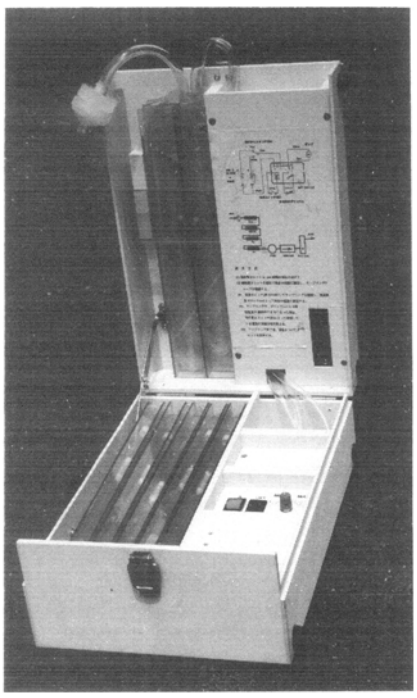


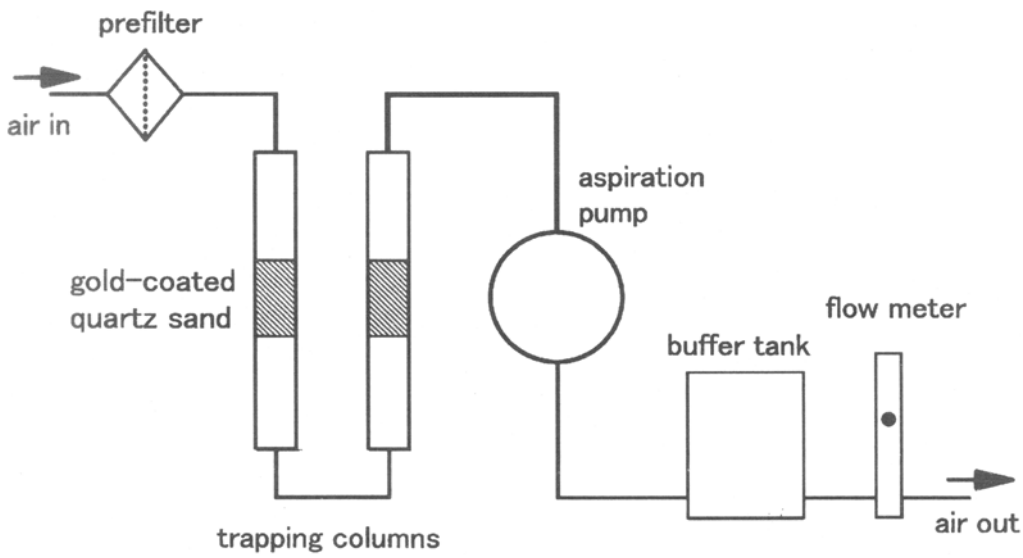
Fig. 1 Air sampling with a portable air sampler. Trapping columns fitted in a transparent cassette are placed in the left section of the upper compartment and connected to an aspirator equipped in the right section of the bottom compartment. A Swinnex holder mounted with a glass fiber filter is attached to the tip of the column on another side. Five reserve cassettes with columns are stored in the left of the bottom compartment.

Mercury collection tube and air sampling

A total mercury collection tube was a quartz column plugged with gold coated quartz sand as a trapping material. The trapping material was prepared as follows. Quartz sand (30 to 60 meshes) was added into chloroaurate solution, dried and then heated at 500℃ in an electric furnace to convert chloroaurate to gold. An aliquot (0.5g) of the gold coated quartz sand thus obtained was packed in a quartz column (outside diameter: 7mm, inside diameter: 5mm, length: 240mm) after exclusion of fine particles under a mesh size of 60. Residual mercury was removed by heating the column at 650℃ with ventilation of mercury free air. Two collection tubes were connected in tandem with a Teflon flexible tube and tightly sealed with a thermal contraction tube at the junction.

Air sample was collected by aspiration at a flow rate of 0.5 l/min through a glass fiber prefilter (Fig. 2). Atmospheric mercury concentrations were corrected based on the trapping efficiency of the collection tube calculated from the amount of mercury detected on both columns. Mercury compounds were trapped at sufficient efficiencies with the collection system in control experiments. When air containing standard amount of elemental mercury (Hg) was aspirated from the upstream of the tandem-connected columns, mercury was recovered on the first column with no leakage to the second column. A coefficient of variation and a range was 15% and 20% of the mean concentration, respectively. Similar results were obtained on $HgCl_2$, CH_3Hg and $(CH_3)_2Hg$ (data not shown).

Alternatively, mercury compounds were also collected with four different collection tubes in series, instead of a pair of gold coated quartz sand tubes, developed for a fractional collection of atmospheric mercury compounds by Takizawa[8].



Fige. 2 collection system for atmospheric mercury with a pair of gold-coated quartz sand trapping columns.

Measurement of mercury

The measurement of mercury was carried out in Akita University for all air samples collected. The collection tube detached from the air sampler was heated for 60 sec at 650℃ and then aspirated at 1 l/min. Total mercury was determined by absorbance of ultraviolet light at a wavelength of 253.7nm using a thermal vaporization-flameless atomic absorption mercury meter[9]. The concentration of mercury compounds in the atmosphere was indicated as the amount of Hg. A blank level was corrected by using a pair of two collection tubes tightly sealed and retained in the air sampler throughout the field survey. The concentration of mercury was indicated after subtraction of the blank level.

Sampling sites and periods

All air samples except those obtained in Akita, Japan were collected in several sites of Federal Republic of Brazil as shown in Fig. 3. The air sampling was carried out in September 1993, November 1994 and March 1996.

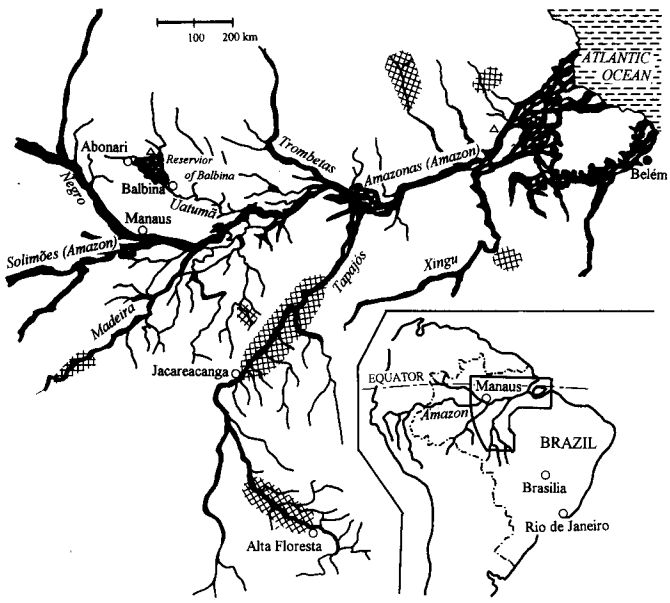


Fig. 3 Air sampling sites in Federal Republic of Brazil. Hatched areas indiccate gold mine clustering sites. ○ : sampling site, △ : tin mine.

Results

Table 1 shows mercury concentrations in samples collected in Balbina (Spots 1, 2 and 3), Abonari, Manaus and Rio de Janeiro using gold coated quartz sand as a mecury trapping material.

Table. 1 Atmospheric mercury concentrations collected with a pair of gold coated quartz sand tubes.

sampling site	aspiration time (min)	volume of air aspirated(m³)	Hg concentration in air sample(ng/m³)
Balbina (Spot 1)	100	0.05	16
Balbina (Spot 2)	315	0.16	7.9
Balbina (Spot 3)	374	0.19	3.4
Abonari	80	0.04	14
Manaus (Spot 1)	525	0.26	7.2
Rio de Janeiro (Spot 1)	290	0.15	7.7

Balbina and Abonari are located in the forest area of the basin of the Uatumã: a tributary of the Amazon, and Manaus is the largest city in middle Amazon. The collection of air samples was carried out in daytime except two (Balbina Spot 3 and Manaus) in which the air samples were collected between midnight and morning. The mean concentration was 9.1ng/m³ for the three sampling spots in Balbina. It was shown that mercury concentrations in Balbina and Abonari were slightly higher than the level of urban area: 7.5ng/m³ that was the mean of Rio de Janeiro and Manaus. Table 1 also shows sampling time duration and volume of aspirated air. The trapping efficiency for mercury was more than 84% with an exception manifesting 57.6%, and the mean was 87.0% after exclusion of maximum and minimum.

Mercury concentrations in Table 2 were obtained using the quadruple collection tubes. Mercury was detected at an average of 4.5ng/m³ in surface air over water of the Amazon river in Manaus, and at 8.0 to 10.0ng/m³ in the air collected in urbanized area of Manaus and Rio de Janeiro. On the other hand, the mercury concentration was relatively low in Brasilia, capital of Brazil. Atmospheric mercury level was 4.7ng/m³ in a control site Akita. The mean concentration calculated from data in Table 1 and 2 was 7.9ng/m³ in Rio de Janeiro (Spots 1, 2 and 3) and 8.6ng/m³ in Manaus (Spots 1 and 2).

Table. 2 Atmospheric mercury concentrations collected with quadruple collection tubes.

sampling site	aspiration time (min)	volume of air aspirated(m³)	Hg concentration in air sample(ng/m³)
the Amazon river (Spot 1)	162	0.08	7.0
the Amazon river (Spot 2)	170	0.09	2.0
Manaus (Spot 2)	129	0.06	10
Rio de Janeiro (Spot 2)	130	0.07	8.0
Rio de Janero (Spot 3)	145	0.07	8.0
Brasilia	120	0.06	3.0
Akita	180	0.09	4.7

Air samples were collected at five gold refineries (goldshops) in Jacareacanga and Alta Floresta located in the basin of the Tapajos where many gold mining sites exist. As shown in Table 3, total mercury concentrations were as high as 380 to 3700ng/m³ in these sampling sites. The difference observed in the concentration of atmospheric mercury may be associated with the surroundings of and actual amounts of mercury released in each working place.

Table. 3 Atmospheric mercury in gold refineries (goldshops) in the basin of the Tapajos with quadruple collection tubes.

sampling site	aspiration time (min)	volume of air aspirated(m³)	Hg concentration in air sample(ng/m³)
goldshop 1 (Jacareacanga)	60	0.03	462
goldshop 2 (Jacareacanga)	60	0.03	3690
goldshop 3 (Jacareacanga)	60	0.03	640
goldshop 4 (Alta Floresta)	60	0.03	382
goldshop 5 (Alta Floresta)	60	0.03	485

Discussion

The average concentration of mercury in the atmosphere is associated with economic activities and industrialization in addition to local emission from natural sources[10]. The combustion of fossil fuels is the most significant source of the anthropogenic release of mercury into the atmosphere. Environmental Agency of Japan conducted a large scale survey that monitored hazardous chemicals in the atmosphere, including mercury compounds determined by gold amalgamization method, at 185 sampling sites throughout Japan, and reported that the mean concentration of total mercury was 2.7, 4.8 to 5.6 and 6.6ng/m^3 in rural, urban and the vicinity of industrial areas, respectively[11]. The background level of total mercury compounds has been determined in atmosphere of rural areas. The concentration ranged from 0.91 to 4.38ng/m^3 with a mean at 1.58ng/m^3 in Mt. Ohdaigahara, Japan[12] and from 1.87 to 3.87ng/m^3 with a mean at 2.5ng/m^3 in the north of Nara Prefecture, Japan[13] by continuous monitoring, as well as from 2.4 to 5.7ng/m^3 in south of Norway[14], and from 3.5 to 4.ng/m^3 in rural areas of Canada[15]. Fukuzaki[16] reviewed published data on the mercury concentration in the air of non-polluted areas including those obtained in the survey of Environmental Agency of Japan, and summarized that the background level is generally around 2 to 3 ng/m^3 in surface air of the ground. Mercury has been detected at relatively higher concentrations in urban areas. The mean concentration of total mercury determined was between 4.1 and 15.0ng/m^3 in highly urbanized cities of Japan including Tokyo, Chiba, Nagoya, Kobe, Amagasaki, Takarazuka, Nara and Kakogawa[13, 17, 18]. Mercury was detected at 6ng/m^3 in the air of residential area of Ghent, Belgium[19], and at 22ng/m^3 in Chicago, US[20].

The atmospheric mercury level was found to be higher in the forest area of the basin of the Uatumã River and on the Amazon River neighboring Manaus than the background level previously reported in rural districts in Japan. Furthermore, the concentration could be higher in the basin of the Uatumã than in Rio de Janeiro and Manaus. On the other hand, atmospheric mercury concentrations of Rio de Janeiro and Manaus were compatible with the reference level that had been reported in urbanized or industrialized areas. In addition, the concentration was similar in Brasilia and in Akita to the level reported in some medium scale cities of Japan. The reliability of the mercury monitoring data in the present study was supported by the agreement of the level observed in Rio de Janeiro, Manaus, Brasilia and Akita with the reference value for urbanized area. In the present study, the variable concentration was apparent on atmospheric mercury of the basin of the Uatumã and the Amazon river. Temporal and weather conditions might be attributed to the varying concentrations of atmospheric mercury as observed in continuous monitorings[12, 13]. It can be concluded that the atmospheric mercury concentration was higher in certain area of Amazon than in the air of general non-polluted area, even if the sampling variations were considered.

Since the Uatumã River was not a gold mining river and air sampling spots of this area are 150 to 200km distant from a large city Manaus, source of the slight increase is not clear in the atmospheric mercury concentration in the basin of the Uatumã. This observation is, however, of interest to consider possible behavior of mercury in Amazon. The global transport of volatile mercury compounds by atmospheric circulation has been shown by the increased levels of mercury in ice samples collected in Greenland and in Antarctica[21, 22]. The temporal and seasonal variation and effects of meteorological and geographic factors should be investigated by large scale continuous monitoring of atmospheric mercury in Amazon in order to evaluate the actual involvement of the atmospheric transport in the wide regional distribution of the mercury. Another possibility that could not be excluded was the existence of natural mercury sources in this area. Increased concentrations of atmospheric mercury have been reported near natural mercury sources, e.g. mercury deposit, volcano and geothermal area[9, 13, 23]. However, no possible candidate was found but a tin mine to the north of the sampling sites (Fig. 3).

Mercury concentration was extremely high, on the other hand, in gold refineries in the basin of the Tapajos, because mercury is vaporized by heating of amalgam with a burner in the gold isolation process. In fact, it has been reported that mercury was detected at significantly high concentrations in the hair of goldminers and workers in goldshops[4]. In WHO Environmental Health Criteria[24], a guideline concentration is 15 μg/m^3 for elemental mercury in the air of general environment, and 50 μg/m^3 for occupational exposure. In Japan, an acceptable mercury concentration limit is provided as 100 μg/m^3 at a generating site without any alkylmercury. Mercury concentrations were below these regulation levels at gold refineries in the Tapajos River basin. Although a body burden of inhalation of metallic mercury should not be underestimated in the working environment, it should be emphasized that the most important pathway of mercury exposure is the intake of fish, which is usually a main protein source for the inhabitants and contains methylmercury as predominant form[5].

While only preliminary data were available, we detected mercury at relatively high concentrations in the atmosphere of a forest area of Amazon. The present observations were in favor of the hypothesis that mercury is distributed widely by the long distant transport of atmospheric circulation after released at gold mining sites.

Acknowledgments

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