Urban mercury pollution in the City of Paramaribo, Suriname

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Abstract Atmospheric mercury pollution related to gold mining activities is a matter of concern in the Republic of Suriname. The first measurements of total gaseous mercury (TGM) in ambient air in Suriname at different sites are presented in this study. Our study shows that Suriname has a TGM mercury background level of 1.45–1.52 ng/m^3, with a mean of 1.4 ng/m^3 which is in agreement with global background concentrations (1.5–2.0 ng/m^3) (Feng et al. Sci Total Environ 304:61–72, 2003; Li et al. Sci Total Environ 395:72–79, 2008). Emissions of mercury from gold buy up shops in the City of Paramaribo result in TGM maximum concentrations of 109.4 ng/m^3 (15 min average) and a mean concentration level of 5.6 ng/m^3 at this urban measurement location. These levels are comparable with that of world cities in Asia and North America. However, per capita Paramaribo loads 3.5–6.5 times more TGM into the atmosphere than Changchun City (Fang et al. Sci Total Environ 330:159–170, 2004) and the occurring spikes are 5.3 times higher and much longer in duration then those in New York City (Carpi and Chen Water Air Soil Pollut 140:371–379, 2002). According to health standard institutions these concentrations represent no risk for the general public. However, a survey inside and in the close vicinity (<100 m) of the gold buy up shops shows mercury concentration levels that surpass the National Institute for Occupational Safety and Health recommended exposure level of 50 μg/m^3 inside and the minimal risk level of 0.2 μg/m^3 of the Agency for Toxic Substances and Disease Registry outside.

Keywords Mercury · Air · Pollution · Urban

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Introduction

Mercury (Hg) has a variety of documented, significantly adverse impacts on human health and the environment. In this paper, we present studies on the mercury pollution in Suriname, a small country in the Amazon region on the north-east coast of South America. Only very limited data on the mercury contamination in Suriname exist. In the Amazon region, large amounts of mercury are released into the environment as a result of small-scale and artisanal gold mining. It is estimated that in Suriname, 20,000 kg/year are discharged into the environment by small-scale and artisanal gold mining (Mol et al. 2001). These amounts are one order of magnitude larger than other important

mercury sources in Suriname, namely bauxite refining industry and biomass burning. The emissions from biomass burning are estimated to be about 30 kg/year (Mol et al. 2001). The emissions of the largest bauxite refining company in Suriname, "Suriname Aluminum Co.," were estimated to be 500–600 kg/year in 2002–2003 and below 150 kg/year in 2005.

Quantitative data assessing the mercury contamination in Suriname are rare. The limited existing data suggest that the contamination is alarming. Total Hg and methyl-Hg concentrations measured in mine wastes, stream sediments, and surface waters in the Brownsweg area indicate that the contamination is similar to the one found near artisanal gold mines in Brazil. Small-scale miners had elevated mercury levels of 27.5 μg/g creatinine in their urine (De Kom et al. 1998). In some Amerindian villages along the Marowijne River, up to 79% of the children had abnormally high hair mercury levels of up to 10 μg/g attributed to the consumption of freshwater fish (Cordier et al. 1998). Mercury levels in hair from mothers delivering in a hospital in Paramaribo showed elevated Hg concentrations in about one third of the mothers and 80% of the newborns had a higher mercury level in hair than their mothers (Mohan et al. 2005).

Studies with regard to mercury pollution in ambient air have not been performed in Suriname so far. However, such measurements would be of interest for the understanding of the background concentrations in the tropics as well as for the determination of urban mercury pollution. According to St Denis et al. (2006), urban air mercury values with regard to Hg^0 in World cities range from 2.48 up to 14.40 ng/m^3. In this study, we have measured mercury in ambient air at three different sites and in addition performed a survey in and around gold buy up shops in the City of Paramaribo. The three main purposes of this study are: determination of the mercury background for comparison, evaluation of the Paramaribo air mercury concentration and evaluation of the mercury occupational exposure in Paramaribo.

Experimental

Operation and methodology

Mercury concentration measurements were performed with a Tekran 2537A stationary mercury analyzer at thre different sites in Suriname and a Lumex RA-915+ portable analyzer for survey in the City of Paramaribo. The Tekran 2537A is a continuous elemental mercury vapor analyzer which is well suited for the measurement of low mercury concentrations in ambient air (Wängberg et al. 2001; de la Rosa et al. 2004). The detection limit is 0.2 ng/m^3.

For quality assurance and quality control reasons, automatic full calibration every 13th hour was enabled, which means cleansing of cartridges, cartridge zero operation, and a span operation procedure. Besides this, a monthly standard operation procedure of cleansing the cartridges was performed. Prior to the real cleansing, the cartridges are filled with demineralised water with a syringe and immersed overnight in demineralised water. The real cleansing takes place the next day in an Ultrasonic bath with a solution of demineralised water and alkali soap. After intake and force out of a solution of demineralised water and alkali soap through the cartridge with a syringe for ten times, the cartridge is put in the ultrasonic bath for 9 min. This procedure is then repeated ten times for each cartridge. After this procedure, every cartridge is rinsed with demineralised water by way of intake and force out for ten times and then dried with pure Argon for 5 min. Agreement of cartridges is also looked upon; if for a sequence of five readings or more one of the cartridges shows a consistent reading higher/lower than 10% of the other cartridge, these data are disregarded.

Integration of mercury levels was programmed at a flow rate of 1.2 L/min for each cartridge. Ambient air is sucked in through a gas cooler, so relative dry air enters the mercury analyzer through a 0.25 in. Teflon tubing with a 0.2-μm particulate filter in the sample line to eliminate possible particulate-bound mercury. For a second zero-air inlet, a particulate filter is followed by two carbon filters to purify the air for calibration and zero-air checks. Measurements were conducted continuously, except under special circumstances such as cleaning of cartridges.

The Lumex RA-915+ operates on differential Zeeman Atomic Absorption Spectrometry (AAS) using high-frequency modulation of light polarization for mercury determination (Garcia-Sanchez et al. 2006; Li et al. 2008). Samples are collected at a controlled mass-flow rate before analysis. The advantage of the Lumex RA-915+ is its portability. With a detection limit of 2 ng/m^3, it is well suited for surveys in urban areas.

In brief the Tekran 2537A pre-concentrates the gaseous elemental mercury on gold cartridges and uses the CVAFS method to determine the mercury concentration while the Lumex RA 915+ determines the gaseous elemental mercury concentration without pre-concentration by way of the AAS method. Because of the setup of the Tekran, we expect this analyzer to measure total gaseous mercury (TGM; $TGM=Hg^0+Hg^{2+}$) and the Lumex analyzer measures gaseous elemental mercury (Hg^0) in the ambient air.

Comparison of data acquired with the Lumex RA 915+ with the background concentration determined by data acquired with the Tekran 2537A is allowed, for the percentage of Hg^0 in TGM is known to be ±95%.
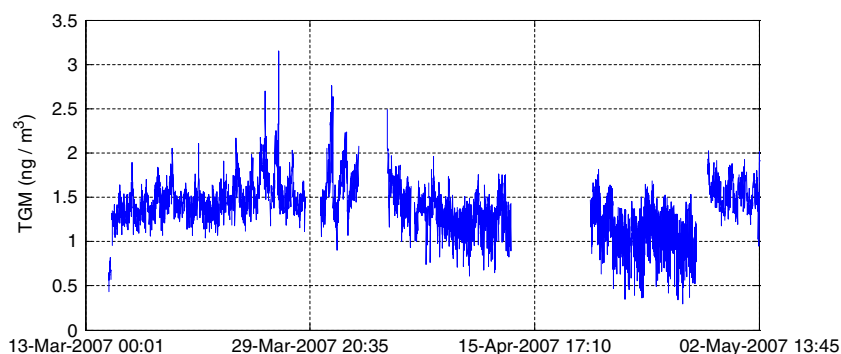
Fig. 1 The black area on the South American Continent in the North is Suriname and the *red and green dots* on the Suriname map represent Paramaribo and Nieuw Nickerie, respectively
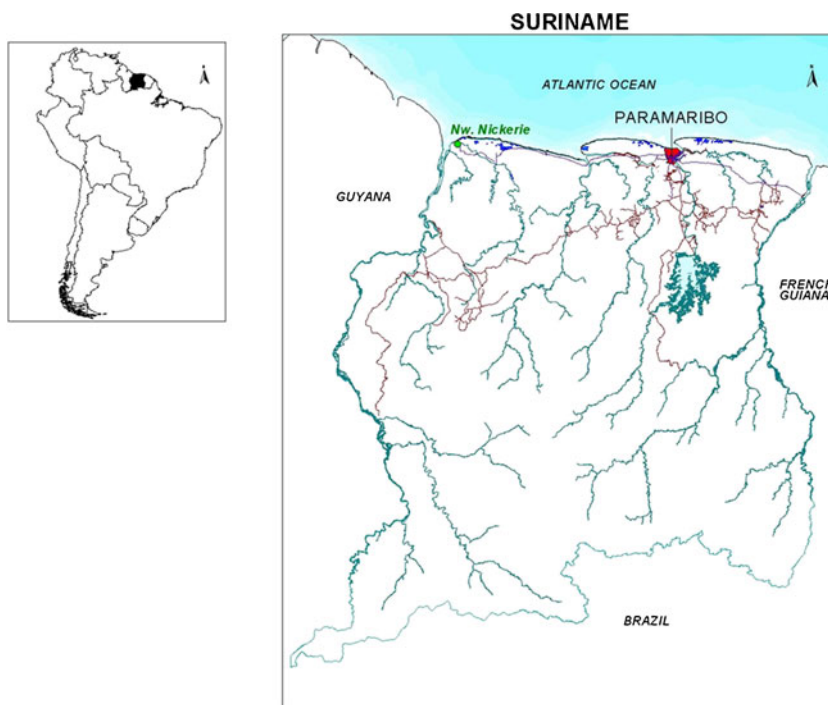
The sampling sites for the stationary Tekran analyzer were chosen to evaluate the mercury concentration in the City of Paramaribo compared with background concentration and was operated at the following three sites:

Site 1 (Background Station, 5°57′ N, 57°02′ W) For the background measurements, the instrument was installed at a costal location in Nieuw Nickerie (Fig. 1) for the time period from 14th March to 1st May of 2007. The sample inlet was placed on a pole about 5 m above the ground, about 300 m away from the Atlantic Coast. Most of the time the Trade winds transport the air directly from the Atlantic to the measurement site and the influence of possible local anthropogenic sources and continental air is minimal. Sampling data from 14th March to 1st May of 2007 were used to determine the mercury background level of Suriname.

Site 2 (Outskirt Station, 5°48′ N, 55°12′ W) This site is located downwind, approximately 7 km south western, at the southern outskirts of the City of Paramaribo (Fig. 1), with no gold buy-up shops or possible polluting sources in the direct vicinity. Sampling data from the 28th October 2006 till 30th November 2006 were used.

Site 3 (downtown station) The downtown station is in the center of the City of Paramaribo (Fig. 1). The mercury analyzer was installed in a hospital (Sint Vincentius Hospital). The period of sampling lasted for 50 days, from the 30th of November 2006 to 18th January 2007.

The survey

The survey in the City of Paramaribo was done to get reliable data with regard to ambient air mercury concen-

Fig. 2 Air Mercury concentration measurements done with the Tekran 2537A mercury analyzer from 14th March to 1st May 2007 at the Background Station (site 1)
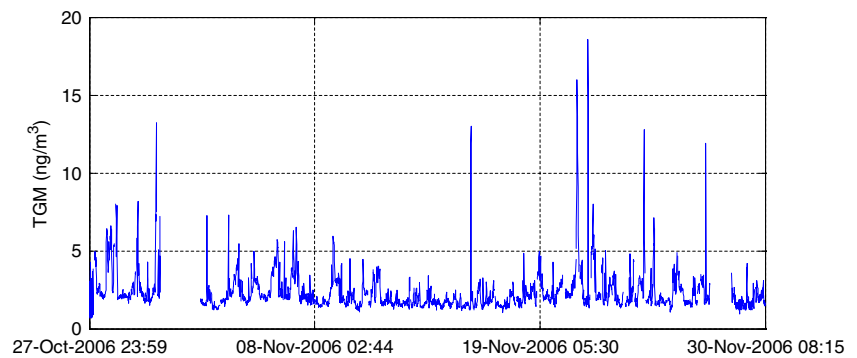
Fig. 3 Air mercury concentration measurements measured with the Tekran 2537A mercury analyzer from 28th October to 30th November 2006 at the Outskirt Station (site 2)

trations and the anthropogenic contribution. Sampling was performed in and around a number of gold buy up shops using a portable LUMEX RA 915+, mercury vapor analyzer. The gold buy-up shops are potentially large sources of mercury pollution because the residual mercury is burned off during the purchase process. Chosen locations for sampling at the shops were at the entrance, in the office, the workplace and outside but within the vicinity (≤100 m) of the shops (Fig. 5 and Fig. 6).

Results

The sites

The background site was used to evaluate the background air mercury level. For the background TGM concentration level in Suriname, data gathered in the period 14th March–1st May 2007 (Fig. 2), are used. Analysis of the data shows that the data set ranges from 0.3 to 3.1 ng/m^3, the mean and median values coincide at 1.4 ng/m^3, and the standard deviation is 0.3 ng/m^3.

For the Outskirt station, the evaluation of a data set for 28th October–30th November 2006 shows that the air mercury concentration has the respective values: mean, 2.4 ng/m^3 and a ranging from 0.7 to 18.6 ng/m^3 (Fig. 3), the standard deviation is 1.3 ng/m^3. The concentration spikes in the data set go up to 18.6 ng/m^3. Airborne mercury concentrations at the downtown station for November

30th–January 8th 2007 had a mean 5.6 ng/m^3 and a range from 0.1 to 109.4 ng/m^3, the standard deviation is 9.0 ng/m^3. Here, concentration spikes in the data go up to 109.4 ng/m^3 (Fig. 4).

The survey

A comparison of the Lumex and the Tekran instruments was performed at the background site over a duration of 2 days. The two instruments agree within 5% of the measured values. Since the Lumex analyzer is not well suited for the low concentrations at the background site a better agreement was not expected, but the comparison demonstrates the comparability of the instruments. The linearity of the Lumex RA 915 Mercury analyzer has been investigated in combination with the Lumex Pyro 915 by way of standard solutions. In the presented study, the Lumex was solely used for the measurements of the pollution around the gold buy up shops. The concentrations range outside the shops is between 500 and 10,000 and inside the shops between 500 and 60,000 ng/m^3. For these concentrations, the Tekran is not applicable. The gold sold to the gold buy up shops contains 5% residual mercury (Veiga and Meech 1999) which is released during melting of the gold. All shops are equipped with retorts and mercury collectors to capture the liberated mercury, but fume hoods and the retorts do not function properly.

With the Lumex RA-915+, a survey was done over a number of five gold buy-up shops. In this survey, the

Fig. 4 Air mercury concentration measurements performed with the Tekran 2537A mercury analyzer from 30th November to 8th January 2007 at the Downtown Station (site 3)
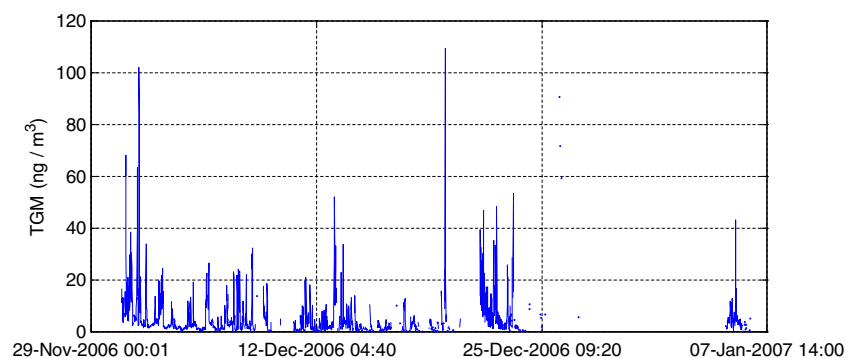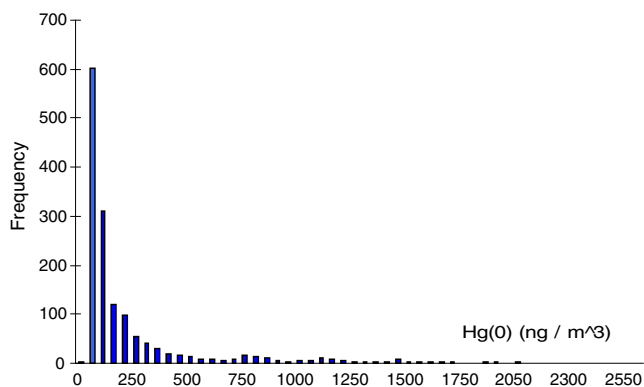
Fig. 5 Measurements performed with the Lumex RA-915+ mercury analyzer during a 30-min walk through downtown Paramaribo in the neighborhood of gold buy-up shops. Peaks were at distances of <100 m from entrances of the gold buy-up shops

entrance, workplace, office, and the outside (≤100 m) were covered.

The air mercury concentration values at the respective locations in and outside the shops covering the following ranges: entrance, 500–40,000 ng/m^3; workplace, 9,000–52,000 ng/m^3; office, 13,000–60,000 ng/m^3; and outside, 500–10,000 ng/m^3 (Fig. 5 for outside walk).

Of three shops, the data are given in Table 1 (Fig. 6). The duration of measurements inside the gold buy-up shops was about 50 min, with a 10–20-min sampling depending on the fluctuation of the concentration in the room. Outside the shop, a 10-min walk to and from the shop was done and along side the shop in the case of shops 2 and 3. In shops 1 and 3, there was some burning, less than 10 min while visiting. Although in shop 2 there was no burning during the sampling, the concentrations were far higher.

Discussion

The background mercury concentration was measured at site 1 in the most western City of Suriname, Nieuw Nieuw Nickerie. Site 1 is located at the Atlantic Coast, where the influence of local anthropogenic sources and continental air is minimal. The statement that site 1 is a clean background site is supported by the data set which shows that no concentration surpasses the 3.5 ng/m^3. Although the Inter
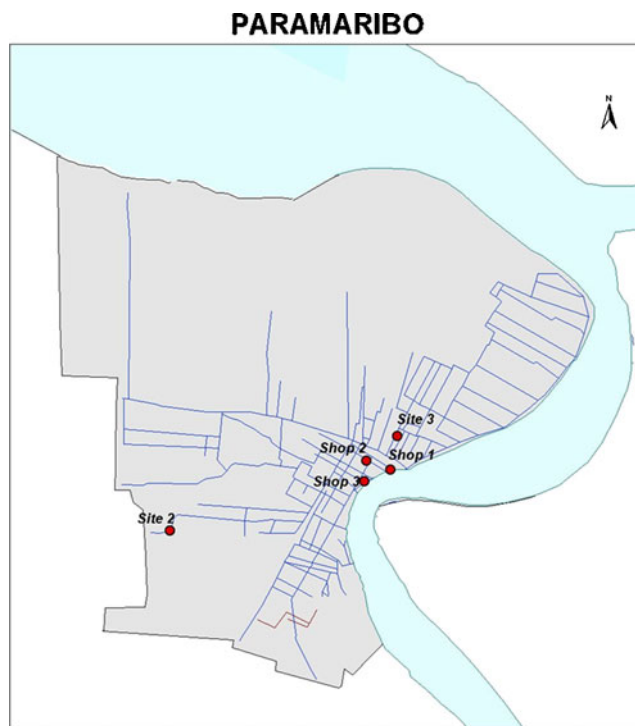

Fig. 6 Location map of the three gold-buy up shops and site 2 at the outskirt and site 3 in the center of the Paramaribo City. The distance from shops 1 to 3 is about 1 km

Tropical Convergence Zone (ITCZ) passes twice over Suriname, at this location (site 1) back trajectories show that most of the time the wind is a trade wind coming from the Atlantic and that the influence of possible local anthropogenic sources and continental air is minimal. Thus the instrument, the Tekran 2537A, sampled air mostly from the trade winds coming from the Atlantic Ocean. Analysis of data shows that the mean and median of the background TGM concentration level in Suriname is 1.4 ng/m^3, this is in accordance with findings of Li et al. (2008) and Schroeder and Munthe (1998). In the City of Paramaribo, the gold miners sell their gold amalgam to the gold buy-up shops. Smelting of the gold amalgam in gold buy-up and jeweler shops releases mercury into the urban air, thereby potentially exposing large populations.

The outskirt and downtown station show elevated concentrations compared with the measurements at the background station in Nieuw Nickerie. Mean values at

Table 1 Gives values at the respective locations in and around the shops; the range indicates fluctuation (see Fig. 6)

Shop Mercury concentration	Shop 1 Hg^0 (ng/m^3±10%)	Shop 2 Hg^0 (ng/m^3±10%)	Shop 3 Hg^0 (ng/m^3±10%)
Entrance	5,000	40,000	12,000
Workplace	9,000–14,000	52,000	24,000–27,000
Office	13,000	60,000	13,000
Outside	5,000–10,000	2,400	500

these sites are 2.4 and 5.6 ng/m^3, respectively, which are 1.7 and 4.0 times the background level. According to St Denis et al. (2006) and Carpi and Chen (2002), these are common urban values. Figures 4 and 5 show sudden distinct elevations of mercury concentration which indicates contributions of local anthropogenic sources. At the outskirt station, concentration values go up to 13 times the background level and at downtown station, up to 78 times. This was expected because of their respective positions with regard to the gold buy-up and jeweler shops.

For reason of insight in the mercury pollution, we will compare these values to that of other cities. With regard to the urban mercury concentration for comparison we can investigate world cities. The yearly average of mercury concentration in the investigated world cities in ambient air ranges from 2.48 to 14.40 ng/m^3, e.g., Toronto-Canada, 2.48 ng/m^3; Tokyo-Japan, 2.70 ng/m^3; New York-USA, 3.80 ng/m^3; Guiyang-China, 8.40 ng/m^3; Seoul-Korea, 14.40 ng/m^3 (Carpi and Chen 2002; Fang et al. 2004). Although Paramaribo is not a world city, nevertheless the measured mercury concentration is within this range. A comparison with these cities should be looked at in more detail, for there are some differences between these world cities and the City of Paramaribo. The above mentioned cities are all densely populated; on the contrary Para-maribo is sparsely populated. There are dry and wet seasons in Paramaribo; the temperatures vary between 21°C and 32°C. The investigated world cities on the other hand have warm and cold seasons, so heating of houses and buildings is a must. In Paramaribo, the mercury pollution is a consequence of the emissions of the amalgam burning in the gold buy up shops and in the aforementioned world cities this is mainly because of domestic and industrial heating (combustion).

A detailed comparison between the City of Changchun (Fang et al. 2004), a metropolitan city in the middle part of Northeast China, and Paramaribo and between Paramaribo and New York (Carpi and Chen 2002) will be made.

Area and population of the urban districts Changchun and Paramaribo are respectively 158 km^2 and 2,920,000 to 183 km^2 and 215,000. This means that Changchun population is almost 16 times the population of Para-

maribo. In both studies, the Tekran 2537A mercury analyzer is used. It is mentioned that TGM (TGM=Hg^0+ Hg^{2+}) was measured in Changchun (Fang et al. 2004); in Paramaribo, we expect the analyzer to also measure total gaseous elemental mercury because of the setup. The percentage of Hg^{2+} in TGM ranges 3.9–5 (Fang et al. 2004). TGM mean concentrations in the non heating and heating season respectively are 13.5 and 25.4 ng/m^3. The Paramaribo Downtown TGM mean concentration is 5.6 ng/m^3 (Table 2).

In the New York and Paramaribo studies the Tekran 2537A is used; in New York gaseous elemental mercury (Hg^0) was measured, with a different time resolution. In the New York measurements, the Tekran was set at a 5-min time resolution and in the Paramaribo measurements it was set at 15 min. In both studies, the data show lots of high spikes, indicating anthropogenic contributions (Table 3).

Although the abovementioned concentrations at these Paramaribo sites are elevated, they do not surpass the environmental and occupational health standards for inhalation exposure to mercury vapor. Namely the ceiling limit at 100 μg/m^3 given by the Occupational Safety and Health Administration, the recommended exposure level (REL) at 50 μg/m^3 given by the National Institute for Occupational Safety and Health (NIOH), and the minimal risk level (MRL) at 0.2 μg/m^3 and action level at 1.0 μg/m^3 given by the Agency for Toxic Substances and Disease Registry.

Ambient air mercury concentration levels at the Para-maribo Stations show concentrations spikes. These spikes values are less than the MRL, but it should be noted that the 15-min sampling average of the Tekran might lose important variability on the timescale of turbulent atmospheric mixing, strong tropical updrafts, and changes in source area due to shifting wind direction. Thus, these values could be much higher locally.

Unlike the mercury levels in the ambient air at the outskirt and downtown stations, the ambient air in Para-maribo in and around gold buy-up shops shows high mercury concentrations. Our survey shows that inside the shops, the mercury concentration reaches high values ranging up to 60,000 ng/m^3. This is more than 40,000

Table 2 Comparison of the districts shows that per capita the Paramaribo community is loading 3.5–6.5 times more TGM into the atmosphere then the Changchun community

Items Districts	Area ratio	Population density ratio	Non-heating season		Heating season	
			TGM loading ratio	TGM loading ratio per capita	TGM loading ratio	TGM loading ratio per capita
Changchun	1	15.75	2.42	1	4.54	1
Paramaribo	1.16	1	1	6.5	1	3.5

The values for Changchun are based on from Fang et al. (2004)

Table 3 Comparison of districts shows that the spikes in the Paramaribo district are not only 5.3 times higher but also at least three times longer in duration

Items Districts	Anthropogenic mercury sources	Lowest and highest urban mean Hg^0 concentration measured (ng/m³) over the district	Measurement resolution ratio	Maximum spikes ratio	Duration ratio of spikes
New York	Waste generation, transport, medical and dental operations	2.7–3.8	1	1	1
Paramaribo	Amalgam burning	2.3–5.3	3	5.3	3

The values for New York are based on Carpi and Chen (2002)

times the background level, 300 times the MRL, and 60 times the action level above which people should evacuate the location immediately and hazardous substance containment and remediation should begin. Given that the concentration of mercury in ambient air in the shops exceeds the action level, the people in these shops are definitely at risk. In the vicinity of the shops (≤100 m), the air mercury concentrations are still so high that they can reach the MRL value of 0.2 μg/m³, so people living and working in the vicinity of these shops are at potential risk.

Metallic mercury is rather volatile, with a saturated atmosphere containing approximately 18 mg/m³ of mercury at 24°C. Therefore, it is quite possible that the NIOSH-REL of 50 μg/m³ can be exceeded, as is shown by our data, in gold buy-up shops. Approximately 80% of inhaled mercury is absorbed through the lungs into the bloodstream, it then becomes oxidized and accumulates in the brain and kidneys with all known health consequences (Li et al. 2008).

The gold sold to the gold buy-up and jeweler shops contains about 5% residual mercury (Veiga and Meech 1999) which is released during melting of the gold. Although all shops are equipped with retorts and mercury collectors to capture the liberated mercury, the mercury vapor concentrations in and outside the shops are high. It was noted that the collectors are in very bad condition and that the fume hoods do not seem to function properly. Furthermore, workers not use proper safety equipment.

With a gold production of 10,000–12,000 kg/year (Hays and Vieira 2007) from small and middle scale gold mining, this suggests large annual emission of mercury vapor into the urban atmosphere. According to Veiga and Meech (1999), 5% of the gold amalgam burned in the gold buy-up shops is mercury, which means that a gold production of 10.000–12.000 kg/year produces an emission of about 527–632 kg which is loaded into the atmosphere.

This load of mercury on to the atmosphere is expected to be the reason for the occurring spikes, so the spikes at the two sites in Paramaribo are attributed to the emissions of the gold buy up shops. According to Carpi and Chen 2002, the spikes could be the consequence of precipitation, whereby the rain increases the deposition of Hg^{2+} to the surface. Divalent mercury is able to undergo an in situ reduction to volatile Hg^0 on surfaces and this process is increased by precipitation. Our investigation shows that there is no positive coupling between the mercury spikes and precipitation.

The precipitation and TGM data in Fig. 7 show that on 8th November, there was a 48-mm precipitation but no spikes, slight increase in precipitation from 16th–21st November no spikes occur, almost the same slight increase from 21st–26th and 30th November and lots of spikes occur.

The shops open at 9 a.m. but business starts around 10 a.m. and lasts till 4 p.m. A set of wind roses (Fig. 8) show that during the whole day, wind from downtown

Fig. 7 The precipitation and TGM data over the month of November 2006 show that there is no correlation between spikes and precipitation
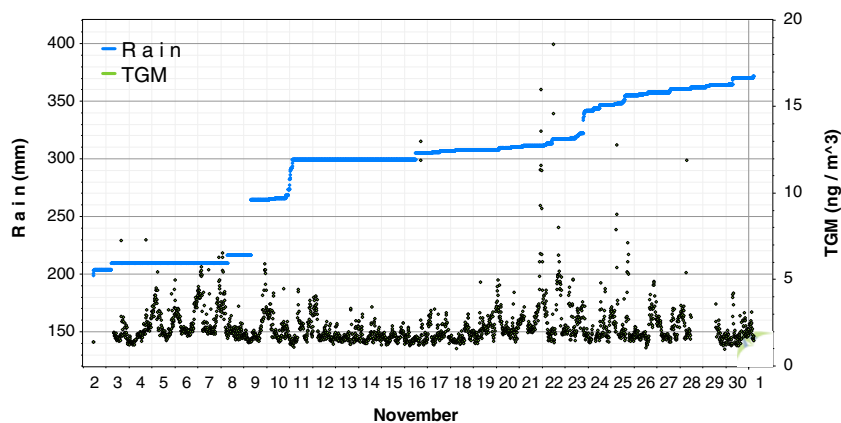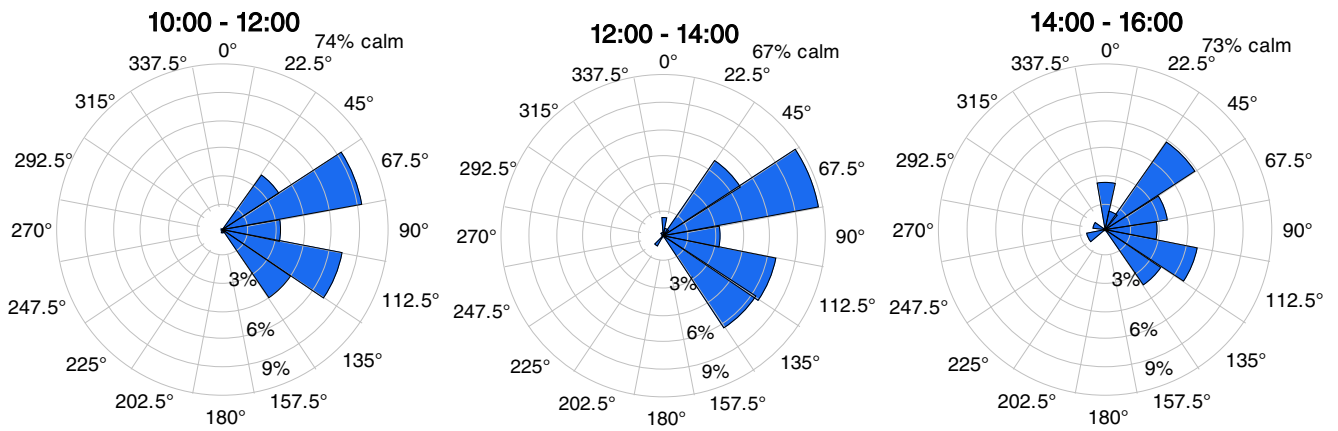
Fig. 8 The wind roses show the average of 2-h intervals over the whole period with regard to the landing of air

Paramaribo is landing at the outskirt site (Fig. 8) which lies South West of the center of the city. In particular between 10.00 a.m. and 14.00 when business is at its highest.

A scatter plot TGM versus wind direction, Fig. 9(left) was put up with data of every half hour and every full hour over the month of November 2006, because the wind data sampling were done on a 10-min interval and the Tekran sampling on a 15-min interval. This scatter plot shows that there is still another contributor to the occurrence of spikes in the mercury data set. According to the wind direction, between South East and South, where these high concentrations come from these spikes could potentially attributed to the emissions of the alumina refining company in Suriname, of which it is known that it loads some hundreds of kilograms of mercury on to the atmosphere per year. This refinery is

located at Paranam about 30 km of the City of Paramaribo, see Fig. 9(right). Because of the distance and the high concentration measured, further investigation is needed with regard to the impact of these emissions on the environment.

Conclusions

Our studies show that Suriname has a total mercury background level of 1.4 ng/m^3, which is in agreement with global background concentrations (1.5–2.0 ng/m^3) (Feng et al. 2003; Li et al. 2008).

In the City of Paramaribo, the detected mean (28th October 2006–8th January 2007) levels of mercury in ambient air varies between 2.4 and 5.6 ng/m^3, this seems to be a common urban background level (Carpi and Chen

Fig. 9 *Left* shows the scatter plot of TGM versus wind direction. High spikes are also coming from the South East. *Right* shows the position of the alumina refinery with respect to site 2
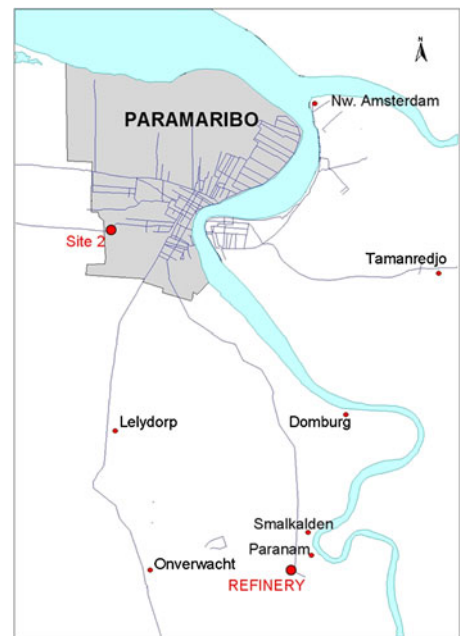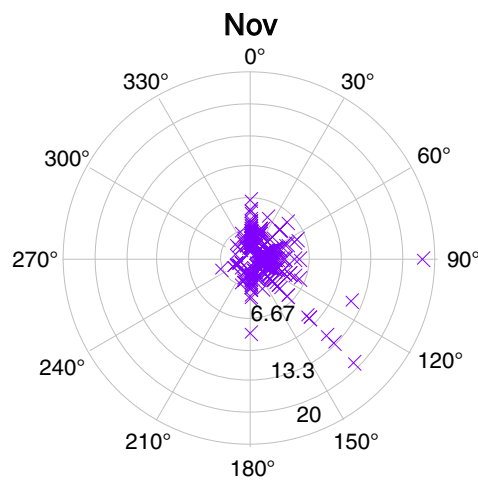
2002; St Denis et al. 2006). Concentration spikes go up to 109.4 ng/m^3 (15 min average) indicating local anthropogenic pollution.

Comparison to world cities shows, e.g., that Paramaribo loads per capita 3.5–6.5 times more TGM into the environment then Changchun. The comparison with New York shows that the mean concentrations are in the same range and that the occurring spikes in Paramaribo are 5.3 times higher and longer in duration.

The ambient air in and outside the gold buy-up shops has high concentrations surpassing the MRL, the action level and even the REL. Notably the mercury concentration of 60,000 ng/m^3 measured in a gold buy up shop surpasses the NIOH recommended exposure level. People working and/or living in the neighborhood of these gold buy up shops are exposed to these high air mercury concentrations and are at potential risk of mercury vapor intoxication.

The ambient air mercury concentrations in Paramaribo depend on wind direction and their location with regard to the gold buy up and jeweler shops and the potential alumina refinery. Available data show that airborne mercury concentrations decrease as one proceeds south from downtown Paramaribo. The mercury loaded on to the atmosphere to our findings does not contain the percentage of Hg^{2+} that activates the positive correlation between occurrence of spikes and precipitation. With regard to the mercury emissions of the alumina refinery and its contribution to higher mercury concentration in populated areas, further investigation is needed in particular when the ITCZ is north of Paramaribo

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