Survey of atmospheric total gaseous mercury in Mexico

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Abstract

While sources of gaseous mercury (natural and anthropogenic) are well known, studies on atmospheric mercury concentrations in Mexico are new. In order to assess the total gaseous mercury (TGM) levels at some characteristic Mexican sites, four locations were selected to start an exploratory survey and begin to assess the TGM behavior. This paper presents data obtained at an urban site (Mexico City), a rural site (Huejutla, Hidalgo), a coastline site (Puerto Angel, Oaxaca) and a closed mining site (Zacatecas City, Zacatecas). The highest TGM average values were found at this last site (71.82 ng m⁻³) together with the urban site (9.81 ng m⁻³). At the rural and coast line sites the lowest TGM values (1.32 and 1.46 ng m⁻³, respectively) were found. According to the ANOVA test, there were significant differences for the TGM values among all the studied sites, except between the coastline and the rural place. A multiple correlation test performed between TGM and some meteorological parameters showed that in sites without anthropogenic mercury sources influence (rural and coast line), the TGM levels are correlated with the temperature and relative humidity, while for the other two sites no clear correlation was found.

Keywords: Total gaseous mercury; Mercury; Meteorological parameters; Mexican polluted sites

1. Introduction

Mercury is present in the environment due to human activities as well as natural sources. Although mercury is relatively abundant on the Earth’s surface, most (70%) of the total gaseous form of mercury found in the atmosphere is anthropogenic (Schuster et al., 2002). Since the beginning of the industrial age, approximately 100–150 years ago, the quantity of mercury mobilized into the atmosphere has been increased between two and five times (Nriagu and Pacyna, 1988; Rada et al., 1989; Lindqvist, 1991; Mason et al., 1994; Hudson et al., 1995).

The physical and chemical characteristics of the metallic gaseous mercury make it a persistent pollutant (with a lifetime of 1–2 years) (Lindqvist and Rodhe, 1985); its deposition, biomethylation and bioaccumulation in aquatic ecosystems represent a serious environmental and health risk (Lutter and Irwin, 2002). Because of high concentrations reported in ecosystems located far away from mercury sources (Che-Jen et al., 2001), some environmental mercury effects are related to long-range transport. Unlike other heavy metals, mercury is present in the atmosphere, primarily in the gaseous...
phase; and therefore the metallic mercury is the predominant specie in rural and remote locations (Ebinghaus et al., 1999).

Developed countries in North America and Europe have reduced their anthropogenic mercury emissions since considerable efforts are devoted to decrease the usage of mercury and strict regulations have been applied to major anthropogenic mercury emission sources (Hylander, 2001). However, it is well known that mercury is still widely used to manufacture consumer goods and in some services around the world. The global mercury market is important and permanent and no substitutes have been found for some uses such as energy saving bulbs; part of this market is illegal or unregulated mainly because mercury is employed for unessential uses as religious and sorcery practices and ornaments in emerging countries, and therefore all these activities also should be considered as potential gaseous mercury sources (Ramı́rez et al., 2000).

Whereas data needed to characterize the temporal distribution of total gaseous mercury (TGM) in the atmosphere is relatively abundant in many regions of North America and Europe (Feng et al., 2003), data for other regions such as Latin America is less available. Mexico is believed to be increasing its atmospheric mercury emissions; however, no comprehensive measurements of ambient atmospheric TGM have been conducted in Mexico (Pilgrim et al., 2000). Our limited knowledge of the trends and cycle of atmospheric mercury is based on measurements from only a few sites. In order to obtain a better understanding of TGM levels in Mexico, four different sites were selected for an exploratory continuous monitoring of TGM over a short time period at the end of the rainy season.

The objectives of this study were: (1) to measure atmospheric mercury at four different sites in Mexico; (2) to determine background atmospheric mercury concentrations at two sites without apparent anthropogenic mercury sources influence.

2. Experimental

2.1. Sites description

Field measurements for atmospheric TGM were conducted during fall 2002 in four different locations in Mexico (Fig. 1): Zacatecas City, Mexico City, Huejutla and Puerto Angel. The first site (ZAC site) was selected because Zacatecas is a City where the main economic activity during 3 centuries was silver and gold mining; because of this activity, millions of tons of mining wastes containing mercury were disposed on the soil in the same time period and it is therefore believed that this region could have high atmospheric mercury pollution. Mexico City (CENICA site) was selected as a monitoring site because it represents a mega-City with residential and industrial zones very close to each other. On the other hand, Puerto Angel and Huejutla (PA and HUEJ sites, respectively) have recently been selected as two new monitoring sites in Mexico for Hg wet deposition, as a result of an extension of the mercury deposition network (MDN) currently operating in Canada and the United States. The TGM monitoring plan and some characteristics of the four sites studied are briefly described below:

(i). ZAC site: The monitoring campaign was from September 17–20, 2002. Measurements were made at the Autonomous University of Zacatecas (22° 44′ N, 102° 28′ W), Zacatecas State. This site is located at S of Zacatecas City (2420 m above the sea level), in a semi-urban place surrounded by rustic brick manufacturers that use mining wastes as raw material; the fuel used for the bricks ovens is not characterized.

(ii). PA site: Measurements were made from October 16–18, 2002. TGM was measured at the weather station in Puerto Angel (16° 47′ N, 96° 28′ W), Oaxaca State. This site is a beach resort localized on the coast of Oaxaca State (13 m above the sea level), this place is surrounded by tropical forest, and no industrial activity is developed nearby.

(iii). HUEJ site: Measurements were made from October 20–23, 2002. TGM was determined at the Technological Studies Center in Huejutla (21° 08′ N, 98° 25′ W), Hidalgo State. HUEJ site (located at 172 m above the sea level) corresponds to a rural location dedicated to farming and almost completely surrounded by agricultural fields.

(iv). CENICA site: The monitoring campaign was performed from October 18–21, 2002. TGM monitoring was carried out at the Environmental Science and Technology Building (CENICA), located at Iztapalapa (19° 21′ N; 99° 04′ W), Mexico.
City. This site, located at SE of Mexico City (2240 m above the sea level), is a place enclosed in mixed residential areas and several industrial activities (steel storage, food processing and storage, among some others) are developed in the surroundings, so this factor makes this area a high traffic zone mainly with heavy trucks.

2.2. Measurement of TGM and meteorological parameters

Measurements of TGM were made with an automatic Mercury Vapor Analyzer Tekran® 2537A. The Tekran® has two gold cartridges in different channels which trap the vapor phase mercury after a pre-selected sampling time, each one is desorbed by thermal action alternately and flushed by a carrier gas (Ar), which is then detected using cold vapor atomic fluorescence spectroscopy ($\lambda = 253.7$ nm). The instrument allows two calibration methods: manual and automatic internal permeation source injection. In this study, the equipment calibration at the beginning of the measurement campaign was done using a manual injection mode (with a Tekran®, 2505 Mercury Vapor Calibration Unit which was allowed to warm up for 24 h); and during the monitoring time, the calibration was done using the internal permeation source, every 23 h. Before the analysis, the particulate matter was removed from gaseous samples by two 47 mm diameter Teflon filter (0.2 µm) located before both the inlet line (3 m length Teflon tubing) and the instrument inlet. The analyzer was operated under 5 min sampling time and 1 L min$^{-1}$ sampling flow, providing a TGM detection range from 0.1 to 10 000 ng m$^{-3}$. TGM data were validated according to guidelines established by the Canadian Atmospheric Measurement Network (CAMNet, 1999) and by the Research Data Management and Quality Control System (RDMQ).

In all cases, meteorological parameters (hourly average temperature ($T$), relative humidity (RH), solar radiation ($I$), wind speed (WS) and wind direction (WD)) were collected from weather stations located near each sampling site with the same frequency (5 min) as the mercury analyzer, whereas the independent variables were the available meteorological parameters ($T$, $I$, RH, WS and WD). In order to find the dependence or relationship between both TGM and meteorological parameters an hypothesis test was conducted to verify the multiple regressions. Analyses of variance ($\alpha = 0.05$) and Duncan’s test were made using the SAS software (SAS, 1989) in order to establish significant differences between TGM averages at each site.

3. Results and discussion

Table 1 and Fig. 2 show a statistical summary of the TGM and meteorological parameters determined during the monitoring periods. It was observed that for ZAC and CENICA sites, TGM average values were significantly higher (41 and 5 times, respectively) compared to concentrations reported on studies that used the same instrumentation at different locations in Europe, North America and polar regions (Kellerhals et al., 2003; Blanchard et al., 2002; Wångberg et al., 2001; Poisant, 2000; Temme et al., 2003). Nevertheless, there is a closed mining site in Nevada, USA, where TGM concentrations of 866 ng m$^{-3}$ were reported (Gustin et al., 1996) using a different monitoring technique. It is observed that the data variability of TGM at ZAC site was higher than at the other three monitoring sites. This result could indicate that the monitoring site is influenced by some nearby mercury vapor phase sources as suggested by Dommergue et al. (2002). For the CENICA site a considerable TGM data variability was observed, possibly due to the fact that this site is located within a polluted city making it a receptor of many still unidentified gaseous mercury sources. For rural (HUEJ) and coastal (PA) sites, TGM averages were significantly lower than TGM averages for CENICA and ZAC sites (near to 6 and 45 times, respectively), the variability of these last data was also significantly lower (Table 1).

The variability of TGM data observed for HUEJ and PA sites was very small, and therefore minimum and maximum TGM values were very close. TGM concentrations found at both sites fall within the normal range of global levels. Confirming this observation, 50% of all TGM data obtained were between 1.1 and 2.9 ng m$^{-3}$ for HUEJ site and between 0.76 and 2.5 ng m$^{-3}$ for PA (Fig. 2). In the case of the two other sites, 50% of the TGM data fell between 20 and 100 ng m$^{-3}$ for ZAC and from 7.5 to 11 ng m$^{-3}$ for CENICA site (Fig. 2), suggesting that these sites are influenced by Hg polluting sources.

TGM measurements made in other regions of the globe indicate that in Mexico there are places with very low TGM concentrations as HUEJ and PA, but also there are sites highly influenced by anthropogenic sources (ZAC and CENICA). Baker et al. (2002),
registered TGM measurements during 6 years at Cape Point, South Africa, and they found a central trend between 1.2 and 1.3 ng m\(^{-3}\); at Guiyang, China, the central trend observed in periods from 14 to 25 days in different seasons was between 6 and 9 ng m\(^{-3}\) (Feng et al., 2002); Dommergue et al. (2002) found TGM values between 0.8 and 1.6 ng m\(^{-3}\) in Grenoble, France; and Poissant et al. (2000) registered during 1 year, a TGM central trend ranging from 1.5 to 2.0 ng m\(^{-3}\) at Quebec, Canada.

Fig. 3 shows the hourly average (geometric) behavior of TGM and \(T\) at each monitoring site, the wide dispersion of TGM data for ZAC and CENICA sites is evident; and some correlation is observed between TGM and \(T\) at PA and HUEJ sites. The strongest correlation between these two variables was found for the PA site (Table 2).

The multiple regression results presented in Table 2 show that for the ZAC site, TGM values were not dependent on the meteorological parameters, and co-linearity is observed between \(T\), \(I\) and WS. For the CENICA site, the statistical analysis indicates that the TGM values are influenced by \(I\), RH and WS values and co-linearity was observed between \(T\), \(I\) and RH variables. The ANOVA and Duncan test prove that the TGM levels found at CENICA and ZAC sites are significantly different between them and from the TGM values found at HUEJ and PA sites (both sites had a very similar TGM average).

For HUEJ site, TGM was influenced by RH and \(T\) values, while co-linearity was observed between RH with \(I\) and WS. In the case of PA site, it was identified that the \(T\) variable has influence on TGM behavior; on the other hand, no co-linearity was observed between independent variables.

Fig. 4 shows the wind directional dependence of the TGM at the monitored sites. Plumes of Hg are slightly observed for ZAC, HUEJ and PA sites, however at HUEJ and PA sites there were no evidence of an anthropogenic mercury source, the average TGM concentrations for both places were of 1.47 and 1.79 ng m\(^{-3}\), respectively. Even though these are not enough data to compare with the global background of around 1.5–2.0 ng m\(^{-3}\), monitoring of wet mercury deposition will be made at these last two sites as part of the MDN to assess transport effects of mercury.

For ZAC site, it can be observed (Fig. 4) that plumes come from the western region of the monitoring site; this result could be attributed to the influence of handcraft bricks production made with local soil/tailings. However, more studies must be carried out at this site in order to determine the main TGM sources.

At the CENICA site no plume direction was observed, which could indicate that the monitoring site...
Fig. 2. TGM concentration range for measured data (I), TGM geometric average values (—) and predominant (50% of total data) TGM concentrations (□) for data obtained at (A) ZAC site, (B) CENICA site (C) PA site, (D) HUEJ site.

Fig. 3. Hourly average of TGM concentrations (solid lines) and temperature (dotted lines) time series at the four monitoring sites. (A) ZAC site, (B) CENICA site, (C) PA site, (D) HUEJ site.
is influenced by several unidentified mercury sources located around the monitor. It is also possible that the laboratories located in the research center emit some quantity of mercury in vapor phase.

4. Conclusions

For the first time, TGM measurements were made in Mexico at four sites with different characteristics. The high variability of TGM values observed for ZAC and CENICA sites is evidence of the influence of nearby anthropogenic sources of mercury. For the first site, no industrial source has been identified so it will be necessary to assess the mining waste reprocessing as a serious mercury source, as well as the influence of nearby production of bricks made with local soil/tailings cooked in primitive furnaces. For the CENICA site, due to the polluted situation of Mexico City derived from an intensive and varied industrial activity, an evaluation at several monitoring points around the City is required. Both sites (ZAC and CENICA) showed significant differences in average TGM concentrations among them, and also with respect to HUEJ and PA sites, which could be related to both sites lacking a direct effect from a nearby anthropogenic mercury source.

The preliminary results obtained from this short period monitoring study, suggest that HUEJ and PA sites could be considered places that fall within the global background TGM values; however, long monitoring periods are required in order to assure that condition.

The relationship between TGM and atmospheric parameters shall not be considered as a prediction tool. However, the statistical analysis of the results shows that at least some meteorological parameters have some bearing on TGM concentration, mainly for sites without anthropogenic mercury source influence.

The TGM results here reported for PA and HUE sites, could be later compared with data on mercury wet...
deposition (currently in measuring stage), in search of a possible correlation between both variables at non-mercury source influence sites.

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