Atmospheric Environment xxx (2009) 1–11

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Mercury species measured atop the Moody Tower TRAMP site, Houston, Texas

Steven Brooks [a,*], Winston Luke [a], Mark Cohen [a], Paul Kelly [a], Barry Lefer [b], Bernhard Rappenglück [b]

[a] National Oceanic and Atmospheric Administration, Atmospheric Turbulence and Diffusion Division, Liaison to Canaan Valley Institute, 456 S. Illinois Ave., Oak Ridge, TN 37830, USA
[b] Department of Earth and Atmospheric Sciences, University of Houston, Houston, TX, USA

ARTICLE INFO

Article history:
Received 3 November 2008
Received in revised form
31 January 2009
Accepted 2 February 2009

Keywords:
Houston
TexAQS-II
Mercury
GEM
RGM
FPM

ABSTRACT

Atmospheric mercury speciation was monitored within Houston, Texas, USA, August 6–October 14, 2006 as part of the TexAQS Radical and Aerosol Measurement Program (TRAMP). On average, all mercury levels were significantly elevated compared to a rural Gulf of Mexico coastal site. Concentrations varied from very clean to very dirty. Multi-day periods of stagnant or low-wind conditions brought elevated concentrations of all mercury species, whereas multi-day periods of strong winds, particularly southerly winds off the Gulf of Mexico, brought very low values of mercury species. Over the entire mercury measurement period, the daily averages of mercury species showed distinct and consistent relationships with the average planetary boundary layer dynamics, with gaseous elemental and particulate-bound mercury near-surface concentrations enhanced by a shallow nocturnal boundary layer, and reactive gaseous mercury concentration enhanced by midday convective boundary layer air entrainment transporting air aloft to the surface. Mercury concentrations were not significantly correlated with known products of combustion, likely indicating non-combustion mercury sources from the Houston area petrochemical complexes. On the morning of August 31, 2006 an observed emission event at a refinery complex on the Houston Ship Channel resulted in extremely high concentrations of aerosol mass and particulate-bound mercury at the TRAMP measurement site 20 km downwind.

1. Introduction

The intensive measurement period of the TexAQS Radical and Aerosol Measurement Program (TRAMP) field study began August 14, 2006 and ended September 30, 2006. The study was conducted in Houston, Texas, USA and was part of the larger TexAQS 2006 intensive air-monitoring campaign. The purpose of the TRAMP program was to sample meteorological and pollutant concentration data, including secondary species such as ozone, to assist the Texas Commission on Environmental Quality (TCEQ) efforts to formulate a Strategic Implementation Plan (SIP) for meeting air quality goals.

Mercury (Hg) data were collected August 6, 2006–October 14, 2006, which included the nominal intensive measurement period. Similar to other measurements, the mercury data sets were collected by a suite of sensors on short towers and climate-controlled shelters on the rooftop of the Moody Tower dormitory building, 70 m above ground level, and within the University of Houston (UH) main campus. While the site is obviously highly urban, it is 2–4 km away from highways and industrial sources, and elevated enough above ground level (70 m) that we consider this to be an "urban background" site.

Mercury species were included to provide a more comprehensive research initiative to better understand the causes of all air pollutants, and their potential interactions in the Houston area. In particular, mercury speciation measurements were conducted to characterize local sources and possible heterogeneous reactions with sea salt aerosols. The study objectives, site selection, participating groups, measurement periods, and all measurements conducted are summarized in the TRAMP overview paper (Lefer and Rappenglück, in this issue)

2. Mercury species

During TRAMP, mercury species were continuously monitored atop the Moody Tower. The mercury speciation included gaseous elemental mercury (GEM, Hg(0)), reactive gaseous mercury (RGM, Hg(II,g)), and fine (PM2.5) particulate-bound mercury (FPM, Hg(II,p)), respectively. Each type of Hg has distinct properties:

- GEM has a long lifetime in the troposphere (6–12 months), has a northern hemisphere background level of ~1.5 ng m^{-3} (90% of the measurement period average), and has the characteristic of long-range transport making it difficult to distinguish local

* Corresponding author. Tel.: +1 304 463 4739.
E-mail address: steve.brooks@noaa.gov (S. Brooks).

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doi:10.1016/j.atmosenv.2009.02.009

from distance sources. GEM is relatively insoluble, therefore is not wet deposited, and near-surface atmospheric concentrations are unaffected by rainfall or surface dew (condensation) events. GEM comprises ~97% of the total atmospheric mercury in the troposphere (e.g. Slemr et al., 2006) and has many natural and anthropogenic sources (volcanoes, enriched soils, coal combustion, biomass burning, etc.). It has been found that for combustion processes, like biomass burning, GEM usually correlated well with CO (e.g. Ebinghaus et al., 2007 and references therein).

- RGM is operationally defined as mercury collected by a KCl coated denuder tube. RGM is typically believed to be dominated by Hg(II) such as $HgCl_2$, HgClX and HgBrX. RGM is typically rare in the lower troposphere 1–2 pg m^{-3} (sub-parts per trillion levels) comprising <1% of total atmospheric mercury (Lindberg and Stratton, 1998). RGM has a high dry deposition rate and is rapidly removed from near-surface air (lifetime in the near-surface air is typically just 1–3 h; Skov et al., 2006). Near-surface RGM concentrations are generally highest when RGM is being actively mixed from aloft to ground level during afternoon boundary layer convection. RGM is also extremely water soluble and is readily removed from the lower troposphere during rain events. In the absence of rain, morning dew on vegetation also has been shown to remove RGM from the very-near-surface air (Malcolm and Keeler, 2002). This effect is absent from the TRAMP data where the measurement height was 70 m above ground level. With the exception of active volcanoes, RGM has negligible natural surface sources and is primarily emitted by coal combustion, waste incineration, cement manufacturing, and industrial processes. RGM can also be produced in-situ by the atmospheric oxidation of gaseous elemental mercury (Lindberg et al., 2002; Swartzendruber et al., 2006). RGM has the potential to convert to FPM in the presence of sea salts and other aerosols due to the high affinity of RGM and NaCl.
- FPM is comprised of oxidized mercury bound to fine (<PM2.5) particles. FPM has a low, but significant, dry deposition rate and, in the absence of rain, a significant lifetime in the near-surface air (2–5 days; Keeler et al., 1995). FPM from local sources concentrates in the near-surface air until it becomes convected out of the region, mixed (diluted) with air entrainment into a growing boundary layer, or, being water soluble, rained-out. FPM is the least studied and least measured form of atmospheric mercury. FPM is typically rare (~1–5 pg m^{-3}; Lu and Schroeder, 1999) in the near-surface air, but more common near the tropopause where rainout is minimal (Talbot et al., 2007). Potential mercury cycling between RGM and FPM has not been fully studied.

3. Sources and regulations

Mercury is released through coal burning, waste incineration, cement production, and, industrial and metallurgical processes. Nationwide, stationary fossil fuel combustion accounts for the majority of anthropogenic emissions (~66%) with coal-fired power plants the largest US source. Each individual source emits a characteristic distribution of GEM, RGM and particulate-bound mercury (PM). Coal-fired power plants, for example, are believed to emit on average 55% GEM, 42% RGM, and 3% PM. These percentages are altered by combustion temperatures, other contaminants in the coal, and, the use of wet and dry flue cleaners, and other emissions' controls. Estimates of total US anthropogenic atmospheric mercury emissions for 1999 are shown in Fig. 1. The percentages listed in Table 1 of local Houston sources are general percentages for that emission type and may not accurately reflect the actual individual source emissions.

Fig. 2 shows the geographical distribution of major Hg sources in the US and Canada. The highest density of mercury sources is found in the Eastern part of the US. Large emission sources are also located in East Texas, mostly associated with coal-fired electricity generation. In the greater Houston area other sources contribute, among them waste incineration and petrochemical processes. Major Houston point sources, from the US Environmental Protection Agency (EPA) National Emissions Inventory 2002, are shown in Fig. 3.

3.1. Regulation of mercury emissions

In 2005 EPA issued the Clean Air Mercury Rule (CAMR) to permanently cap and reduce atmospheric mercury emissions solely from coal-fired power plants. This rule forced limits on

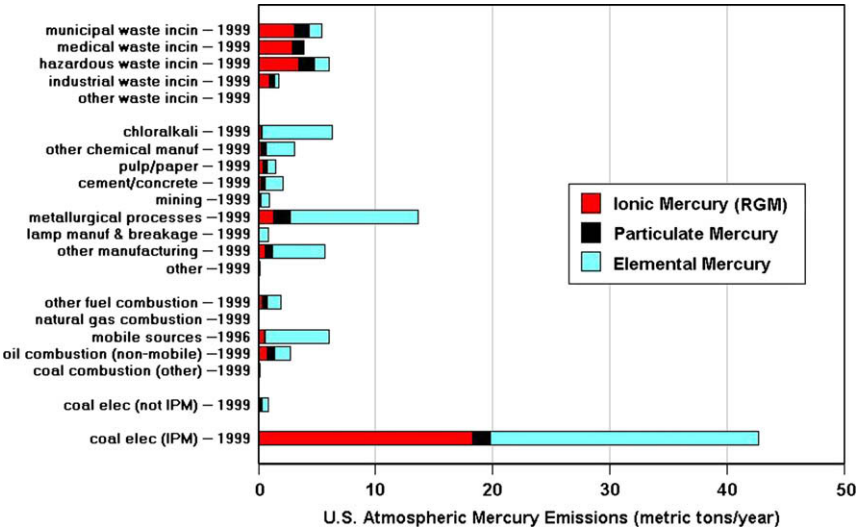

Fig. 1. Estimated 1999 US Atmospheric Anthropogenic Mercury Emissions and typical emission source strengths for the Hg species (USEPA National Emission Inventory 1999). Most sources emit significant amounts of gaseous elemental Hg. Only waste incineration emits mostly reactive gaseous Hg and particulate-bound Hg. The largest emissions of RGM and GEM are associated with coal-fired electricity generation.

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Table 1
The Houston area USEPA National Emission Inventory Hg sources (2002) with general percentages of Hg species emitted.

	Direction	Distance	Type	Emission height	% GEM	% RGM	% PM
Houston Ship Channel	ENE	15–25 km	Waste incineration	~100 m	20	55	25
			Chlor-Alkali[a]	NA	95	~0	5
			Refineries	10–50 m	50	25	25
Port Arthur, TX	ENE	120 km	Waste incineration	~100 m	20	55	25
			Metallurgical	10–50 m	80	10	10
Lake Charles, LA	ENE	170 km	Manufacturing	10–50 m	80	10	10
Parish power plant	SW	25 km	2460 MW, coal fired	~200 m	55	42	3
Fayette power plant	W	110 km	1641 MW, coal fired	~200 m	55	42	3

[a] This Oxy Vinyls Deer Park Chlor-Alkali plant, although listed in the USEPA National Emissions Inventory of 2002, has been idle since 2002.

mercury emissions from new and existing coal-fired power plants, required stack monitoring, and created a market-based cap-and-trade policy to reduce total coal-fired power plant emissions in two phases: 2010 and 2018. In February 2008 the US Court of Appeals for the D.C. Circuit vacated CAMR, stating that the EPA did not have the authority to exempt power plants from MCAT-based standards with a cap-and-trade system. The state of Texas had previously adopted the EPA CAMR through a state implementation plan. It is uncertain, at this time, how the Texas SIP will be influenced by the court-ordered nullification of the EPA CAMR.

3.2. Texas statewide and Houston area mercury emissions reduction efforts

The mercury emissions' issues in the Houston region reflect the regulatory processes ongoing nationwide. The current emissions inventory is the USEPA 2002 National Emissions Inventory with significant national and local Houston sources highlighted in Figs. 2 and 3, respectively.

There are plans by several Texas utility companies to reduce coal-fired power plant mercury emissions. For instance, TXU Corporation, which operates the majority of power plants in Texas, announced plans to reduce mercury pollution by the installation of carbon sorbent injection systems on all nine of their existing coal-fired plants and on any new plants they construct. Installation of these systems was scheduled to begin in 2008 and to be completed by 2011.

Austin Energy and the Lower Colorado River Authority intend to install emissions' controls at the coal-fired Fayette power plant, located to west of Houston (see Fig. 3) by 2018. It is planned to install new scrubbers on the remaining two scrubber-less stacks. These scrubbers are expected to cut Fayette mercury emissions by 30%.

The coal-fired Parish power plant is located to the south-west of Houston (see Fig. 3). In a plan submitted to the Texas Commission of Environmental Quality on June 21, 2006, NRG Energy stated it will install a new scrubber at the Parish power plant in 2010 with a second new scrubber in 2014. According to the NRG Energy plan, the additions of these two scrubbers at Parish power plant will "significantly reduce sulfur dioxide and mercury emissions".

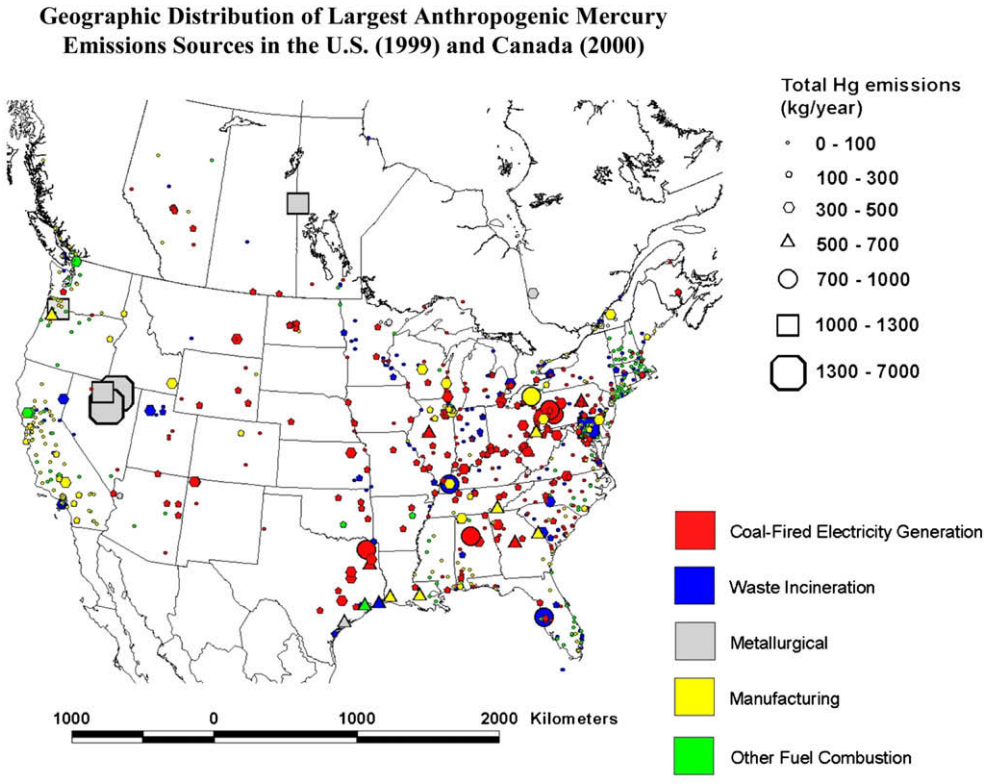

Fig. 2. Distribution of significant anthropogenic mercury emissions' sources in the US and Canada. The majority of mercury sources are found in the Eastern half of the US. However, large emission sources are also located in the Eastern part of Texas, mostly associated with coal-fired electricity generation. Data are from the USEPA National Emissions Inventory 1999 and Environment Canada Inventory 2000.

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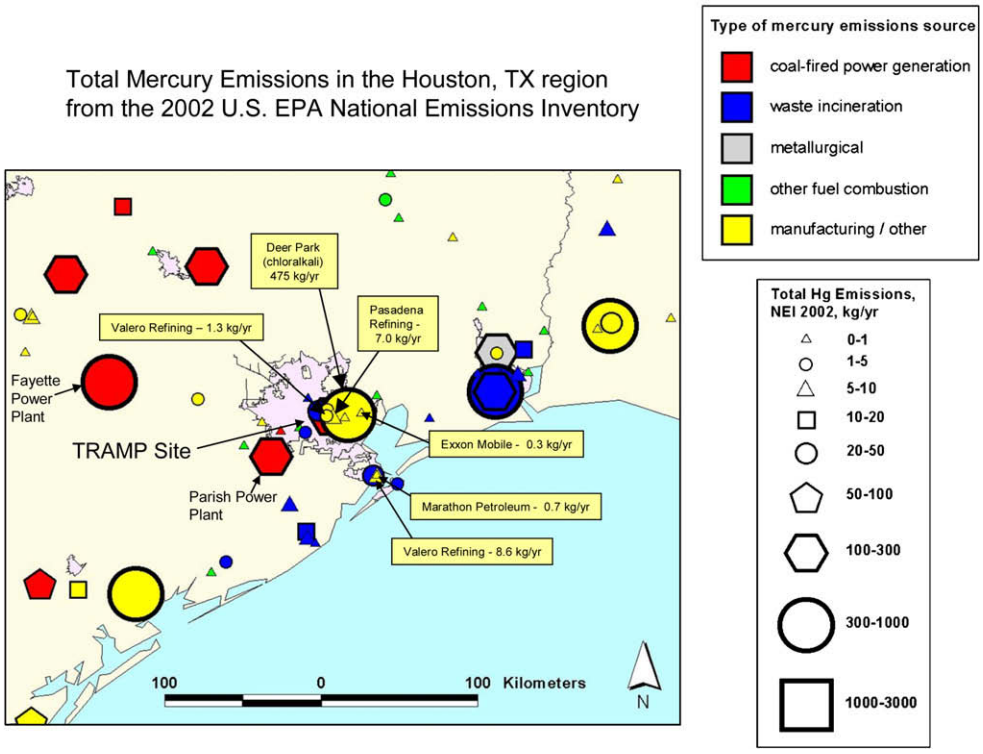

Fig. 3. Houston area mercury sources with the TRAMP measurement site location. Coal-fired power generation sites, including the Parish and Fayette plants, are located to the south and west of the TRAMP site. Waste incineration, manufacturing and petrochemical processes are located to the north and east of the TRAMP site predominately near the Houston Ship Channel.

3.3. Houston area petrochemical facilities

While many coal-fired power plant utilities within Texas are planning to reduce mercury emissions, the mercury emissions from petrochemical processing facilities are more difficult to characterize. These are not covered by the Clean Air Mercury Rule, and emission reductions are unlikely due to their low national priority. The mercury content of crude oil varies considerably, spanning 3 orders of magnitude. Wilhelm et al. (2007) analyzed 170 crude oil samples at US refineries, and determined total mercury to be in the range from below their analytical detection limit (<0.5 g kg^{-1}) to approximately 600 g kg^{-1}, with a mean of 7.3 g kg^{-1}. Extrapolating to national usages, total mercury in crude oil is roughly 20 times less than the total mercury in coal. However, it is thought that crude oil mercury is primarily released during refining processes, with the majority of mercury emissions from coking. The Houston area performs 13.3% of all US refining, and 19.2% of all US crude oil coking. Most of this local refining is concentrated near the Houston Ship Channel.

The Lyondell refinery, the refinery closest to the TRAMP measurement site, processes approximately 1.8 million barrels of heavy crude per week. Heavy crude oil, as opposed to light crude, requires coking. Using the average mercury content of crude oil of 7.3 g kg^{-1}, a very conservative estimate as heavy crude oil tends to have higher mercury levels, the Lyondell refinery mercury emissions could potentially be as high as 1.8 kg week^{-1}. This mercury emission would then be similar to a small capacity coal-fired power plant.

Our estimate of petrochemical facilities emission heights is 10–50 m above ground level with the highest emissions' elevations occurring from the tops of the coking towers. The Parish and Fayette coal-fired plant stacks are approximately 200 m above ground level. Under average conditions these local sources will be consistantly internal to the planetary boundary layer. However, under very stable nocturnal conditions the coal-fired plant emissions will enter the free troposphere directly. This effectively isolates the Hg(II) species from the surface until mixed downward by daytime boundary layer entrainment.

Direct evidence of potential petrochemical processing emissions of mercury was obtained during TexAQS-II from high-time-resolution ($\sim$1 s) measurements of GEM made from the NOAA ship Ronald H. Brown (Cowling et al., 2008). These measurements, although concurrent and part of TexAQS-II, were not part of the TRAMP project. Measurements of oxidized Hg species were not made. Concentrated plumes of GEM up to concentrations of $\sim$250 ng m^{-3} believed to be from at least one point source were observed repeatedly in the Houston Ship Channel and once in the Beaumont–Port Arthur area. While the magnitude of the detected plumes varied widely, the Houston Ship Channel plume was detected during each of four transects of the Houston Ship Channel under southerly to easterly winds. Surprisingly, these measured GEM concentrations did not significantly correlate with the measured concentrations of any other measured species (SO_2, NO_x, CO, Ozone, etc.) on the Ronald H. Brown, suggesting that the mercury sources impacting these locations were sources other than stationary combustion sources such as coal-fired power plants. In addition, Cowling et al. (2008) stated that the elevated GEM concentrations are not consistent with the latest TCEQ emission inventories, or the EPA National Emissions Inventory of known sources.

Furthermore, the very high ($\sim$250 ng m^{-3}) plume-based gaseous elemental mercury concentrations observed at the NOAA ship, Ronald H. Brown, within the Houston Ship Channel were not observed at any time atop the Moody Tower, indicating large local

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source(s) isolated near the Houston Ship Channel Industrial Complex, ~20 km from the TRAMP site.

4. Methods and quality assurance

Mercury species were measured on the UH Moody Tower between August 06 and October 14, 2006 using a Tekran ambient air Hg speciation system. Due to an instrumentation problem, data from September 24th–26th were not collected. The mercury speciation sensor suite consisted of Tekran models 2537a/1130/1135 for the determination of gaseous elemental mercury (GEM, Hg(0)), reactive gaseous mercury (RGM, Hg(II,g)), and fine particulate mercury (FPM, Hg(II,p); Fitzgerald and Gill, 1979; Landis et al., 2002; Lu et al., 1998) with detection limits of 0.01 ng m^{-3}, 1.0 pg m^{-3}, and 1.0 pg m^{-3}, respectively. To ensure proper operation of the individual components, the sensor suite was activated in three stages with only GEM (model 2537a) measurements initially started, followed by the addition of RGM (model 1130) measurements a few hours later, followed finally by FPM (model 1135) measurements a few hours after RGM.

The system was set to collect RGM and FPM for 1 h, while concurrently collecting and analyzing 5 min GEM samples. At the end of the hour the system analyzed the preconcentrated RGM and FPM over a period of 1 h. The resultant data set is twelve 1-h RGM and FPM samples daily, and the same 12 h of 5 min GEM samples. The GEM, RGM, and FPM data presented in this paper are all hourly data, with the GEM samples averaged over the RGM and FPM collection hour. Effectively, the sampling system runs 50% of the time and analyzes, without sampling, 50% of the time. Therefore not all short duration (~hour) mercury events are temporally resolved.

The mercury system was leak tested and zero-air tested at least daily during the first week of operation and after all glassware and filter changes. Otherwise it was leak-checked weekly. A Tekran model 1102 air-drier unit was utilized to supply air to the zero-air generation system (Tekran 1130 pump unit) to avoid known problems with moisture and the iodated carbon canisters which provide the zero-air for system flushes. Tekran model 2537a internal permeation source calibrations were performed at 52-h intervals. The sensor suite inlet was located 1.5 m above the rooftop trailers, at the southern edge of the rooftop area, and well away from the building's ventilation and air conditioner exhausts. No significant trend in GEM was detected between moderately windy and stagnant periods that would indicate a potential source, such as a broken mercury thermometer or leaking fluorescent lighting tube, in the immediate (1–10 m) vicinity.

5. Results

Fig. 4 shows hourly results of Hg measurements obtained atop the Moody Tower. GEM was found in the typical urban range of 1.5 to about 4.0 ng m^{-3}. The highest GEM value was 4.4 ng m^{-3} observed on August 23 under stagnant wind conditions when other TRAMP chemical measurements were also elevated. RGM varied from <DL to ~60 pg m^{-3} with typical afternoon peaks (~1500 CST). The maximum value was obtained on August 24 with light under SE winds (~1.4 m s^{-1}). FPM varied from <DL to ~80 pg m^{-3} with typical early morning hours peaks (~0400 CST). The highest FPM value was observed on August 31 along with extremely high values of VOCs, SO_2, aerosol mass, and most other primary pollutants.

For comparison purposes, mercury speciation results at Grand Bay, Miss., obtained in summer 2007 are included with the Houston summary results in Table 2. The Grand Bay, Miss. Site in 2007 was located 3 km from the Gulf of Mexico in low-lying Pine Savannah

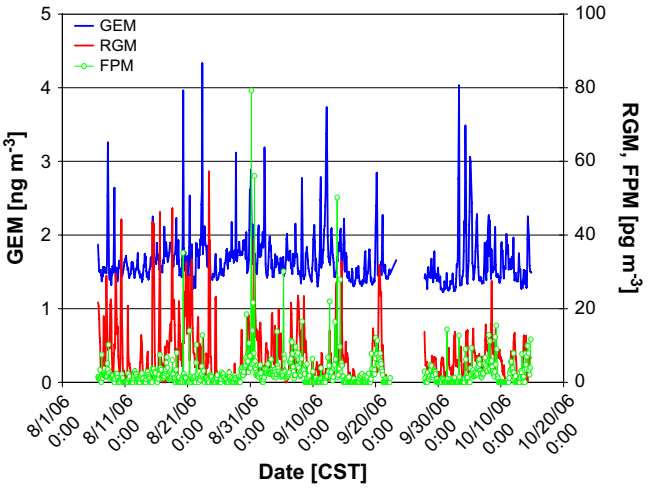

Fig. 4. Hourly mercury species concentrations for entire TRAMP study.

within the NOAA Grand Bay National Estuary Reserve. It is a relatively remote, rural site with a similar latitude and climate to the Houston area. On average, Houston mercury species concentrations were 17%, 60%, and 39% higher compared to Grand Bay, Miss. for GEM, RGM, and FPM, respectively.

During TRAMP UH conducted regular rawinsonde balloon launches to determine the vertical atmospheric structure and the Planetary Boundary Layer (PBL) height (for details see Rappenglück et al., 2008). To compare with the average diurnal mercury concentrations, the resultant the PBL heights were weighted and hourly averaged. These results were smoothed to generate an "average" boundary layer height diurnal cycle shown with the mercury species in Fig. 5. This figure includes the entire mercury data set binned and diurnally averaged for the mercury species. GEM begins a slow build-up after midnight with the shallow PBL trapping GEM emissions in the near-surface air. At ~0730 CST the PBL begins to grow, mixing the near-surface air with air aloft. This causes near-surface GEM to drop until ~1200 CST when the PBL reaches its daily peak depth. At ~1900 CST when the PBL decreases and converts to a nocturnal boundary layer, the GEM surface emissions again cause a slow build-up of GEM in the near-surface air. FPM shows a similar trend to GEM, likely with similar cause-and-effect.

Table 2
Measurement results from TRAMP (Bold) and the rural NOAA site, Grand Bay, Miss. for summer 2007 (in parentheses) for comparison. In every case, with the exception of maximum RGM concentration, mercury concentrations, and their standard deviations were greater in the summer of 2006 in Houston compared the summer of 2007 at Grand Bay, Miss. Most notably maximum TRAMP FPM was nearly four times the Grand Bay maximum concentration, and TRAMP GEM maximum was nearly double the maximum Grand Bay concentration.

	Detection limit	Avg.	Max.	Min.	Std. dev.
Gaseous elemental Hg (ng m^{-3}) 1 h averages	**0.01**	**1.66** (1.41)	**4.33** (2.40)	**1.22** (1.02)	**0.36** (0.23)
Reactive gaseous Hg (pg m^{-3}) 1 h samples	**1.0**	**6.9** (4.3)	**57.3** (70.2)	**0.0 (<DL)** (0.0 < DL)	**7.9** (6.1)
Fine particulate-bound Hg (pg m^{-3})1 h samples	**1.0**	**2.5** (1.8)	**79.2** (21.1)	**0.0 (<DL)** (0.0 < DL)	**5.2** (3.1)

<DL = below detection limit.

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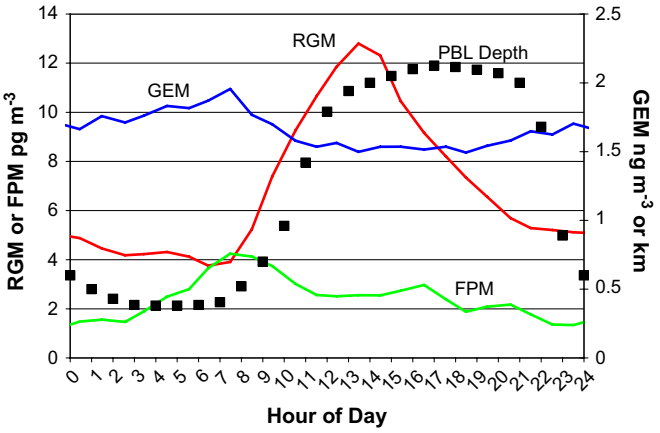

Fig. 5. Hourly diurnal averages for the mercury species and the planetary boundary layer (PBL, or mixing layer) depths. GEM and FPM begin a slow build-up after midnight with a shallow nocturnal PBL trapping GEM and FPM emissions in the near-surface air. At ~0730 CST the PBL begins to grow mixing the near-surface air with air aloft resulting in decreases for GEM and FPM, and an increase in RGM in the near-surface air.

RGM, a species that readily dry deposits, shows a much different diurnal signal. Daily RGM minima occur at ~0630 CST. During the nighttime more RGM is deposited than is emitted to the near-surface air, as demonstrated by RGM decreasing during the nighttime. At ~0730 CST the PBL begins to grow, mixing the air aloft in the PBL. This causes near-surface RGM to dramatically increase when air aloft (isolated from the surface during the nighttime hours and high in RGM) is mixing downwards towards the surface. RGM peaks at ~1300 CST when the PBL entrainment rate decreases abruptly. Dry deposition of RGM then dominates and the near-surface RGM concentrations drop through the remainder of the day and night. We can conclude that at the TRAMP site, on average within the near-surface air, the surface emissions of GEM and FPM tend to dominate over surface sinks, and the surface sinks for RGM dominate over the surface emissions.

Generally high RGM and FPM concentrations were most often associated with wind directions (ENE) from the Houston Ship Channel Industrial Complex. Fig. 6 shows the wind roses for the three mercury species. The maximum GEM concentration (not shown), and the higher median concentrations for FPM occurred when the wind was blowing from the direction (NE) of the Houston Ship Channel Industrial Complex. During daytime enhanced values for RGM (and also FPM) occurred with E wind direction. Higher FPM values also pointed to the downtown Houston area (N) and to SSW, potentially associated with the Parish power plants. The lowest median concentrations of RGM and FPM usually occurred with winds out of the south and west.

As shown in Fig. 7 during the seven-week mercury campaign, all mercury species were, on average, lower on the weekends (Saturdays and Sundays) compared to the weekdays. If we assume that GEM enhancement is its concentrations above its northern hemispheric background levels of ~1.5 ng m^{-3}, weekend mercury species enhancements are only ~60% of weekday enhancements. Assuming 1 pg m^{-3} background levels for RGM and FPM, weekend enhancements are ~68% and ~61% of weekday enhancements for RGM and FPM, respectively. These indicate a greater work week (Monday–Friday) source of all mercury species. Vehicular output of all Hg species is generally considered to be negligible. Therefore this suggests that industrial Monday–Friday emission sources may be large contributors to the elevated mercury concentrations observed during our study.

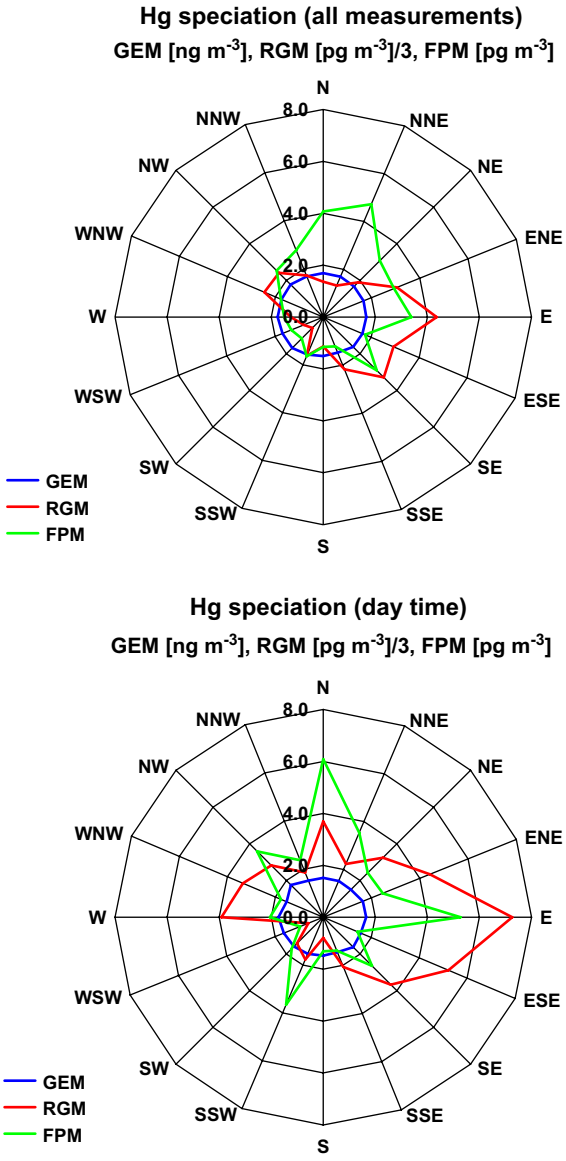

Fig. 6. Wind roses for GEM, RGM and FPM, respectively for all measurements (above) and for daytime (0800–2000 CST) measurements only (below).

5.1. Remarkable events

Houston air varies from very clean to very dirty, with Hg species following the general multi-day polluted and clean periods with the other TRAMP chemical measurements. Overall, the mercury speciation measurements showed several very-clean, and several highly-polluted, multi-day periods. Here we examine two "clean" periods and two "dirty" periods.

On clean days GEM concentrations were near northern hemispheric background level (~1.5 ng m^{-3}). RGM was nearly absent on clean days, with the exception of minor RGM peaks in early afternoon hours when air aloft is mixed downward. FPM was also nearly totally absent, but with nearly identical peaks in the afternoons. "Clean" periods were most often associated with persistent southerly winds which advect marine background air masses from the Gulf of Mexico. This air tends to be low in both primaries such as CO and non-methane hydrocarbons (Rappenglück et al., in this issue) and secondaries such as ozone and formaldehyde (Rappenglück et al., 2008, in this issue).

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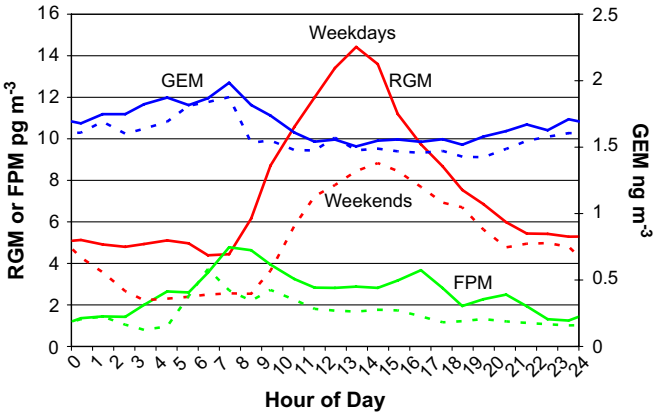

Fig. 7. Diurnal averages of mercury species on weekdays (Mon.–Fri.) verses weekends (Sat. and Sun.). Weekends and Weekdays showed similar diurnal cycles, with all weekday average concentrations exceeding weekend concentrations.

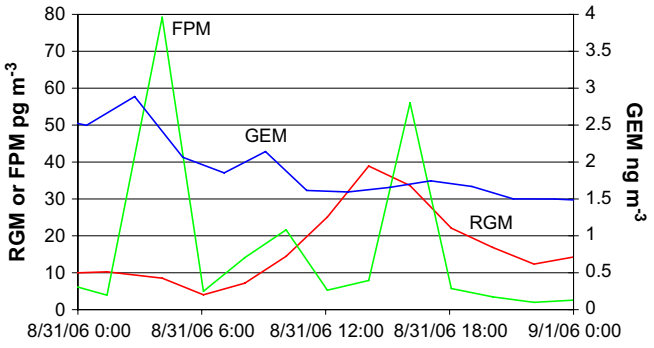

Fig. 8. Hourly mercury species on August 31. An "emissions event" was observed at a refinery complex near the Houston Ship Channel early on 8/31. Most pollutants were elevated at the TRAMP site through most of 8/31. GEM was elevated and FPM was highly elevated in the morning hours, and FPM was again highly elevated in the afternoon. RGM concentrations were only slightly elevated, and maintained the PBL driven diurnal cycle observed on most days.

The highest concentrations of all mercury species were most often associated with low-wind days with wind directions from the Houston Ship Channel Industrial Complex. During "dirty" periods GEM and FPM showed episodic spikes not associated with boundary layer dynamics, while RGM, dominated by dry surface deposition, although elevated, maintained its same boundary layer-driven diurnal cycle.

Two "dirty" event periods warrant analysis: 8/31–9/2 2006 and 9/11–9/15 2006. During the morning of 8/31 it is probable that an "Upset Event" occurred at a refinery complex on the Houston Ship Channel Industrial Complex. The TRAMP site on 8/31, particularly in the early morning hours (0300–0500 CST), experienced extreme pollution events. Wind speeds were very low ($\sim$2 m s^{-1}). Back trajectories and wind direction analyzed showed the TRAMP site as generally downwind of the Houston Ship Channel through most of 8/31, although back trajectory computations suffer significant accuracy problems under these very low-wind speed conditions. Also on 8/31 a noteworthy "dirty" flare was observed by the Baylor University Piper Aztec research aircraft along the Houston Ship Channel in the morning hours (Alvarez et al., 2007).

Typically pollutants are emitted in massive quantities from the Houston Ship Channel petrochemical facilities solely during upsets, and during scheduled maintenance, start-up, or shut-down (Allen et al., 2004; Nam et al., 2006). These so-called "emission events" typically involve releases from flaring and cooling towers, and secondarily from process vents and fugitive releases, typically at low heights (10–50 m) above ground level.

Our observations during the late morning of 8/31 are consistent with a Houston Ship Channel "emission event". As shown in Fig. 8, FPM concentrations peaked at 79 pg m^{-3} around 0400 CST coinciding with peak levels of total aerosol mass and organic mass measured by Aerodyne aerosol mass spectrometry (Wright et al., in this issue), C2–C10 non-methane VOCs, CO (600–700 ppb), and NO (100–120 ppb). By 0530 CST these primary pollutant events had subsided and were replaced around 0930 CST with spikes in HCHO (23 ppb) and PAN (3.6 ppb). Ozone increased to $\sim$100 ppb at 0930 CST (e.g. Flynn et al., in this issue), and later peaked at 127 ppb in the late afternoon ($\sim$1600 CST). This late afternoon activity was accompanied by a second FPM peak (56 pg m^{-3}) coincident with a broad RGM peak (38 pg m^{-3}).

Over the multi-day period 9/11–9/15 2006 (Fig. 9) TRAMP chemical measurements showed that the site experienced the highest averages of NO_2, NO_y, CO and SO_2 of any multi-day period of the study. In addition, on 9/14 the site experienced the study's highest PAN and Formaldehyde concentrations. Levels of FPM peaked at $\sim$50 pg m^{-3} late on 9/13, the second highest FPM measurement of the study period. This multi-day period experienced the lowest average wind velocity, and once again, back trajectories indicate significant time (30–40% of the period) that the TRAMP site was downwind of Houston Ship Channel.

Clean events were noted on 8/25–8/29 2006 (Fig. 10) and 9/16–9/19 2006 (Fig. 11). 8/25–8/28 featured predominately strong southerly winds directly from the Gulf of Mexico and the study's lowest multi-day average concentrations of NO, NO_2, NO_y, CO, Ozone, and SO_2. At no time during this period were winds from the ENE, the direction of the Houston Ship Channel. All mercury species were near background levels. The single spikes visible in the RGM and GEM time series are likely from the Parish power plant plume.

"Clean" period 9/16–9/18 2006 also experienced strong southerly winds off the Gulf of Mexico with similar results. These lower levels of all pollutants are also associated with increased wind speeds during these periods which had a clearing effect on the aerosol and chemical pollutants. Fig. 11 shows comparisons of the mercury species diurnal averages of the "dirtiest" period (8/31–9/1) and the "cleanest" period (9/16–18). During the "cleanest" period GEM, RGM, and FPM were often near their background level of $\sim$1.5 ng m^{-3}, 1 pg m^{-3}, and 1 pg m^{-3}, respectively.

The "clean" periods shown in Fig. 10 (8/26–8/29) and Fig. 11 (9/16–9/18) all show RGM and FPM daily minima at night and maxima at midday. While the afternoon enhancements of RGM and FPM are relative small ($\sim$5 pg m^{-3}) they are consistent day-to-day. This likely indicates midday boundary layer entrainment of RGM and FPM from aloft. These "clean" periods occurred with south

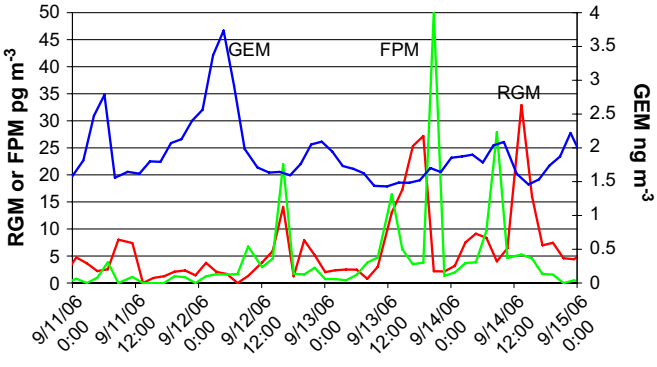

Fig. 9. The longest "dirty" period at the TRAMP site, 9/11–9/15 2006.

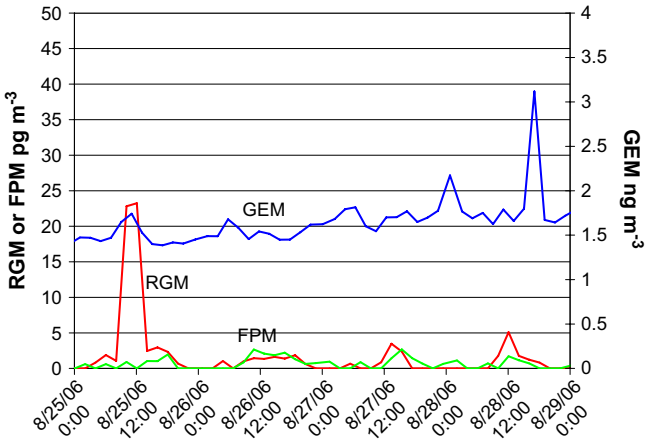

Fig. 10. The longest "clean" period at the TRAMP site, 8/25–8/29 2006.

winds from the marine environment implying that free tropospheric air aloft coming off the Gulf of Mexico is slightly enriched in oxidized mercury. Previously significant Hg(II) concentrations have been measured in the "marine" free troposphere by Swartzendruber et al. (2006) at Mt Batchelor Observatory and by Talbot et al. (2007) over the North Pacific. Both these studies indicate GEM oxidation over a period of days and significant oxidized mercury concentrations in the free marine troposphere.

5.2. Rain events

Rainfall typically removes and wet deposits RGM and FPM species from the mid- to lower troposphere, while dry deposition removes predominately RGM from the near-surface air. Severe or Supercell thunderstorms, common in the Houston area during the summer months, can extend upwards to the tropopause and can wash-out nearly all tropospheric RGM and significant FPM. The ratio of wet to dry deposition depends strongly on the frequency of rain events and the thickness of the rain layers. The TRAMP study period experienced a total of six rainfall events of >2 cm. For the rain event of 9/23–24 the associated mercury data are missing due

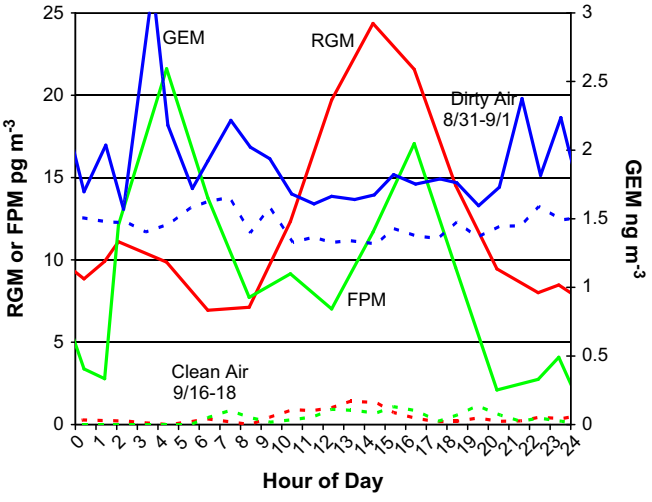

Fig. 11. Comparisons of the diurnal averages of the mercury species from the "dirtiest" period (8/31–9/1) and the "cleanest" period (9/16–9/18). During this "cleanest" period GEM, RGM, and FPM were near their background level of ~1.5 ng m^{-3}, 1 pg m^{-3}, and 1 pg m^{-3}, respectively.

Table 3
Rain events and RGM and FPM concentrations.

Date	Type	Time (CST)	Duration (h)	Amount (cm)	FPM prior	FPM after	RGM prior	RGM after
8/19	Thunder	0800	3	6	8	2	9	<DL
8/22	Thunder	2100	1	3	<DL	1	17	<DL
9/9	Rain	~midday	6	3	<DL	<DL	2	<DL
9/11	Thunder	1200	2	2	2	<DL	7	<DL
10/12	Thunder	2300	3	3	<DL	<DL	2	<DL

to an instrument problem. For the other five events, RGM, being highly water soluble, was totally removed (<DL) from the near-surface air and FPM dropped to low levels (<DL – 2 pg m^{-3}). Nearly all measurements of RGM below our detection limit were associated with rain events. Table 3 shows the five rain events, and the corresponding RGM and FPM concentrations. Periods of minor rain had similar affects, but the removal of FPM and RGM were less complete. Fig. 12 shows the mercury species for the 5 rain event days in Table 3.

6. Comparisons to other TRAMP measurements

While the mercury species concentrations followed the general "clean" and "dirty" multi-day time periods of most other pollutants, overall the TRAMP mercury species concentrations hour-by-hour were not significantly correlated to other measured pollutants. This is a similar finding to the TexAQS-II GEM measurements on the NOAA ship Ronald H. Brown described previously, where the observed GEM plumes within the Houston Ship Channel did not significantly correlate with the measured concentrations of other measured species (e.g. CO, SO_2, and NO_x).

Cowling et al. (2008) suggested historically contaminated soils as a possible source of the high GEM values measured within the Houston Ship Channel. Our measurements atop the Moody Tower would tend to rule-out contaminated soils, as soils' emissions are nearly all GEM and our most notable enhancements are in RGM and FPM. RGM and FPM were not measured on the NOAA ship Ronald H. Brown.

Toluene occurs naturally at low levels in crude oil and is usually produced in the processes of making gasoline utilizing a catalytic reformer process and is likely associated with episodic venting events. Fig. 13 shows toluene versus GEM, RGM and FPM on an hourly scale over the entire study period. The higher toluene concentrations (>1500 ppt) correspond to our peak hourly GEM, RGM and FPM concentrations. At the lowest concentrations of toluene (<200 ppt), all GEM concentrations are <1.8 ng m^{-3} and FPM concentrations are also very low (<5 pg m^{-3}). Elevated GEM concentrations (>3.0 ng m^{-3}) occurred only at toluene concentration > 1000 ppt. Otherwise there are no significant overall hour-by-hour correlations between toluene and GEM, RGM or FPM, suggesting only generally "clean" periods when toluene, GEM and FPM are uniformly low, and "dirty" periods when toluene is elevated and the mercury species are episodically at their highest values of the study period. RGM concentrations, driven by high dry deposition rates at the surface, and afternoon boundary layer entrainment rates, are episodically elevated in the afternoon hours even during low toluene (<50 ppt) periods. Correlation analyses with other VOCs (except isoprene) in the Houston area (see Leuchner and Rappenglück, in this issue) yielded similar relationships with the mercury species.

The mercury data collected at this site are not consistent with the often observed situation in which Hg(II) species emitted by stationary combustion sources (such as coal-fired power plants) impact the site and therefore tend to be correlated with other

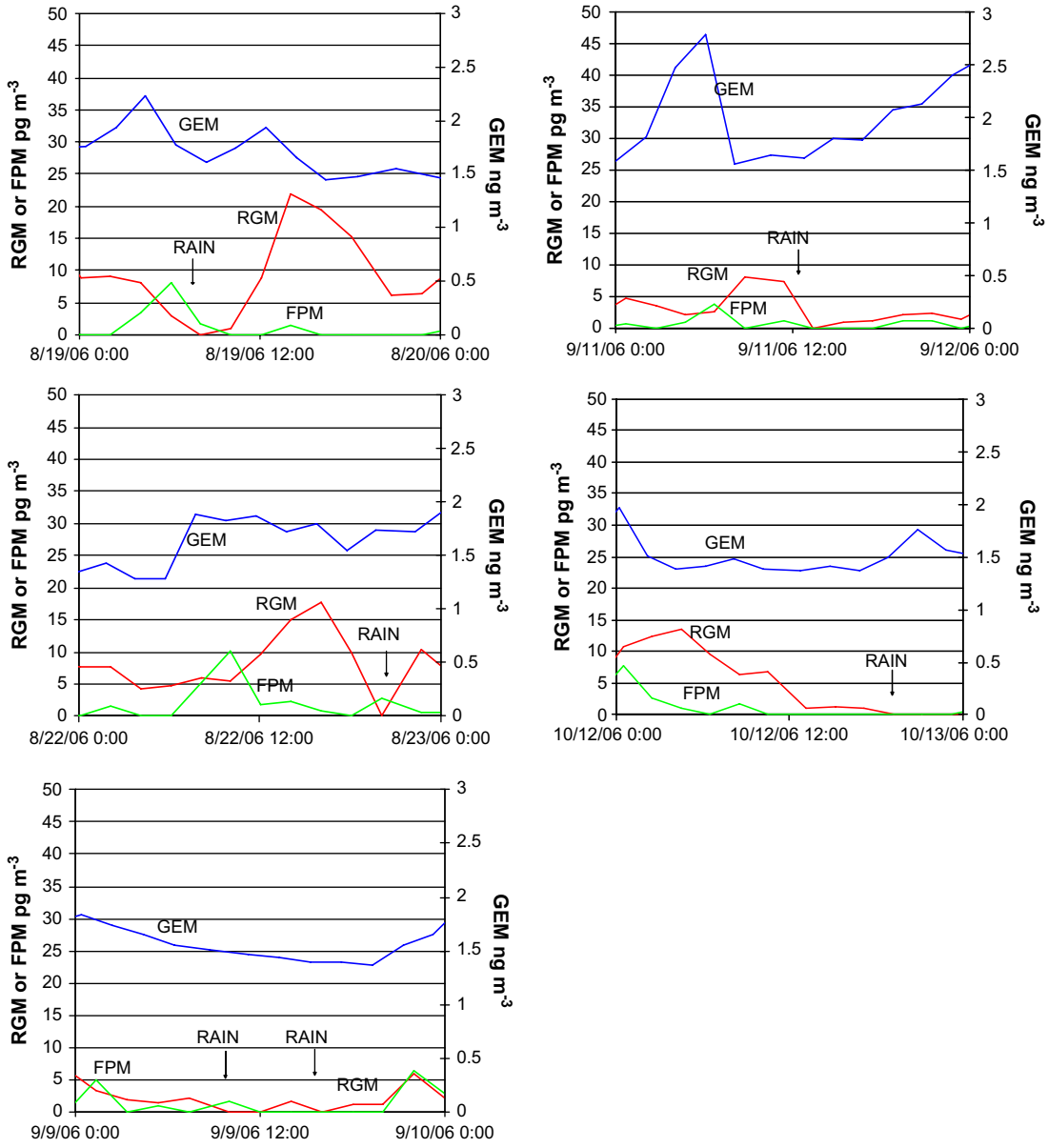

Fig. 12. Mercury concentrations during the five rain event days listed in Table 3. RGM, being highly water soluble, was washed-out to below our detection limit (<1 pg m^{-3}) during these events. FPM levels were reduced significantly. GEM, being non-water soluble, was unaffected by rain events.

combustion products, such as SO_2, NO_x and CO. The absence of any RGM to SO_2/NO_x/CO correlation (see Fig. 14) as observed at most other sites (Beltsville, MD; Grand Bay, Miss.; Oxford, MD; etc.), indicates significant non-combustion sources. These sources are likely petrochemical processing. Supporting this assumption is the noted decrease in all Hg species on weekends days compared to the weekdays (Fig. 7) indicating significant Monday–Friday related sources.

7. Summary

Mercury levels at Houston varied from very clean to very dirty. Multi-day periods of stagnant or low-wind conditions from the ENE (the direction of the Houston Ship Channel) brought elevated concentrations of all mercury species along with higher concentrations of VOCs, NO_x, CO, SO_2 and aerosols. Multi-day periods of strong winds, particularly southerly winds off the ocean, were characterized by very low values of mercury species, and low values of the primary pollutants, VOCs, NO_x, CO and SO_2.

While the concentrations of mercury species correlated with "clean" and "dirty" multi-day periods, the hour-by-hour correlations between the mercury species and VOCs, NO_x, CO, SO_2, etc. are lacking, indicating non-combustion mercury sources(s).

An exception was the morning of 8/31 coincident with a probable "upset emissions event" at a refinery complex in the Houston Ship Channel. At 0400 CST the TRAMP site experienced peak concentrations of total aerosol mass, organic aerosol mass, CO (600–700 ppb), NO (100–120 ppb), HONO (~2 ppb), and FPM (79 pg m^{-3}). GEM and RGM were also elevated but not significantly, indicating either direct FPM emissions or a favoring of FPM formation due to the extremely high levels of total aerosol mass and organic aerosol mass.

Over the entire mercury measurement period, August 6–October 14, 2006, the daily averages of mercury species showed

Please cite this article in press as: Brooks, S., et al., Mercury species measured atop the Moody Tower TRAMP site, Houston, Texas, Atmospheric Environment (2009), doi:10.1016/j.atmosenv.2009.02.009

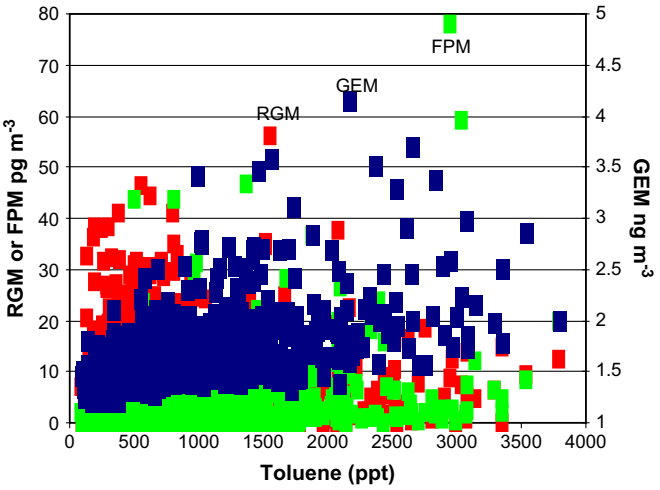

Fig. 13. Toluene versus GEM, RGM and FPM on an hourly scale.

distinct relationships with the average PBL dynamics with GEM and FPM building-up after midnight with a shallow PBL trapping GEM and FPM emissions in the near-surface air. As the PBL grows during the day, GEM and FPM decrease. RGM, a species that readily dry deposits, shows a much different diurnal signal. Daily RGM minima occur at ~0630 CST. During the nighttime more RGM deposited than was emitted to the near-surface air, as demonstrated by RGM decreasing during the nighttime. During the day as the PBL grows, air aloft (isolated from the surface during the nighttime hours and higher in RGM) is mixed downwards towards the surface. RGM peaks at ~1300 CST when the PBL entrainment rate begins to decrease. Dry deposition of RGM then dominates and the near-surface RGM concentrations drop through the remainder of the day and night.

Significant rainfall events totally removed (washed-out) RGM from the near-surface air, and significantly washed-out FPM. The frequent rain and thunderstorm events of the gulf coast and Houston region coupled with our observed elevated levels of RGM and FPM (both water soluble) will certainly enhance mercury wet deposition in the Houston area.

Comparing the TRAMP Summer 2006 mercury data set to the closest comparable site, Grand Bay, Miss. in a rural area of the gulf coast covering Summer 2007, the TRAMP mercury levels on average were 17%, 60% and 39% higher for GEM, RGM, and FPM, respectively. This indicates higher mercury emissions' sources in the Houston area (urban) compared to Grand Bay, Miss. (rural).

The coal-fired power plants most likely to affect Houston mercury levels are the Parish Plant to the SW, and the Fayette Plant to the west. Both plants are scheduled to install mercury reduction equipment in the coming decade to reduce mercury emissions by 30% at Fayette (Austin Energy and Lower Colorado River Authority press release), and by a "significant" amount at Parish (NRG plan submitted to TCEQ). In addition, TXU, Texas' largest coal-fired power plant operator, has pledged to install mercury reduction equipment at its nine existing coal-fired plants within Texas and on any future Texas plant (TXU press release).

While coal-fired power plant mercury emissions are expected to drop, mercury emissions from petrochemical processes, and refinery upset events are less likely to decrease. The enhanced mercury concentrations on weekdays as compared to weekends, the probable refinery "emissions event" on 8/31, the grossly elevated GEM levels (to 250 ng m^{-3}) observed repeatedly within the Houston Ship Channel by the NOAA research ship Ronald H.

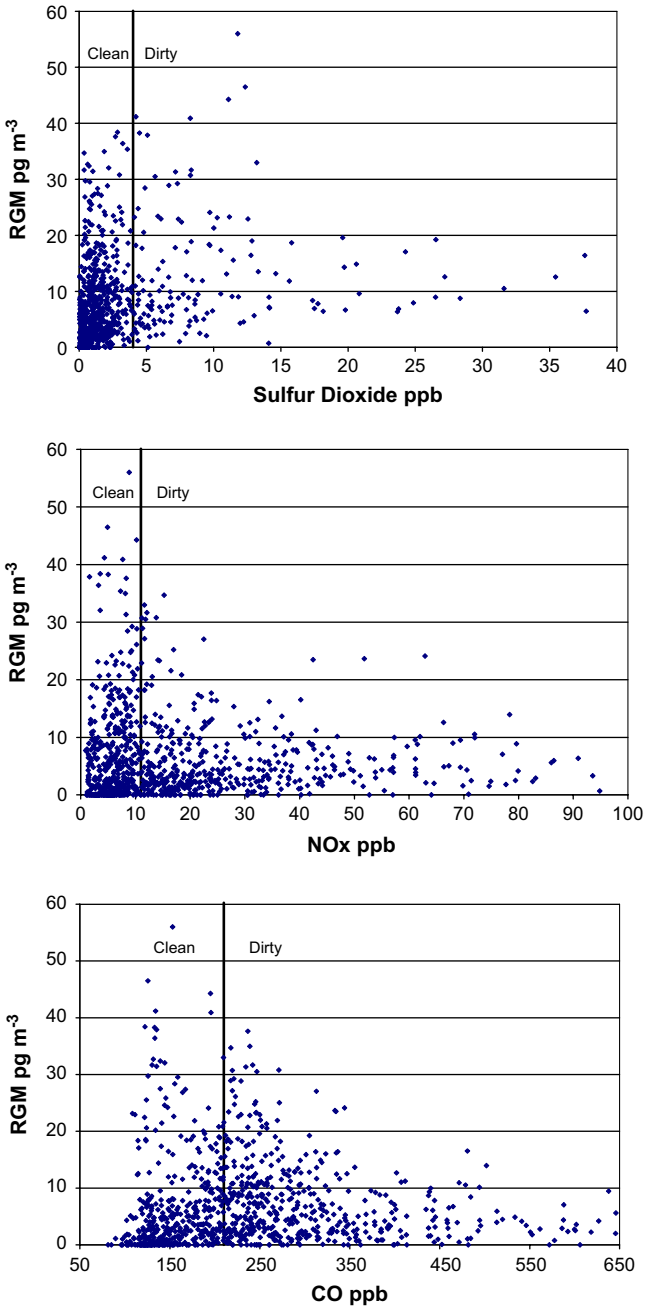

Fig. 14. RGM concentrations versus SO_2, NO_x and CO. While the multi-day "clean" and "dirty" periods suggest some relationships, there exists no overall correlation for the entire data set. This lack of overall correlations to primary combustion pollutants (SO_2, NO_x, and CO) suggests non-combustion mercury sources, such as petrochemical processing, and different sinks.

Brown, the lack of correlation between mercury species and combustion species (NO_x, CO, SO_2, etc.) at both the ship Ronald H. Brown and the TRAMP Moody Tower site, and the wind roses for the mercury species all indicate significant mercury sources from industrial processing in the vicinity of the Houston Ship Channel. Nationwide the mercury content in consumed coal is roughly 20 times the mercury content of consumed crude oil. While the mercury in coal is released nationwide, the mercury in crude oil is thought to be released primarily during refining. The concentrated refineries on the gulf coast, including Houston, may add significantly to the region's mercury loadings.

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Acknowledgements

The authors would like to express their gratitude to the Houston Advanced Research Center (HARC) for supporting and funding Project H78 and the Texas Commission on Environmental Quality (TCEQ) for supporting and funding this research under grant 582-5-64594-FY07-02.

References

Allen, D., Murphy, C., Kimura, Y., Vizuete, W., Edgar, T., Jeffries, H., Kim, B.-U., Webster, M., Symons, M., 2004. Variable Industrial VOC Emissions and their Impact on Ozone Formation in the Houston–Galveston Area. Project H13 Final Report. Texas Environmental Research Consortium, Houston, TX. <http://www.epa.gov/ttn/chief/conference/ei13/uncertainty/allen.pdf>.

Alvarez, S., Kauffman, L., Compton, T., Zanin, G., Shauck, M., Buhr, M., 2007. H-63 Aircraft Measurements in Support of TexAQS II. Project H63 Final Report. Texas Environmental Research Consortium, Houston, TX.

Cowling, E., Furiness, C., Dimitriades, B., Parrish, D., 2008. Final Rapid Science Synthesis Report: Findings from the Second Texas Air Quality Study (TexAQS II). A Report to the Texas Commission on Environmental Quality by the TexAQS II Rapid Science Synthesis Team. Prepared by the Southern Oxidants Study Office of the Director at North Carolina State University, 31 August 2007. <http://www.tceq.state.tx.us/assets/public/implementation/air/texaqs/doc/rsst_final_report.pdf>.

Ebinghaus, R., Slemr, F., Brenninkmeijer, C.A., vn Velthoven, P., Zahn, A., Hermann, M., O'Sullivan, D.A., Oram, D.E., 2007. Emissions of gaseous mercury from biomass burning in South America in 2005 observed during CARIBIC flights. J. Geophys. Res. Lett. 34, L08813. doi:10.1019/2006GL028866.

Fitzgerald, W.F., Gill, G.A., 1979. Sub-nanogram of mercury by two-stage gold amalgamation and gas phase detection applied to atmospheric analysis. Anal. Chem. 15, 1714.

Flynn, et al. Impact of clouds and aerosols on ozone production in Southeast Texas, in this issue.

Keeler, G., Glinsorn, G., Pirrone, N., 1995. Particulate mercury in the atmosphere: its significance, transport, transformation and sources. Water Air Soil Pollut. 80, 159–168.

Landis, M.S., Stevens, R.K., Schaedlich, F.H., Prestbo, E., 2002. Development and characterization of an annular denuder methodology for the measurement of divalent reactive gaseous mercury in ambient air. Environ. Sci. Technol. 36, 3000–3009.

Lefer, B., Rappenglück, B. TRAMP overview, in this issue.

Leuchner, M., Rappenglück, B. VOC source–receptor relationships in Houston during TexAQS-II, in this issue.

Lindberg, S.E., Stratton, W.J., 1998. Atmospheric mercury speciation: concentrations and behavior of reactive gaseous mercury in ambient air. Environ. Sci. Technol. 32, 49–57.

Lindberg, S.E., Brooks, S.B., Lin, C.-J., Scott, K.J., Landis, M.S., Stevens, R.K., Goodsite, M., Richter, A., 2002. The dynamic oxidation of gaseous mercury in the arctic atmosphere at polar sunrise. Environ. Sci. Technol. 36, 1245–1256.

Lu, J.Y., Schroeder, W.H., 1999. Sampling and determination of particulate Hg in ambient air: a review. Water Air Soil Pollut. 112, 279–295.

Lu, J.Y., Schroeder, W.H., Berg, T., Munthe, J., Schneeberger, J., Schaedlich, F., 1998. A device for sampling and determination of total particulate mercury in ambient air. Anal. Chem. 70, 2403–2408.

Malcolm, E., Keeler, G.J., 2002. Measurements of mercury in dew: atmospheric removal of mercury species to a wetted surface. Environ. Sci. Technol. 36, 2815–2821.

Nam, J., Kimura, Y., Vizuete, W., Murphy, C., Allen, D.T., 2006. Modeling the impacts of emission events on ozone formation in Houston, Texas. Atmos. Environ. 40, 5329–5341.

Rappenglück, et al. In-situ ground-based and airborne formaldehyde measurements during the TRAMP study, in this issue.

Rappenglück, B., Perna, R., Zhong, S., Morris, G.A., 2008. An analysis of the vertical structure of the atmosphere and the upper-level meteorology and their impact on surface ozone levels in Houston, TX. J. Geophys. Res. 113, D17315. doi:10.1029/2007JD009745.

Skov, H., Brooks, S.B., Goodsite, M.E., Lindberg, S.E., Meyers, T.P., Landis, M.S., Larsen, M.R.B., Jensen, B., McConville, G., Christensen, J., 2006. Fluxes of reactive gaseous mercury measured with a newly developed method using relaxed eddy accumulation. Atmos. Environ. 40, 5452–5463.

Slemr, F., Ebinghaus, R., Simmonds, P.G., Jennings, S.G., 2006. European emissions of mercury derived from long-term observations at Mace Head, on the western Irish coast. Atmos. Environ. 40, 6966–6974.

Swartzendruber, P.C., Jaffe, D.A., Prestbo, E.M., Weiss-Penzias, P., Selin, N.E., Park, R., Jacob, D.J., Strode, S., Jaeglé, L., 2006. Observations of reactive gaseous mercury in the free troposphere at the Mount Bachelor Observatory. J. Geophys. Res. 111, D24301. doi:10.1029/2006JD007415.

Talbot, R., Mao, H., Scheuer, E., Dibb, J., Avery, M., 2007. Total depletion of Hg° in the upper troposphere–lower stratosphere. Geophys. Res. Lett. 34, L23804. doi:10.1029/2007GL031366.

Wilhelm, S.M., Liang, L., Cussen, D., Kirchgessner, D.A., 2007. Mercury in crude oil processed in the United States (2004). Environ. Sci. Technol. 41 (13), 4509–4514.

Wright, et al. Extensive aerosol optical properties and aerosol-mass related measurements during TRAMP/TexAQS 2006 – implications for PM compliance and planning, in this issue.

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