Interactive comment on “In situ measurements of speciated atmospheric mercury and the identification of source regions in the Mexico City Metropolitan Area” by A. P. Rutter et al.

A. P. Rutter et al.

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Anonymous Referee #1 Received and published: 23 July 2008

General Comments: 1) "This paper shows some interesting correlations between mercury sources in the Federal Pollutant Release and Transfer Register (PRTR) and receptor type modeling at two sites in the Mexico City area. The paper certainly provides important information that is worthy of publication. However, some improvements could be made as described in the specific comments below."

We have responded to the suggestions for improvements on an individual basis below.

2) "Just looking at the concentration traces for GEM and RM, it is obvious that the
urban site is heavily impacted by industrial emissions. Even the rural site seems to be impacted based on the GEM measurements."

We tend to agree with the review but feel that it is important to recognize that the impact of GEM and RM on the sites may be obvious to researchers with extensive experiences looking at atmospheric mercury data but that the impact of GEM and RM on the sites would not necessarily be obvious to the readership of ACP and the boarder atmospheric science community. The manuscript seeks to demonstrate how data analysis tools can be used with atmospheric monitoring data to clearly show the impacts of local sources of mercury on atmospheric concentrations. Clearly, the ability to demonstrate the impact of local sources to a broader community is an important need that must be addressed. To this end, no changes have been made in response to this comment.

3) "The discussion of the Concentration Field Analysis (CFA) maps and the way their indicated source regions correlate with sources in the Federal PRTR seemed to me to be a little too detailed. After all the discussion, I am still left wondering if the CFA is trustworthy. I think it is generally accepted that the inventory of sources in that region is not complete and there are a multitude of other sources of atmospheric mercury in that area. All sources are affecting the receptor site. If there are systematic errors in the back-trajectory analysis, the CFA source regions would be displaced. It could be that a source missing from the Federal PRTR is actually the cause of a source region indicated by the CFA. It would help if there was some way to show the WRF-generated wind fields are accurate. Can the wind measurements at the two receptor sites be compared to the WRF simulation?"

Reply 1 - Like all atmospheric and meteorological models, there are uncertainties in the WRF simulations of wind transport, especially for a situation as complex as the Mexico City basin. Detailed comparisons of MM5 simulations with both surface and radiosonde observations were carried out for the MCMA-2003 campaign (de Foy et al., 2006a; de Foy et al., 2006b). In addition, the particle paths obtained using FLEXPART were compared with pilot balloon measurements (de Foy et al., 2006c). These
results suggested that the model did in fact represent the basin meteorology within the expected uncertainties of both numerical models and observation networks. The CFA method was evaluated using transport of carbon monoxide: the emissions sources in Mexico City have been well characterized and were correctly identified by the method. It was then used to identify possible sulfur dioxide sources and suggested industrial impacts from known sources on the MCMA (de Foy et al., 2007). For MILAGRO, CFA has been used to analyze ATOFMS data pointing to possible source regions for aerosols of varying composition (Moffet et al., 2007). Given these past evaluations of the model, we feel that the WRF and CFA results are accurate within the uncertainties described in the text. Given the existing evaluation of the model and method in Mexico City, we do not think that additional time series of surface data would contribute to the existing validations. To help clarify this point, the following modification to the manuscript have been made:

The text starting at Line 26, p 13136 (lines 313-315 of the revised manuscript), has been changed to read as follows: "...was performed. The CFA method was evaluated using transport of carbon monoxide: the emissions sources in Mexico City have been well characterized and were correctly identified (de Foy et al., 2007; Stohl et al., 2005). Figure 3a to d present...".

A reference to (Fast et al., 2007) has been added in Line 22, p13134 (lines 258-260 of the revised manuscript). The text now reads: "A thorough review of the meteorology during the MILAGRO campaign was presented by (de Foy et al., 2008; Fast et al., 2007) who revealed that..."

Reply 2 - The authors don’t entirely understand this comment. We agree that there are likely many mercury emission sources missing from the PRTR, and that these unregistered sources could be the cause of source regions identified by the CFA that do not correspond to known sources. We have already stated this in the text at numerous locations, and therefore think that no changes are necessary to further clarify this:
i) Lines 1-2, p 13138
ii) Lines 6-8, p 13138
iii) Lines 11-13, p 13138
iv) Lines 22-24, p 13138
v) Lines 2-4, p 13138
vi) Lines 15-19, p 13141.

Reply 3 - Firstly the authors disagree with the comment that "All sources are affecting the receptor site". There may have been areas of the MCMA containing unregistered mercury emission sources that did not impact the measurement sites during the 17-day study because the winds may not have allowed for transport between the source and measurement locations. The authors are keen to avoid misinterpretation of the CFA results with respect to the identification of source regions and their relationships to the PRTR, and therefore feel that it is necessary to add the following sections of text in the specified locations:

i) Line 6, p13137 (lines 322-334 of the revised manuscript) after "the study.", and before, "The method..."

"It is important to recognize that the CFA results from this study provide perspective of how point sources in and around the MCMA affect atmospheric mercury concentrations at the measurement sites. However, the CFA cannot evaluate the impact of the emissions from mercury point sources that did not, or only rarely impacted the measurement sites during the 17-day study. Such point sources may have impacted atmospheric concentrations in other regions of the MCMA more or less substantially than was observed at the measurement sites used in this study. Relationships between point sources and measurement sites may also change throughout the year as seasonal variations in weather patterns occur. In order to properly assess the impacts of mercury point sources to the MCMA, a more extensive monitoring campaign and CFA will need to be conducted in which multiple monitoring sites throughout the region are established and operated for at least one calendar year."

ii) Line 18, p 13141 (Line 463 of the revised manuscript) between "occurring..." and "...in Region W"

"...in all of the source regions, but particularly..."
4) "I am glad to see that PHg and RGM are being considered as one semi-volatile species (reactive mercury or RM). The dynamic partitioning of Hg compounds between the gas and aerosol forms is something that I feel has not gotten enough attention. However, I do not think we can preclude elemental mercury as one of the constituents of PHg. We know that powdered activated carbon can remove GEM from industrial exhausts. Some types of atmospheric particulate matter may very well be able to bind with GEM at atmospheric concentrations, especially when the concentrations are as high as those measured in this study. The importance of elemental Hg as a constituent of PHg might be negligible, but then again it might not be. I think this issue deserves at least some mention."

We agree with the reviewers in the comment that PHg and RGM should be considered a single semi-volatile species, which is what was done in the subject manuscript. However, we do not agree with the statement that GEM should be treated as a species that partitions to the particle-phase like reactive mercury. Although it is true that GEM can be absorbed to activated carbon in flue gas control technologies, activated carbon is not a good representation of atmospheric aerosols. Furthermore, to our knowledge the adsorption of GEM to atmospheric EC has not been demonstrated in the peer reviewed literature. The authors of the subject manuscript have extensive experience measuring the gas-particle partitioning of atmospheric mercury, and in numerous studies conducted by us and other research groups, GEM partitioning to atmospheric aerosols was not observed as an important process in industrial exhaust plumes: these data sets all provided several examples where large episodic GEM increases in industrial exhaust plumes were not corroborated with concomitant increases in PHg, indicating that GEM partitioning to atmospheric aerosol is unlikely to be an important process (Gabriel et al., 2005; Hall et al., 2006; Manolopoulos et al., 2007; Manolopoulos, 2006; Rutter et al., 2008; Yatavelli et al., 2006). To clarify this point to the reader, we have made the following changes to the text in the specified places:

i) Lines 6 through 15, p 13128 (lines 77- 90 of the revised manuscript) have been
"Reactive mercury (RM; defined operationally as the sum of PHg and RGM) is typically considered to be predominantly oxidized mercury compounds which are semi-volatile and water soluble (Lin and Pehkonen, 1999; Schroeder and Munthe, 1998) meaning that source emissions will impact local ecosystems through wet and dry deposition (Lin and Pehkonen, 1999; Schroeder and Munthe, 1998; Seigneur et al., 2003) Previous atmospheric modeling work has assumed that gaseous elemental mercury (GEM) partitioned to elemental carbon (EC) in urban atmospheric aerosol, thereby contributing to PHg. To our knowledge the adsorption of GEM to atmospheric EC has not been demonstrated as a significant source of PHg. Likewise, several previous publications have provided several examples where large episodic GEM increases in industrial exhaust plumes were not corroborated with concomitant increases in PHg, indicating that GEM partitioning to atmospheric aerosol is unlikely to be an important process (Gabriel et al., 2005; Hall et al., 2006; Manolopoulos et al., 2007; Manolopoulos, 2006; Rutter et al., 2008; Yatavelli et al., 2006). Once in anoxic aquatic environments the oxidized component of RM can be converted to..."

5) "The levoglucosan analysis that is described appears to be a combination of at least two referenced methods, extraction by the method of Sheesley et al. and analysis by the method of Nolte et al. Is there a prior work that discusses the overall process used here, or is this a novel approach?"

The reviewer is correct that the levoglucosan analysis a hybrid method that is based on work by Sheesley et al., 2004 and Nolte et al., 2002. The hybrid method was used and documented by Stone et al., 2007 reference (now Stone et al., 2008) and is now used as the appropriate reference for the analysis of levogluosan used in the current study. To update this reference, the following changes has been made:

i) To reflect the conversion of the Stone et al., 2007 ACPD article to a full ACP publication, Line 7, p 13132 (lines 188-189 of the revised manuscript), has been changed to
"... biomass burning (Schauer and Cass, 2000; Simoneit et al., 1999; Stone et al., 2008). The particulate matter..."

The reference section has also been updated to reflect this change at line 30, p 13148 (reference section of revised manuscript):

ii) Line 17, p 13132 (lines 199-202 of the revised manuscript), has been changed to read:
"...was available. The samples were analyzed for Levoglucosan using the method described in previous publications (Nolte et al., 2002; Sheesley et al., 2004; Stone et al., 2008) and so will be only briefly discussed here. The filters were spiked with..."

6) "In the second paragraph of section 3.1, it is stated that only 4 of the 19 RM plume events correlated with GEM plume events at the urban receptor, indicating that most of the plumes came from sources that emit primarily RM, or that the speciation of emissions changed with time. The concentrations for GEM are very large compared to RM. A local peak of 500 pg m\(^{-3}\) in RM is easily discernable, but the same peak in GEM would barely be noticeable given its concentration scale is 50 times greater in this highly polluted environment. I do not believe the level of detail in the GEM concentration plot in Figure 1 is adequate to support this notion, at least not in the graphic I was able to download."

The authors agree with the reviewer's comment that a source which emits large amounts of RM could also be emitting GEM at concentrations that are only very slightly in excess of the urban background concentrations, and therefore not easily observed in Figure 1, but which would still mean that by mass, the source was emitting primar-
ily GEM. In this study we are only concerned with identifying point sources that emit enough RM and GEM that substantially impact the measurement sites above the urban background concentrations in order to start developing a quantitative understanding of the source-receptor relationships in the MCMA. To address this comment the text has been changed between lines 15 and 18, p 13134 (lines 250-255 of the revised manuscript) to read:

"However, only four of the 19 RM plume events correlated with substantial GEM plume events, indicating that most of the plumes came from sources that emitted enough RM to produce large impacts on atmospheric concentrations, but that did not emit enough GEM to change concentrations significantly above the urban background. It is also possible that the speciation of emissions from some facilities may have changed with time."

7) "In section 3.3, it is stated that the minimum hourly GEM concentrations measured in this study (2.0 ng m-3 urban and 1.8 ng m-3 rural) were compared to those in previous studies, it was decided that the sites were too influenced by emission sources to extract reliable threshold concentrations from the data. I take this to mean that both sites were always influenced by at least one emission source (industrial or surface evasion) and that there was no time at which the measured concentrations were low enough to indicate a normal background condition. Yet, a GEM threshold of 1.4 ng m-3 was chosen from published measurements from other locations in Mexico (de la Rosa et al., 2004). I fail to understand how this lower threshold would be of any use in any analysis of this highly polluted environment. I understand the source apportionment is based on Rutter et al. (2008), but that work was done where 1.4 ng m-3 concentrations were observed occasionally. More explanation of the source apportionment and the purpose for the threshold value is needed."

A review of GEM monitoring data collected throughout the western northern hemisphere (Rural values in Table 3; (Ebinghaus et al., 2002; Kim et al., 2005; Slemr et al., 2003; Swartzendruber et al., 2006; Weiss-Penzias et al., 2006)) shows that GEM
concentrations average at about 1.5 +/- 0.2 ng m-3 (1SD) when no anthropogenic or natural point or area sources are influencing the air mass. This concentration therefore represents the northern hemispheric background. If concentrations are seen in excess of this concentration range, it is likely because of some point or area sources. Furthermore, we know from the referenced article (de la Rosa et al., 2004) that concentrations not statistically different from this average are observed in unimpacted parts of Mexico. The drive behind the source apportionment analysis was to determine how much of the atmospheric mercury measured in the MCMA was due to local anthropogenic or natural influence, and how much was due the long range transport into the region. We therefore think that the threshold concentration we selected was entirely appropriate to achieve this goal.

In order to better explain why we selected 1.4 ng m-3 as a threshold value for delineating between local source contributions and the regional background we have changed the text at lines 12 - 14, p 13140 (lines 421-429 of the revised manuscript) "...indicative of the regional background. A review of GEM monitoring data collected throughout the western northern hemisphere (Rural values in Table 3; (Ebinghaus et al., 2002; Kim et al., 2005; Slemr et al., 2003; Swartzendruber et al., 2006; Weiss-Penzias et al., 2006)) revealed that GEM concentrations averaged at about 1.5 +/- 0.2 ng m-3 (1SD) when no local anthropogenic or natural sources (point or area) were influencing the air mass. This concentration therefore represents the western northern hemispheric background. When minimum hourly concentration averages measured during this study (urban GEM=2.0 ng m-3; rural GEM=1.8 ng m-3) were compared to the western northern hemisphere background, it was decided that ...

And at lines 20-22, p 13140 (lines 435-439). "...with the passing of time. To obtain a GEM threshold concentration that represented the regional background in Mexico, published measurements made outside of Mexico City at a rural location and pacific coastal location were used (de la Rosa et al., 2004). The GEM threshold concentration was determined to be 1.4 +/- 0.1 ng m-3, which was not statistically different than the
western northern hemispheric background. A paucity...

Editorial issues: 8) "The acronym MILAGRO is used in the first paragraph of the Introduction, but is not defined until later."

The text has been changed at line 21, p 13127 (lines 64-65 of the revised manuscript) to read:

"...during the MILAGRO (Megacities Initiative: Local and Global Research Observations) sampling campaign..."

9) "Figure 2 and Table 2 show much the same data, with one additional plume (#20) and plumes #14 and #18 subdivided in the Table. Maybe Figure 2 could show these added features and Table 2 would no longer be necessary."

The authors included Table 2 to allow modelers to use the PHg/RGM partitioning data that is represented in Figure 2. Furthermore, Table 2 presents the RM:GEM ratios for each plume, demonstrating a considerable variation in this parameter. The 2002 US EPA emission inventory (USEPA, 2002) uses a table of constants to allow modelers to describe the PHg : RGM : GEM speciation ratios in point sources emissions as a function of process type. Therefore the RM:GEM ratios presented in Table 2 are valuable to modelers, and also provide insight into the reliability and utility of the USEPA speciation factors.

No changes to the text have been made in response to this comment.

10) "Also, Table 2 is mentioned in the text before Table 1."

Table 1 is first referred at line 17, p 13129 and is before the first reference to Table 2 which appears at line 11, p 13137. No changes to the text were made in response to this comment.

11) "Regarding Figures 3a to 3d, the discussion in section 3.2 says the Federal District boundary is a dashed line, but it looks like a solid gray line in the downloaded images."
The text has been changed at line 14, p 13137 (line 337 of the revised document) to read
"... Federal District boundary (gray line),"

12) "Figures 4a to 4c show a column of data with the heading "UNC" that is not explained in the text. I assume this shows some measure of uncertainty, but more description is needed."

The last sentence in the caption to Figure 4 (lines 574-575 of the revised document) was changed to read "Uncertainties (presented in the column titled "unc" in the inset tables) were derived..."

and at line 11, p 13141 (lines 454-456 of the revised manuscript) to read
"...17-day study period. The uncertainties presented in each table under columns labeled "unc" are the results of the previously described sensitivity analyses. The calculations revealed..."

Anonymous Referee #2 Received and published: 5 September 2008

General Comments: 1) "This paper reports on a 17-day study of atmospheric mercury concentrations and speciation at a rural and urban site in Mexico City. The study goals were to correlate the concentration plumes that were detected with reported local point sources in order to provide a rationale for mitigation of the point source mercury emissions. The results of the study did establish source regions that contributed to the plumes although specific sources could not be identified. In addition, the contributions from the Popocatepetl Volcano could not be separated from anthropogenic contributions under the study conditions. The paper was well-organized and written and the figures and tables support the conclusions made."

No response to these comments is necessary from the authors.

Editorial Comments: 2) "Only two small typos were evident:
one on page 13135, line 5 [reviewer refers to line 7, rather than line 5] "to transport from (not for) the industrial sources"

The text has been changed at line 7, p 13135 (lines 265-266 of the revised manuscript) to read:

"...to transport from the industrial sources..."

and page 13138, line 25 "was composed of a large area"

The text has been changed at line 25, p 13138 (line 378) to read:

"Source region W was composed of a large area..."


Interactive comment on Atmos. Chem. Phys. Discuss., 8, 13125, 2008.