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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.

Anonymous Referee #1

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General Comments: 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.

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. The discussion of the Concentration Field Analysis (CFA) maps and the way their indicated source regions correlate with sources

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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?

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.

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?

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

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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.

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.

Regarding editorial issues:

- The acronym MILAGRO is used in the first paragraph of the Introduction, but is not defined until later.
- 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. Also, Table 2 is mentioned in the text before Table 1.
- 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.

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- 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.

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

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