

## Response to Referee #1

We greatly appreciate all of the comments, which have improved the paper. Our point-by-point responses are provided below.

### Anonymous Referee #1

Receptor models have been used to trace sources, long-range transport and atmospheric processes of atmospheric speciated Hg in many previous studies. This review presents a comprehensive synthesis of the previous studies. In this review, the principles, mathematical model, advantages, disadvantages and achievements were introduced. I think this review could help to better use the receptor models in future studies. It is recommended that this paper should be published in ACP in a final version. I have no major questions on the manuscript. There are several minor points should be considered before final publication.

1. Line 266-267: I am not very clear about the conclusion on the effect of larger  $n_{ij}$  on the lower PSCF values near the receptor. I think this should be depending on the threshold, source regions and trailing effect. PSCF values generally indicate the relative contributions of source regions, and larger threshold would likely generate lower PSCF values at most of the potential source regions. If the areas close to receptor were located downwind the major source regions, I think larger  $n_{ij}$  may overestimate the PSCF values for nearby areas.

Response: We think a larger number of trajectory endpoints in a particular grid cell ( $n_{ij}$ ) may lead to lower PSCF near the receptor location in some cases because  $n_{ij}$  increases as grid cells approach the receptor location where all the trajectories converge. This may affect the PSCF calculation according to Eq. 4 because of the large denominator. However, as mentioned by the reviewer, there are other factors potentially affecting the PSCF calculation, such as the concentration threshold, which has been discussed in the revised paper (last paragraph of 2.2.1).

2. Line 419-426: I think the authors may discuss the uncertainties related to contribution of the Hg-O<sub>3</sub> photochemistry to receptor measurements. It is currently unclear whether O<sub>3</sub> is the major oxidant in the transformation of Hg in continental boundary layer. I doubt that many of the good correlations between O<sub>3</sub> and GEM and GOM may be partially attributed to the co-occurrence of photochemistry processes of O<sub>3</sub> and GOM. It is also possible that other oxidants or processes may contribute to the transformation of GEM to GOM.

Response: When two or more variables in a component have the same sign and strong loadings because of a strong correlation between those variables, caution should be used to assign a causal relationship. Most PCA studies identified a Hg photochemistry component based on the presence of GOM, O<sub>3</sub>, and/or relative humidity. A different study extracted a PCA component in their dataset containing GOM, BrO and O<sub>3</sub>, which represented oxidation of GEM as well (Ren et al., 2014); however it is still not clear from this profile whether BrO or O<sub>3</sub> was the major oxidant. It could be interpreted as a co-occurrence of O<sub>3</sub> and GOM photochemical reactions or a combined effect from several oxidants. In the revised paper, we have discussed this example (3rd paragraph of 3.1.1). A more general wording, like "GEM oxidation", is used instead of "Hg-O<sub>3</sub> photochemistry" in the revised paper because there are many oxidants of GEM and it's not known which one is predominantly involved in GEM oxidation and whether the reactions are occurring in the gas, liquid, and/or solid phase.

3. Section 3.1.2: the authors should also discuss other photochemical processes involved in the atmospheric Hg transformation. For example, Timonen et al. (2013) and other previous literatures identified new sources of GOM in the free troposphere and boundary layer over ocean. This type of GOM events showed an anti-correlation between GOM and O<sub>3</sub>, indicating halogens chemistry plays an important role. Also, Faïn et al. (2009) did not observed clear correlation between GOM and O<sub>3</sub> during high GOM events in the free troposphere. These findings may suggest many oxidants may play a combined effect. I think the Hg-O<sub>3</sub> chemistry may not well explain the speciated Hg at high-altitude sites.

Response: On p.5512 line 19 of the ACPD paper, we discussed a study by Swartzendruber et al. (2006) that suggests the transport of GOM from the free troposphere was a source of GOM at a high altitude site based on a PCA component with GOM, ozone, and water vapor. Although the PCA component contained GOM and ozone, the study concluded that the Hg-O<sub>3</sub> reaction rate is likely too slow to produce the elevated GOM concentrations observed and suggested there may be other GOM production mechanisms. The presence of ozone in the PCA component is indicative of free troposphere transport, and not necessarily its role as an atmospheric oxidant. We have clarified this in the revised paper (1<sup>st</sup> paragraph of 3.1.2).

The revised paper has also incorporated the findings by Faïn et al. (2009) and Timonen et al. (2013), who also studied GOM processes at high altitude locations. Faïn et al. (2009) observed elevated GOM events that were negatively correlated with GEM and occurred during low relative humidity, while GOM was not related to other air pollutants or O<sub>3</sub>. These observations may be consistent with GEM oxidation or deep vertical mixing of free troposphere air enriched with GOM. Timonen et al. (2013) found that different air masses may be associated with different types of Hg processes. Dry upper troposphere transport was associated with elevated O<sub>3</sub> and GOM, which may be indicative of GEM oxidation by reactive bromine. GEM oxidation by O<sub>3</sub>, halogens, and heterogeneous chemistry may occur during long-range transport of emissions from Asia. GEM oxidation by reactive halogens can also occur in clean air masses from the Pacific. (1<sup>st</sup> paragraph of 3.1.2)

4. Section 3.1.2: I suggest the author may provide the TGM/CO ratio, and it may be an important components associated with forest fire smoke. The TGM/CO ratios of forest fire were found to be significantly different from air flows from anthropogenic air plume and could be used in PCA analysis. Also, for ratios of TGM/CO, TGM/CO<sub>2</sub>, TGM/CH<sub>4</sub>, etc were also different from different regions. Can these components be used in PCA models?

Response: The TGM/CO ratio for biomass burning plumes can be determined to support a biomass burning source inferred from PCA results. The median TGM/CO ratio ranged from 1.3 to 9.2 pg m<sup>-3</sup> ppb<sup>-1</sup> based on data collected from flights over different regions (Slemr et al., 2014), which can be compared with TGM and CO data measured at a receptor location. A low TGM/CO ratio (1-2 pg m<sup>-3</sup> ppb<sup>-1</sup>) can be clearly attributed to biomass burning plumes, whereas a higher TGM/CO ratio (> 6 pg m<sup>-3</sup> ppb<sup>-1</sup>) is indicative of anthropogenic emissions (Slemr et al., 2014). However this involves additional analysis to determine the subset of receptor measurements impacted by biomass burning.

A potential way the TGM/CO ratio could be used in the PCA models is to differentiate between biomass burning and anthropogenic/industrial sources when there is a component with only TGM and CO and no other chemical species markers are available. This involves calculating the Absolute Principal Components Scores (APCS) for the component with high loadings on TGM and CO. The APCS can be converted to a pollutant's source mass contribution to each receptor measurement according to

Thurston and Spengler (1985), which is in the same units as the pollutant's concentration. The TGM/CO ratio can be calculated from TGM and CO's source mass contributions and then compared with the emission ratios for biomass burning and anthropogenic plumes (Ebinghaus et al., 2007; Weiss-Penzias et al., 2007; Slemr et al., 2014). Few TGM/CO<sub>2</sub> and TGM/CH<sub>4</sub> emission ratios have been reported by Slemr et al. (2014). The APCS approach could be used to gain insight on where the plumes originated from. However, it is not clear from the TGM/CO<sub>2</sub> and TGM/CH<sub>4</sub> emission ratios whether it is attributed to a biomass burning or anthropogenic source due to the limited data available. We have briefly described this idea in the revised paper (last paragraph of 3.1.2).

5. Section 3.3; I suggest that the authors may discuss what kind of receptors are suitable for using of PSCF and CWT models. In my opinion, the PSCF model is aimed to study the long-range transport. Therefore, the models may not work well at receptors with strong local impact. In addition, clear spatial distributions of anthropogenic emissions are also important for accurate simulations.

Response: Based on the trailing effect and trajectory model uncertainties discussed in previous PSCF and CFA/RTWC/CWT studies, these models are more suitable for receptor locations that are potentially impacted by regional or long-range sources rather than locations that are downwind of major local sources. We recommended in section 4 of the ACPD paper that an alternative method to assess local source impacts could involve the analysis of local wind measurements. It also depends on which atmospheric Hg species are measured at the receptor location. If only PBM are measured, these models are more suitable for receptor locations that are potentially impacted by regional sources and less suitable for distant/long-range sources because of the shorter residence time of aerosols. Regarding the spatial distribution of sources relative to the receptor site, several studies conclude that these back trajectory receptor models are more accurate at identifying the direction of potential sources rather than the distance of sources to the receptor location (Han et al., 2007; Rutter et al., 2009; de Foy et al., 2012). Another receptor location consideration is that the goal in most of the PSCF and CFA/RTWC/CWT studies were to identify potential Hg point sources, but these models can also be used at receptor locations that are potentially impacted by area sources (e.g. Hg emissions from lakes, ocean, forest fires, traffic, etc.) as shown in de Foy et al. (2012). These discussions have been included in the revised paper (last paragraphs of sections 3.3 and 3.5).