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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric speciated mercury concentrations on an island between China and Korea: sources and transport pathways" *by* G.-S. Lee et al.

Anonymous Referee #2

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This discussion paper describes concentrations and trends in TGM, GOM, and PBM at Yongheung Island, Korea, a gas-particle partitioning model dependent on temperature and relative humidity, and the use of correlation analysis, conditional probability function, GOM/PBM ratios, potential source contribution function, and a trajectory cluster source contribution approach to identify long-range and local transport of Hg emissions impacting the site. The study attempted various ways to analyze the data including the use of a newer approach; however there are issues with the methodologies that could lead to inaccurate results and interpretation. This paper needs to emphasize the uncertainties and other factors not accounted for in the study that could impact the results. More explanations should be provided when the various modeling results don't agree

with each other. There are large discrepancies in the gas-particle partitioning model between this study and a previous study, and the model does not fit the data well. More work is needed to improve the model fit.

Specific Comments:

Abstract: L4: I suggest using the actual name of the sampling site, Yongheung Island, Korea, in the abstract and title.

L15-19: The sentences should be revised after considering the specific comments on the GOM/PBM ratio and the gas-particle partitioning model.

P32932 L25: Does this sentence only apply to aquatic systems? Can Hg deposit on to soil and then transform to methylmercury?

P32933 L6-8: "GOM has short atmospheric residence times (∼day) and, consequently, its ambient concentration is mainly impacted by local sources." This sentence is not entirely correct because the free troposphere can be a source of GOM (Weiss-Penzias et al., 2009; Timonen et al., 2012), which does not necessarily originate from local sources.

P32933 L26-28: "Since GEM makes up the bulk of the total Hg in ambient air its formation through reduction processes of divalent Hg may not be important." Previous studies suggest this reduction reaction is important in power plant plumes (Lohman et al., 2006; Landis et al., 2014).

P32933 L28: I suggest using, "However, the secondary formation of GOM through the oxidation of Hg0 followed by the gas-particle partitioning formation of PBM can contribute significantly to their ambient concentrations."

P32934 L2: Is this the total global anthropogenic emissions?

P32935 L20: Delete "a"

P32936 L8-17: GOM and PBM were not collected using the automated Tekran speci-

ation system, which can sample and analyze GOM and PBM at higher temporal resolution. Why did you choose a 12 hour sampling period? Previous studies suggest a longer sampling period can lead to sampling artifacts (Malcolm and Keeler, 2007). Please explain why you then switched to 2 hour sampling in the 7th sampling period.

P32937 L21: Please mention the type of cluster analysis that HYSPLIT uses. How many trajectory clusters were selected? What distance measure was used?

P32938 L6: What were the criteria values used for TGM, GOM and PBM? For n, did you use all wind data or only the data above a certain wind speed? Typically, low wind speeds are excluded. There are some important details in the methodology that are missing. GOM and PBM were measured every 12 hours, but wind direction data were collected every 5 minutes. The concentrations and wind data should be paired in time when they are used to calculate CPF. How did you treat the wind data so that it corresponds with the GOM or PBM measurement? The wind directions and concentrations can change a lot over a 12-hr period. It would not be accurate to use a 12-hr average wind direction or a 12-hr concentration for each 5-min wind measurement.

Equation (2): I suggest deleting the P[Bij]/P[Aij] because it is not defined in the description.

P32938 L15: Similar to the comments for the CPF method, you should state the top 25th percentile concentrations used and provide details on how the hourly trajectory and the 12 hour GOM and PBM concentration data were treated. The large difference in the temporal resolution of the trajectory and mercury data would lead to inaccurate results.

P32939 L7-9: What were the causes of the concentration peaks? I suggest excluding the PBM concentration peak because this was the only sampling period where 2 hr PBM measurements were made; the rest of the periods were 12 hr measurements.

P32940 L22: It should be “secondary”

Equation (4): The denominator should be GOM (Rutter and Schauer, 2007), not gaseous Hg which could mean GEM and GOM.

Equation (5): The PBM/GOM ratio is not normalized by PM2.5 unlike in the partition coefficient, Kp. Is this parameter still representative of gas-particle partitioning? If PM2.5 is available, it would be good to generate a Kp equation and compare it to previous Hg gas-particle partitioning models (Rutter and Schauer, 2007; Amos et al., 2012; Cheng et al., 2014), which have been predominantly based on data from North American sites.

Another issue with equation (5) is that independent variables should be used in multiple linear regression. However, temperature and relative humidity are typically correlated. I suggest reporting the partial correlations to show the magnitude of the relationships for temperature and RH separately. This is possibly why RH and the PBM/GOM ratio are not related, but when you apply the regression model with both temperature and RH a relationship was found with the PBM/GOM ratio. If the partial correlation of RH is very small, then RH should not be included in the regression model.

P32941 L14: Are these 12-hr average temperature and relative humidity values used to generate the regression model, since PBM and GOM were only measured twice a day? This should be mentioned. It could be a reason for the poor model fit since temperatures can vary greatly throughout the day.

R2 for the regression model should be reported rather than R because it gives the variance explained by the model. The R2 value of 0.24 is considered small. Based on this, the model does not fit the data well compared to previous gas-particle partitioning models. More work should be done to improve the model fit.

What is the application of equation (5)? Can it be used to predict PBM given GOM, temperature, and RH at any location? Can this model be used in chemical transport models? If so, it is necessary to validate this model with data from other locations.

Aerosol composition should also be discussed in this paragraph as another important factor affecting gas-particle partitioning, which has not been considered in this study.

P32941 L25-27: Why would the presence of anthropogenic sources affect the relationship between PBM/GOM and temperature and relative humidity? Please provide more explanation and why the coefficients for temperature and RH in the equation are so much lower than those obtained by Han et al. (2014).

P32942 L7: It should be "and undergo deposition during transport". Is this point entirely correct given that GEM is rapidly oxidized by reactive Br and can undergo dry deposition?

P32942-32943 CPF results for GOM: The explanation says GOM concentrations are due to the local power plants from the south direction even though there is no correlation between GOM and SO2. But you haven't explained why the CPF plot in Fig. 5 show highest GOM concentrations from the SE and ESE directions (not in the south direction). What are the potential Hg sources from these wind directions?

P32943 L10: It should be "the number of samples"

3.2.1 GOM/PBM ratio:

P32944 L5: It should be CPF

P32944 L10: I suggest referencing Lynam and Keeler (2005) because this study also used this ratio to analyze the role of long-range transport.

The GOM/PBM ratio doesn't seem to characterize long-range transport specifically. The inverse of this ratio (PBM/GOM) was also used in section 3.1 to characterize gas-particle partitioning. How would you differentiate between long-range transport and gas-particle partitioning? Lower GOM/PBM ratio associated with westerly and northerly airflows could also indicate higher gas-particle partitioning because of colder airflows from the north and differences in aerosol composition. A lower ratio does not necessarily indicate greater deposition of GOM; it could be GOM partitioning to

aerosols. Please provide the correlation coefficient (r) between GOM/PBM ratio and CO instead of only the p-value because the p-value doesn't describe the relationship between the GOM/PBM ratio and CO.

P32944 L16-17: Like previous comments, how did you compare the GOM/PBM ratios with the wind direction data when the temporal resolution of data is so different? GOM/PBM are based on 12-hr measurements but wind directions are measured every 5 min. It would not be accurate to use a 12-hr average wind direction or a 12-hr concentration for each 5-min wind measurement.

3.2.2 PSCF Results:

P32945 L2: It should be "the largest Hg emissions in China"

P32945 L2: It should be "which emerged as prominent source areas"

The results mentioned in P32945 L10-12 seem inconsistent with the GOM/PBM ratio results, which suggest long-range transport from China. Here, the PSCF plot shows long-range transport of GOM from China was not important. Which result is correct and what are the reasons for the discrepancy? The trajectory duration of 3 days in the PSCF model is also a limiting factor to identifying long-range transport. In this paragraph, you should also discuss the back trajectory uncertainties because that affects the PSCF distribution.

P32945 L13-18: Please look into whether shipping ports are potential sources of GOM in the Yellow Sea.

3.2.3 Trajectory cluster analysis:

P32945 L25: What is the reason for choosing five clusters, instead of other number of clusters? Based on Fig. 8, there is a lot of overlap in the trajectory direction between different clusters. Also, does the cluster analysis model provide any statistics on the spatial variance between clusters and within a cluster? How did the model determine that five clusters was the most optimal number?

The average concentrations of GOM and PBM for each trajectory cluster are shown in Table 4. You can include the GOM/PBM ratio here to show whether the ratio is lowest for cluster 4, the cluster associated with long-range transport.

Equation (6): Is there a reference for this equation or is it an original receptor modeling approach? One issue with this equation is the use of the average concentration for each cluster. The concentrations associated with the trajectories in each cluster could have large variability. How representative is the average concentration for each of the trajectory cluster? I suggest providing the concentration range and the number of trajectories belonging to each cluster. Another issue that needs to be mentioned is the back trajectory uncertainties, which will likely affect how the trajectories are distributed between the clusters and the calculation of the source contributions for each cluster. A previous study (Stohl, 1998) suggested the uncertainties may be 20% of the distance travelled by the trajectories. Fig. 8 shows a lot of overlap in the trajectories between different clusters (e.g. 1&2 and 3&5) and if one considers the trajectory uncertainties, there would be even greater overlap. Furthermore, a longer trajectory duration (> 3 days) should be selected if the goal is to identify long-range transport. The discussion on P32947 should consider the impact of these uncertainties on the results.

P32947 L3: The small n in equation (6) has not been defined.

P32947 L9: The link does not proceed directly to the information.

P32947 L17 and L24: The use of the word “mass” doesn’t seem correct because only the average concentration for each cluster was used to calculate the contribution for each cluster. As mentioned in the previous comment, the concentrations associated with the trajectories in each cluster could have large variability and certainly doesn’t represent the total mass.

P32947 L20-25: The cluster analysis source contribution method produced different results from CPF and PSCF for GOM. Can you explain the discrepancy in the results?

Conclusions:

P32948 L10: CPF is based on wind directions and PSCF is calculated from back trajectories. Both of these existing methods do consider wind data. Therefore, it is not clear how the trajectory cluster source contribution approach is more advantageous. I suggest revising this sentence.

P32948 L16-25: The GOM/PBM ratio does not seem to be an effective tool for identifying long-range transport because it is too similar to the PBM/GOM ratio that was used to characterize gas-particle partitioning. While it’s possible that the two processes occur simultaneously, that is not always the case. It’s also possible gas-particle partitioning and local transport of emissions occur concurrently. Furthermore, aside from temperature and RH, aerosol composition is also an important factor affecting gas-particle partitioning which has not be accounted for in this study.

Figure 2: There needs to be some gaps in the time-series plot because each of the sampling periods was only $\sim$6 days and the measurements were not continuous. For the caption, I suggest revising to “TGM, GOM, and PBM concentrations measured during the eight sampling periods. TGM was measured every 5 min while GOM and PBM were measured every 12 h except for the 2 hr measurements during May 2014.”

Figure 4: For the caption, I suggest revising to “Relationship between the ratio of PBM/GOM and temperature and relative humidity (RH) (n = 81)”

Figure 5: It would be more convenient for readers if you labelled the plots instead of the description in the caption.

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