

Referee #2

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 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.

We are grateful for the precise and valuable comments. We have responded to the major issues raised by the referee including gas-particle partitioning model, the ratio of GOM/PBM to determine the contribution of local vs. regional sources, and the overlapping trajectories between clusters, and have accordingly revised the manuscript. Please see the responses to the specific comments below.

Specific Comments

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

The actual name of the sampling site is now used in the abstract.

“In this study, speciated Hg concentrations were measured on Yongheung Island, the western most island in Korea, located between China and the Korean mainland.....”

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

Please see the responses below.

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

We have added the discussions regarding possible Hg exposure from rice consumption as well as fish consumption in the revised manuscript. We have revised and added the following sentences.

“Many studies show that one of the major sources of MeHg in aquatic and terrestrial system is atmospheric deposition of inorganic Hg (Landis and Keeler, 2002, Mason et al., 1997). Fish consumption has been considered for the major exposure pathway of Hg for humans (Mergler et al., 2007; UNEP, 2013). In Korea, You et al. (2012) showed that MeHg concentrations in blood were affected by fish consumption as well as by gender difference. However, rice consumption was also found to be the predominant pathway of MeHg exposure for the inhabitants residing in a highly contaminated area of China (Zhang et al., 2012).”

- 4. 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.**

In response to this comment, we have added the following sentence.

“Besides the anthropogenic sources, the free troposphere has been identified as an important GOM source (Huang and Gustin, 2012; Weiss-Penzias et al., 2009; Timonen et al., 2012).”

- 5. 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).**

We agree with the referee that GEM production from GOM reduction is important in plumes where the percentage of GOM to total Hg is much higher (30~70%) than in ambient air (typically less than 5%); however, in ambient air where GOM typically contributes less than 5% of TGM, we do not think that GOM reduction caused a significant increase on GEM concentrations. We clearly stated “*in ambient air*” in the original manuscript.

- 6. 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.”**

We have revised as suggested. Thank you.

7. P32934 L2: Is this the total global anthropogenic emissions?

Yes. We have added the term, “global”.

8. P32935 L20: Delete “a”

We deleted as suggested.

9. P32936 L8-17: GOM and PBM were not collected using the automated Tekran speciation 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.

Unfortunately we did not have an automated Tekran speciation system. Therefore, we chose the sampling time of 12hrs to lessen the labor for most of periods. We are well aware of the possible artifact caused by longer sampling duration. Malcolm and Keeler (2007) found Hg loss from filters over the course of the long sampling periods. Our group also found 11.4% PBM decrease when zero air was passed through a sampled filter at a flow rate of 1 Lpm for 4 hr (Wang et al., 2013). We think that there were some negative artifacts associated with our PBM measurements, and that any loss of PBM is assumed to be the same for each sampling period as in the study of Feddersen et al. (2012). For the 7th sampling period, we chose 2 hour sampling despite the intense labor needed in order to measure the PBM concentration on a shorter time resolution; therefore, the PBM concentration measured in this study except in 7th sampling period are likely to have some negative artifacts.

In response to this comment, we have added the following sentences in section of 2.2 Sampling and analysis.

“Also, it should be noted that the concentrations of PBM measured during 12-hrs of sampling time (all sampling periods except in the 7th) may have been biased due to Hg loss from filters over the long sampling period; however for model development any loss of PBM is assumed to be the same for each sampling period.”

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

Trajectory cluster analysis was performed by HYSPLIT program. For every combination of

trajectory pairs, the cluster spatial variance (SPVAR) is calculated, which is the sum of the squared distances between the endpoints of the cluster's component trajectories and the mean of the trajectories in that cluster. Then the total spatial variance (TSV), the sum of all the cluster spatial variances, is calculated. The pair of clusters combined are the ones with the lowest increase in total spatial variance. The iterations continue until the last two clusters are combined, resulting in N trajectories in one cluster.

In our study, we chose 5 clusters based on the change of TSV with the number of clusters (Fig. R1) since the iterative step just before the large increase in the change of TSV typically gives the final number of clusters (Draxler et al., 2014).

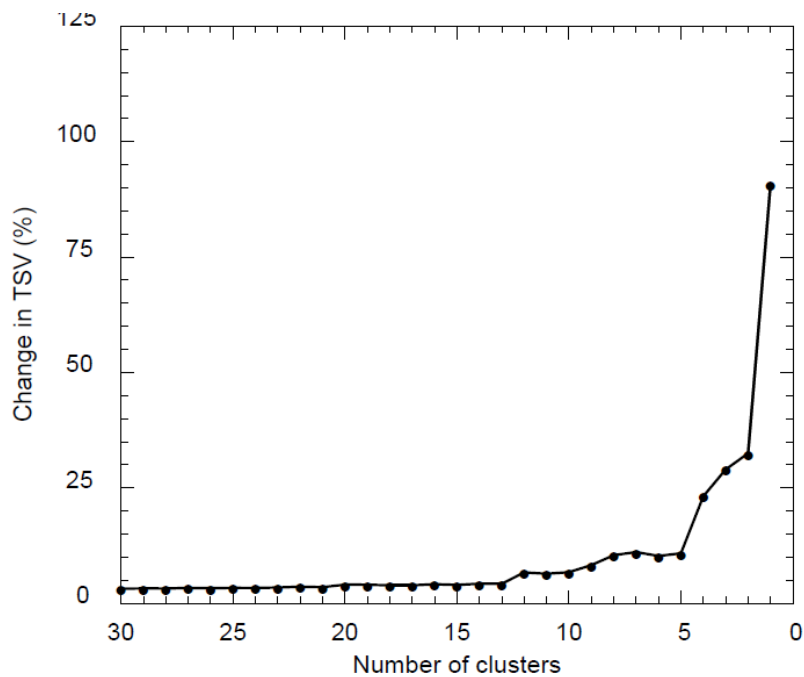


Fig. R1. Change in TSV as clusters are combined in this study.

In response to this comment, we have added some description about TSV method in section 2.3, as follows, given the relevant references, and provided the figure of change in TSV with the number of clusters in the Supplementary file as Fig. 4S.

“The clustering of trajectories is based on the total spatial variance (TSV) method. TSV is the sum of all the cluster spatial variances (SPVAR) which is the sum of the squared distances between the endpoints of the cluster's component trajectories and the mean of the trajectories in that cluster.

In this study, five clusters were chosen based on a large increase a large increase in TSV for larger clusters (Fig. 4S), as described in Draxler et al. (2014) and Kelly et al. (2012)."

- 11. 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.**

We used the top 10% and the top 25% of TGM concentrations and compared the results as shown in Figure 5. For GOM and PBM, we used only the top 25% as the criteria because the numbers of samples for both species were significantly less than for TGM due to their longer sampling duration, as in indicated on Line 9 in Page 32943 in the original manuscript.

For n, we excluded the calm condition ($WS < 1$ m/s). In response to this comment, we have added the following sentences.

"In this study, 16 sectors were used ($\Delta\theta = 22.5^\circ$), and calm winds ($WS < 1$ m/s) were excluded from the calculation because of isotropic behavior of the wind vane for such conditions. For TGM, two threshold criteria of the upper 10 and 25 percentile were chosen while only the upper 25 percentile was used for GOM and PBM concentrations due to the smaller number of samples."

As the referee indicated, the GOM and PBM were measured for 12-hr duration whereas the meteorological data were measured every 5 min at the sampling site and hourly averages were used for source identification in this study. We used 1hr-averaged WS and WD data for 12hr-averaged GOM and/or PBM concentrations, so in total 12 WS and/or WD were used for one averaged GOM and/or PBM concentrations to create CPF graphs. If the time durations for Hg measurements and meteorological data were identical it would be easier to interpret; however, this does not always happen. There are many studies using different time scale for measurements of pollutants and for meteorological data. For example, Galindo et al. (2011) showed CPF plots using 24-hr PM_{2.5} samples with weather data of 10-min time resolution. Kim et al. (2007) and Amato and Hopke (2012) also provided CPF results using daily source contribution estimates

from daily PM2.5 observation with much finer duration wind data.

In response to this comment, we have explained the different temporal resolution between GOM and PBM data and WD data in the revised manuscript.

12. Equation (2): I suggest deleting the $P[B_{ij}]/P[A_{ij}]$ because it is not defined in the description.

We think that addition of definitions for $P[B_{ij}]$ and $P[A_{ij}]$ is helpful for the reader to understand the PSCF calculation so we have added the definition of $P[B_{ij}]$ and $P[A_{ij}]$ in the revised manuscript, as follows. Thank you.

“If N is the total number of trajectory segment endpoints over the study period and if n segment trajectory endpoints fall into the ij th cell, the probability of this event ($P[A_{ij}]$) is calculated by n_{ij}/N . If m_{ij} is the number of segment endpoints in the same ij th cell when the concentrations are higher than a criterion value, the probability of this high concentration event, B_{ij} , is given by $P[B_{ij}] = m_{ij}/N$.”

13. 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 difference in the temporal resolution of the trajectory and mercury data would lead to inaccurate results.

Please see our response to the comment no. 11. We have added the possible uncertainty that might be caused by different temporal resolution between trajectory and mercury data, as follows.

“Since GOM and PBM were measured for 12hr for most time periods, hourly trajectories were matched to the 12hr-averaged GOM and PBM concentration; therefore, in total 12 back-trajectories represented one averaged GOM or PBM concentrations. The different temporal resolution between trajectory and concentration data might increase the uncertainty of trajectory-based approaches; however, there have been many successful studies using different time scales for measurements of pollutants and for meteorological data (Amato and Hopke, 2012; Galindo et al., 2011; Kim et al., 2007).”

14. 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.

We agree with the referee. We have calculated the 12hr-averaged concentrations for the 7th

sampling period to maintain consistency of the sampling duration to identify the general trends of Hg species, and revised the first paragraph of the section 3.1 in the revised manuscript.

15. P32940 L22: It should be “secondary”

This has been corrected. Thank you.

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

In describing K_p , we used “ Hg_{gas} ” instead of GOM because some previous studies suggested that all gaseous mercury species including GEM may deposit on particles, although most studies suggested that the adsorption of GEM on particles was negligible due to its high vapor pressure. In this study, we used only GOM concentrations for Hg_{gas} in equation (4); however, Hg_{gas} is more appropriate than GOM to indicate the general definition of K_p in the equation (4).

17. Equation (5): The PBM/GOM ratio is not normalized by PM2.5 unlike in the partition coefficient, K_p . Is this parameter still representative of gas-particle partitioning? If PM2.5 is available, it would be good to generate a K_p 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.

We did not directly use K_p because the total ambient aerosol mass concentration ($\mu g m^{-3}$) was not measured; however, we obtained and used the PM_{10} concentration measured at the nearest national air quality monitoring station. If we assume that PM_{10} concentration can be representative of the total ambient aerosol mass, K_p can be calculated. When we used K_p instead of the PBM/GOM ratio the coefficient of determination, R^2 increased to 0.29 ($R=0.54$). We think that this increase was because the PM_{10} concentration was considered, and this result more strongly suggests the significance of gas-particle partitioning.

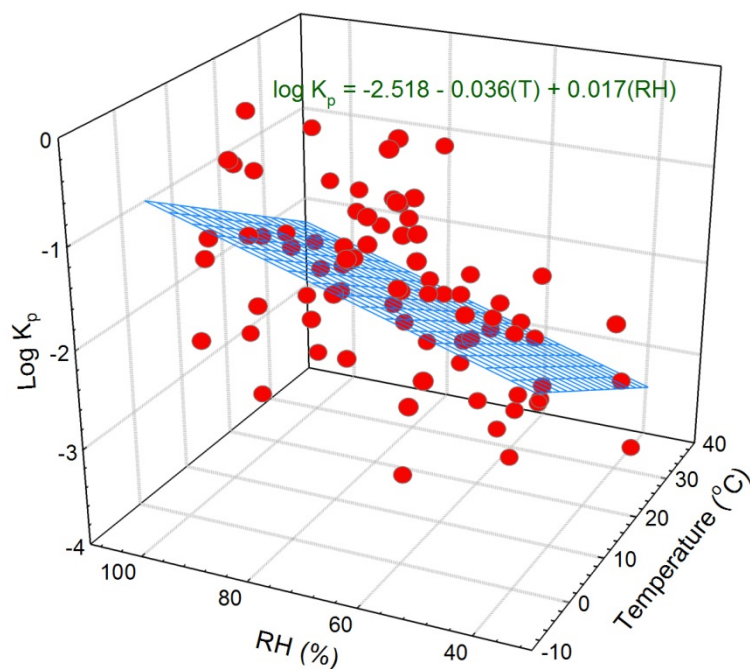


Fig. R2. The gas-particle partitioning coefficient, K_p , related to atmospheric temperature and relative humidity (RH) (n=81).

As the referee indicated, the relative humidity is affected by temperature (T) because RH is a function of the vapor pressure and two independent variables should be independent to each other in regression analysis. When the hourly variations of both variables are depicted one usually finds that the RH changes inversely with T; however, this negative correlation becomes much weaker for longer time durations such as 12hr used in this study. For our dataset, there is no statistical correlation between temperature and RH (Pearson R= -0.142, p-value= 0.191). We also performed the partial correlation with T and RH separately. T had a statistically negative correlation with $\log(K_p)$ (the Pearson R= -0.416, $R^2= 0.173$, p-value<0.0001) and RH showed a statistically positive correlation (the Pearson R= 0.390, $R^2=0.152$, p-value<0.0001) (Fig. R3). The partial correlation graphs are now provided in the supplementary material as Fig. 1S. When multi-linear regression was used for K_p with T and RH variables the coefficient of determination, R^2 increased to 0.29 (R=0.54); therefore, we think that multi-linear regression is better to predict the secondary formation of PBM.

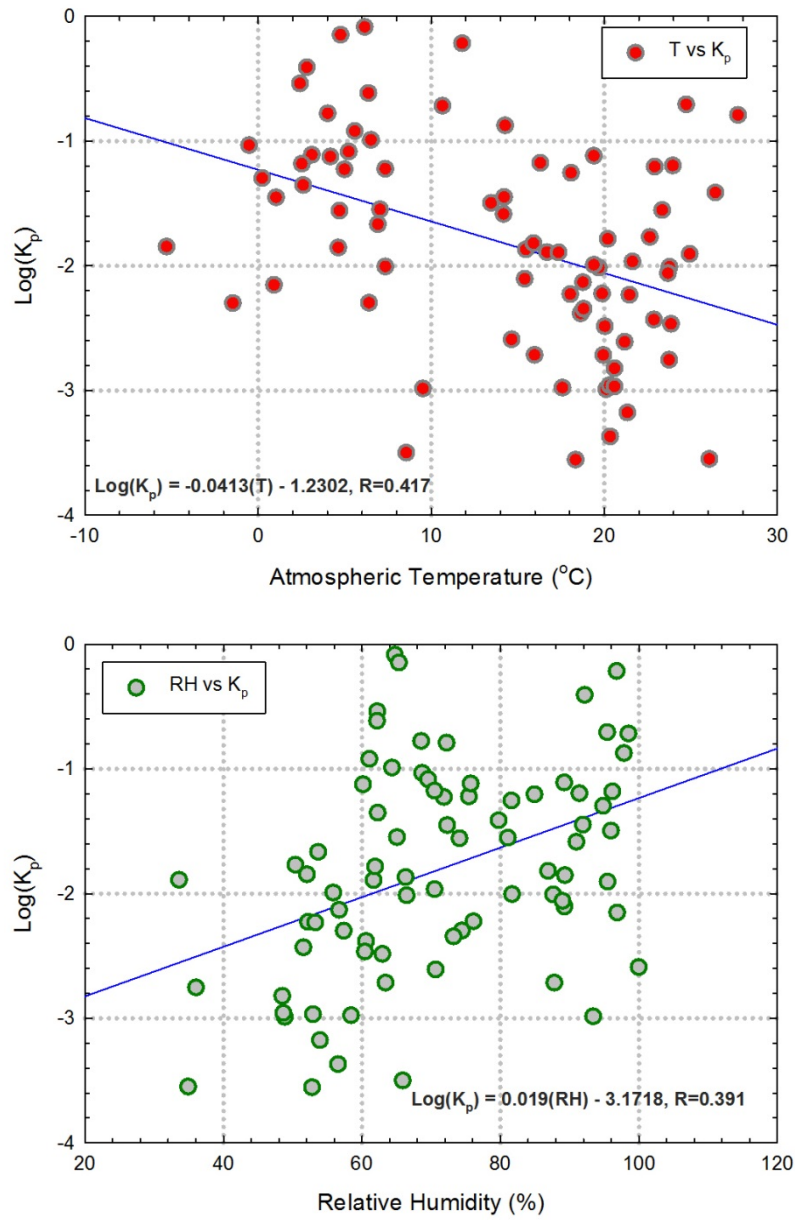


Fig. R3. The partial linear regression between K_p and temperature (upper panel) and between K_p and RH (lower panel).

In response to this comment, we have replaced the ratio of GOM/PBM to K_p with consideration of PM10 concentration, changed equation (5), mentioned the results of the partial correlations with T and RH, and provided the figures of the partial correlations in the supplementary file.

18. 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.

We used 12hr-averaged temperature and relative humidity, and do not think that this time scale seriously affected the result of multi-linear regression as shown in many other studies (Die et al., 2015; Xie et al., 2014).

The correlation coefficient, R is used to identify whether there is statistical correlation and dependence between X and Y or not while the coefficient of determination, R² indicates how well data fit a statistical model, identifying whether the dependent variable, Y is statistically explained by the independent variable, X. Therefore, we believe that both R and R² are appropriate in this context, and have added to “R²” in the revised manuscript.

As we responded to the previous comment, K_p considering PM10 concentration was used instead of the ratio of PBM/GOM in the revised manuscript. We think the equation derived in this study can be used in chemical transport models. Amos et al. (2012) found an empirical gas-particle partitioning relationship between K_p and T using the Hg data obtained from five monitoring sites in United States and Canada and two laboratory experiments, and the average equation was:

$$\text{Log}(K_p) = (10 \pm 1) - (2500 \pm 300)/T, \quad R^2 = 0.49$$

In our study, a similar equation was derived from the correlation of K_p with a single variable, T (K).

$$\text{Log}(K_p) = 13.5 - 3362.7/T$$

The coefficients, β and y₀, in the equation derived by Amos et al. (2012) ranged from -1600 to

3300 and 6 to 13, respectively, in various monitoring sites similar to those found in this study.

Also, the referee mentioned that the R^2 is too low and the model does not fit the data. The R^2 of the new equation of K_p in the revised manuscript increased to 0.29, and Amos et al. (2012) found a similar range of R^2 from 0.16 to 0.57 at various monitoring sites. Somewhat lower R^2 in this study is probably caused by smaller number of samples, different composition of aerosol, different GOM species, and/or longer sampling duration, but it is obvious that there is a statistical relationship between K_p and T and RH. Whether the model fit the data well or not is decided by a statistical test, and the p-value was less than 0.0001 in this study.

In response to this comment, we have compared our equation with the previously derived equations in the revised manuscript.

19. 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).

One possibility is that the anthropogenic source near the sampling site in this study weaken the relative contribution of gas-particle partitioning to the variation of ambient PBM and GOM concentrations because both Hg species can be also strongly affected by anthropogenic emissions. In the study of Amos et al. (2012) the highest R^2 was shown in the Experimental Lakes Area (in Canada) and Reno, NV where no large anthropogenic source of Hg are located.

We have provided more explanation in the revised manuscript.

20. 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?

It is true that GEM is oxidized by atomic Br(g) with a relatively high kinetic coefficient, and the combination of GEM and Br atoms can serve as a pathway for mercury depletion in the polar atmosphere. A few researchers have shown a significant bromine-induced oxidation of GEM in the mid-latitude marine boundary layer over the Dead Sea, Israel (Ariya, 2011; Obrist et al., 2011), also; however, the atmospheric Br concentrations in the marine boundary layer is a subject of great scientific debate because the global importance of Br has yet to be properly evaluated as there is a lack of understanding of the concentration profiles of this halogen (Subir et al., 2011). Atmospheric lifetime of GEM currently ranges from 0.5 to 2 years.

In order to respond to this comment, we have revised the sentences, as following.

“Correlations between Hg and other pollutant concentrations are often used to identify sources. For example good correlations with SO₂ and CO typically indicate the impact of coal combustion (Pirrone et al., 1996; Han et al., 2014), and a strong correlation between Hg and CO has often been used as an indicator for long-range transport because both pollutants have similar sources and do not easily decompose by reaction and undergo deposition during transport (Weiss-Penzias et al., 2003, 2006; Kim et al., 2009) although a few recent studies showed the significant bromine-induced oxidation of GEM in the mid-latitude marine boundary layer as well as in the polar atmosphere (Ariya, 201; Obrist et al., 2011).”

21. 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?

The high GOM concentrations were associated with the wind from S to E in the CPF plot of Figure 5. As indicated in Figure 1, the major coal plants areas are located in the southern direction comprising from SW to SE from the sampling site. The industrial and metropolitan areas of Korea are located in the eastern direction from the sampling site (Fig. 1).

In order to eliminate any confusion, we have replaced the term “south” to “southerly direction”.

“Much larger SO₂ emissions in China raise the background SO₂ concentration in the region and may mask any correlation between GOM and SO₂ even if coal fired power plants located in the southerly direction from the sampling site impacted GOM concentrations.”

22. P32943 L10: It should be “the number of samples”

We have revised as suggested.

23. 3.2.1 GOM/PBM ratio: P32944 L5: It should be CPF

We have revised as suggested.

24. 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.

We believe that the GOM/PBM ratio is dependent on the relative contribution of local vs. regional transport based on our results. As the referee indicated, Lynam and Keeler (2005) also found that high GOM/PBM was observed with influences from local sources and low GOM/PBM ratios appeared with influence from regional sources in Detroit. They provided only one-day data for each case to determine the relative contribution of local vs. regional sources using the ratio of GOM/PBM while we used more than 80 data points to support the same theory. In Korea, Kim et al. (2009) also found the significant increase of the PBM/GOM ratio during high PM_{2.5} concentration events caused by regional transport from China.

The referee is concerned about using the ratio of GOM/PBM as an indicator for long-range transport and the inverse ratio (PBM/GOM) as an indicator for gas-particle partitioning at the same time (although we have used K_p instead of the ratio of PBM/GOM in the revised manuscript). As the referee mentioned, a lower GOM/PBM ratio associated with westerly and northerly airflows could be derived by higher gas-particle partitioning because of colder airflows from the north and differences in aerosol composition. We believe that this kind of coincidence events might happen but do not seem to occur very often. Average temperatures for each WD are shown below, which are not very different (Fig. R4).

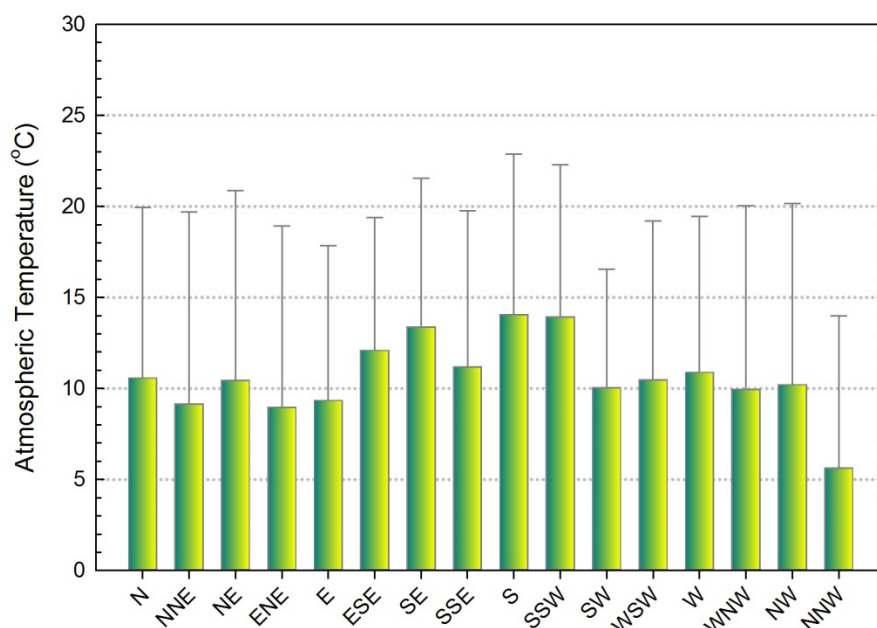


Fig. R4. Atmospheric temperature for each WD category. The error bar indicates the standard deviation.

We do not think that it is a problem to use the K_p for an indicator as gas-particle partitioning and to use the ratio of GOM/PBM as an indicator for the contribution of local vs. regional sources at the same time. As we indicated in the conclusions, our results show that the secondary formation of PBM becomes more important as the significance of regional transport increased. Lynam and Keeler (2005) also found that the secondary production was highly favored when the air underwent regional transport rather than local transport.

The correlation coefficient between CO and GOM/PBM was not very high ($R=0.27$: please note Fig. R5 below), but this negative correlation was statistically significant at a significance level of 0.1 as indicated in the manuscript. Strong correlation between CO and GOM/PBM ratio is not observed because the GOM/PBM ratio is affected by not only long-range transport but also by other factors such as various chemical reactions. That is why other studies including Lynam and Keeler (2005) and Kim et al., (2009) did not use the whole dataset to indicate the contribution of regional transport using the GOM/PBM ratio. The important thing is that our results clearly show that the GOM/PBM ratio was dependent on the wind direction, and a higher proportion of PBM relative to GOM with regional transport is rationale based on their atmospheric residence time, as also mentioned in Lyman and Keeler (2005).

In respond to this comment, we have added the references of Lynam and Keeler (2005) and Kim et al., (2009) to compare to our results. We have also provided the graph of correlation between CO and PBM/GOM ratio in the supplementary file as in Fig. 3S.

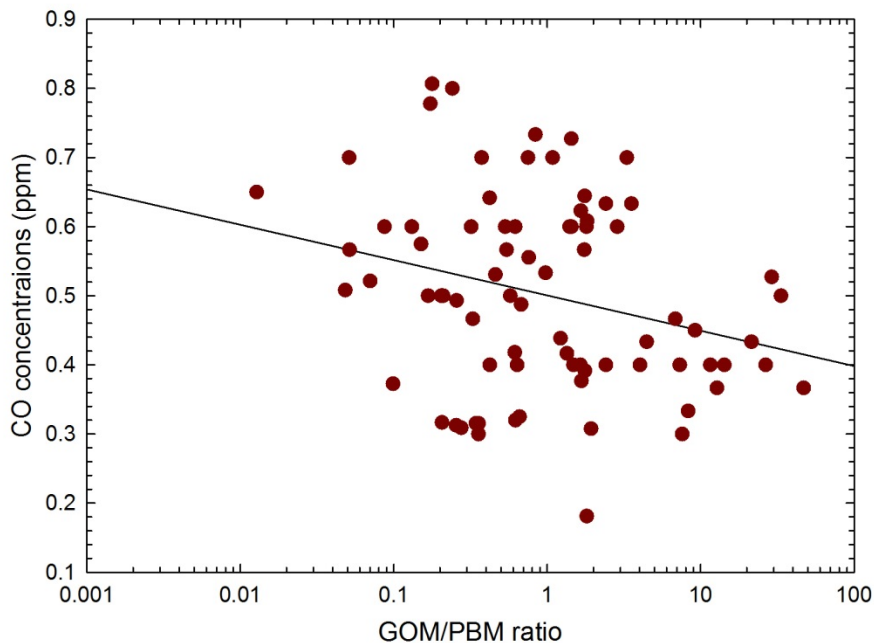


Fig. R5. Correlation between CO concentration and the ratio of GOM/PBM.

25. 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.

As we responded to the previous comments, we used much finer time scale of WD data for 12hr-averaged GOM and PBM concentrations. If the time durations for Hg measurements and meteorological data were identical it would be better to interpret; however, this does not always happen. There are many studies using different time scale for measurements of pollutants and for meteorological data. For example, Galindo et al. (2011) showed the possible source direction using 24-hr PM_{2.5} samples with weather data of 10-min time resolution. Kim et al. (2007) and Amato and Hopke (2012) also provided the source direction using daily source contribution estimates from daily PM_{2.5} observation with much finer wind direction data.

26. 3.2.2 PSCF Results: P32945 L2: It should be “the largest Hg emissions in China”

We have revised as suggested.

27. P32945 L9: It should be “which emerged as prominent source areas”

We have revised as suggested.

28. 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.

Long-range transport of GOM from China was not important (as shown in PSCF); therefore, when the effect of long-range transport increased, GOM concentrations should decrease as compared with PBM concentration, resulting in the decreased ratio of GOM/PBM. Therefore, the PSCF result is consistent with the GOM/PBM ratio result.

There are many references discussing the back-trajectory uncertainties. We have added a short discussion about the back-trajectory uncertainties and provided appropriate references in the revised manuscript.

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

That is a good suggestion, and we have added that shipping ports can be potential sources of Hg in the revised manuscript.

30. 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?

As we responded to the comment No. 10, we chose five clusters based on the change of TSV (Fig. R1) since the iterative step just before the large increase in the change of TSV typically gives the final number of clusters. Many other studies have used the same method to determine when to

stop the cluster process (Kelly et al., 2012; Piñero-García et al., 2015). We have provided the figure depicting the change in TSV vs. number of clusters in the supplementary file. Also, we think that five clusters can characterize well the usual air mass types over Korea.

As the referee indicated, trajectories between different clusters are indeed overlapped; however, it is inevitable that some of the trajectories are overlapped between clusters since the number of trajectories is large. In a lot of studies including Dimitriou and Kassomenos (2015), Delcloo and De Backer (2008), Piñero-García et al., (2015), and many more, we found overlapped trajectories between clusters. Please also refer our response to the comment No. 32.

31. 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.

The figure of the mean trajectory for five clusters shown in Figure 8 was accidentally used using 48-hr back-trajectories; therefore, Figure 8 and the relevant Table 4 have been changed in the revised manuscript, as follows (Fig. R6 and Table R1). The re-calculated contributions of Korean vs. out-of-Korean sources were slightly changed, but overall results are consistent.

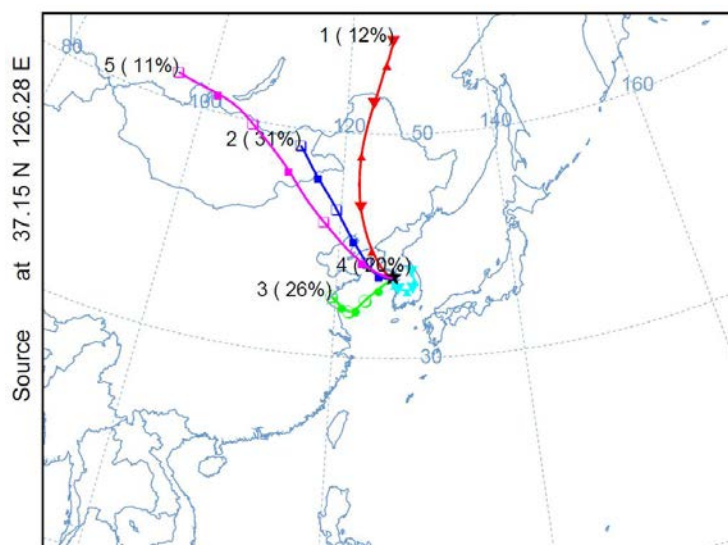


Fig. R6. The mean back-trajectory and contribution for each cluster.

Table R1. Estimated contribution of Korean and out-of-Korean sources on variations of speciated Hg concentration

Cluster	Cluster frequency (%)	Average concentration*			Source contribution (%)			Korean (%)			Out-of-Korean (%)		
		TGM	GOM	PBM	TGM	GOM	PBM	TGM	GOM	PBM	TGM	GOM	PBM
1	12	2.2	6.9	7.7	9.6	10.5	8.6				9.6	10.5	8.6
2	31	2.8	8.3	12.6	31.5	32.5	36.5	15.7	16.3	18.2	15.7	16.3	18.2
3	26	2.9	8.1	10.0	27.3	26.6	24.3	13.7	13.3	12.1	13.7	13.3	12.1
4	20	2.6	9.0	12.3	18.9	22.8	23.0	18.9	22.8	23.0			
5	11	3.2	5.5	7.4	12.8	7.6	7.6				12.8	7.6	7.6
Korean								48.3	52.3	53.4			
Out-of-Korean											51.7	47.7	46.6

The average GOM/PBM ratios for each cluster are 0.9, 0.7, 0.8, 0.7, and 0.7 for the cluster 1 to 5, respectively (note that the cluster 4 now represents local transport in the revised figure and table), showing no significant difference. We have also obtained 5 clusters from the 48-hr back trajectories, and the GOM/PBM ratio associated the local transport was 0.8 while those associated with regional transport were 0.5 and 0.6.

No significant difference of the ratio of GOM/PBM is probably because of other influencing factors; one of which is the overlapping trajectories between different cluster categories. In addition, the clusters associated with regional transport (cluster no. 1 and 5 in the Figure 8 of the revised manuscript) originated from China, passing through the North Korea before arriving at the site. North Korea is very close to the sampling site; therefore, the sources in North Korea are regarded as out-of-Korean sources (in Table 4); however, this is not really long-range transport considering the close distance between North Korea and the sampling site, resulting the over-estimation of the ratio of GOM/PBM.

In order to remove any confusion, we have replaced “long-range transport” to “regional transport” in the revised manuscript.

32. 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.

There is no reference for the equation 6 as we developed this approach. We used the average concentrations in equation 6 because the average can statistically represent the data. We do not think that the concentration range can better represent the characteristic of data than the average, but the box-and-whisker plots for each Hg species are shown below (Fig. R7). When considering

that cluster 4 is associated with the local transport from inland Korea and the cluster 1 and 5 are associated with the regional transport from outside of (South) Korea, the maximum and 75th percentile values as well as the arithmetic average are higher in cluster 4 for GOM and PBM than those in the clusters 1 and 5. We tried the same approach using the geometric mean, and obtained a similar result (shown below, Table R2). Also, we have used equation 6 with 48hr back-trajectory duration which is typically associated with GOM and PBM because of their shorter atmospheric residence time (Xu and Zhang, 2015), and obtained consistence results (Table R3).

We have now provided the box-and-whisker plots in the supplementary file.

We are well aware of the uncertainties of trajectories. The error in calculating trajectories is caused by a numerical and a physical component. The physical component of the error is related to how well the numerical field estimates the true flow field while the numerical error is composed of the integration error and resolution error. There is no way to track the physical error without independent verification data, but a few papers attempted to estimate the numerical error. Stohl (1998) and others suggested that the growth of trajectory position errors with travel time caused by interpolation is approximately linear. While Stohl (1998) suggested the uncertainties may be 20% of the distance travelled by the trajectories Draxler (1996) found that the final error was about 10% of the travel distance with an experiment using a balloon at a travel time of a little more than 100 hr. Trajectory errors vary considerably from case to case as shown in Stohl (1998), and should be considered when interpreting the results. However, the trajectory error is inevitably a part of all trajectory-based studies. We have added the paragraph about limitation of trajectory-based studies in the section of 3.2.3, and also mentioned the uncertainty of source apportionment approach based on cluster analysis in the “Conclusion and Implication” section.

The referee is concerned about the overlapping of trajectories between different clusters; however, as we responded to comment no. 30 because the cluster analysis accounts for variations in transport speed and direction simultaneously, there should be some overlapping of paths between the different clusters. In this study, cluster 2 and 5 were divided based on the speed rather than the direction (Fig. R6); therefore, the paths of trajectories overlapped between these two clusters. Many other studies also found the overlapping of the trajectories between different clusters. Dorling et al. (1992) presented applications of trajectory clustering, which is one of the earliest studies for cluster analysis of trajectories, and the trajectories were clearly overlapped between 9 different clusters. In a lot of other studies including Dimitriou and Kassomenons (2015), Delcloc and De Backer (2008), Piñero-García et al., 2015), and many more, there were also the

overlapped trajectories between clusters.

For using longer trajectory duration, we think that 72hr is appropriate for all Hg species considering the short atmospheric residence time of GOM and PBM and trajectory numerical error enhanced by travel distance. However, we agree on that the travel time of 72hr is not enough for identifying long-range transport, and we have replaced “long-range transport” to “regional transport”.

The percentage of trajectories for each cluster is shown in the Figure 8 and Table 4.

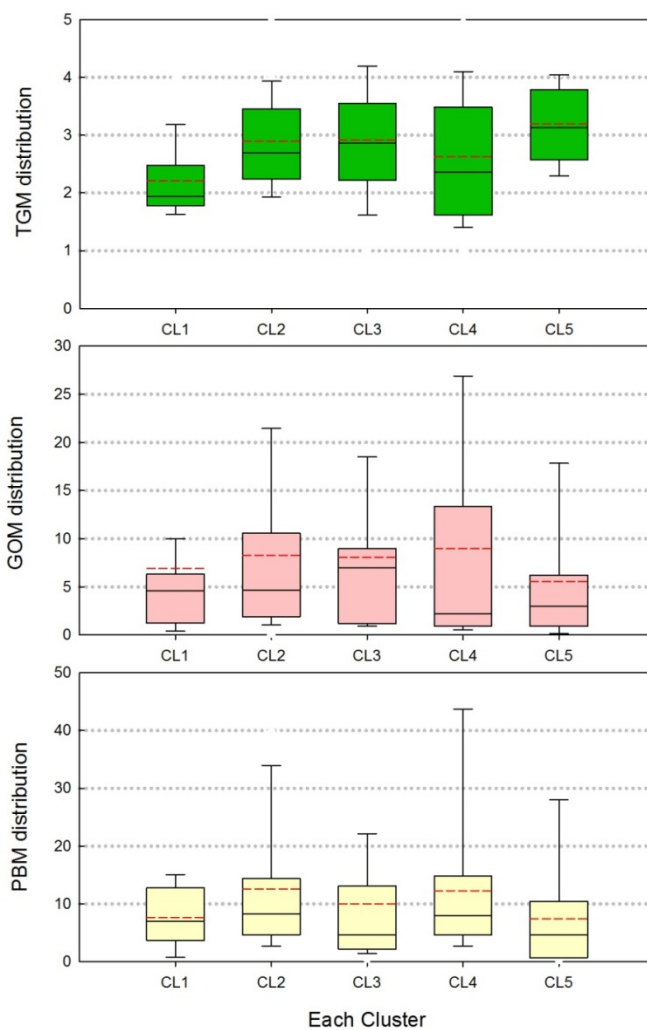


Fig. R7. Box-and-whisker plot of all Hg species for five clusters.

Table R2. Estimated contribution of Korean and out-of-Korean sources on variations of speciated Hg concentration using geometric average.

Cluster	Cluster frequency (%)	Geometric mean			Source contribution (%)			Korean (%)			Out-of-Korean (%)		
		TGM	GOM	PBM	TGM	GOM	PBM	TGM	GOM	PBM	TGM	GOM	PBM
1	12	2.1	3.1	5.3	9.6	9.4	9.5				9.6	9.4	9.5
2	31	2.8	4.4	8.4	32.3	34.3	38.9	16.1	17.2	19.4	16.1	17.2	19.4
3	26	2.7	4.7	5.5	27.0	31.1	21.5	13.5	15.5	10.7	13.5	15.5	10.7
4	20	2.4	3.7	8.2	18.2	18.9	24.6	18.2	18.9	24.6			
5	11	3.1	2.3	3.5	12.9	6.3	5.7				12.9	6.3	5.7
Korean								47.9	51.5	54.7			
Out-of-Korean											52.1	48.5	45.3

Table R3. Estimated contribution of Korean and out-of-Korean sources on variations of speciated Hg concentration using 48hr trajectories

Cluster	Cluster frequency (%)	Arithmetic mean			Source contribution (%)			Korean (%)			Out-of-Korean (%)		
		TGM	GOM	PBM	TGM	GOM	PBM	TGM	GOM	PBM	TGM	GOM	PBM
1	12	2.2	3.7	7.9	9.3	5.7	9.1				9.3	5.7	9.1
2	25	2.8	10.0	10.7	25.0	32.0	25.8	12.5	16.0	12.9	12.5	16.0	12.9
3	24	3.0	8.9	12.4	25.5	27.5	28.6	12.7	13.8	14.3	12.7	13.8	14.3
4	13	3.2	5.4	9.3	15.0	9.0	11.6				15.0	9.0	11.6
5	25	2.8	8.0	10.4	25.2	25.7	25.0	25.2	25.7	25.0			
Korean								50.4	55.5	52.1			
Out-of-Korean											49.6	44.5	47.9

33. The discussion on P32947 should consider the impact of these uncertainties on the results.

We have added the paragraph about limitation of trajectory-based approach. Overlapping issues of back-trajectories between clusters have been considered in the “Conclusion and Implication” section in the revised manuscript.

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

The small n is the number of clusters, which is 5 in this study. We have added in the revised manuscript.

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

We have replaced it to other references as shown below.

Kim, I.S., Lee, J.Y., and Kim, Y.P.: Impact of polycyclic aromatic hydrocarbon (PAH) emissions from North Korea to the air quality in the Seoul Metropolitan Area, South Korea, Atmos. Environ., 70, 159-165, 2013.

NI, Nautilus Institute for Security and Sustainable Development: Rural energy survey in U nhari Village, the Democratic People’s Republic of Korea (DPRK): Methods, results, and implications, Berkely, California, USA, 2001.

NI, Nautilus Institute for Security and Sustainable Development: The DPRK Energy Sector: Estimated year 2000 energy balance and suggested approaches to sectoral redevelopment, Berkely, California, USA, 2003.

36. 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.

We have replaced “mass” to “concentration variation”. Please see our response to the comment no. 32 and no. 38.

37. 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?

The cluster analysis source contribution considers both concentration and the frequency of the trajectory while CPF and PSCF do not; therefore, the cluster analysis results augment the CPF and

PSCF results which only use concentrations that are in the top 25th percentile. Please see our response to the comment no. 38.

- 38. 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.**

CPF and PSCF indeed consider the wind direction, but what they do not consider is the frequency of wind direction or the overlapping of the paths of trajectories. In other words, if high Hg concentration is not often observed with westerly winds the CPF and PSCF values for westerly direction cannot be high even though the westerly winds are dominant throughout the sampling periods. Contrary of this, if the Hg concentration is high with easterly winds, both CPF and PSCF identify the eastern areas as important source areas although the winds are, in fact, hardly blowing from east. In this case, it is true that the sources located in eastern direction from the sampling site are probably important for enhancing Hg concentration, but it cannot be said that their contribution affecting the “concentration variation” of Hg seen by the site is also high.

The trajectory cluster source contribution considers both concentration and directional frequency of back-trajectories to evaluate the quantitative contribution of Korean and out-of-Korean sources to the variation of measured Hg concentrations.

We have added more explanation in the section of “Conclusion and Implications”.

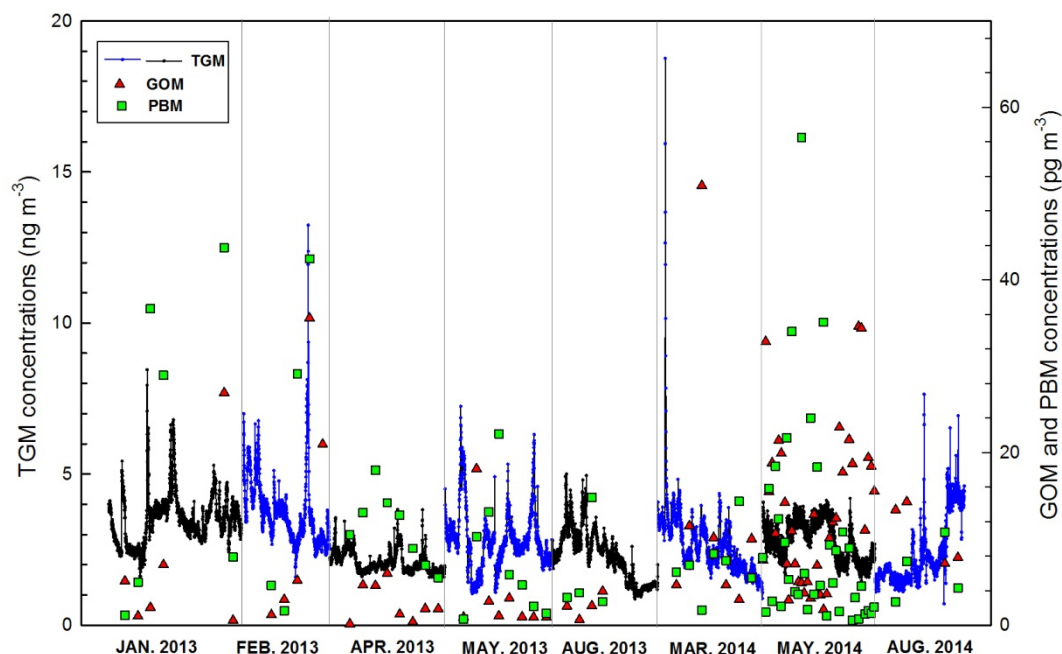
- 39. P32948 L16-25: The GOM/PBM ratio does not seem to be an effective tool for identifying long-range transport because it is too similar to the PBM/GOM ratio that was used to characterize gas-particle partitioning. While it’s possible that the two processes occur simultaneously, that is not always the case. It’s also possible gas-particle partitioning and local transport of emissions occurs 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.**

Please see the responses to the comment no. 17, 18, and 24.

- 40. Figure 2: There needs to be some gaps in the time-series plot because each of the sampling periods was only ~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.”

There are gaps between the sampling periods in Figure 2, but it is hardly visible because the number of TGM data are very large. In order to distinguish the TGM concentration in each sampling period, we have used different colors for TGM concentration in two consecutive sampling periods. For the caption, we have revised as suggested.



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

As we responded to the previous comment, we have replaced the ratio of PBM/GOM with “ K_p ” and subsequent changes have been made in the revised manuscript.

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

We have revised as suggested.

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