

Response to Reviewer #1 comments

We appreciate the reviewer's constructive comments which helped us to improve the manuscript. Our point-by-point responses are provided below (in blue).

1. In this work, Authors aimed to identify the factors affecting ambient Hg concentrations (in the form of gaseous-GEM, oxidised-GOM and particulate-bonded-PBM) at a receptor site using PMF and PCA approaches. They also tried to summarize the similarity and differences in PMF factors and PCA components, to evaluate the PMF model performances for Hg forms, investigate the impact of meteorological parameters on PCA results, assess the sensitivity of PMF results and performance to different treatment of missing data and low concentration values of speciated Hg.

Anyway, despite the attention paid in missing/<MDL data treatments, lacks are present in describing how the PMF model was performed. In this case, a rigorous categorization of the variables is important along with the definition of the Total Variable (which allows estimating the contribution of a chemical species to a reference variable, PM for example). In addition, a preliminary analysis of some parameters like Q, IM and IS versus the number of factors, allows the user to obtain useful information on the correct solution for PMF. All these information are not reported in the work. Finally, the authors performed an analysis of the performance of the PMF model, considering the observed/predicted forms of Hg. In this case, PMF outputs clearly shown that the model was not able to well reconstruct the variables GEM, GOM and PBM. Then in my opinion, further elaborations need in order to improve the solution and the relative stability. In conclusion, I believe that the manuscript could not be considered matured for publication in its present form considering the reasons indicated above. It could be improved with further PMF analysis. In addition, even if in this work a different data treatments have been done, the datasets analysed have already been published and this limits the novelty of the results (Cheng et al., 2013). I also give some specific comments that could be useful for eventual re-writing of the paper.

Response: We agree with the reviewer that more analysis of the PMF model outputs would be useful. In fact, the analyses of Q, IM and IS versus the number of factors were conducted. Similarly, the percent concentrations reconstructed by all factors were monitored for each of the three Hg forms. However, these analyses were not included in the submitted manuscript. A brief description of how the optimal number of factors was determined is now included in the Methods section. Detailed analysis is presented as Supplemental Information (SI), which support the stability of PMF runs, and justify the final solution and the number of factors chosen. Several alternative PMF settings have been attempted to improve the model performance on reproducing observed GOM and PBM, including changing the category of GOM and PBM and retaining different number of factors. However, little improvement was observed in the model performance on reproducing GOM and PBM. In the revised manuscript (Results and Discussion), we have added PMF uncertainties for modeling pollutants that undergo various transformation processes, unlike the modeling of only aerosols. PMF does not account for chemical reactions that may occur as it travels from source to receptor.

In the SI, we have added the following: “The number of PMF factors needs to be chosen according to the understanding of the sources impacting the samples utilized. When the background information is not enough to determine the number of factors, several methods could be used to determine the range of the number of the factors. The maximum individual column mean (IM) and the maximum individual column standard deviation (IS) of the scaled residual matrix can be used to identify the range of the number of factors. IM and IS will show a drastic drop when the number of factors increase up to a critical value (Lee et al., 1999). The optimal number of factors should be no less than the critical value. The trend of dQ also provides useful information on deciding the number of factors. When dQ becomes small as the number of factor increases, there might be too many factors (Hopke, 2000; Brown et al., 2015). Runs with different numbers of factors in the range determined by IM, IS, and dQ should be conducted. The model performance and the interpretability of factors in each run should be evaluated. The optimal PMF solution should be a compromise of those indexes and the interpretability of the factor profiles and their comparability with those from the literature (Belis et al, 2015 b; Cesari et al., 2016).

The IM, IS, and Q values are provided in the SI of the revised manuscript as follows. “The IM and IS were calculated to determine the number of factors. The IM and IS dropped dramatically in 2009 when the number of factor increased to 3 (Figure S1). In the line plot of Q(Robust) and Q(true) vs number of factors (Figure S2), no significant decreases were found when the number of factors is larger than 5 in 2009. Therefore, the PMF was run using the number of factors from 3 to 5 in 2009. In 2010, the decrease of IS value was gradual while the IM value experienced a drastic drop when the number of factors increased to 3 (Figure S3). The trend of the Q(Robust) and Q(True) in 2010 is similar to 2009 (Figure S4). Therefore, the PMF runs with the number of factors from 3 to 5 were also conducted in 2010. The number of the factors selected (4) is a compromise of the trends of these indexes and the physical meanings of the factors obtained following Cesari et al. (2016). A detailed comparison of the physical meanings of different solutions can be found in Liao (2016).”

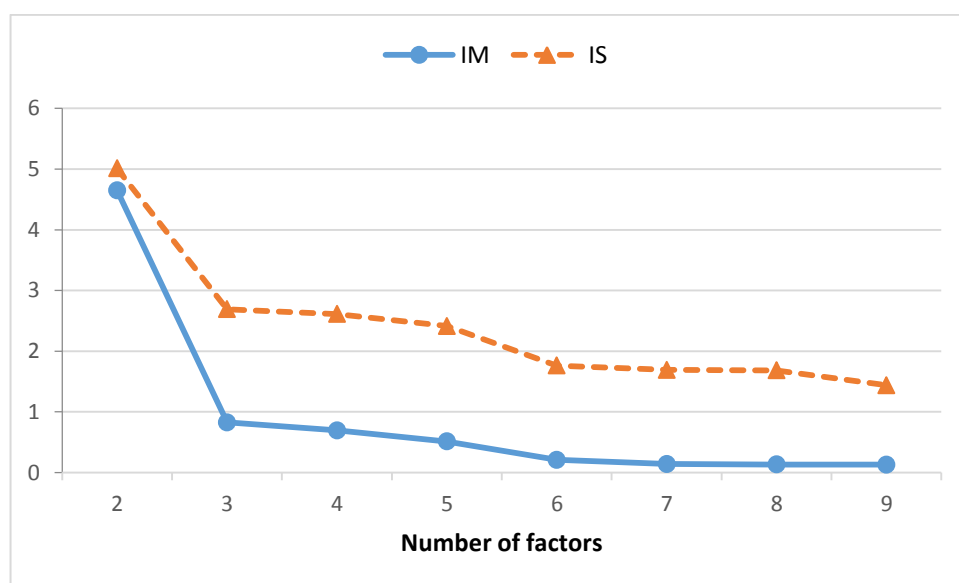


Figure S1: IM and IS vs number of PMF factors in 2009.

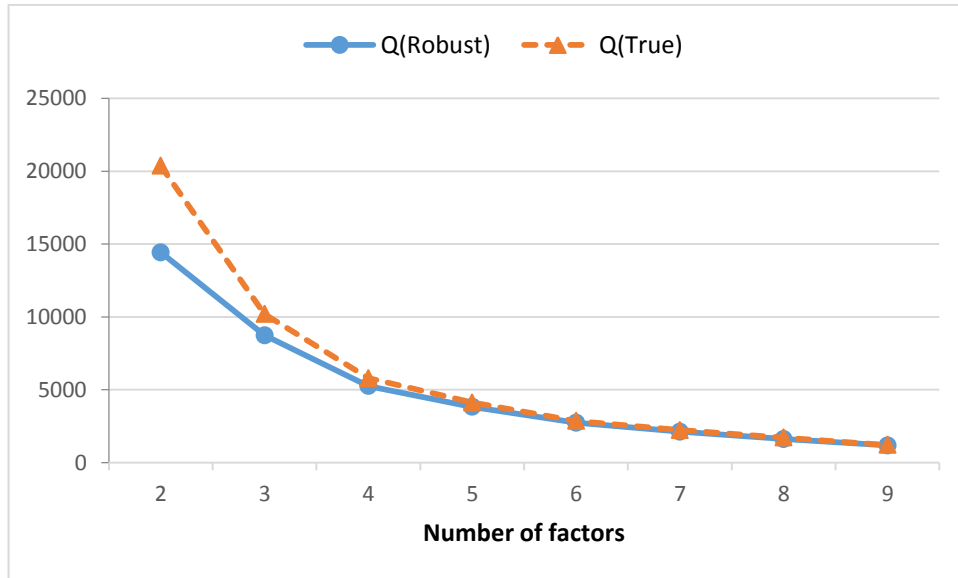


Figure S2: Q(Robust) and Q(true) vs number of PMF factors in 2009.

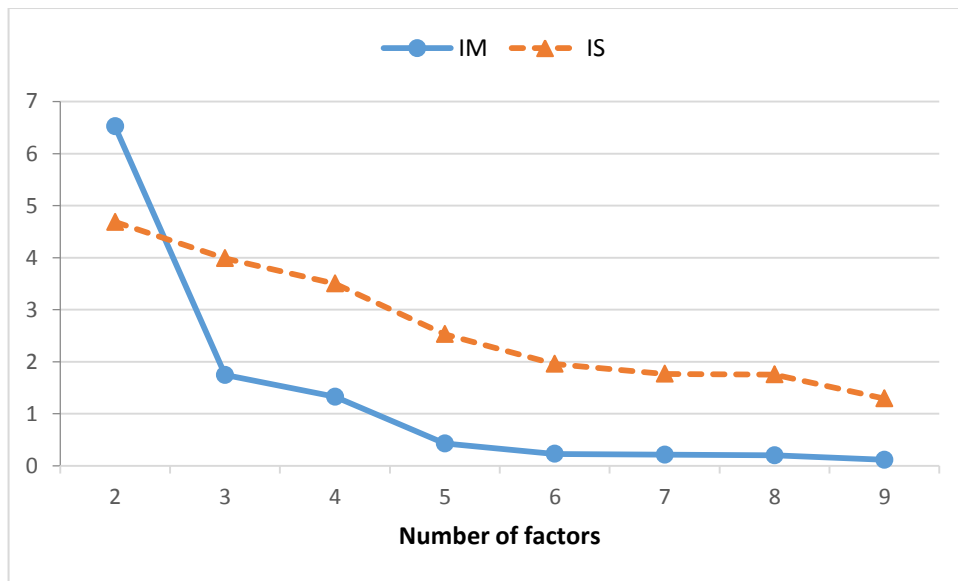


Figure S3: IM and IS vs number of PMF factors in 2010.

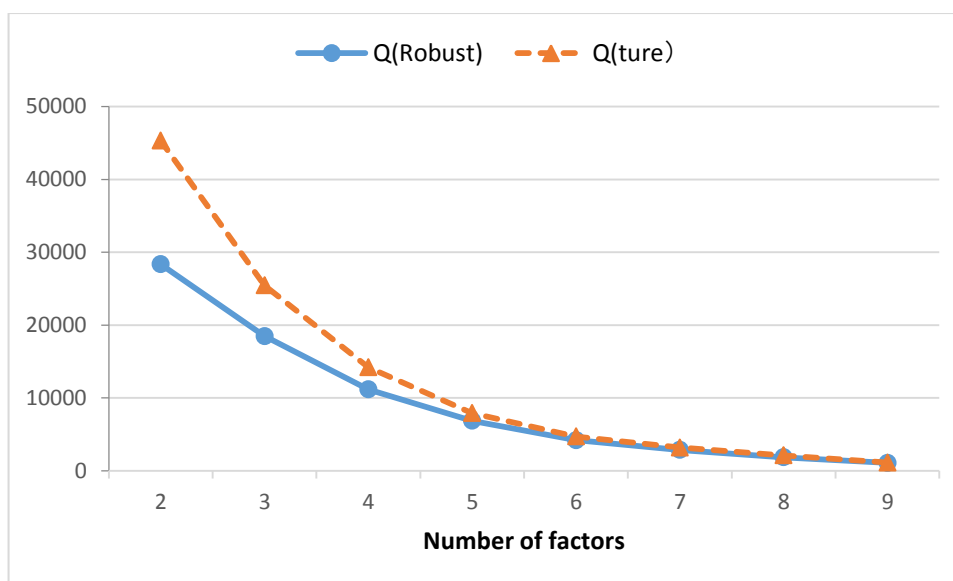


Figure S4: Q(Robust) and Q(true) vs number of PMF factors in 2010.

The same dataset was used in a PCA study (Cheng et al., 2013), while this paper focuses on PMF and comparison between PMF and PCA results. Furthermore, the variables used, treatment of missing data and number of component are different. In Cheng et al. (2013)'s study, pairwise exclusion was used to make the full use of the dataset. The marine tracing species were excluded in 2009 while SO₂, HNO₃, and all ions were excluded in 2010 because they were not related with mercury. However, listwise exclusion and all species were used in order to be compared with the PMF results in this study. The method used to retain the number of components for further analysis was different. Fixed number (4 and 3 for 2009 and 2010, respectively) of components was retained in Cheng et al. (2013)'s study but the Kaiser criterion (eigenvalue>1) was used to retain the number of components in this study. Those are presented in Table 4. All these differences could result in the differences in the PCA results. In short, the comparison of the results suggests that the PCA results are sensitive to the input parameters. In terms of the differences in the results, four components were extracted in Cheng et al. (2013)'s study in 2009. Three out of four components, including Combustion/Industrial Source, Gas-particle partitioning of Hg, and Gas-phase Oxidation of Hg, were similar as the components in Case 09-C&M. The component loadings of the components Combustion/industrial Source and Gas-phase Oxidation of Hg in 2009 were similar in this study and in Cheng et al. (2013)'s study. The component loadings of the components Condensation on Particles in Winter (Cheng et al., 2013) and Gas-particle Partitioning of Hg (this study) in 2009 were very different. Only the negative association between temperature and PBM was the same between Cheng et al. (2013)'s study and this study. Three components were extracted by Cheng et al. (2013) in 2010. However, none of the major variables of these three components is similar to the five components identified in this study in Case 10-C&M. In a PM₁₀ source apportionment study using PMF and PCA at three European sites (Cesari et al., 2016), the authors reported that PCA results are more sensitive to the air contaminants present as input variables. In the revised manuscript, a reference has been added (Liao, 2016) for a detailed comparison of PCA results in this study and that in Cheng et al. (2013).

Specific comments

2. Page 2, line 64: Author could cite some example regarding works that assessed model performances of RM, such as Cesari et al., 2016 Environ Sci Pollut Res 23:15133–15148 and Belis et al. 2015 Atm Environ 123:240-250.

Response: Thank you for your suggestion, those papers are included in the revised manuscript, Method as well as Results and Discussion sections.

3. Page 3, line 88. A map could be useful in order to understand the sampling site position together with the sources, listed in the paper, affecting that area.

Response: A map (Figure 1) has been added as suggested, including the sampling site, all Hg sources and all major sources of NO_x and SO₂ in Nova Scotia.

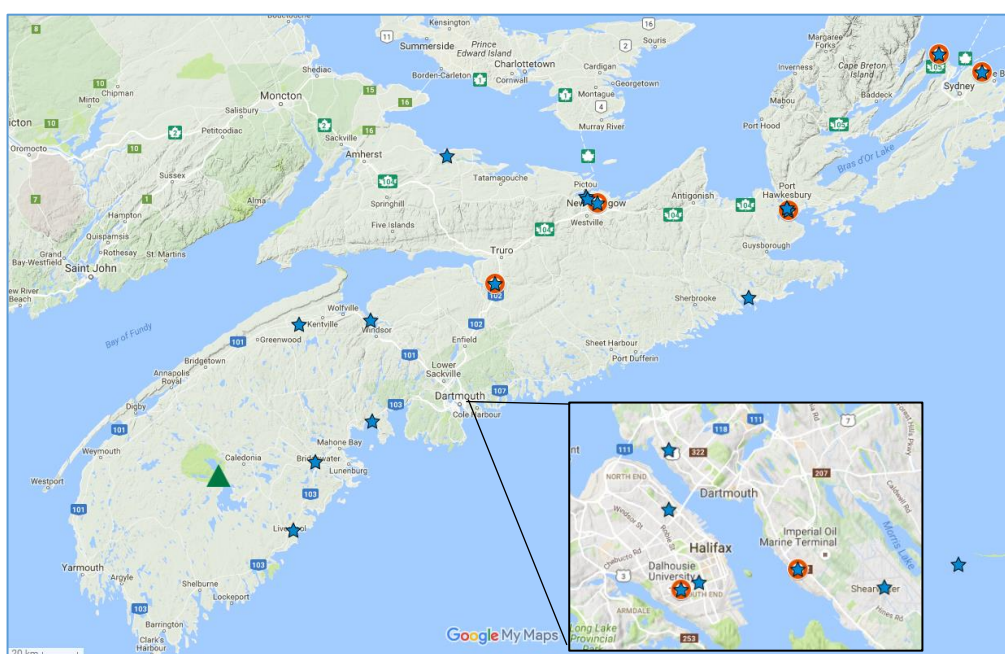


Figure 1: Map showing the locations of sampling site (▲), the top 19 SO₂ or NO_x point sources (average of 2009 and 2010) (★), and all mercury point sources in 2009 and 2010 (○), in Nova Scotia.

4. Page 4, line 111. Authors should indicate the amount of aerosol mass characterized.

Response: The total aerosol mass characterized in each year has been reported in the Methods section of the revised manuscript. The mass of total ions in 2009 accounted for 80% of the PM mass. The total ions were added in Table 1 and Table 2 for 2009 and 2010, respectively.

5. Page 6, line 130. Authors should better indicate in the text the dimensions of the datasets analysed and if these dimensions respect the conditions requested in order to obtain statistically stable SA analysis. From literature, we have that these conditions are: the minimum required number N of samples $N > 30 + 0.5 * (V + 3)$ where V is the number of species considered (Henry et al., 1984 Atmos Environ 18:1507-1515), and the more

restrictive condition $N > 50 + V$ (Thurston and Spengler, 1985 Atmos Environ 19:9-25.).

Response: Dimension of datasets has been incorporated in Tables 3 and 4 as suggested. We have also added in the main body the conditions requested in order to obtain statistically stable source apportionment results (Henry et al., 1984; Thurston and Spengler, 1985), and stated that our datasets meet the more restrictive requirement by Thurston and Spengler (1985) in both years, by a margin of 90-300 in 2009 and 216-300 in 2010.

6. Page 6, lines 176-180. Authors wrote that one of the objectives of this work is to identify the factors affecting ambient Hg concentrations using PMF model. In this sense, authors should explicit what chemical specie they used as Total Variable in PMF analysis: PM or Hg (GEM or GOM or PBM)?

Response: This is now clarified in the Methods section as suggested. We did not use total variable because this study focused on speciated mercury. Commonly used total variables include PM as pointed out by the reviewer. However, input variables in this study include both PM ions and gaseous pollutants. Furthermore, a total variable should be set to “weak” as recommended by USEPA (US EPA, 2014) thus may not have much impact on the PMF results.

7. Page 6, line 185: Please, give some examples of stability indexes for model runs.

Response: Included now in Supplemental Information. As pointed out in the PMF User’s Guide (US EPA, 2014), when the Q (robust) values over several runs are highly variable, the stability of the result is poor. In this study, the differences of the Q (Robust) value between different runs were all smaller than 5 indicating that the results were quite stable in both years.

8. Page 7, line 194. Please, indicate the dimensions of the analysed dataset and if these datasets are the same considered for PMF analysis.

Response: Included in text now under the Methods section, as suggested. The dimensions of the reference cases in PMF model and PCA are the same. After including the meteorological parameters in PCA input, the dimensions of the input data are slightly smaller.

9. Page 7, line 209. Authors should explicate why the 4-factors solution is the best solution. I am wondering if they have analysed the trend of some parameters (such as dQ, IM and IS, see Lee et al, 1999 Atmos Environ 33: 3201-3212; Viana et al., 2008 Atmos Environ 42:3820-3832; Brown et al., 2015, Sci Total Environ 518-519: 626-635) with the number of factors, from 4 to 8 for example, in order to obtain some “objective” information about the best solution. If not, please consider to perform this analysis in order to justify the choice of 4-factors solution.

Response: Included now as Supplemental Information, please see response to comment #1.

10. Page 9, line 267. Again, what species, PM or Hg-form, has been considered as Total

Variable? If the T.V. is the PM, how is possible to obtain a factor contribution for 2010?

Response: This is now clarified as suggested; please see response to comment #6.

11. Page 10, lines 302-307. The coefficients of determination together with Figures S1-S2 show that the model in this case is not able to reconstruct the Hg – concentrations. The reason could be different, depending on, for example, the reduced number of samples (a solution could be to merge the two datasets), or the high percentage of missing values/data lower than MDL. In my opinion, Authors should check the categorization of the variables, performed considering both the S/N value and the percentage of missing values or lower than MDL: for example, in my opinion GOM could be considered as a BAD variable. Again, the choice of a different number of factors could help in obtaining a better reconstruction. Authors should perform other runs with the aim to improve the output of the model. The same observations are for the dataset Case 2010.

Response: Included now as supplemental Information. The S/N ratio was not used in this study because the uncertainties of all variables were set to a fixed fraction of concentrations as suggested in the PMF user's guide. Because this study focuses on speciated mercury, all three mercury forms should be included in the input. Also, categorizing GOM and PBM to "weak" would have a similar reproduction of GOM and PBM concentrations compared to the cases categorizing them as "strong". Therefore, they are categorized as strong in this study. Different numbers of factors were also analyzed and the 4-factor result had the best interpretability. Therefore, 4 was used as the number of factors.

12. Page 14, line 440. Referring to PC3 in table 8, how can you explain the opposite load values of GOM and Temperature? Photochemical production of GOM happens with high temperature and solar radiation, so I would imagine this variable having the same sign.

Response: This is now clarified as suggested in the Results (section 3.2). "The additional negative loading of temperature (-0.52, Table 8) and positive loading of wind speed (0.52, Table 8) in major variables may indicate colder air flows from the north containing more O₃ and GOM (Cheng et al., 2013). This is reasonable because Hg sources in Nova Scotia were mainly located north of the sampling site (Figure 1)."

References

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