Response to Anonymous Referee #1

Referee comment on "Odds and ends of atmospheric mercury in Europe and over northern Atlantic Ocean: Temporal trends of 25 years of measurements" by Danilo Custódio et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-753-RC1, 2021

This paper presents trends in total gaseous mercury concentrations in Europe and the North Atlantic Ocean and the regional sources affecting TGM inferred from concentrationweighted trajectory (CWT) analysis and the Positive Matrix Factorization (PMF) model. Ten to twenty-five years of TGM data at six locations were analyzed in the study. Given the long term data available, there needs to be a more detailed and deeper analysis of the data than the one currently presented. The paper summarized the distribution and general statistics for the 10-25 year period. There should be more detailed analysis comparing TGM data over various time periods and among the sites and examining changes in the frequency of Hg depletion events, etc. as well as the explanations for the TGM variability. Long term declines in TGM appear to be related to decreasing anthropogenic Hg emissions; however, Hg emissions data from the region were not presented in the paper.

Response: The authors thank the comments. New statement was added in order to improve the article and a more detailed analysis was included.

One of the major point highlighted by the reviewer is the necessity of discussing anthropogenic emission. The author agree on the relevance of such discussion. An accurate emissions inventory is essential for interpreting trends in atmospheric concentrations and assessing the effectiveness of mercury pollution control policies. However, the observed GEM/TGM trend is not consistent with the global anthropogenic emissions inventory. As reported by Lyman et al. (2020 and references in) the uncertainties in inventories range from -33% to 60%.

The emission issue was intensively discussed during the article preparation among the authors. Indeed, the is a conundrum in the trend displayed by the emission inventory.

Listen different partners the conclusion was that having trend analysis for the emission inventory could be not suitable for comparison with the observed one. Due to gaps, errors and inconsistencies in the data from different periods, I would be afraid that a trend evaluation of atmospheric mercury based on inventories could be misleading. Emission inventory relies on data provided by countries and emission sectors.

There is a protocol, however it explicitly informs that national agencies can use its on method.

Many countries just do not provide data, so it is estimated. It used different parameters to estimate, like population density, vegetation, ecosystem. Sometimes there is even interpolation when data are not available for some sectors in some regions or period.

Even in Europe, the emission assessment for sectors as power plants, industrial installation, oil and gas production sites, waste units can follow proxies and methods that have changed over time. (Thus, the sector classification can be changed).

Strong deviations can be observed for following years as for example, 2015-2016 when the spatial resolution of 1/10° x 1/20° in longitude and latitude was applied to 30° W – 60° E and 30° N – 72°N in many atmospheric pollutant species inventories.

In addition, even emission estimated based on remote sensing techniques have be tremendously improved.

Since the emission inventory are more committed with a better description and accuracy of sources rather than its method coherence throw the years, and the gathering of data has been constantly improved, the apparent trend displayed by emissions inventory can be mainly caused by the improvement in the emission catalogue. This is the main argument for not having the emission data discussed in the manuscript. It may not represent the observed trend.

Others comments above mentioned by the reviewer are replied in the specific comments.

The detailed methodology for the CWT and PMF analysis are missing. It is unclear why back trajectory data are combined for the five sites rather than analyzing the data for the sites individually. CWT results likely differ from one site to another. The PMF analysis in this paper was very similar to the one conducted by Custodio et al. (2020) published in this special issue for the 5-year period at Mace Head, and does not seem to provide substantially new results and insights.

Response: The source apportionment and CWT are only methods exploited in order to bring insights into the trend evaluation, which is the aim of the article. Rather than a detailed methodology description, which will take an extensively part of the article, the author stands for addressing the references of the full description of the method. However, the authors agree that further description of the method helps the reader understanding and evaluate the finding. Therefore, we appreciate the comment and new information in the factorization and factors obtained were added.

The PMF results are also not as detailed as those in Custodio et al. (2020) despite a longer time-series in this study.

Response: A longer times series has no analytical or computation implication for the initial condition considered in the PMF factorization (in terms of factors, seeds, analytical uncertainties). It basically increases the number of equations, propagating the factors backwards in time. However, key failures as residual and reconstruction performance are important for the reader to evaluate the mass reconstruction. This information was added in the new version.

The baseline factor extracted from the PMF model needs to be described in detail given that this factor explains the largest proportion of the TGM variability. It was not clear from the paper which pollutant markers were used to assign a PMF factor to the baseline factor. The lack of a clear definition of the baseline factor makes it challenging to evaluate the effectiveness of mercury control measures that have been implemented. In my view, the source apportionment results should provide a better understanding of the different anthropogenic source sectors contributing to TGM and whether their contributions have changed over time, and if there are emerging Hg sources that we need to be concerned about. The role of re-emissions of previously deposited Hg is also not well understood.

Response: Baseline factor refers to a background factor, a factor where TGM display an established well mixing ratio. The authors are taking the reviewer comment into account and improving the factor description.

The new version of the manuscript brings the full profile of the sources obtained from the factorization, which reconstructed the TGM mass. The chemical profile obtained for each factor is now presented on the supplement.

The authors understand the importance of the re-emission role; however, it is important to highlight that we are dealing with a receptor model. The solution is constrained by the data that you have, which will allow the propagation of the eigenvector. The axis rotations without a re-emission marker will not solver such "source". The same can be said about better speciation of sources. We are totally in line with the reviewer idea that a better understanding of the different anthropogenic source sectors contributing to TGM is needed and should be sought. However, more source marker is needed to develop and permit better source apportionment. Custodio et al. (2020) give a contribution on decluttering atmospheric mercury sources by PMF, but their solution is far from being the ultimate. In addition, the authors want to declare that there is no improvement in the source apportionment method used in this study. We only applied the method presented by

Custodio et al. (2020) to exploit the TGM trend. This study was conceptualised as Part II of the aforementioned article, even been the authors not being the same.

Specific comments

Abstract. It is not necessary to describe the PMF model in the abstract. It is more meaningful to focus on the PMF factors extracted and what sources they represent. Please also clarify the last sentence of the abstract.

Response: Thanks for the comments. The abstract was reworded.

Lines 57-65. The updated review paper on atmospheric mercury (Lyman et al., 2020) should be discussed and cited. This review paper summarized trends in TGM and provided potential explanations for the trends.

Response: We appreciated the comment. The aforementioned reference was considered in the new version.

Lines 67-70. The paper by Custodio et al. (2020) is a five year study of the TGM during the 2013-2018 period, while historical mercury releases are discussed in Horowitz et al. (2014). The timescales are very different; thus it does not seem reasonable to attribute the TGM decrease over that period to historical changes in mercury releases.

Response: The aforementioned statement stands for compliance with those articles findings rather than a trend comparison.

Lines 71-73. There have been several studies examining long-term trends in TGM and relating that to mercury emissions trends. Please discuss and reference these studies and provide some explanations on how this study is different.

Response: As far the authors know, this is the first publication deploying time series decomposition, combining Lagrangian transport and receptor model in the evaluation of TGM/GEM trend.

Lines 77-79. Were 5-day trajectories analyzed over the 25-year period? Please clarify.

Response: We analysed trajectories arriving at Mace Head with a backward length of 120 h. Two trajectories per day for a period of 25 years. An improved statement was added in the section 2 subsection, "back-trajectory".

Line 80. Delete "On this raw,"

Response: Sentence reworded. Thanks.

Line 81. Please clarify the meaning of "baseline factor"

Response: A factor with a high load of long-lived anthropogenic species was labelled by Custodio et al. (2020) as a baseline factor. Such a name was picked up because it was the main factor at Mace Head station, a background site with a lower impact of nearby anthropogenic sources. (The factor was labelled as "Aged TGM", however, it was renamed baseline factor as requested by the reviewer community in a previous paper). Further consideration on the factor meaning and interpretation is given in lines 377-384.

Line 128. It is useful to label the TGM sites on a map and show the spatial distribution of the mercury point sources in Europe.

Response: Thanks for the comment. The sites' names were added in Figure 2.

Line 130-146. Please clarify which analyzer model was used to measure TGM and the sampling interval of the TGM data. There should also be some discussion on quality control, calibration and maintenance of the analyzers.

Response: All sites used Tekran 2537 (A and/or B) instrument. A new statement is presented.

Line 150. Was the CWT analysis conducted at five or six stations? Long term TGM data are available at six stations as mentioned in the previous section.

Response: The CWT was performed at six stations. The mistake was corrected. Thanks.

Lines 151-152. Some justification for the back trajectory model parameters are needed. It seems that two trajectories per day is not sufficient given that TGM data are available every 5 minutes. Why did you choose a start time of 0:00 and 12:00 local time and two arrival heights?

Response: For the CWT, it was considered TGM/GEM in a time resolution of 12h. As well, it was obtained trajectories arriving at the stations representing the average time of 12h. A higher resolution would require intense computing power since the time series is quite long and has six combined sites. In addition, considering the trajectory uncertainties, it was not observed significant difference among trajectories closely collocated in time. Thanks for the comment. The statement was reworded.

Line 161. "For a 120-hour trajectory duration, 84 trajectory segment end points were calculated." It's not clear how the 84 end points were obtained. There should be 120 trajectory segment endpoints for each 120 h trajectory.

Response: 84 is the maximum in segments that hysplit can provide (1.42h/segment).

Line 169. PMF stands for Positive Matrix Factorization.

Response: Indeed. Thanks.

Lines 171-175. It is unclear as to which year(s) of data the PMF model was applied to. Why was PMF applied to only the Mace Head site and not the other five sites? If the purpose is to examine changes in the sources affecting the TGM sites, then PMF should be applied to the yearly data or different time periods rather than the 25-year period.

Response: PMF is applied to daily data. We reconstructed daily data at Mace Head for a period of 25 years. It was performed only for Mace Head because the site has the best database, disposing of a better tracer gases speciation (markers).

Lines 177-184. The introduction to the CWT method should have been discussed in the back trajectory section where the CWT calculation was described.

Response: The sections were reworded. Thanks.

Figure 1. The time-series shown is not very meaningful as it is difficult to see the variations due to the large number of data points.

Response: Figure 1 is a summary dedicated to presenting data distribution, central tendency, and timely availability of data. Since the dataset is trended, any comparison should consider the period of missing data. The period with a lack of data is displayed in the aforementioned figure. In addition, the time variability as seasonality and trend (which need further data decluttering) are discussed and showed in later figures.

Lines 188-215. A more detailed analysis of the TGM data is needed given that there are almost 25 years of data measured at six sites. For example, a comparison of the TGM data over the three time periods, comparisons between sites, changes in the frequency of Hg depletion events, etc.

Response: *The presented analysis of the measurements compares the sites only as far as needed for the application of the CWT and PMF modeling. A detailed analysis proposed by the reviewer would need a separate paper.*

In addition Hg depletion is taken in this study as a modulated phenomenon. Indeed, changes in the frequency of depletion phenomena and in the strength of its events would be an essential component in the atmospheric mercury reducibility and should be decluttering in future investigations. Comparison and evaluation of the non-monotonic trend in different periods is presented in section 3.2

Line 218. Please label the site names on one of the maps.

Response: Label with the name of sites added in figure 2.

Line 252. LSQF has not been defined.

Response: Indeed. Thanks.

Lines 264-273. Some studies in North America (Weiss-Penzias et al., 2016) and Mace Head (Weigelt et al., 2015) observed a smaller decreasing trend in TGM during the recent decade. Was this observed at the six sites analyzed in this study? Explanations on long term TGM trends were provided by Lyman et al. (2020) and should be discussed in this paper.

Response: Yes, the period studied by Weiss-Penzias et al. and Weigelt et al. 2015 is contemplated in this study and new insights are stated. Lyman et al. (2020) is cited and discussed in section 3.2 of the new version.

Lines 281-294. The discussion of the trend at Villum is quite interesting. From Figure 3, there was a substantial increase in TGM from 2010 to 2014, which you attribute to melting of sea ice and subsequent GEM emissions. However, what caused the abrupt decline in TGM from 1.7 to 1.0 ng/m3 after 2014? Was that related to changes in sea ice?

Response: The abrupt decline corresponds mainly to the re-establishment of atmospheric circulation normality, and consequently, stopping the ice mass discharge. However, I am afraid that linking the abrupt decline in mercury at Villum after 2014 to sea ice would sound a bit speculative in the face of the presented results. More data would need to support such a conclusion.

Line 295. Did you analyze the CWT results for each site separately? The probable source regions are likely different depending on the site. Why were the CWT results combined for all sites?

Response: Combining back trajectories from different sites enhance and allows a broader evaluation of hotspots and regional sources of mercury besides avoiding a computation problem concerning the edges of the CWT where the density of trajectories are low. It is irrelevant the factor of CWT be different in different sites since it will not constrain the concentration density on a second site since concentrations are weighted by the frequency of air mass.

Lines 316-342. It would be useful to include a plot of the annual Hg emissions from central Europe and discuss the changes in anthropogenic emissions alongside with changes in TGM.

Response: See response to the first comment.

Line 348-349. "We compared the regional patterns of TGM with other pollutants (CO, CO2, CH4, O3, CHCl3, CCl4, and CFCs) also measured at Mace Head and find that TGM shows a similar pattern concerning source location as the other species closely related to anthropogenic sources." Are these results shown in the paper? Have you analyzed the trends for these co-pollutants and are they decreasing?

Response: The regional pattern of TGM is displayed in Figures 2 and 4. The regional patterns for the other mentioned species are not showed in this paper since they are well represented in the literature, included by satellite data products. All species considered in the factorization, which have trended in time-series, upward (CH4, N2O) or downward (CFCs), are detrended in the factorization.

Lines 352-367. This discussion of the CWT results and Figure 4 were discussed in the previous section. This discussion should be combined with the previous section.

Response: The discussion of Figure 4 was moved to 3.2 as proposed by the reviewer. Thanks for the comment.

Line 376-377. "The source apportionment indicates a baseline factor characterized by high load of anthropogenic species accounting for 65% of TGM mass." Has the percentage change over time? Was the PMF analysis conducted on the yearly data or the entire 25 year period?

Response: The PMF was conducted on daily data. The change over time based on a monthly average is displayed in Figure 5 and discussed in section 3.3. A new statement improving the description of PMF is presented in the new version of the article.

Line 383. It is not clear from the discussion how the baseline factor was extracted from the dataset. What pollutant markers were used to assign a PMF factor to the baseline factor? Please show a plot of the factor profiles from the PMF analysis.

Response: An additional plot with the "fingerprint" for the factors obtained from the PMF solution are presented in the supplement of the article. Thanks for the comment.

Line 390. What was the magnitude of the trend for the combustion factor and was it greater or smaller compared with the baseline factor?

Response: The magnitude of the trend for the combustion and ocean factors are displayed in Figure 5, together with the trend for the baseline factor.

The lack of a clear definition of the baseline factor is an issue especially if the objective was to evaluate the effectiveness of mercury control measures. The focus should be on understanding the different anthropogenic source sectors contributing to TGM and whether their contributions have changed over time, and if there are emerging sources that we need to be aware of. Also, what is the role of re-emissions of previously deposited Hg? Are the source apportionment tools able to improve the understanding of Hg re-emissions?

Response: We agree with the reviewer that a factorization solving the anthropogenic and emerging sources would be very valuable. However, we are not quite there yet. The prospect of improving our source apportionment method is to use more source markers. The propagation of the eigenvector from axis rotations can develop and permit better source apportionment. However, more source markers are still needed considered.

References:

Custodio, D., Ebinghaus, R., Spain, T. G., and Bieser, J., 2020. Source apportionment of atmospheric mercury in the remote marine atmosphere: Mace Head GAW station, Irish western coast, Atmos. Chem. Phys., 20, 7929–7939, https://doi.org/10.5194/acp-20-7929-2020

Lyman, S. N., Cheng, I., Gratz, L. E., Weiss-Penzias, P., and Zhang, L., 2020. An updated review of atmospheric mercury. Science of the Total Environment, 707, 135575, https://doi.org/10.1016/j.scitotenv.2019.135575