Dear Prof. Dommergue (ACP Editor):

We are submitting a second revision of our manuscript (EGUSPHERE-2024-2895), entitled "Natural Surface Emissions Dominate Anthropogenic Emissions Contributions to Total Gaseous Mercury at Canadian Rural Sites", for potential publication in Atmospheric Chemistry and Physics as part of the special issue, Mercury science to inform international policy: the Multi-Compartment Hg Modeling and Analysis Project (MCHgMAP) and other research.

We have addressed all the comments provided by Reviewer #2. Please see the enclosed authors' response to reviewers for details. The re-submission also includes a manuscript and supplement file with tracked changes. Thank you for taking care of the review process for this paper.

Sincerely,

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Response to Reviewer #2

We appreciate the comments from this reviewer and have provided responses to all comments and improved on the manuscript.

Thank you to the authors for having addressed my comments. I have two comments.
First, Reviewer #1 made an excellent suggestion about pooling data from all years for the PMF analysis. Using data from all years not only increases statistical power but also makes sense in terms of interpreting the results. A constant factor profile enables comparability across years and allows for the identification of trends in the same set of factors throughout the study period at individual sites. Interannual variation in source composition is reflected in the time-dependent factor scores.

When running PMF annually, the top six factors were determined based on their contribution to the total variance of TGM in each year. In principle, interannual variations in the contribution of the top factors and in the annual total variance of TGM could compromise the comparability of the quantitative contributions of factors between years. However, in this case, the authors obtained the exact same top six factors every year despite running PMF separately for each year. This suggests that these six factors were consistently dominant throughout the entire study period. It is likely that their results would not differ significantly if they had pooled data from all years together.

Response: In response to the previous suggestion from Reviewer #1, we had added the results from pooling data from all years (single run) for the SAT site to Supplement section S1, which confirmed there was no significant change to the findings of the study. We have now carried out the single runs for the other two sites (EGB and KEJ). The single run factor profiles and TGM source contributions for all sites are now presented in the main paper. We have replaced the previous discussions, figures, and tables of the yearly runs in the main paper and supplement.

The model-observation agreement from the single run was equally as good as those of the yearly runs for the SAT and KEJ sites; however, it was not the case for the EGB site. TGM source contributions for EGB were compared between the single run and yearly runs, and the discussion was added in the main paper (section 4.1). The section reads:

4.1 PMF yearly runs vs. single time series run

Additional PMF runs were conducted separately for each year, and the TGM source contributions for the six factors were compared with those of the single time series run. While the results between the two sets of runs were comparable for SAT and KEJ, clear differences were found for EGB. The PMF modelled TGM concentrations derived from the yearly runs were better correlated with the observed TGM (R^2=0.71; Fig. S8) than that from the single run (R^2=0.43; Fig. S1). Furthermore, the yearly runs produced a better fit of the interannual variability and long-term trends in TGM. In the yearly runs, the mean relative contribution of anthropogenic emissions to annual TGM was 27.5% at EGB, which was greater than the single run scenario. The Hg pool (63%) contributed the most to annual TGM followed by terrestrial GEM re-emissions (15.4%), crustal/soil

dust (8.7%), local combustion (5.9%), road salt (4.1%), secondary sulfate (1.8%), and wildfires (1.3%), respectively. These percentages are lower for the Hg pool and GEM re-emissions and are higher for crustal/soil dust, local combustion, road salt, and secondary sulfate compared to those of the single run. In the yearly runs, TGM contributions from the Hg pool was the main driver of the observed TGM trend, whereas there was no dominant driver of the TGM trend from the single run.

Figure S9a illustrates the model-observation discrepancies occurred in 2005-2009 and 2012-2013 in the single run. During 2005-2009, TGM contributions from the Hg pool, local combustion, crustal/soil, and road salt for the single run were smaller compared to those of the yearly runs (Fig. S9b). In 2012-2013, TGM contributions from the Hg pool and GEM re-emissions for the single run were greater than those of the yearly runs. The differences between the single and yearly runs may be caused by various reasons. The underestimation of the Hg pool and local combustion contributions suggests a constant factor profile assumption in the single run may not be valid over the long term because of changes in the emissions control technology affecting the speciation profiles as discussed in Zhang et al. (2016). Perhaps the estimated TGM abundance in the Hg pool factor and local combustion factor should be higher in the earlier period. For crustal/soil, road salt and GEM re-emission contributions, dust emissions and GEM (Hg^0) flux are highly variable. These processes could depend on land disturbance from agricultural activities at EGB, road salt applied, and meteorology. For GEM flux, it is also affected by soil temperature and its Hg content, moisture level, organic matter content, vegetation and litterfall cover, Hg uptake, and ambient Hg concentration. The TGM content in dust is affected by gas-particle partitioning. These complex processes are perhaps not well captured in the factor profiles and contributions for terrestrial re-emissions in the single run but are better modelled in the yearly runs. It is recommended that short-term runs be performed across the time series to confirm the single run PMF results are robust.

Zhang, Y., Jacob, D.J., Horowitz, H.M., Chen, L., Amos, H.M., Krabbenhoft, D.P., Slemr, F., St. Louis, V.L. and Sunderland, E.M.: Observed decrease in atmospheric mercury explained by global decline in anthropogenic emissions, Proc. Natl. Acad. Sci., *113*(3), 526-531, 2016.

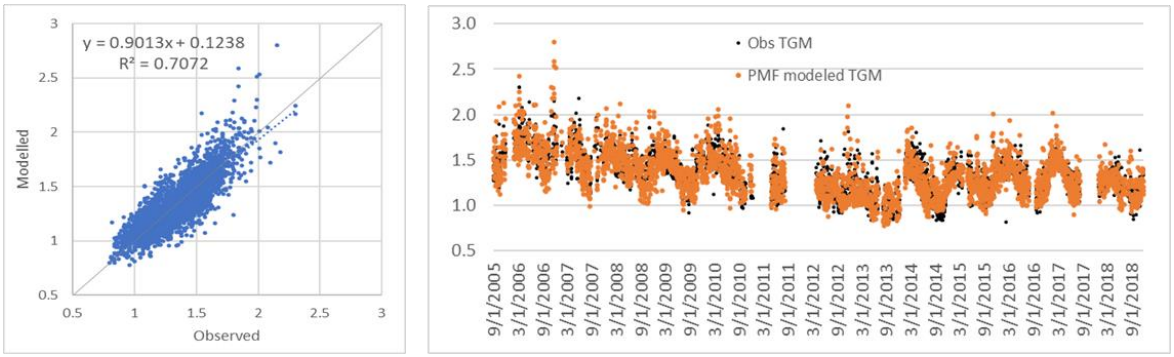

Figure S8: Comparison of PMF modelled and observed 24-h TGM (ng m^{-3}) for EGB using regression analysis (left) and time series analysis (right). PMF modelled TGM are based on yearly runs across the time series.

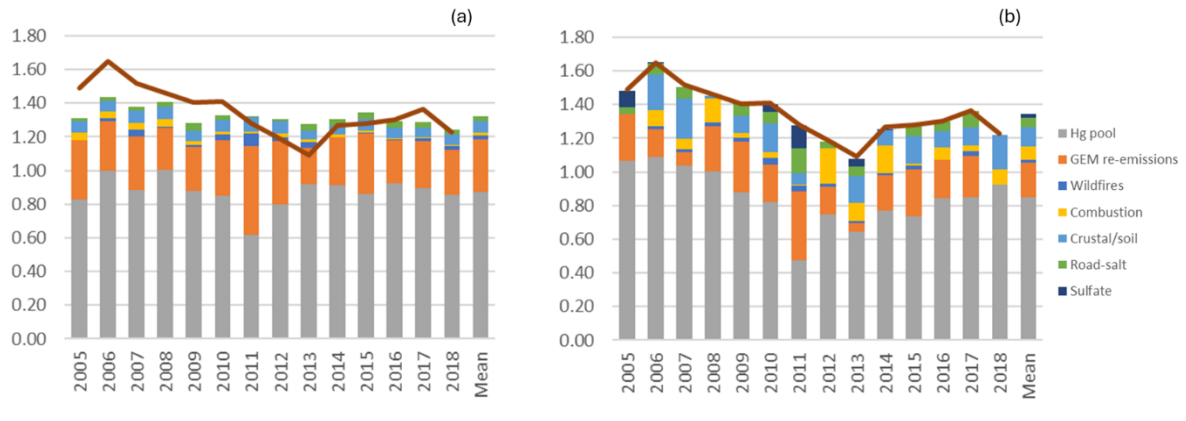

Figure S9: TGM annual source contributions (ng m^{-3}) at EGB for (a) single run and (b) yearly runs for 2005-2018. Bar graphs: PMF modelled TGM; red line: mean observed TGM.

I am unclear about what the authors mean by "variation" in their statement of "while the variability from year to year gives us an indication of the uncertainty in those profiles", and why they consider such variation to be "uncertainty in those profiles."

Response: Regarding the previous response to Reviewer #1, we agree that the statement was misleading. We are referring to the slight differences in the TGM concentrations in the factor profiles among the years when we performed the yearly runs. By contrast, the single run produces one profile which is constant across the time series. The factor profiles between the yearly runs and single run should be comparable if those six factors are prevalent throughout the time series as this reviewer noted, and this is a method that could be used to confirm the single run results are robust.

Second, the description of Figure 1 is inaccurate. What does "annual TGM" refer to? If it pertains to annual median values, then only EGB started to show a decreasing trend from 2009 to 2013 with the other two locations showing declines in later years. SAT started to see a return to higher values in 2014, while KEJ showed no such return, as its data ended in 2016. Additionally, it was unclear whether the decreasing trends before 2013 were statistically significant. Why were the values so different in 2006 and 2007 between EGB and KEJ?

Response: In the text, annual TGM refers to annual mean TGM. This has been clarified in sections 3.1.1, 3.2.1, and 3.3.1. The Fig. 1 caption now reads: "Box-whisker plots of annual summary statistics of 24-h average TGM concentrations (ng m^{-3}) at Egbert (EGB), Kejimkujik National Park (KEJ) and Saturna (SAT)". Based on the annual mean values, TGM decreased from 2009 to 2015 and then returned to higher concentrations in 2016 and 2018 at SAT. At EGB, the annual mean TGM decreased from 2005 to 2013 and then rebounded in 2014 with concentrations remaining stable during 2014-2018. At KEJ, the annual mean TGM decreased significantly from 2005 to 2006. A parabolic pattern was observed thereafter with concentrations increasing during 2006-2011 and then decreasing during 2012-2016.

Sections 3.1.1, 3.2.1, and 3.3.1 provide an overview of the TGM concentrations without examining the statistical significance. Note the long-term trends analysis (including the magnitude of the

trend and p-values showing the statistical significance level) is presented in sections 3.1.5, 3.2.5, and 3.3.5. It is clear from Fig. 6 (blue line graph) there was a decreasing trend in the observed TGM between 2006 and 2013 for EGB.

The large TGM difference between EGB and KEJ in 2006-2007 can be explained by the Hg emission patterns. Around EGB, Hg emissions based on the Canadian National Pollutant Release Inventory were high during 2006-2007 and only decreased sharply after 2008 followed by an increase starting in 2010 (Fig. S4). Around KEJ, Hg emissions decreased sharply in 2006 and then again in 2007 (Fig. S7), which was due to emissions reductions and the closure of a power plant.

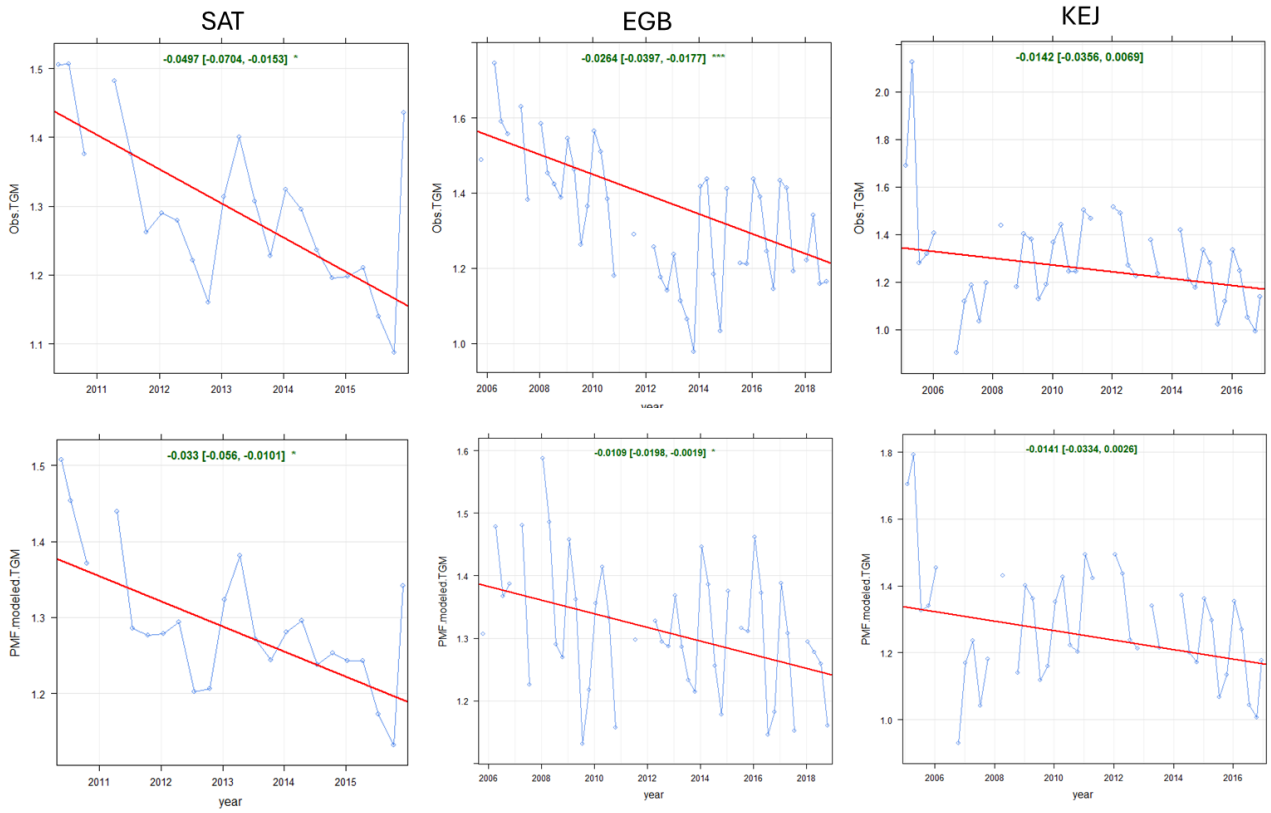

Figure 6: Long-term trends in observed and PMF modeled TGM concentrations at SAT, EGB and KEJ. Blue line: observed or modeled TGM; red line: trendline; green text: slope of the trendline (ng m^{-3} yr^{-1})

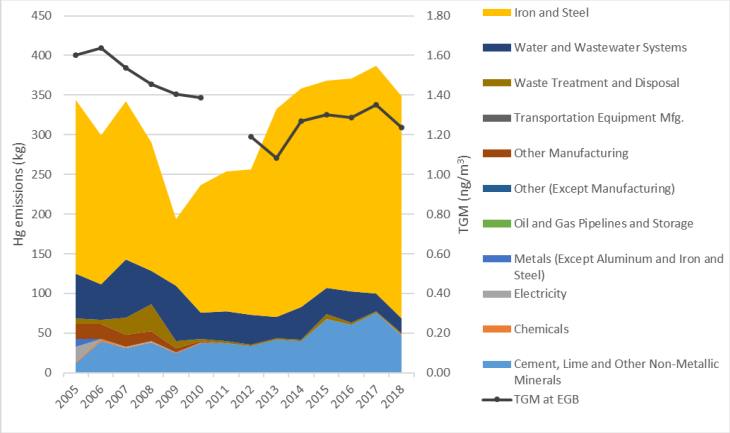

Figure S4: Hg emission sources within 150 km of EGB in Province of Ontario (ECCC NPRI, 2023)

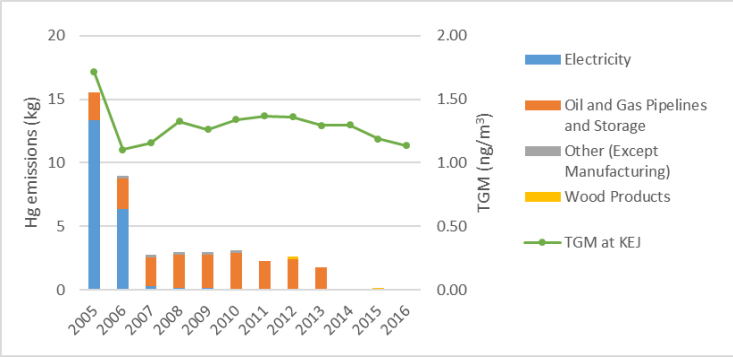

Figure S7: Hg emission sources within 150 km of KEJ in Provinces of Nova Scotia and New Brunswick (ECCC NPRI, 2023)