

Authors' Response to Reviewers

By Irene Cheng, Amanda Cole, Leiming Zhang, and Alexandra Steffen (Environment and Climate Change Canada)

Reviewer 2

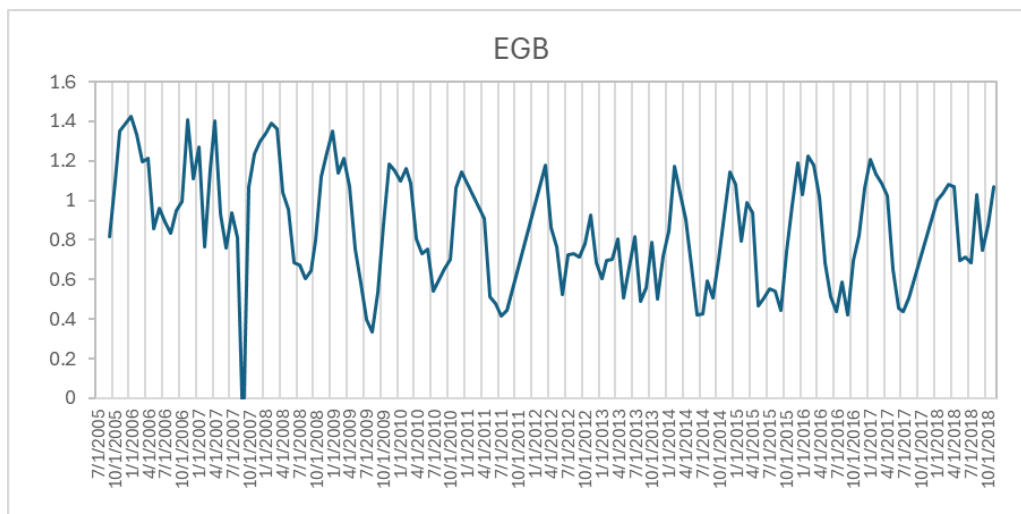
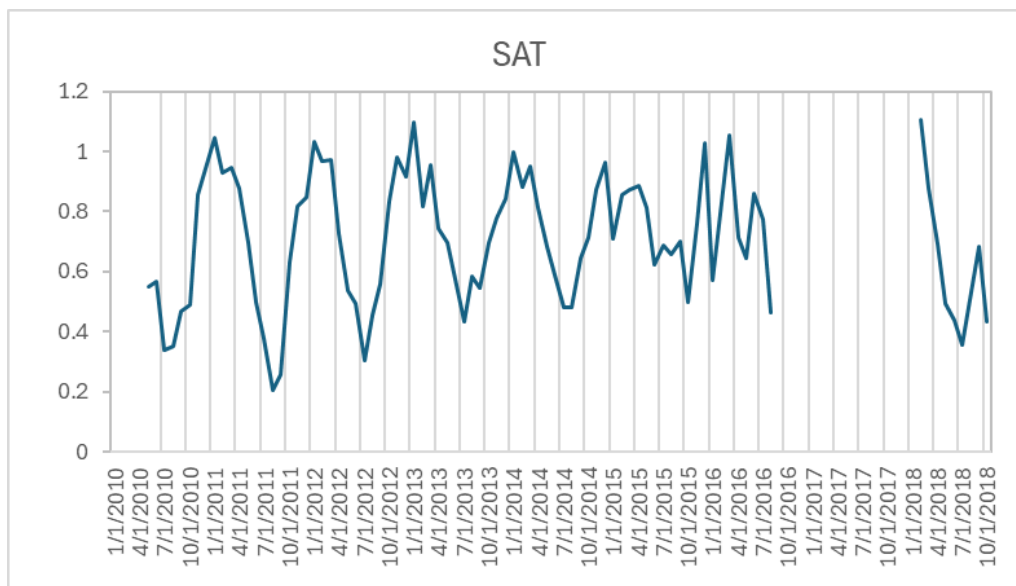
We appreciate the comments from this reviewer and have provided responses to all comments and improved on the manuscript.

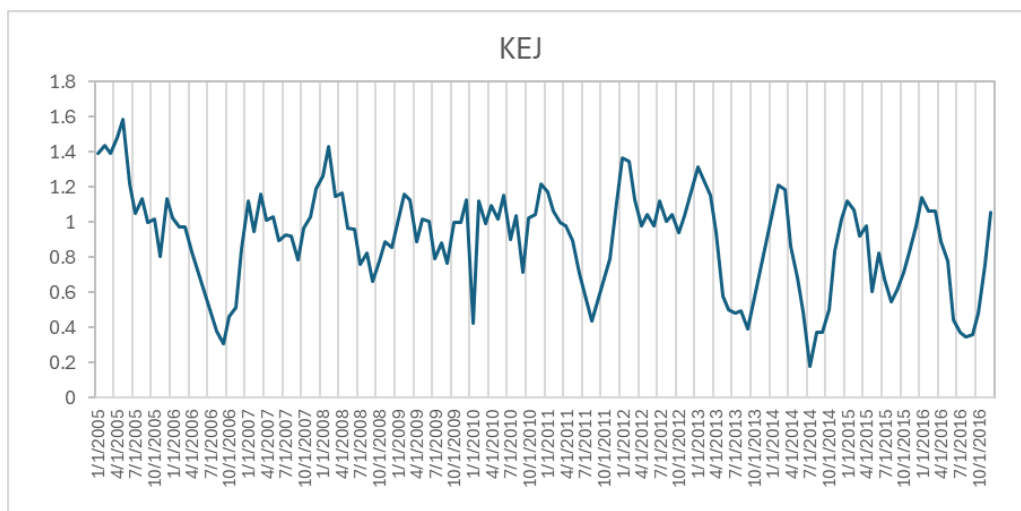
Cheng et al. performed a thorough analysis of TGM from three Canadian sites using PMF. I have a couple of concerns. First, I am not entirely convinced how some of the factors were identified, i.e., the background factor and the reemission/biomass burning factor. The background factor was identified because of the high abundance of CO and TGM, and the authors cited Weiss-Penzias et al. (2007) to back the decision. What was their definition of “background”? I took it as the baseline level at the site. Did they look into the correlation between CO and TGM? Chances are the two are correlated due to their similar seasonal patterns. CO has always been used as an anthropogenic tracer in the literature. The very reference, Weiss-Penzias et al. (2007), they cited used the CO-TGM correlation to demonstrate the impact of Asian pollution. Therefore, the authors' decision to use CO as a background tracer did not make sense to me. Numerous studies in the literature used TGM-CO correlation at sites to identify anthropogenic influence; yet the two compounds do not really share common sources. There is in fact a deeper meaning to this correlation, which is, in this reviewer's opinion, that the relationship really reflects the anthropogenic or wildfire burning emission ratios of TGM and CO over a studied region. Regarding the reemission/biomass burning factor, there were quite jarring inconsistencies in the concentrations of supposedly fire tracers. As is commonly known, biomass burning emissions can enhance CO, TGM, and K^+ . However, Fig. 2 showed K^+ at ~10%, similar to the values for the local combustion and fresh SSA factors and lower than the K^+ values (~15%) in the background, secondary sulfate and aged SSA factors, and also showed the lowest CO in this factor.

Response: In the revised paper, the ‘background’ factor was renamed to the Hg pool, which was discussed in section 2.2 and 3.1.2. This factor encompasses natural, anthropogenic, and re-emitted Hg mostly from the northern hemisphere that is subject to long range transport. It is not associated with any specific point sources, and CO is not being used as an anthropogenic tracer. As this reviewer noted, the Hg-CO relationship may be indicative of anthropogenic or biomass burning. CO is an indicator of the Hg pool and long-range transport because its lifetime is in the order of a few months, which allows for it to be transported over long distances (Jeffery et al., 2024). Given the relatively small magnitude of combustion sources near these rural and remote sites, it is not surprising that the CO emissions from these sources contribute a relatively small proportion of the total CO observed, which is dominated by the hemispheric background. This characteristic is similar to that of GEM and TGM. This has been clarified in the revised paper (section 3.1.2), which reads “The Hg pool was identified based on the high abundance of CO (56%). The Hg pool consists of natural, anthropogenic, and re-emitted Hg mostly from the Northern Hemisphere that is subject to long range transport (Selin and Jacob, 2008). CO is emitted from fossil fuel combustion and wildfires. It has a longer lifetime in the order of a few months compared with SO_2 , which allows for it

to be transported long distances by advection (Jeffery et al., 2024) and accumulate in the hemispheric background. This characteristic is similar to that of GEM and TGM.”

Based on monthly mean TGM contributions from the Hg pool, the seasonal patterns are more in line with anthropogenic emissions associated with winter heating across the northern hemisphere. TGM contributions from the Hg pool show a conspicuous seasonal cycle with a peak in the colder months and minimum in the warmer months (see graphs below). At SAT, the range in TGM contributions for the cold and warm season are 0.75-0.93 ng m⁻³ and 0.42-0.74 ng m⁻³, respectively. The range refers to the interannual variability. At EGB, the ranges were 0.67-1.35 ng m⁻³ for the cold season and 0.47-0.93 ng m⁻³ for the warm season. At KEJ, the ranges were 0.86-1.28 ng m⁻³ for the cold season and 0.38-1.03 ng m⁻³ for the warm season. If this factor was driven by wildfires, the warm (fire) season contributions would have been greater than those of cold season. Previous chemical transport modeling studies using the GEM-MACH-Hg model show only a small Hg contribution from wildfires at these sites (Fraser et al., 2018).





Hg re-emissions and wildfires were identified from a factor with a strong temperature signal (Figures 2, 8, and 12). This reviewer noted that Fig. 2 showed the K^+ percentage at $\sim 10\%$ in this factor, which is similar to the percentages in other factors. This may be because this factor is only partially due to wildfires, and re-emissions of GEM would not be associated with K^+ . As well, K^+ can also be released from crustal dust, soil and vegetation (Zhang et al., 2008) and is very common in pollen (Lee et al., 1996). Considering the site in question is coastal, the source of K^+ may include sea-salt aerosols. Potassium is also associated with coal combustion (Yu et al., 2018), although this is less likely the case for the rural-remote sites in this study. Thus, the sources of K^+ are wide-ranging, and it is not necessarily a strong indicator of wildfires especially if the wildfire area is far away from the monitoring site. This discussion was added to the revised paper (section 3.1.2), which reads “The K^+ percentage for biomass burning and re-emissions was comparable to those in other factors. This may be because this factor is only partially due to wildfires, and re-emissions of GEM would not be associated with K^+ . As well, K^+ can also be released from the continental crust, soil and vegetation (Zhang et al., 2008), and is very common in pollen (Lee et al., 1996). Since SAT is a coastal site, the source of K^+ may include SSA. Potassium is also associated with coal combustion (Yu et al., 2018), although this is less likely the case for the rural-remote sites in this study.” The novel approach that was applied in this study was using Fire Radiative Power (FRP) satellite data to screen wildfire contributions to TGM. This approach does not rely solely on presumed fire tracers; it also accounts for concurrent wildfire observations in the region surrounding each site. We examined correlations between observed K^+ concentrations and FRP on a daily and monthly scale for the SAT site. No strong relationships were found (r^2 of 0.0003 daily and 0.049 monthly), suggesting that K^+ was not the best fire tracer for the studied sites.

Fraser, A., Dastoor, A., and Ryjkov, A.: How important is biomass burning in Canada to mercury contamination?, *Atmos. Chem. Phys.*, 18(10), 7263-7286, 2018.

Jeffery, P. S., Drummond, J. R., Zou, J., and Walker, K. A.: Identifying episodic carbon monoxide emission events in the MOPITT measurement dataset, *Atmos. Chem. Phys.*, 24, 4253–4263, <https://doi.org/10.5194/acp-24-4253-2024>, 2024.

Lee, E. J., Kenkel, N., and Booth, T.: Atmospheric deposition of macronutrients by pollen in the boreal forest, *Ecosci.*, 3(3), 304-309, 1996.

Yu, J., Yan, C., Liu, Y., Li, X., Zhou, T., and Zheng, M.: Potassium: a tracer for biomass burning in Beijing?, *Aerosol Air Qual. Res.*, 18(9), 2447-2459, 2018.

Zhang, L., Vet, R., Wiebe, A., Mihele, C., Sukloff, B., Chan, E., Moran, M. D., and Iqbal, S.: Characterization of the size-segregated water-soluble inorganic ions at eight Canadian rural sites, *Atmos. Chem. Phys.*, 8, 7133–7151, <https://doi.org/10.5194/acp-8-7133-2008>, 2008.

Second, what does the “secondary sulfate factor” really mean? If I am not mistaken, it could indicate the role of secondary production of TGM. If it was correct, then the assumption of chemistry being negligible would be invalid. I’m curious how such a paradox can be reconciled.

Response: The secondary sulfate factor is indicative of regional Hg emissions and chemical transformation including oxidation and gas-particle partitioning. This is because the strong sulfate presence in a factor has been associated with regional emissions and oxidation of SO₂ from previous source apportionment studies (Liu et al., 2003; Keeler et al., 2006; Gratz and Keeler, 2011; Pancras et al., 2013). In previous studies, back trajectory analyses were produced for the studied sites (except SAT because of modeling over complex terrain) to estimate the fractional contributions of wind direction sectors to atmospheric sulfate deposition. The analyses showed the EGB and KEJ sites were frequently impacted by regional transport. There were regional contributions from the south-southwest sectors and west-northwest sectors for the EGB site and from the southwest and northwest sectors for the KEJ site (ECCC, 2004; Zhang et al., 2008). Additional explanation on the secondary sulfate factor were included in the revised paper (section 3.2.2), which reads “The secondary sulfate factor is indicative of regional Hg emissions and chemical transformation including oxidation and gas-particle partitioning. This is because the strong sulfate presence has been associated with regional emissions and oxidation of SO₂ from previous source apportionment studies (Liu et al., 2003; Keeler et al., 2006; Gratz and Keeler, 2011; Pancras et al., 2013). Previous back trajectory analyses showed the EGB site was frequently impacted by regional transport (ECCC, 2004; Zhang et al., 2008).”

The PMF model assumes a constant source profile, which may be violated in the case of chemical species undergoing transformation during transport from the source to receptor site, e.g. using gaseous elemental Hg (GEM) or gaseous oxidized Hg (GOM or RGM) data. As stated in section 2.2, TGM is the sum of GEM and GOM, which tends to be less impacted by chemical reactions. We have also limited the input of reactive or secondary species into PMF where possible; ozone and nitrate are also monitored at the sites but were not included in the PMF model. SO₂ and sulfate are necessary tracers to distinguish between local combustion vs. regional emissions and fresh vs. processed sea salt.

Environment and Climate Change Canada (ECCC): 2004 Canadian Acid Deposition Science Assessment, Meteorological Services of Canada, <http://www.publications.gc.ca/pub?id=9.688243&sl=0>, 2004.

Gratz, L. E., and Keeler, G. J.: Sources of mercury in precipitation to Underhill, VT, *Atmos. Environ.*, 45(31), 5440-5449, 2011.

Keeler, G. J., Landis, M. S., Norris, G. A., Christianson, E. M., and Dvonch, J. T.: Sources of mercury wet deposition in eastern Ohio, USA, *Environ. Sci. Technol.*, 40(19), 5874-5881, 2006.

Liu, W., Hopke, P. K., Han, Y. J., Yi, S. M., Holsen, T. M., Cybart, S., Kozlowski, K., and Milligan, M.: Application of receptor modeling to atmospheric constituents at Potsdam and Stockton, NY, *Atmos. Environ.*, 37(36), 4997-5007, 2003.

Pancras, J. P., Landis, M. S., Norris, G. A., Vedantham, R., and Dvonch, J. T.: Source apportionment of ambient fine particulate matter in Dearborn, Michigan, using hourly resolved PM chemical composition data, *Sci. Total Environ.*, 448, 2-13, 2013.

Zhang, L., Vet, R., Wiebe, A., Mihele, C., Sukloff, B., Chan, E., Moran, M. D., and Iqbal, S.: Characterization of the size-segregated water-soluble inorganic ions at eight Canadian rural sites, *Atmos. Chem. Phys.*, 8, 7133-7151, <https://doi.org/10.5194/acp-8-7133-2008>, 2008.

The manuscript is quite tedious to read. The approach is mechanical. The interpretation of the analysis results is somewhat arbitrary. There is potential to this study, but the authors might want to put more effort into thinking through the interpretation of their results.

Response: The manuscript text has been revised and condensed with greater emphasis on the interpretation of the PMF factors and major results of the study. We have provided clarification on using CO as a tracer of the Hg pool and long-range transport (section 3.1.2) and discussions on the secondary sulfate factor and additional K⁺ sources to explain the presence of the ion in other PMF factors (section 3.2.2).

Few source apportionment studies have estimated the relative contributions of sources to TGM over different time scales including annual, seasonal, daily, and on a long-term basis. These results, while detailed and statistical in nature, may be of interest to other readers. We have refined the long-term trends section to focus on the main causes of the long-term annual TGM concentrations, which is a fundamental policy question of the Minamata Convention on Mercury. Additional discussions on long-term TGM source contribution trends for the cold and warm seasons were moved to Supplement S4.