

Review of “Atmospheric mercury observations from Antarctica: seasonal variation and source and sink region calculations” by K. Aspmo Pfaffhuber et al., submitted to Atmospheric Chemistry and Physics (doi:10.5194/acpd-11-29117-2011).

General Comments

This paper presents an analysis of gaseous elemental mercury (GEM) and ozone (O₃) measurements made at the Norwegian Antarctic Research Station, Troll (TRS) from 2007–2011. The Lagrangian particle dispersion model FLEXPART is used to analyze potential source and sink regions for GEM and O₃ corresponding with the TRS measurements. The authors’ analysis suggests, among other features of the spatial distribution of GEM sources/sinks, a sink for GEM over the Antarctic plateau during summer. The spatial distribution of the summertime GEM sink appears to differ significantly from that found during springtime. This observation, together with the coinciding O₃ source/sink distributions indicates that the chemistry responsible for summertime GEM depletion over the Antarctic plateau is distinct from springtime GEM depletion in the Arctic and Antarctic linked primarily to halogen chemistry over coastal regions. The demonstrated spatial correlation between FLEXPART ‘footprint’ emission sensitivities associated with GEM depletion and O₃ production over the Antarctic plateau during summer, in relation to measurements during four consecutive summer seasons at TRS, is in fact quite remarkable. The authors highlight that summertime GEM depletion in the Antarctic differs significantly from behavior observed in the Arctic.

The data and results presented in this paper are important for our understanding of the global distribution of Hg. The results argue strongly for further study of GEM depletion over the Antarctic Plateau during summer, which quite possibly could lead to surprising new insight into the photochemical processes governing removal of Hg from the atmosphere.

My primary criticism is that information presented in parts of the Methods section is somewhat ambiguous regarding the conditions under which the GEM measurements were performed. However, it seems that the inclusion of a few additional explanatory sentences will be sufficient to resolve this issue.

The paper is recommended for publication in Atmospheric Chemistry and Physics after the above mentioned issue is addressed (see “Specific Comments” below) and after additional minor technical corrections are made as indicated under “Technical Corrections”. The authors are further encouraged to present some additional O₃ data to enrich the presentation of their results (see “Specific Comments” below).

Specific Comments

1. Section 2.2: The authors state that “The internal calibration source was checked against manual injections once per year”. A reader familiar with atmospheric Hg measurements would conclude from this statement that a saturated Hg vapor primary standard was used. However, for completeness it should be explicitly stated that such a standard was used. Was the primary standard a Tekran 2505 module or some other saturated Hg vapor source? It should be indicated whether the injections were performed on ambient air or on zero air. Additionally, the accuracy of the measurements as determined by the permeation source verification procedures should be quoted. This information is highly valuable to the mercury community for the purpose of

understanding the comparability of measurements made by different groups and at different study locations.

2. Section 2.2: The authors state that “More details on the instrumental set-up and quality control can be found in Hansen et al. (2009), Berg et al. (2003) and Aspmo et al. (2005)”. The Aspmo et al. (2005) paper describes atmospheric Hg measurements performed in the Arctic at the Zeppelin station with a Tekran 1130 module upstream of the GEM analyzer. From this reference and the information presented in the current paper it is unclear which part of the Aspmo et al. (2005) experimental description is relevant to the methods discussed in the current paper. Furthermore, there are notable discrepancies between the instrument configurations described in Aspmo et al. (2005) and in Berg et al. (2003) (e.g. regarding sample line heating and particle filtration). Given the above ambiguities, it is necessary that the authors be more specific regarding which parts of their experimental setup were described in the cited references. For instance, it should be clearly indicated how the inlet was filtered, whether the sample line was heated, and whether a soda-lime trap was used. This information will help facilitate comparison of methods employed in this work with those used in other studies (see also Comment 3 below).

3. Section 2.2: There currently exists some uncertainty regarding the fraction of gaseous oxidized mercury (GOM) which is measured with GEM by the Tekran 2537 analyzer when GOM species are not removed from the sample stream (e.g., by the Tekran 1130 module). When the fraction of GOM measured is unknown it is difficult to determine whether the measurement represents GEM only or a larger fraction of total gaseous mercury (TGM). When the inlet is filtered and the sample stream is passed through soda-lime traps, it is assumed that particle-bound Hg (PHg) and GOM compounds are effectively trapped and that the measurement is in fact representative of GEM. The authors present their data as a record of GEM measurements, yet they do not provide adequate information on how the Hg inlet was filtered and whether soda lime traps were used. A few brief comments on the GEM/TGM distinction and how PHg/GOM was removed from the sample stream would be helpful for completeness.

4. Section 2.3, Paragraph 2: The authors state “Conversely, when using the lowest decile of the data, $R_{10}(i, j) > 0.1$ indicates a likely sink in grid cell (i, j) , and $R_{10}(i, j) < 0.1$ a source”. By analogy to the discussion on interpreting values of $R_{90}(i, j) >$ or < 0.1 , it seems that it is more correct to say that $R_{10}(i, j) < 0.1$ indicates the absence of a sink, rather than a source.

5. Section 3.2, Paragraph 2: The authors state that “In spring and summer (August–February) GEM concentrations are highly variable ranging from 0.02 to 6.04 ng m⁻³ and with mean concentrations of 0.86 ± 0.24 ng m⁻³”. Contrary to this statement, Figure 2 shows a maximum GEM concentration of 3 ng m⁻³. No mention of whether values above 3 ng m⁻³ were excluded from Figure 2 is made. This discrepancy should be clarified.

6. Section 3.2: Although a main focus of this paper is a comparison between the seasonally averaged spatial distributions of GEM and O₃ sources and sinks, the presentation of the data could be enriched by inclusion of some quantitative information on the O₃ measurements. It would be helpful to present the O₃ data as is done for GEM in Figures 1 and 2. Also, it seems that an inclusion of some summary statistics on the O₃ measurements (e.g., annual/seasonal mean/median) would be valuable to the reader for comparison to other measurements made in the Antarctic region. The decision to include such additions depends on the authors’ discretion.

7. Sections 2.3 and 3.4: It is unclear whether values of the 10th and 90th percentile GEM and O₃ concentrations were computed separately for each season or if these values were computed for the entire dataset, which was then divided into seasons before constructing the plots of R_{10} and R_{90} in Figures 3 and 4. The distinction seems important, as it should influence the calculation of R_{10} and R_{90} . Please clarify this issue. Also, it would be helpful to specify the 10th and 90th percentile values of the GEM and O₃ concentrations that were used in determining the R_{10} and R_{90} distributions.

8. Section 3.4, Paragraph 1: The authors state that “In the Antarctic case, the spring-time oceanic sink appears to be weaker (Fig. 3f)”. The text seems to imply a comparison with the springtime oceanic sink in the Arctic based on the results of Hirdman et al. (2009), yet the data presented in Figure 3 and elsewhere in the paper seem to be insufficient to support this conclusion. This statement needs clarification. Perhaps reference to Figure 1 in Hirdman et al. (2009) and/or a comparison of springtime oceanic R_{10} values determined for Zeppelin and TRS would be helpful.

9. Section 3.4, Paragraphs 3 and 4: Here the authors begin to discuss specific regions of the Antarctic, in addition to the Antarctic Plateau, including the Ross and Weddell Seas. For readers less familiar with the geography of Antarctica an annotated map highlighting the different regions discussed (or a reference to such a map published previously) would be helpful for following the discussion. It is entirely the authors’ choice whether to include such a figure/reference.

10. Section 3.4: A time series plot showing the anti-correlation between GEM and O₃ during a summertime GEM depletion episode would be a valuable addition to the authors’ discussion of the relationship between GEM depletion and O₃ production over the Antarctic Plateau during summertime. Including such a plot would be helpful, but it is not necessary that the authors do so.

11. Section 3.4, Paragraph 5: The authors state that “The high concentrations of GOM observed at the coastal sites by Temme et al. (2003a) and Sprovieri et al. (2003) **must** have been transported from the Antarctic Plateau to the measurement location”. It seems that without further analysis of the Temme et al. (2003a) and Sprovieri et al. (2003) measurements, in line with the analysis of the TRS data, this assertion should be softened to read “**were likely to**” rather than “**must**”.

12. Section 4, Paragraph 1: The authors state that “Significant long-term decreases in GEM concentrations are observed at many monitoring sites both in the Northern Hemisphere and at Cape Point, South Africa as a response to decreasing mercury emissions”. This statement does not appear to be true in general. As discussed in Slemr et al. (2011) decreases in atmospheric Hg concentration over the past ~15 years cannot be explained by changes in anthropogenic emissions, which are expected to have been nearly constant over this time period, but could be due to decreasing ‘legacy’ Hg emissions. The authors should be clearer regarding which emissions have likely been decreasing.

13. Section 4, Paragraph 4: The authors state that “The Antarctic Plateau is a highly oxidizing environment in summer; resulting in efficient release of NO_x from the snowpack leading to high NO mixing ratios. The NO/NO₂ cycling rapidly enhances radical concentrations, such as OH, which further leads to increased O₃ production”. The wording here seems somewhat convoluted. I suggest that the authors revise these sentences to read more similar to the discussion in Section 3.4, Paragraph 5, which better describes snowpack NO_x emission as a precursor to highly

oxidizing conditions in the summertime Antarctic Plateau mixed layer (as discussed for example in Davis et al., 2008).

14. Section 4, Paragraph 4: The authors state that “This **shows** that the elevated summertime concentration of oxidized mercury species observed by others at coastal locations results from different chemical processes than those causing AMDEs”. As in Comment 11, the authors are advised to be more cautious in extending the conclusions drawn from their results to different data sets collected at different locations in the Antarctic without further analysis. Using the word “**suggests**” rather than “**shows**” here seems more appropriate.

Technical Corrections:

1. Section 1, Paragraph 2: “A long-term monitoring program **of GEM** was initiated...” should be reworded.
2. Section 3.1, Paragraph 1: “whereas the distribution is shifted towards lower concentrations **as** TRS...” should read “**at**”.
3. Section 3.1, Paragraph 1: “mercury emissions sources are located **on** the Northern Hemisphere...” should read “**in**”.
4. Section 3.4, Paragraph 3 and References: Kaleschke et al. (2005) is cited in the text, while Kaleschke et al. (2004) is cited in the Reference list. Please check this reference.
5. Section 3.4, Paragraph 5: “because GEM and O₃ **anti-correlates**” should read “**are anti-correlated**” or similar.
6. Section 4, Paragraph 2: “Spring and summer **shows** highly variable GEM concentrations...” should read “**show**”.
7. References: Please correct typographical errors in the Davis et al. (2008) reference.
8. References: The Priddle (2002) reference needs to be properly alphabetized.

References

Slemr, F., Brunke, E.-G., Ebinghaus, R., and Kuss, J.: Worldwide trend of atmospheric mercury since 1995, *Atmos. Chem. Phys.*, 11, 4779–4787, doi:10.5194/acp-11-4779-2011, 2011.