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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric mercury observations from Antarctica: seasonal variation and source and sink region calculations" *by* K. Aspmo Pfaffhuber et al.

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We thank the anonymous referee for helpful comments to improve the quality of the manuscript. Please see our responses below.

Specific comments from the reviewer:

Comment 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

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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.

Authour comment (AC): We have added the suggested clarifications to the text.

Comment 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).

AC: We have added some text to clarify the above mentioned ambiguities, and removed instrument setup reference to Berg et al., 2003 and Aspmo et al., 2005.

Comment 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

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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.

AC: At Troll an extra Teflon filter was placed at the inlet of the sample line, but no soda lime trap was used. HgP is removed by this filter and we also claim that GOM is removed with this extra filter and thus only GEM is collected (Steffen et al., 2002). Without this extra filter total gaseous mercury (TGM) would have been collected, which includes both the GEM and GOM species (Ebinghaus et al., 2002). In a study at Ny-Ålesund (Berg et al., 2003) a cold Teflon grid was used in front of a denuder collecting GOM (referred to as RGM in the paper). Large parts of the GOM were collected on this grid, which is due to the cold surface and or GOM's high affinity to any surface.

Comment 4. Section 2.3, Paragraph 2: The authors state "Conversely, when using the lowest decile of the data, R10(i, j) > 0.1 indicates a likely sink in grid cell (i, j), and R10(i, j) < 0.1 a source". By analogy to the discussion on interpreting values of R90(i, j) > or < 0.1, it seems that it is more correct to say that R10(i, j) < 0.1 indicates the absence of a sink, rather than a source.

AC: We agree with the reviewer and the sentence is changed to the following: Conversely, when using the lowest decile of the data, R10(i ,j) > 0.1 indicates a likely sink in grid cell (i ,j), and R10(i ,j)<0.1 a source or at least the absence of a sink.

Comment 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

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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.

AC: The authors apologize for the inconvenience of a typographical error; the highly variable GEM concentrations range from 0.02 to 3.04 (not 6.04 as stated in the text). This typo is corrected in the text.

Comment 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.

AC: We have added O3 box plots to figure 1 (in the new version of the manuscript figure 2), similar to the GEM box plots. We have chosen to leave O3 time series out of figure 2 (now figure 3) in order to keep this figure as simple as possible. However, we have chosen to add one new figure showing GEM and O3 concentration time series for short time periods during different seasons, as partly suggested in comment 10. This new figure shows the small concentration variability in winter, the strong correlation between GEM and O3 in spring and the anti-correlation in summer.

Comment 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 R10 and R90 in Figures 3 and 4. The distinction seems important, as it should influence the calculation of R10 and R90. Please clar-

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ify 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 R10 and R90 distributions.

AC: The calculations of the 10th and 90th percentiles for the GEM and ozone concentrations have been made for each month separately over each of the years with available measurements. Thereafter, the results for the months in each of the predefined seasons have been combined together over the whole time period (2007-2010) after which we calculated the Rp fields shown in Figures 3 and 4. This clarification is also added to the text in section 2.3. We have chosen not to specify percentile values in a separate table as suggested, because these values are represented in the box plots for GEM and O3 in figure 2b and d as the whiskers above and below the box.

Comment 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 R10 values determined for Zeppelin and TRS would be helpful.

AC: We have added a reference to figure 1e in Hirdman et al., 2009 and included the maximum R10 values in both studies.

Comment 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.

AC: We agree that readers may not be familiar with the Antarctic geography, and have

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decided to include a map highlighting the areas discussed in the manuscript. This is figure 1 in the revised manuscript.

Comment 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.

AC: We agree, this would be helpful to the reader, consequently we have added such a plot. See also our reply to comment 6.

Comment 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".

AC: We agree that our initial statement needs to be softened; "must" is replaced with "were likely".

Comment 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 $\sim$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.

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AC: We agree, this statement was poorly explained. The text is changed according to the referee's suggestion.

Comment 13. Section 4, Paragraph 4: The authors state that "The Antarctic Plateau is a highly oxidizing environment in summer; resulting in efficient release of NOx 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 NOx emission as a precursor to highly oxidizing conditions in the summertime Antarctic Plateau mixed layer (as discussed for example in Davis et al., 2008).

AC: Due to a discussion with C.D. Holmes the conclusion is slightly changed and as a result of this discussion the snowpack NOx emission being coupled to GEM depletion is toned down in the text in general and left out of the conclusion.

Comment 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.

AC: We agree that we should be more cautious extending our results to other studies. We have changed the wording according to the referee's suggestion.

Technical Corrections

Comment 1. Section 1, Paragraph 2: "A long-term monitoring program of GEM was initiated..." should be reworded.

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AC: We are not completely sure what the referee want however, the sentence is changed to the following: To extend the global mercury database and improve the current understanding of the atmospheric transport, transformation and removal processes of GEM over Antarctica, long-term monitoring of GEM at the Norwegian research station Troll was started in 2007.

Comment 2. Section 3.1, Paragraph 1: "whereas the distribution is shifted towards lower concentrations as TRS. . ." should read "at".

AC: Done

Comment 3. Section 3.1, Paragraph 1: "mercury emissions sources are located on the Northern Hemisphere. . ." should read "in".

AC: Done.

Comment 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.

AC: The reference should be Kaleschke et al., 2004. This is changed in the text.

Comment 5. Section 3.4, Paragraph 5: "because GEM and O3 anti-correlates" should read "are anti-correlated" or similar.

AC: Done

Comment 6. Section 4, Paragraph 2: "Spring and summer shows highly variable GEM concentrations. . ." should read "show".

AC: Done

Comment 7. References: Please correct typographical errors in the Davis et al. (2008) reference.

AC: Done

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Comment 8. References: The Priddle (2002) reference needs to be properly alphabetized.

AC: We do not fully understand what the referee means by “properly alphabetized”. However, we have added the total number of pages of the report.

References:

Steffen, A., Schroeder, W., Bottenheim, J., Narayan, J. and Fuentes, J.D.: Atmospheric mercury concentrations: measurements and profiles near snow and ice surfaces in the Canadian Arctic during Alert 2000, Atmos. Environ., 36, 2653-2661, 2002.

Ebinghaus, R., Kock, H.H., Temme, C., Einax, J.W., Lowe, A.G., Richter, A., Burrows, J.P. and Schroeder, W.H.: Antarctic springtime depletion of atmospheric mercury, Environ. Sci. Tech., 36, 1238-1244, 2002.

Berg T., Sommar J., Wängberg I., Gårdfeldt K., Munthe J. and Schroeder W.H.: Arctic mercury depletion events at two elevations as observed at the Zeppelin Station and Dirigibile Italia , Ny-Ålesund, spring 2002. J. Phys. IV France 107, 151-154, 2003.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 29117, 2011.