“New insights into the atmospheric mercury cycling in Central Antarctica and implications at a continental scale” by H. Angot et al.

Response to referee comments by Referee #1.

We thank this anonymous referee for insightful questions and comments. We provide below a point-by-point reply to the comments (points raised by the referee in bold, changes made in the manuscript in red).

1. General comments

The manuscript is well written and presents a novel dataset of atmospheric mercury and mercury in snow interstitial air covering slightly more than one annual cycle. Mercury measurements from Antarctica is generally scarce in particular good data covering more than the summer season, so this manuscript will definitely be a longed for addition to the pool of mercury data for the scientific community, both for experimentalists and modelers. The references used are recent and relevant. The structure of the result and discussion chapter is complicated. The text jumps between different environmental compartments (atmosphere and snow interstitial air) and seasons, which makes it ponderous to follow the discussion. The authors should consider re-arranging the sections within the results and discussion chapter.

We agree with the referee regarding the structure of the results and discussion chapter. In the revised manuscript we have changed the structure as follows in order to avoid jumps between different environmental compartments (atmosphere and snow interstitial air) and seasons.

3. Results and Discussion

3.1 Hg(0) concentrations in ambient air

- 3.1.1 Spring
- 3.1.2 Summertime
  - a) Oxidation of Hg(0) in ambient air and Hg(II) deposition onto snowpack
  - b) Multi-day depletion events of atmospheric Hg(0)
  - c) Hg(0) diurnal cycle
- 3.1.3 Fall
- 3.1.4 Winter

3.2 Hg(0)/Hg(II) redox conversions within the snowpack

- 3.2.1 Sunlit period
- 3.2.2 Winter

4. Implications at a continental scale

2. Scientific comments

- Line 65-70: The manuscript text says that the Antarctic plateau was first considered to be chemically inactive for atmospheric species including Hg and a paper from 2008 is cited. The manuscript test further says that it turned out to be highly active, now citing a paper from 2001 and 2007. To me there is a lack of logic in this argument.

We agree. In the revised manuscript we now refer to an older reference:

"The Antarctic plateau (...) was first considered to be chemically-inactive and a giant cold trap for atmospheric species~~, including mercury~~ (e.g., Lambert et al., 1990). It turned out to be highly photochemically active (Davis et al., 2001; Grannas et al., 2007)…"

- Line 131: Was mercury saturated manually? I assume you mean manually injecting saturated mercury.

Yes indeed. This has been corrected in the revised manuscript.

- Line 144-146: QA/QC; Interesting that you use internal standard on the 2600, what was used as internal standard? Why not use commercially available control samples?

These questions have been addressed in the revised manuscript:

"The instrument was calibrated with the NIST SRM-3133 mercury standard. Quality assurance and quality control included the analysis of analytical blanks, replicates, and internal standards (Reference Waters for mercury: HG102-2 at 22 ng/L from Environment Canada)."

- Line 202-204: This was an elegant way of defining seasons!

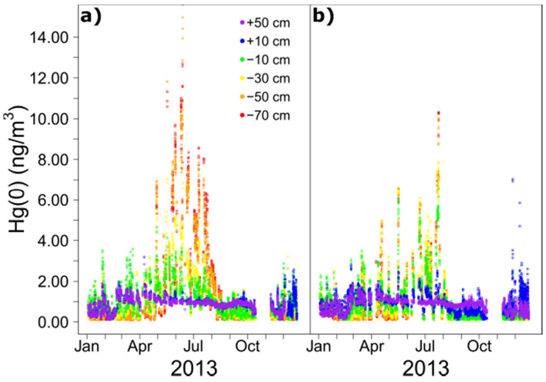
Thank you.

- Line 211-212: Troll can hardly be called a coastal site as it is situated almost 250 km from the coast and at almost 1500 masl. However, due to its location Troll experiences air from both the Antarctic plateau and the southern Ocean, but it is not a coastal site.

We agree that Troll can hardly be called a coastal site. This has been corrected in the revised manuscript:
"(…) Hg(0) concentrations are lower than annual averages reported at near-coastal or coastal Antarctic stations..."

- Line 259-263: I like the figure showing the vertical distribution of Hg(0) concentrations, however I think it could also be interesting for the audience to present a figure showing time series of Hg(0) in SIA as well. The atmospheric Hg(0) time series seems well covered in other figures.

A Figure displaying the annual variation of Hg(0) concentrations in the snow interstitial air collected at the various inlets of the two snow towers has been added in the revised manuscript:



"Figure 10: Annual variation of hourly-averaged Hg(0) concentrations (in ng/m^3) in the snow interstitial air collected at the various inlets of the two snow towers: **a)** snow tower #1, **b)** snow tower #2. Note that we regularly experienced technical problems on snow tower #2 leading to missing values."

- Line 356 and throughout the paragraph: I am not quite sure but I believe it is general consensus regarding the use of the term "depletion event" being oxidation of Hg resulting from bromine photochemistry and high correlation with tropospheric ozone depletions. The multi-day low concentrations described in chapter 3.5 are a different mechanism and should consequently be called something else.

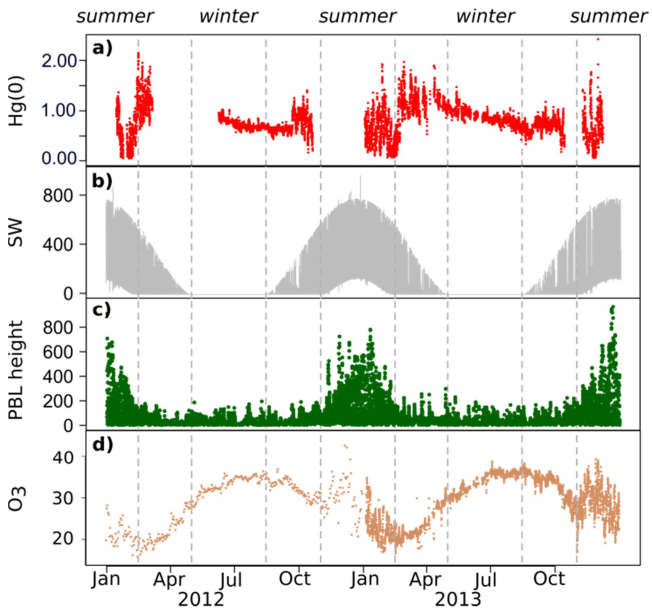
We are not sure that renaming a depletion of mercury specific to this site is warranted. A "depletion event" is just a depletion of Hg(0), and is not specific to the halogen chemistry. We do understand that some may associate it but "depletion event" is a more generic term than that.

- Line 391 and throughout chapter 3.6: A mechanism for reduced Hg(0) during winter is proposed, and it is also mentioned that this reductions are not observed at Troll or Neumayer. Any thought on why this reaction mechanism does not occur at Troll or Neymayer? Do you believe this reaction mechanism occur throughout the Antarctic plateau?

The reason why this reaction mechanism does not occur at Troll or Neumayer is unclear. This could be due to meteorological conditions on the Antarctic plateau (e.g., temperature, relative humidity, boundary layer dynamics). Further research is clearly needed. Our sense is that this reaction mechanism might occur throughout the Antarctic plateau, but the spatial distribution of Hg(0) measurements should be improved.

- Additionally, as you have O3 measurements it would be interesting to have them presented in fig 12 alongside Hg(0) since O3 is suggested to be involved in the Hg(0) wintertime decrease.

Figure 12 shows that – despite the overall decreasing trend in winter – Hg(0) concentration exhibited abrupt increases when moist and warm air masses from lower latitudes occasionally reached Concordia Station. Key parameters are therefore Hg(0), integrated water vapor, and temperature. We do not think that adding O_3 measurements here would be relevant. However, the annual variation of O_3 measurements in 2012 and 2013 has been added in Figure 3 of the revised manuscript.



"Figure 3: Annual variation in 2012 and 2013 of a) hourly-averaged Hg(0) concentrations (in ng/m^3) at 500 cm and 25 cm above the snow surface in 2012 and 2013, respectively, b) downwelling shortwave (SW) radiation (in W/m^2), c) planetary boundary layer (PBL) height (in m), and d) ozone (O_3, daily mean in 2012 and hourly mean in 2013) mixing ratios (in ppbv). The vertical dashed lines represent seasonal boundaries."

- The authors should perhaps also have a look at a very recent paper by Nerentorp Mastromonaco et al., 2016 (Atmospheric Environment) where winter depletions are present and to check whether this may have any relevance for the winter decreasing trend observed in this study.

Thank you for the suggestion. Nerentorp Mastromonaco et al. (2016) observed Atmospheric Mercury Depletion Events (AMDEs) during Antarctic winter over sea ice areas and proposed a dark mechanism in the marine boundary layer. It should be noted that such events have never been reported on the Antarctic continent (coastal or inland stations). Given the distance of Concordia station from sea ice areas a similar dark mechanism seems unlikely.

3. Technical comments

- Line 412: Several characters in the equation disappear in print

Thanks for noticing that. We will make sure there is no such problem in the final version of the manuscript.

- Figure 6: It is difficult to tell the difference between summer and spring/fall colours in the figure and I would very much like to see something similar to box and whisker plots to be able to tell the concentration distribution at each height at each season.

The color for spring/fall values has been changed in the revised manuscript. It should now be easier to tell the difference between summer and spring/fall colors. The concentration distribution at each height at each season can be inferred from the Figure we have added in the revised manuscript (see comment line 259-263).

- Figure 9: Hg(0) concentrations, which measurement height do the results represent?

This has been added in the caption of the revised manuscript:

"Figure 7: Hourly (local time) mean variation, along with the 95% confidence interval for the mean, of: **a)** Hg(0) concentration (in ng/m^3) at 25 cm above the snow surface, **b)** downwelling shortwave (SW) radiation (in W/m^2) according to the MAR model simulations, **c)** temperature (in °C) at 3 m above the snow surface, **d)** wind speed at 3 m above the snow surface (in m/s), **e)** planetary boundary layer (PBL) height (in m) according to the MAR model simulations, **f)** friction velocity (u_*, in m/s), and **g)** Eddy diffusivity (K, in m^2/s) in summer (red), fall (green), winter (blue), and spring (purple). Note that the hourly mean variation of Hg(0) concentration in summer is similar at the three inlets of the meteorological tower".

- Figure 11: Same comment as above, please indicate at which height the Hg(0) measurements are from.

This has been added in the caption of the revised manuscript:

"Figure 6: Top: January and February 2012 cycle of: **a)** hourly-averaged Hg(0) concentrations (in ng/m^3) at 500 cm above the snow surface, **b)** Integrated Water Vapor (IWV, kg/m^2), **c)** Temperature (in °C) at 10 m above ground level, and **d)** ozone (O_3, daily mean) mixing ratios (ppbv). Hg(0) was low from 19 January to 8 February (period highlighted in red) while O_3 showed no abnormal variability. Bottom: January and February 2013 cycle of: **e)** hourly-averaged Hg(0) concentrations (in ng/m^3) at 210 cm above the snow surface, **f)** Integrated Water Vapor (IWV, kg/m^2), **g)** Temperature (in °C) at 10 m above ground level, and **h)** ozone (O_3) mixing ratio (ppbv). Hg(0), IWV, and temperature were low from 5 to 20 February (period highlighted in red) while O_3 showed no abnormal variability. Note that Hg(0) concentrations exhibited the same pattern at the three inlets of the meteorological tower from 5 to 20 February 2013".

- Figure 12: same comment as above.

This has been added in the caption of the revised manuscript:

"Figure 9: Year 2012 wintertime record of: **a)** hourly-averaged Hg(0) concentrations (in ng/m^3) at 500 cm above the snow surface, **b)** Integrated Water Vapor (IWV, kg/m^2), and **c)** Temperature (T, °C) at 10 m above ground level. Hg(0), temperature, and IWV increased from June 12 to 15 (in red) suggesting transport of moist and warm air masses originating from lower latitudes."

4. References

Davis, D., Nowak, J. B., Chen, G., Buhr, M., Arimoto, R., Hogan, A., Eisele, F., Mauldin, L., Tanner, D., Shetter, R., Lefer, B., and McMurry, P.: Unexpected high levels of NO observed at South Pole, Geophysical research letters, 28, 3625-3628, 2001.

Grannas, A. M., Jones, A. E., Dibb, J., Ammann, M., Anastasio, C., Beine, H. J., Bergin, M., Bottenheim, J., Boxe, C. S., Carver, G., Chen, G., Crawford, J. H., Domine, F., Frey, M. M., Guzman, M. I., Heard, D. E., Helmig, D., Hoffmann, M. R., Honrath, R. E., Huey, L. G., Hutterli, M., Jacobi, H.-W., Klan, P., Lefer, B., McConnell, J. R., Plane, J. M. C., Sander, R., Savarino, J., Shepson, P. B., Simpson, W. R., Sodeau, J., Von Glasow, R., Weller, R., Wolff, E. W., and Zhu, T.: An overview of snow photochemistry: evidence, mechanisms and impacts, Atmospheric Chemistry and Physics, 7, 4329-4373, 2007.

Lambert, G., Ardouin, B., and Sanak, J.: Atmospheric transport of trace elements toward Antarctica, Tellus B, 42, 76-82, 10.1034/j.1600-0889.1990.00009.x, 1990.

Nerentorp Mastromonaco, M., Gårdfeldt, K., Jourdain, B., Abrahamsson, K., Granfors, A., Ahnoff, M., Dommergue, A., Méjean, G., and Jacobi, H.-W.: Antarctic winter mercury and ozone depletion events over sea ice, Atmospheric Environment, 129, 125-132, 2016.