“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 #2.

We would like to thank the anonymous referee for its time and useful comments towards the improvement of our manuscript. 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

This paper describes year-round measurements of Hg(0) in the atmosphere and snow on the Antarctic plateau along with ancillary measurements. These comprise a novel data set that is very valuable for understanding the global atmospheric (and cryospheric) mercury cycle. Given the value of these data and the difficulty in duplicating them, I would encourage the authors to make the complete data set available in some capacity (e.g. as a supplementary file, or a link to a data repository) in order to aid modellers, etc., in using these measurements to advance further research.

Mercury data reported in this paper are available upon request at http://sdi.iia.cnr.it/geoint/publicpage/GMOS/gmos_historical.zul. This has been added in the acknowledgments of the revised manuscript.

The analysis and interpretation is largely sound, with a few gaps as identified in the comments below. I do agree with the first reviewer that the organization of the Results and Discussion could be improved. I recommend the publication of this paper after the minor issues discussed below have been addressed.

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. Specific comments

- l. 38-39: "according to observations at coastal Antarctic stations" is vague; this is used elsewhere in the paper (l. 488) and is not very enlightening. Can you summarize the evidence you are using to draw this conclusion? Perhaps in Section 3.7? There are references there but the observations are not described.

"According to observations at coastal Antarctic stations" refers to the following sentence in Section 3.7 (Section *4* in the revised version of the manuscript, see previous comment regarding the structure of the Results and Discussion chapter):

"Conversely, low Hg(0) concentrations that were not correlated or anti-correlated with O_3 were observed at Neumayer and Troll (Temme et al., 2003; Pfaffhuber et al., 2012), while elevated Hg(II) concentrations (up to 0.33 ng/m^3) were recorded at Terra Nova Bay in the absence of Hg(0)/O_3 depletion (Sprovieri et al., 2002)".

In an attempt to clarify this point, we have added (1) a reference to this sentence in lines 482-484 of the revised manuscript and (2) a reference to this Section in the conclusion:

(1) "but can be sporadically observed elsewhere explaining the aforementioned observations at Neumayer, Troll, or Terra Nova Bay ~~(Temme et al., 2003; Sprovieri et al., 2002; Pfaffhuber et al., 2012)~~".

(2) "According to observations at coastal Antarctic stations (see section 4), the reactivity observed at Concordia Station can be transported at a continental scale by strong katabatic winds".

- l. 53: "rapid deposition" is relative. You later describe a reservoir of gaseous Hg(II), which can hardly be expected if the deposition lifetime is very rapid.

We agree. This has been corrected in the revised manuscript: "leading to the formation and subsequent ~~rapid~~ deposition"

- Section 2.3: What is the estimated precision of your Hg(0) measurements?

This has been specified in the revised version of the manuscript: "Based on experimental evidence, the average systematic uncertainty for Hg(0) measurements is of ~ 10 % (Slemr et al., 2015)".

- Section 3.1: (a) This is titled "seasonal variation" but mostly summarizes annual values and spatial/vertical differences.

This title has been removed in the revised manuscript (see previous comment regarding the structure of the Results and Discussion chapter).

(b) Can you identify what the ± values are? Standard deviation? Confidence limits on the mean?

± values refer to standard deviations. This has been clarified in the revised manuscript: "In summer, the mean atmospheric Hg(0) concentration was 0.69 ± 0.35 ng/m^3 (mean ± standard deviation)."

(c) What statistical test was used to determine that your values were lower than the Troll and Neumayer – Mann-Whitney as well?

None. This would require the entire distribution of Hg(0) concentrations at Troll and Neumayer. A two-sample z-test for comparing two means could be used. However, this test assumes that the two populations are normally distributed.

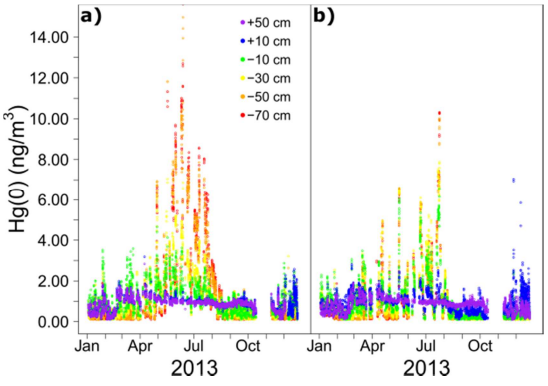
- How did the 25 cm inlet met tower values compare with the 50 cm and 10 cm snow tower inlet values overall? Fig. 6 suggests there was some offset between the met tower and snow tower inlets, at least in winter and possible spring/fall. Is the sampling coverage the same? Could there be an effect of heated/non-heated lines, or the length of the sampling lines?

Overall, the 25 cm inlet met tower values are lower than the 50 and the 10 cm snow tower inlet values. Values at the 50 and 10 cm snow tower inlets might be biased high due to contamination from the deeper inlets. Indeed, as mentioned in section 2.2 of the manuscript, sampling lines were purged continuously at 5 L/min on the met tower but intermittently at ~ 2-3 L/min on the two snow towers.

- Fig. 3: Why did you choose the 25 cm inlet to show? Can you add a time series or two (shallow/deep) for the snowpack data?

The decision to show Hg(0) at the 25 cm inlet is arbitrary. There is little variation of Hg(0) with height on the meteorological tower. Displaying all of the Hg(0) data (i.e., at the three inlets of the meteorological tower) makes this Figure difficult to read.

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."

- Fig. 4: I only see error bars on a few points. Are these the only ones with replicates? How many replicates were done in those cases? A line or two in the caption to explain this would be helpful.

All samples were analyzed in replicates of three. Standard error is most of the time smaller than the width of the dot explaining why you only see error bars on a few points. This has been clarified in the caption of the revised manuscript:

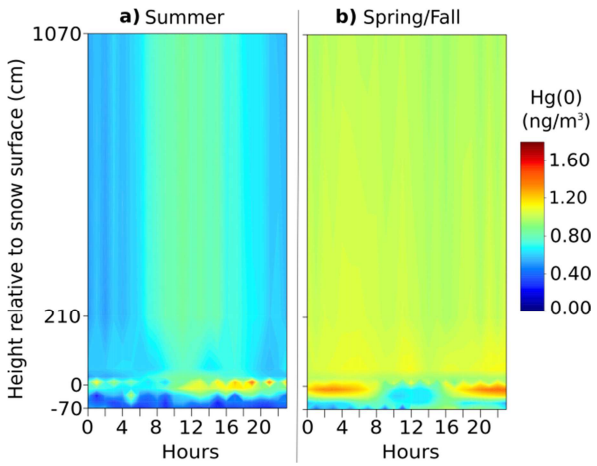
"Figure 5: Total mercury concentration (ng/L), along with standard errors, in surface snow samples collected weekly at Concordia Station from February 2013 to January 2014. Dark period (winter) highlighted in grey, sunlit period highlighted in yellow. Total mercury concentrations were elevated (up to 74 ng/L) in November-December 2013 (summer). All samples were analyzed in replicates of three. Standard errors are frequently smaller than the width of the dots."

- Section 3.2: You refer to "continuous" oxidation in the summer. What do you mean by that? It is clear there is net oxidation, but I am not sure you have shown it is continuous.

Yes, indeed. The term "continuous oxidation" has been removed throughout the revised manuscript.

- Fig. 7: This figure is a nice attempt to visualize the data, but it is rather confusing. Does the shading represent some sort of unspecified interpolation? Do the top boxes represent the met tower and the bottom the snow tower? In that case, why do the top boxes extend down below zero and the bottom ones not go up to 50 cm? If not, why don't the top and bottom agree within the overlap region?

We agree that this figure, as it is, might be confusing. It has been modified in the revised version of the manuscript:



"Figure 12: Hourly (local time) mean atmospheric and interstitial air Hg(0) concentrations in a) summer, and b) spring/fall. The vertical axis is the height of measurement relative to the snow surface (in cm). Color contours show Hg(0) concentrations (in ng/m^3). Concentrations at 25, 210, and 1070 cm above the snow surface were acquired on the meteorological tower while concentrations at 50, 10, -10, -30, -50 cm, and -70 cm were collected on snow tower #1. Data were cubic spline interpolated using software R."

- Fig. 8: I think this figure is not crucial to the paper, since it is only being used to support a suggested mechanism for a single extreme value. I think you can make that suggestion without an additional figure, though it is up to your discretion.

We agree. This Figure has been removed in the revised manuscript.

- Section 3.3.2: You mention a shift from oxidation to reduction at the beginning of winter, but it would be very helpful to see the time series of Hg(0) at depth (as mentioned above) – is it a sudden drop to a stable "winter" value, or is there a longer trend over the winter to accompany the atmospheric decline?

As mentioned above, 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. It is a sudden drop and not a longer trend over the winter to accompany the atmospheric decline.

- Section 3.4.1: Your summary is a bit confusing (ll. 339-343). I think you are saying by "continuous" that (i) has a week diurnal cycle and by "important" that (iii) has a strong diurnal cycle, resulting in the observed concentration pattern. Can you say this more clearly? I'm not sure what "important" means in (ii). Clearly it is important to the surface snow THg, but I'm not sure how this is related to the Hg(0) diurnal cycle.

The summary has been modified in the revised manuscript:

"In summary, the observed summertime Hg(0) diurnal cycle in ambient air might be due to a combination of factors: i) ~~a continuous~~ the intense oxidation of Hg(0) in ambient air due to the high oxidative capacity on the plateau – as evidenced by low mean Hg(0) concentrations (see section 3.2.1.a), ii) ~~important~~ subsequent Hg(II) deposition onto snowpack – as evidenced by elevated total mercury levels in surface snow samples (see section 3.2.1.a), and iii) ~~important~~ emission of Hg(0) from the snowpack during convective hours. Fig. 8 summarizes the processes that govern mercury exchange at the air/snow interface. Redox processes occurring within the snowpack are discussed in details in section 3.2."

- Section 3.4.2: Where is this Hg(0) building up from? Presumably the snow, but it's not mentioned. Why is the fall concentration higher than spring? The reservoir of Hg in the summer snow?

Yes indeed, we believe that Hg(0) is building up due to emissions from the snowpack. This has been clarified in the revised manuscript: "We believe that the shallow boundary layer could cause Hg(0) concentrations in ambient air to build up to where they exceeded levels

recorded at lower latitudes in the Southern Hemisphere because Hg(0) – emitted from the snowpack – was dispersed into a reduced volume of air, limiting the dilution".

The fall concentration is higher than spring indeed likely due to the reservoir of mercury in the summer snow. It should be noted that in both 2012 and 2013 mercury depletion events occurred at the end of summer likely leading to Hg(II) deposition on the snowpack.

- Fig. 9g: What inlet is the Hg(0) cycle from?

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".

- Section 3.5: It's a bit odd to refer to Fig. 10e first. I suggest you rearrange the figure to make this 10a.

We agree. The Figure has been rearranged in the revised manuscript.

- Section 3.6: (a) Given you have a single winter of data, and the decline is not seen at the other stations, can you eliminate instrument drift (e.g. trap poisoning)? Were the external calibrations before and after the winter consistent?

The instrument failed in 2014 but the decreasing trend has also been observed at Concordia Station in 2015. The data are presented in a paper that will soon be submitted in *Atmospheric Chemistry and Physics* (Angot et al., in preparation). Additionally, the decreasing trend has also been observed at Dumont d'Urville and data are presented in a companion paper (Angot et al., 2016). These results give us confidence that the decline is not due to an instrument drift.

(b) Why do you not include dry deposition of Hg(0) as a possible mechanism for this decrease? Given the low BL, what deposition flux would be needed to remove the observed amount of Hg(0)? How does this compare to other observations/calculations (Cobbett et al 2007, Zhang et al 2009)? I think it's quite similar. It would also account for the gradient in the decrease (3.6.2).

You are absolutely right. Dry deposition of Hg(0) is a possible mechanism for this decrease. This has been added in the revised manuscript:

"The observed declining trend could also be attributed to the dry deposition of Hg(0) onto the snowpack. The dry deposition velocity is defined as follows (Joffre, 1988), as the ratio between the deposition flux F (ng/m^2/s) and the concentration C (ng/m^3):

$$v_d = \frac{F}{C} \qquad (2)$$

Denoting the height of the boundary layer h and the Hg(0) concentration at the beginning of winter C_0, the evolution of the concentration versus time is thus given by the following ordinary differential equation:

$$C = C_0 \, e^{-(v_d/h)t} \qquad (3)$$

During winter (t = 107 days), the Hg(0) concentration gradually decreased from C_0 ~ 1.03 ng/m^3 to C ~ 0.73 ng/m^3 at 25 cm above the snowpack, in a mixing layer of 25 m high. According to Equation (3) the associated dry deposition velocity is 9.3 10^{-5} cm/s. This result is in very good agreement with dry deposition velocities reported for Hg(0) over snow (Cobbett et al., 2007; Zhang et al., 2009)."

(c) Speaking of which, you don't report in 3.1 if there are any seasonal differences in the three met tower inlets. Your discussion of the winter data suggests there would be.

This has been added in the revised manuscript:

Lines 209-213: "No significant difference was observed between annual averages of Hg(0) concentrations measured at the three inlets of the meteorological tower in 2013 (p value = 3.1.10^{-14}, Mann-Whitney test). It should be noted that Hg(0) concentrations at the three inlets were significantly different in winter only (see section 3.1.4)."

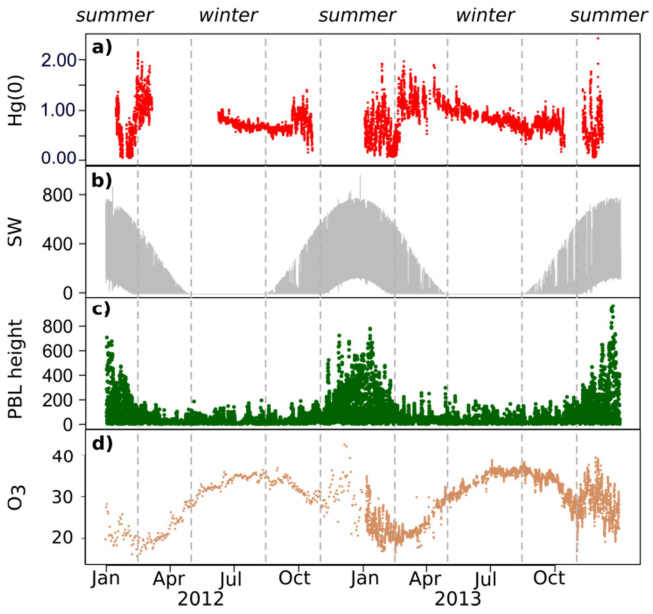
Lines 372-376: "In 2013, the height of measurement had a significant influence on the decline over time of Hg(0) concentrations (ANCOVA test, p value < 0.05), with a steeper decrease at 25 cm than at 1070 cm. Additionally, wintertime Hg(0) concentrations were significantly lower at 25 cm than at 1070 cm (p value < 0.05, Mann-Whitney test)."

(d) This section is poorly organized. I suggest removing the sub-sections since you basically discount the gas-phase reaction without doing so explicitly.

Sub-sections have been removed in the revised version of the manuscript.

(e) l. 402: Why don't you report your O3 data instead of (or as well as) referring to another paper? Also, are there O3 data at Troll or Neumayer that suggest that a winter reaction with O3 would not also happen there?

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 reason why the Hg(0) decline throughout winter 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.

- Section 3.7: A bit more detail about the observations that are attributed to transport from the plateau (ll. 457-462) would be helpful, as mentioned above.

See response above.

- Section 4: (a) I'd like to see a mention of the intriguing winter subsurface Hg(0) peak in here.

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

"Additionally, Hg(0) concentrations increased with depth in the snow interstitial air in winter likely due to a dark reduction of Hg(II) species accumulated within the snowpack during the sunlit period."

(b) Maybe change "heating" to "snowpack ventilation" or "ventilation and heating" in l. 479.

This has been changed in the revised manuscript: "Summertime Hg(0) concentration in ambient air exhibited a pronounced diurnal cycle likely due to large emissions from the snowpack as a response to daytime snowpack ventilation."

(c) In l. 481 I would change "likely" to "possibly"…. And do you really think gas-phase oxidation is even that likely? Your earlier discussion suggests not. You may need to add dry deposition of Hg(0) as well, depending what you find.
Indeed, the decreasing trend observed in winter is most likely due to the dry deposition of Hg(0). This has been changed in the revised manuscript (abstract and conclusion).

3. Specific comments

l. 32: change "never been observed" to "not been reported"

Done.

l. 46: change "contamination" to "contaminant"

Done.

l. 246: change "bound" to "bind"

Done.

l. 315: change "significant and daily" to "significant daily"

Done.

l. 316: change "all along" to "throughout"

Done.

l. 358: suggest changing "explosions" to "so-called 'bromine explosions'" to avoid leaving unfamiliar readers with the impression there are actual explosions.

We agree. This has been corrected in the revised manuscript.

l. 378: change "these depletions of Hg(0)" to "the depletions of Hg(0) reported here"

Done.

4. References

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Cobbett, F. D., Steffen, A., Lawson, G., and Van Heyst, B. J.: GEM fluxes and atmospheric mercury concentrations (GEM, RGM and Hg(p)) in the Canadian Arctic at Alert, Nunavut, Canada (February–June 2005), Atmospheric Environment, 41, 6527-6543, http://dx.doi.org/10.1016/j.atmosenv.2007.04.033, 2007.

Joffre, S. M.: Modelling the dry deposition velocity of highly soluble gases to the sea surface, Atmospheric Environment (1967), 22, 1137-1146, http://dx.doi.org/10.1016/0004-6981(88)90343-5, 1988.

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