Atmos. Chem. Phys. Discuss., 12, C9115–C9125, 2012
www.atmos-chem-phys-discuss.net/12/C9115/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Dynamic recycling of gaseous elemental mercury in the boundary layer of the Antarctic Plateau" *by* A. Dommergue et al.

A. Dommergue et al.

dommergue@lgge.obs.ujf-grenoble.fr

Received and published: 7 November 2012

We acknowledge both reviewers for the work they did on our manuscript. As advised, we spent a lot of time to shorten and re-write some sections of the discussion. We hope that it will help to clarify our ms.

You will find below our detailed reply to all comments (starting with a + sign). We have also attached a proposal for a revised version including modification that were suggested by the referees.

Anonymous Referee #1

General Comments: This paper presents two weeks of continuous atmospheric Hg0 measurements from the Dome-C monitoring site on the high Antarctic plateau. These

represent some of the only available continuous measurements of atmospheric Hg in Antarctica to date. This is an important contribution to the peer-reviewed literature given that this is an area of study that needs further attention and exploration. The article is very well written, and despite a relatively small dataset the authors provide a very informed discussion of the possible processes that might be influencing their observations, based upon a thorough review of the existing literature. Some of this discussion is lengthy, and could be tightened so that it is easier for the reader to follow along and separate the findings from the present study from those in the existing literature. After consideration of the few comments provided below, this manuscript is recommended for publication.

+Following referee #1' s comments we worked a lot on clarifying and shortening the discussion. We now propose a result section and we divided the discussion into subsections. We acknowledge the reviewer for this advice and we hope that the revised manuscript will be now clearer.

Abstract: Are the Hg0 values reported in the abstract 5-minute values? Or are they average values (e.g. hourly)?

+That is right that the presentation of our data may be confusing. As mentioned in the methods section (2.1), 8 inlets (2 in the atmosphere and 6 inside the snowpack) were actually connected to the Tekran 2537 analyzer with an alternate sampling every 10 min. One additional inlet was connected but data were not used, resulting in 9 inlets and a total sampling sequence of 90min. Therefore, each inlet was theoretically sampled on a 90min basis interval. Because of internal calibrations, sampling interval for a considered inlet was not constant during the campaign. In order to present data with a fixed time step, we decided to interpolate our dataset on each inlet at a 90 min interval and we verified by comparing raw data and binned data that such a linear interpolation did not led to any artifact. Single data that are presented of discussed are 10-minutes values. There was a mistake in the ms where it was written that a 5 minutes sampling time was used. We corrected this mistake.

p.18136, Line 12: What is meant by the phrase "an atmospherically clean area"? It seems that it is meant to refer to location in which the air is not impacted by any emissions from the station, but the way it is phrased sounds a little odd. It might be enough to just say: ": : : measurements were performed in an upwind area that is 800 m south of the station"

+The words are not well chosen indeed. It was meant to say that measurements were carried out in the so-called "clean air sector". We propose to use the reviewer's sentence instead.

p.18136, Line 22: Is the reported detection limit for the Tekran 2537 based upon the detection limit reported for the Tekran, or was it calculated from the internal calibrations and manual injections?

+It is LOD as reported by the Tekran. While very interesting we did not perform any analytical work on the tekran to calculate detection limit. So we change our wording saying that :" With this configuration mode, a detection limit of about 0.1 ng m-3 is expected".

p. 18137, Line 16: Where is the American Tower located relative to the Hg measurement location?

+We did not mention it, but the American Tower is located 600m north-west of the measurement site, on the same side of the Concordia base (upwind). We propose to add this information.

p. 18138, Lines 8- 10: You might want to remind the reader that you will, in fact, still present the samples collected along the trail between DDU and DC, because at a first read it sounds like all samples from the study were thrown out. Can you present any quantitative information about the field blanks collected along the logistic trail?

+We performed two field blanks. Two bottles were transported from our lab to the field site half filled with milliQ water. They were opened and closed in the field. They were

taken back to the lab together with all the snow samples. They were treated and analyzed like other samples. Average raw area was 500 (no unit) for those field blanks while the limit of quantification was around 582 for this analytical session (around .9 ng/L). It shows that the transportation, collection, and wash procedures did not contaminate the samples in a significant way. We have added details about the procedure and the levels of contaminations. We propose to add a sentence to clarify that the samples from the logistic trail were used.

Results and Discussion: Figure 2: Are the 5-minute Hg0 measurements presented in this figure as hourly averages? Or are they 90-minute averages? You should explain this somewhere in the figure title and/or in the methods section if hourly averages are to be used in the discussion. Also, should there be small gaps in the data every day during the period when the internal permeation source calibration occurred?

+As explained in details above, we did not use any averages. We rather use single measurements and interpolate between the measurements. Please refer to our comment above.

Figure 3: Why did you use 90-minute bins instead of hourly bins?

+With the exception of automatic calibrations intervals, each inlet is sampled for 10min at a 90min interval. Our 90bins allow to interpolate raw data to a common timeline and to compensate for 40min gaps occurring during calibrations.

Sections 3.2 – 3.4: These discussions on how meteorological conditions and atmospheric chemistry in the Antarctic atmosphere might be influencing the observed Hg0 concentrations are interesting and important, and the authors have clearly performed a thorough review of the existing relevant literature. However, the discussion as it is currently presented is very lengthy and at times it is difficult to distinguish between what is being obtained from measurements in this study and what is conjecture from the existing literature. As a reader, it is easy to get lost in the discussion and the references and lose sight of the important findings or hypotheses. One way to address this could be to have separate Results and Discussion sections, and then try to tighten up some of the Discussion so that it is easier for the reader to follow along and understand the key points that the authors wish to make.

+We have taken into account reviewer's advice and we hope that he/she will find the discussion clarified.

Technical corrections: Figure 1 should say "locations" instead of "localization". p. 18145, line 7: The word "univoqually" should perhaps be "unequivocally"

+Corrections were done. âĂČ

Referee 2.

The manuscript presents the results of 8 days of continuous gaseous Hg(0) measurements in air, and in interstitial air below the snow surface, at Dome C in Antarctica. As these are only the second set of atmospheric measurements from the Antarctic Plateau (since the advent of automated measurement systems) the results are certainly of interest. The variations in concentration Hg(0) observed with the time of day, and also from day to day do indeed indicate that the processes influencing Hg(0) concentrations in the atmospheric mixed layer on the Antarctic Plateau are dynamic. The article is generally well written although some of the Results and Discussion section is rather long-winded and at times somewhat repetitive. I also think that some of the conclusions the authors draw are more suppositions than conclusions as detailed below. Two previous studies, one on the Plateau and one on the coast appear to draw different conclusions from their results. Brooks et al. (2008) state that it is the air above the mixing layer which is enriched in oxidised Hg compounds, and most probably where GEM is oxidised, and that entrainment resulting from higher atmospheric turbulence during the day than the night, allows this oxidised mercury deposits to the snowpack where, in part at least, it is reduced and re-emitted to the mixing layer. Pfaffhuber et al. (2012) identify summer air masses with low GEM concentrations (and high ozone) at the Troll Research Station as free tropospheric air descending over the Plateau and then being

transported to the station. This article however argues that mercury oxidation is occurring in the mixing layer, and I think therefore that the discussion needs to be more rigorous and to include a section explaining how mixing layer oxidation is a plausible explanation in light of the other groups' results. Some specific points that need to be addressed before publication are listed below. I think the Abstract and Conclusions make statements that are not strictly borne out by the evidence that the authors have obtained. These are referred to in the relevant sections below.

+We thank the reviewer for the helpful comments. We took into account all the comments and we worked on shortening the discussion. We paid attention to be consistent about what are the results and what are the speculations. We thus reworded the conclusion and were more rigourous in the abstract.

Section 2.2 "Field blanks obtained at DC contained unexpectedly high levels of THg. We were forced to discard the whole set of data. Quality controls showed no contamination for snow samples collected on the logistic trail however." These sentences seem written almost with the intention of making the reader extremely curious! The authors should give more details here, maybe a brief description of the procedure, the level of blank contamination etc.

+We have added details about the procedure and the levels of contaminations.

This is an important point especially because the authors state in the Abstract that fast Hg(0) oxidation leads to enrichment of the upper snow layers in divalent Hg, which is actually slightly misleading as the snow samples were not collected where the Hg(0) measurements were made, and in fact the closest sample was taken 131 km away. In the Conclusions they state "Dramatic losses of Hg(0) were daily observed in the boundary layer suggesting fast oxidation processes. This oxidation was exacerbated during low irradiation periods in a confined mixing layer and led to the increase of Hg(II) levels in surface snow" and continue "The coincidental observation of oxidation ....", so that the suggestion becomes a fact. This is not what Section 2.2 describes, oxidation was not observed in as much that oxidation products were not measured in the air or on the snow surface at Dome Concordia. Rapid changes in Hg(0) concentration were observed which the authors ascribe to hypothetical oxidation processes. The wording both in the Abstract and in the Conclusions need to be changed to reflect the description of what measurements were actually performed.

+The reviewer is right. We have deleted all the part mentioning “enrichment of the upper layer”’, and use careful wording such as: we suspect a deposition on the snow surface. We also now less affirmative about oxidation processes and we suggest and hypothesize them. Abstracts and conclusion were changed accordingly.

Section 3.2. This section is rather long-winded and at times repetitive, it should be rewritten and shortened. The authors find that low turbulence (highly stratified) atmospheric conditions coincided with decreased Hg(0) concentrations, and that increased mixing coincided with higher Hg(0) concentrations. Brooks et al. (2008) found the same for RGM and Fine Particulate Mercury (FPM), some comment should be made on this as at it appears to be counter intuitive.

+This section has been rewritten and shorten. +We admit that this point can be counter intuitive. However, atmospheric turbulence in Antarctic can directly be related to solar downward radiation. The warming-up of snow surface and lower atmospheric boundary layer then generate turbulence responsible for vertical mixing. In our study, it is clear that we observed an increase in Hg(0) concentrations with solar irradiance, which is expected when considering photo-reduction of Hg(II) species in snow. Surprisingly (since data were obtained with a Tekran 2537), there is no Hg(0) data shown in Brooks et al. (2008) and therefore we believe that our Hg(0) results are not necessary in contradiction with their study. In addition, Brooks et al. (2008) do not present daily patterns of the boundary layer (or the turbulence/Richardson), so it is very delicate to comment on this paper. Brooks et al. (2008) speculated RGM and FPM deposition from the free troposphere. We do not have any RGM nor FPM measurements to speculate on the behavior of these species. Based on our data and on the modeling study, it seems that

we observed processes occurring in the very lower boundary layer. As suggested by the reviewer here and in the general comments, we added a subsection (4.2.1) explaining our suggestions about local reactivity and how they differ from previous studies that speculate vertical transport (such as advection from overlaying layer).

The authors refer to the background Hg(0) concentration in Pfaffhuber et al. (2012) as being a possibly typical value for the atmospheric layers above the mixing layer. This is not really an appropriate reference as Pfaffhuber et al. (2012) actually suggest that higher ozone, lower Hg(0), air that arrives at the Troll Research Station in the summer is actually air originating from the free troposphere above the Antarctic Plateau.

+The reviewer is right. We no longer use this reference for background values. We added a short paragraph as advised by the reviewer to discuss on local vs advection processes (4.2.1).

Section 3.3 This section is also overlong and not very concise, the authors may wish to consider dividing it into subsections or shortening it, or both.

+We reworded the section and divided in two shorter subsections.

I think the Brooks et al. (2008) paper estimates an Hg(0) evasive flux of 8.1 ngmôĂĂĂ2 hrôĂĂĂ1, and not 10.

+That is right, we do not know how 8.1 became 10 here.

I tried to estimate a flux from the increase in the Hg(0) concentration shown in figure 2 and the modeled mixing height in figure 4. There appear to 16 points for each hour in figure 2, is this correct?

+There are 16 points for each day (one point every 90min), we believe that is want the referee meant.

I estimated very roughly that the flux observed at Dome C was around 20 ng/m2 .hr-1. A graph showing flux estimates over time, obviously with the caveat that the mixing layer height is derived from a model might be a useful addition to this section.

+The suggestion is very interesting. We do not want to go too far into that topic because we did not make accurate measurement fluxes for three reasons: First, the sampling height for Hg(0) are probably not well designed. It would have been better to use an inlet right at the snow surface and one a little bit higher (50 cm) such as the design used in Steen et al (2009) . Second, we would need at least micrometeorological measurements at the same place (sonic anemometer for example) to derive turbulent fluxes. Thirdly, estimation of fluxes for a reactive species is often biased. Indeed, reactivity can significantly vary with height (for example if a strong gradient of radicals exists). We however did a calculation that is similar to what the reviewer suggests though it is not a figure. We also changed the discussion to make it clearer that we observed two processes: (i) an emission of Hg(0) after the sunrise, and (ii) a decrease of Hg(0) in the afternoon. We also precise in section 4.1 that our instrumentation was not sufficient to calculate Hg(0) fluxes.

Section 3.4. When discussing the possible gas phase oxidation mechanisms of Hg(0) the authors might wish to include a reference to the recent article by Dibble et al. (2012).

+This is a very interesting suggestion and we weren't aware of that paper when we wrote the ms. We added this reference and a short comment in section 4.2.2.

On page 18145 I imagine the authors meant 'unequivocally'. +Yes, correction has been made.

Section 3.4.1 is rather long and could be shortened. I think Lyman and Jaffe (2012) simply quote Holmes et al. (2010).

+Yes we agree. Citation has been changed following reviewer's suggestion. Section 3.4.1 has been shortened and now refers to 4.2.2.

Section 3.4.2 makes reference to Brooks et al. (2008), and says that Hg oxidation rate

peaks some time after the solar maximum. Which is indeed what Brooks et al. (2008) says, however as Brooks et al. (2008) are suggesting that this occurs above the mixing layer and the authors here are making the case that it occurs within the mixing layer, it is perhaps not really an ideal reference.

+That is right. This reference has been removed from the revised section.

The second paragraph is not very clear, the authors might like to rethink it. There is also a reference to O'Concubhair et al. (2012) which describes the dark oxidation of dissolved Hg(0), 'via freeze-induced' pathways. The authors say that it is not clear if oxidation occurs during freezing, however O'Concubhair et al. (2012) state that "DGM is oxidised to Hg2+ ions when frozen in the presence of ..." which seems quite clear. The paragraph was reworded and we removed the part of the sentence that was not accurate. Section 4. The conclusions state "Dramatic losses of Hg(0) were daily observed in the boundary layer suggesting fast oxidation processes. This oxidation was exacerbated during low irradiation periods in a confined mixing layer and led to the increase of Hg(II) levels in surface snow." But no oxidised mercury compounds were measured at Dome C either in the air or in the snow, and the suggested oxidation process appears to have become a definite one. I feel that the authors should be a little more reserved in their statements, particularly as this study seems to lend themselves to a different interpretation than previous studies.

+As mentioned earlier, we reworded the discussion, conclusion and abstract so that we are less definite.

References: Steen, A. O., Berg, T., Dastoor, A. P., Durnford, D. A., Hole, L. R., and Pfaffhuber, K. A.: Dynamic exchange of gaseous elemental mercury during polar night and day, Atmos. Environ., 43, 5604-5610, 2009.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C9115/2012/acpd-12-C9115-2012-

supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 18133, 2012.