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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.

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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.

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. 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.

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.

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 originiating from the free troposphere above the Antarctic Plateau.

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.

I think the Brooks et al. (2008) paper estimates an Hg(0) evasive flux of 8.1 $\mathrm{ng\,m^{-2}\,hr^{-1}}$, and not 10. I tried to estimate a flux from the increase in the Hg(0) concentration shown in figure 2 and the modelled mixing height in figure 4. There appear to 16 points for each hour in figure 2, is this correct? I estimated very roughly that the flux observed at Dome C was around 20 $\mathrm{ng\,m^{-2}\,hr^{-1}}$. 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.

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). On page 18145 I imagine the authors meant 'unequivocally'.
Section 3.4.1 is rather long and could be shortened. I think Lyman and Jaffe (2012) simply quote Holmes et al. (2010).
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. 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* Hg^{2+} *ions when frozen in the presence of ...*" which seems quite clear.

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 seem to lend themselves to a different interpretation than previous studies.

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