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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Overview of mercury measurements in the Antarctic troposphere" *by* A. Dommergue et al.

Anonymous Referee #3

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Review of Atmos. Chem. Phys. Discuss., 9, 26673–26695, 2009

Overview of mercury measurements in the Antarctic troposphere By Dommergue et al..

This paper has a stated goal of looking at Hg cycling in the Antarctic as it has been in the Arctic. They note that "only sporadic measurements have been made" in this region. They go forward to point out that "an effort has been first made to study the processes of AMDEs on coastal sites" in Antarctic and that "more recently, the Antarctic plateau turned to be a new focus of attention".

General Comment: Although the basic idea behind this paper is sound, this reviewer does not believe the authors have followed through with an implementation plan that

does justice to the title they have chosen or to the many other scientific studies that have already been reviewed and published in the scientific literature. It is quite disjointed in many places; and most importantly, it has failed to present a clear picture of the differences as well as any similarities between the two distinct environments in which Hg has been investigated in Antarctica,e.g., coastal areas and the plateau. It also has failed to make clear the differences as well as similarities of each of these Antarctic environments versus that in the Arctic. Finally, it has not been made clear what specific unresolved issues remain at each of these polar sites, especially the Antarctic. This is a major responsibility of any Overview paper. Equally important, the experimental/methods section of this paper is far too weak. Again, this is an important responsibility of any Overview paper. The manuscript has considerable speculation in it, which does not necessary make it unacceptable; however, when it is used, the authors must clearly state this in the text. In addition, speculation should not be offered if it is in direct conflict with other data/results in the reported literature unless the authors can convincingly show that these earlier results are in error. Overall, this reviewer believes this manuscript needs a major overhaul before it can be seriously considered for publication.

Specific Concerns: Section 1 Too much of this text is focused on the Arctic. The title of the paper is An Overview of Antarctica. Any details on the Arctic should be primarily given in section 2.3 which should be laid out to present a comprehensive comparison of these two different worlds with the Antarctic being broken up into two distinct environments. (Thus, this section can be significantly shortened.)

Section 2 Results and Discussion Comment: It makes little sense to have Methods and Definitions under a heading of Results and Discussion. In addition, the section 2.1.2 is quite inadequate given the title of this paper, "An Overview". An "Overview paper" should, at a minimum, provide extensive references that discuss the several different measurement techniques used in the detection of the different forms of Hg. In addition, some form of a summary should be provided in the paper which clearly states both the

detection limits of each method as well as provides a significant discussion of both systematic and random errors. Very important also is providing a discussion concerning Hg calibration techniques for its different forms. Finally, there needs to an expansion of the existing text in which an effort has been made to discuss the various data sets in Table 1. This , in particular should address the problems Hg measurements at low temperatures which the authors have made a very good start on. However, not provided is information regarding older measurements and whether or not any of these studies had a high probability of suffering from instrumental sampling errors/uncertainties, and, if so, what might be the magnitude of these errors. Thus, the question can be asked can we really make legitimate comparisons between these different data sets? As an Overview paper, this reviewer believes the authors need to give the reader a better idea of what the state-of-the-science is in making Hg measurements and whether all previous data are of equal value. The text would imply that they are.

Section 2.2.1 A picture of available data (poor title) Comment 1: Some of this text should be placed in the section Discussion of Methods. Also, confusing is the fact that the authors immediately start comparing Arctic with Antarctic measurements. Preferred here is text that is focused on Antarctic measurements since as already stated this paper's title is "An Overview of Antarctica —. Again, present the bulk of the Arctic data and/or discussion in section 2.3.

Comment 2: This whole section could, in fact, be eliminated and the specifics put into Sections 2.2.2 and 2.2.3.

Section 2.2.2 Comment 1: The authors need to clarify the sentence containing "polynyas and coastal, or flaw, leads provide frequently freezing sea ice surfaces". It would seem that there are both grammar problems here as well as jargon words that the average reader will not recognize. Also, how are we to understand the sentence, "In fact mer cury processes in Antarctica probably begin with marine bromine emissions." Probably ? And which processes are you referring to? And, are you saying this in the context of coastal areas only or are you trying to generalize this to both the plateau as

well as coastal areas?

Comment 2: Figure 2 is a rather misleading figure at first glance. One sees evidence of a very large gradient in BrO based on color changes in the figure until one realizes that in moving from green to red the concentration of BrO only changed by $\sim$30%. This is because most of the BrO is in the stratospheric column. Thus, the BrO levels in the troposphere appear to be at near the detection limit of the observations. This Figure needs to be re-done and something needs to be said about the uncertainty in the tropospheric column number density. As noted above there appear to be very large uncertainties in the troposphere.

Comment 3: In the sentence "It in fact, seems reasonable to suppose that BrO or another halogen-containing radical or compound is responsible for an increase in Hg0 oxidation and the formation of less volatile Hg(II) compounds (Boudries and Bottenheim, 2000)." By "suppose" do you mean "hypothesize"? If so, it would be far preferred to use a more scientifically meaningful word. Also the authors are talking about the Antarctic but then they give a reference to an Arctic study. It would be so much clearer to the reader if they would simply state: "based on the available data we are here inclined to hypothesize that in Antarctic coastal areas the enhanced oxidation of Hgo is similar to that which has been observed in the Arctic (Boudries and Bottenheim, 2000) and speculation here is that it also involves BrO or other halogen containing radicals or compounds".

Line14 "This suggests that the oxidation of Hg0 to RGM, and a concurrent production of O3, has already occurred before the air parcels were advected to the sampling site. The authors proposed a gas-phase oxidation of Hg0 by potential oxidants (i.e. OH, HO2, NO3) associated with high levels of NO. These oxidants result from photodenitrification processes in the snow-pack (Zhou et al., 2001) which may maintain the high RGM concentrations that were observed."

Comment 1) As it relates to other Hg oxidizing species such as OH, HO2 and others,

the authors appear to be unfamiliar with the recent Chablis observations at Halley Bay where OH and HO2 were measured and the extensive measurements of these same species at South Pole by (Mauldin et al., 2001, 2004, 2009). Interesting the study reported by the co-author Brooks in 2003 at South Pole was done at the same time that OH was measured. It seems to this reviewer that the authors have not really explored their suggestion about other Hg oxidizing agents given the supporting measurements that now exist. Nor have there examine any of the kinetic data involving these radical species and Hg which also I understand is available at some level.

Comment 2) Reference Zou et al., 2001- Once again the authors have used a reference involving Arctic observations to justify a discussion involving Antarctic data when there exist extensive observations of the photo-denitrification phenomenon in Antarctica (e.g., Jones et al., 2000, 2001, Davis et al., 2001, 2004).

Comment 3) With the extensive amount of sunlight during summer months and the extremely high absorption cross section for NO3 this species is highly unlikely to have a concentration level that it could influence Hg chemistry.

Comment 4: Why were measurements at McMurdo listed in Table 1 but never discussed. This makes little sense to the reviewer particularly in view of the fact that this appears to be the only case where the same investigator (using the same techniques) reported Hg measurements at both a coastal site and at the South Pole. These two sets of measurements, therefore, should have minimized systematic errors developing in evaluating the two sites.

Comment 5: There was no mention in section 2.2.2 (as discussed above, section 2.1) whether the use of different experimental techniques at some of the different coastal sites may have contributed to some of the disagreement found between these sites.

Section 2.2.3 In the sentence starting with: “This delay could be due to the requirement of “seed” reactive halogens to drive the recycling of halogens from the surface snow (Simpson et al., 2007; Piot and von Glasow, 2008).”

Comment 1: The references cited appear to be primarily focused on addressing the Arctic environment and more particularly in addressing the coastal environments. Thus, are the authors suggesting that halogen chemistry plays a major role in plateau boundary layer Hg chemistry. If so, they need to first examine the extensive plateau O3 studies published that show throughout the summer months the plateau is a net source of O3 (e.g., Crawford et al., 2001, Helmig et al., 2008, Oltmans et al., 2008, Legrand et al., 2009). Photochemistry leading to net O3 production and halogen chemistry that destroys O3 don’t mix!

The text beginning with: “Another recent study showed at Concordia (Courteaud et al., 2009) that GEM ground levels were both affected by the snowpack recycling and the variations of the boundary layer height. Contrarily to South Pole station, the daily diurnal cycle of the UV irradiance at Concordia significantly modulates the GEM levels with a significant local GEM production (through photochemical processes occurring at the snow surface) when a thin boundary layer (<50 m) is maintained. Later, the high solar radiations lead to a strong increase of the boundary layer height. GEM levels are 20 then diluted in a strongly Hg_-depleted air.”

Comment 2: It is interesting that one of the co-authors, S. Brooks, reported making Hg observations at South Pole in 2003 at the same time that extensive sodar observations (Neff et al., 2008) were recorded. The latter measurements revealed that numerous boundary depth changes occur continually at South Pole throughout the summer months even though no diurnal variations occur in the incident solar flux. In particular, one may ask: why have the authors avoided any discussion of these results since they clearly show that major boundary layer depth changes occur in the absence of significant solar variations? For example, Brooks et al., Hg measurements at South Pole also should have revealed some relationship to boundary layer changes if the authors Concordia arguments are valid.

The text starting: “Given the dry conditions of the Antarctic Polar Plateau (burial/snowfall rate is _10 cm/yr) only _10% of the deposited mercury is buried (se-

questered), resulting in some 60 metric tons Hg annually based on concentrations and flux rates presented in Brooks et al. (2008a)."

Comment 3: It would be interesting to estimate what the possible magnitude of the combined systematic/random errors in the Brooks et al., plateau measurements and then determine what the possible upper limit value might be on the amount of Hg buried. For example, would the 10% number shift to 30 or 40%?

The text starting with: "This dynamic mercury cycle on the Polar Plateau is driven by the surrounding sea ice as a vast bromine source, Southern Hemisphere Hg emissions, the sun, and the cold Spring/Summer temperatures.

Comment 4: This reviewer completely fails to see how the authors can draw the conclusion that bromine is the one of the key ingredients in plateau Hg recycling given the available evidence. As pointed out by the reviewer previously, the available evidence from the South Pole studies shows no indication of a role of bromine throughout the summer plateau months. The authors themselves make the statement: "However mechanisms of reactivity are not fully understood". Furthermore, they earlier made other arguments regarding coastal Hg chemistry that it was still unclear which of the halogens (Cl, Br, or I) is (are) the important ones in Hg processing.

The text starting with: "While Arctic and Antarctic coastal sites experience episodic mercury depletion events which occur predominantly in the late winter and early spring, the Polar Plateau experiences nearly-constant mercury events, peaking in the summer."

Comment 5: This sentence is quite confusing. Specifically, the expression, "nearly constant events". What events? Also figure 3 actually shows for the peaking of Hg activity occurring in early fall on the plateau

Text starting with: "Holmes et al. (2006) shows that subsiding air from any part of the troposphere could bring to the surface, gaseous Hg(II), formed by reactions with Br,

together with elevated ozone."

Comment 6: Holmes et al., speculation, although interesting, is as stated above by this reviewer completely at odds with all field data reported at South Pole. For example, the O3 data systematically show a decrease in concentration with an increasing in altitude above the ice surface (Crawford et al., 2001, Helmig et al., 2008) with only a few days (3-5) in early December showing very small influxes of upper tropospheric or stratospheric air (e.g., as evident in small increases in Be7). The South Pole data also show no evidence of bromine in that for virtually the entire summer there appears to be evidence of some degree of net photochemical O3 production.

Section 2.3

Comment: As stated in my general remarks this section needs to be entirely rewritten in that any comparison between the Arctic and Antarctic must be carefully pieced together such that coastal Arctic results are compared primarily with coastal Antarctic data not the plateau. The Antarctic coastal results should then be carefully compared with the Antarctic plateau. As currently written this section gives the reader many unclear messages and sometimes even quite misleading messages.

Section 3.0

As in the case of section 2.3 section 3.0 should also be rewritten once the other problems in the text are fixed. As stated above, the conclusion section must make clear which conclusions apply to which polar environment and talking about at least three different environments as covered in this manuscript.

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