Atmos. Chem. Phys. Discuss., 7, S7358–S7371, 2007
www.atmos-chem-phys-discuss.net/7/S7358/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "A synthesis of atmospheric mercury depletion event chemistry linking atmosphere, snow and water" *by* A. Steffen et al.

A. Steffen et al.

Received and published: 28 November 2007

Comments from reviewers re: ACPD- 2007-0227 Reviewer #1: R. Macdonald (Referee)

This manuscript predominantly reviews the advances made in atmospheric mercury chemistry in polar regions over the past decade or so. It is well written and gives the reader a clear sense of the academic excitement following the discovery of AMDEs by Schroeder et al. in the mid 1990s. Indeed, many of the authors included in this review have played a large role in unravelling polar sunrise photochemical processes. The chemistry of atmospheric reactions is well described as is the potential significance of mercury deposition into fragile polar ecosystems. Clearly, the research in this topic

has been a growth industry and Steffen et al. point out in a number of places important research remaining to be done before we understand the entire process linking atmospheric depletion to uptake in ecosystem. Having said that, I think this paper does have an Achilles heel - in particular, the link to water. 1. The weakness of our understanding of how mercury enters water and what it does once there is not the fault of the authors, but if this paper is to claim in its title that it will link atmosphere, snow and water, there needs to be a better presentation of the difficulties with the waterside including the problem of making aquatic measurements for trace Hg species. I say this especially because the research on AMDEs has been justified by reference to their potential ecological significance and, yet, we still seem not very far advanced in determining that significance despite the brilliant atmospheric chemistry that has been done since 1996. In a review written prior to the discovery of AMDEs, we proposed that there were two priorities in the context of Arctic contamination, one of which was Hg (Macdonald and Bewers, 1996). At that time, mercury was already established as a global contaminant with ą or more of the Hg cycling in atmosphere/upper ocean due to human activities (e.g., see Mason et al., 1994). But the question for polar research was whether or not mercury deposition somehow favours polar locations thereby making the poles global mercury sinks. It seems clear that the unique deposition of Hg at polar sunrise is significant (50 to 300 tonnes in the Arctic is proposed), but is the net deposition into the water anywhere near that large (see Kirk et al., 2006), and how might that deposition be altered by change in ice climate? These questions are crucial and depend almost completely on water-column work.

2. The authors present in Table 3a fairly long list of mercury measurements in polar waters; the problem with this table is that 2a) it presents no data (only detection limits) 2b) it gives no evaluation of confidence in the data given the difficulties with mercury measurements 2c) most of the ocean data are for the North Atlantic, giving a false impression that much has been done in the Arctic Ocean. Actually, we are in a very poor position to say much about mercury geochemical cycling in the Arctic Ocean and I think that needs to be more clearly expressed.

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3. The second issue, allied with problem of Hg speciation and trends in polar oceans, is whether or not AMDEs lead to biological uptake. Scott (2001) has shown that some of the deposited Hg is bioavailable, but what is the efficiency of transfer from air to snow to water to biota? Without these answers, the AMDE remains an interesting academic phenomenon with unknown relevance to Hg trends found in wildlife (e.g., Lockhart et al., 2005; Stern and Macdonald, 2005) or humans (Johansen et al. 2004). Specific comments P10841 L 25; the rich history of Hg measurements in snow, ice and water seems misleading to me.

4. Certainly, where is the rich history of Hg measurements in polar waters?

5. P10844-45L25-2. The arctic is actually quite well populated in some regions, and heavily industrialized in parts of the Siberian sector.

6. P10845 L10-14. Although upper layer Hg enrichment in Arctic marine sediments is often taken to indicate industrial input, it may not always be so (Gobeil et al., 1999).

7. P10846 L15-17. Hg and POPs deposition have a similar component - phase partitioning. Cold condensation is, accordingly, a bit of a misnomer as the POPs do not ‘condense out’ any more than Hg ‘condenses out’; they both partition onto particles which then settle out in some manner. Some (perhaps most) of the Hg deposition is forced by the photochemistry, but Hg deposits in other parts of the world where there are no AMDEs. I would recommend rewriting this sentence a bit more carefully.

8. P10866 L20-25. The importance of more long-term measurements of atmospheric Hg in the Arctic. No doubt more measurements would help to validate model and seek geographical variation, but is this the most important thing to do if one had money enough to establish more stations?

9. It would help the reader if the various proposed research tasks could be ranked in order of importance with some rationale placing in context the understanding of risks

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to ecosystems posed by mercury.

10. P10866 L25-26. I’m not sure what is meant by ‘this information’. Assessments of fluxes and trends have been made already, so I presume they can be made. The question then is of confidence in those fluxes.

11. P10869 L11-18. So what do these observations mean?

12. P10869 L26. The use of the word solubility, which is usually defined as “A measure of how much of a given substance will dissolve in a liquid”. Normally, one thinks of solubility at saturation, but I think what is meant here is not solubility, per se, but rather Henry’s Law partitioning behaviour (or kaw). This crops up elsewhere as well.

13. P10872 L15-28. Are these ‘net’ depositions in an annual context?

14. P10879 L24-27. I would agree with the first part of the sentence, but there is not much in the section detailing ‘subsequent transfer to other compartments of the ecosystem.’

15. P10881 L6 -10. And how did these models perform compared to DEHM?

16. P10881 L12. Insoluble or unfavourable air to water partitioning?

17. P10881 L11-20. What about deposition to water? Although deposition to water might involve RGM and PHg, what about the reverse flux; does that depend on Hg(0) and MHg? If so, is that flux controlled by the water side or the air side (e.g., Nightingale, 2003). It might help the discussion here to give a diagram showing a schematic of the fluxes.

18. P10882 L5-10. It would seem appropriate to point out here that future efforts in modeling should focus on incorporating re-emission of Hg from snow and ice.

19. P10883 L22. From the above comment, it seems to me that a current challenge for these models is to get the correct net deposition by properly incorporating the re-

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emission fluxes? The issue of transfer to ecosystems needs to be addressed by measurements at this point in time, more than by modeling, in my opinion.

20. P10886 L20. Figure 6 seems to me to be un-necessary as the same information is presented, or could be presented, in Figure 3. Furthermore, the text describes some knowledge about methyl mercury which is represented in Figure 3 but not in Figure 6.

21. P10893 L1-2. The question of Hg and MHg concentrations scaling with water flow is interesting and important for climate change; this deserves more text in this document (see also Stanley et al., 2002; Bishop et al,1995)

22. P10894 L9. Understanding the springtime pulse of MeHg is important from theperspective of marine mammal uptake, but the authors need to recommend the lines of research required to make that connection. Furthermore, climate change will likely have its greatest impact on MHg production through the organic carbon cycle, perhaps mediated through change in hydrological conditions - especially where such change causes submergence of soil.

23. P10894 Section 6.4. This section is appallingly thin. For the Arctic, we can say that 1/3 of the area is covered by ocean; the margins of that ocean are where the AMDEs exert their influence because they need seawater halogens (influence extends only 25-75 km inland; P10877); the other 2/3 drainage basin in the Arctic feeds its material, including Hg, into the same margins of that ocean. And so, with respect to Hg deposition and ecosystem consequences, I would say that the ocean is quite a bit more than a ‘considerable’ portion of Polar Regions. The authors should also provide more specific guidance on the sorts of research required for oceans and their priorities in line with what they have provided elsewhere for atmospheric-snow components. I admit a fondness for oceans, but my point is this: the Arctic Ocean contains a large, vulnerable ecosystem living under the threat of very poorly understood risks from Hg. Those risks stem from 1) a potentially high net deposition of Hg via AMDEs, 2) Concentrating and methylating processes within the water column,

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sediments and ice and 3) climate change. Presently, AMDEs could deposit as much as 300 tonnes/yr of Hg to the surface; a lot of it might get into the water - or almost none of it (Kirk et al., 2006)). The science community needs better guidance than “more research be focussed on the cycling of Hg in and around these oceans.”

24. P10895 line 23.If a great leap has taken place, it is in atmospheric research on AMDEs; if there has been a great leap in understanding the cycle in the ocean or the passage of deposited Hg into ecosystems, it is not evident in this review.

25. P10895 Section 7 Conclusions and future directions. Again, I would recommend prioritizing this research. What are the key research activities required to understand risks of Hg to polar ecosystems and humans?

26. References Bishop, K., Y.-H. Lee, C. Pettersson, and B. Allard (1995) Methylmercury output from the Svartberget catchment in northern Sweden during spring flood. Water Air and soil Pollution, 80, 445-454.

Gobeil, C., R.W. Macdonald, and J.N. Smith (1999) Mercury profiles in sediments of the Arctic Ocean basins. Environmental Science and Technology, 33, 4194-4198.

Lockhart, W.L., G.A. Stern, R. Wagemann, R.V. Hunt, D.A. Metner, J. DeLaronde, B. Dunn, R.E.A. Stewart, C.K. Hyatt, L. Harwood, and K. Mount (2005) Concentrations and trends of mercury in tissues of beluga whales (Delphinapterusleucas) from the Canadian Arctic from 1981 to 2002. Science of the Total Environment, 351-352, 391-412.

Macdonald, R.W., and J.M. Bewers (1996) Contaminants in the arctic marine environment: priorities for protection. ICES Journal of Marine Science, 53, 537-563. Nightingale, 2003. The Oceans and Marine Geochemistry (Ed.H. Elderfield); Chapter 6.03, Gases in Seawater, pp 49-81.

Stanley, J.B., P.F. Schuster, M.M. Reddy, D.A. Roth, H.E. Taylor, and G.R. Aiken (2002) Mercury on the move during snowmelt in Vermont. Eos, Transactions, American Geo-

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physical Union, 83 (5), 45, 47-48.2.

Stern, G.A., and R.W. Macdonald (2005) Biogeographic provinces of total and methyl mercury in zooplankton and fish from the Beaufort and Chukchi Seas: Results from the SHEBA drift. Environmental Science and Technology, 39, 4707-4713.

27. Typos etc. P 10840 L 6 Much work ˇ Ehas occurred but these processes are not yetˇE

28. P10844 L 17; typos/missing words

29. P10853 L12; remove in the

30. Page 10858 L7 remove and P10866 L3; they

31. P10870 L26. How do you repeat a hypothesis?

32. P10871 L8-11; rewrite for clarity

33. P10871 L18-20; rewrite for clarity

34. P10883 L4. Remove ‘that’

35. P 10886 L27 Rewrite for clarity.

36. P10889 L12 loose should be lose.

37. P10891 L 14. In its oxidized form, Hg isˇE

38. P 10895 L18. Insert and after oceans.

Response from the authors to reviewer #1 – Robie Macdonald: 1. The comment from this reviewer is valid and well taken. The focus of this paper is to review the research that has been undertaken in terms of AMDEs since their discovery. The challenge has always been the “so what” about AMDEs and while there has been much speculation on their potential ecological significance there has been little progress made to actually link the atmospheric chemistry to the elevated levels of Hg in

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the ecosystem. There are many gaps of information to link the former 2 issues and the authors agree that one of these gaps is the role of the oceans. The purpose of this review is to investigate the work that has been done on the atmosphere and into the snow pack and will review briefly the small amount of work undertaken in the North Sea and some lakes. Thus, the title of the paper and comments throughout the text, have been changed to reflect a more focussed review about the atmosphere and its role to the surface. The title of the paper has been changed to “A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow”. The following comments have been changed in the text to reflect this shift of focus: a. “As well, the role that the snow pack, oceans, fresh water and the sea ice in the cycling of Hg are presented” to “As well, the role that the snow pack and the sea ice in the cycling of Hg are presented”. b. The following text was added in the introduction “In 1996, a review was published that clearly identified mercury as a heavy metal of great concern because of its anthropogenic mobilization during the last century and its ability to bioaccumulate and biomagnify Arctic marine wildlife (Macdonald and Bewers, 1996). This paper further recommended that work was urgently needed to verify trends of mercury in various media including the atmosphere, the oceans, the water system and the biota”. c. The following was removed from the text in the introduction “Scenarios for deposition of Hg to the polar marine and terrestrial environments after AMDEs will be provided”. d. The following sentence was changed in section 3.3.2: “Aqueous monomethyl mercury (MeHg) concentrations are reported in levels from a few tenths…” e. Section 6.4 – title was changed from “mercury in polar oceans” to “mercury in polar waters”

2. Table 3 was included to provide the reader with a summary of aqueous measurements that have been undertaken in the Arctic. Because this table is included in the methods section, the authors did not intend for this table to illustrate data or concentrations but more to the point - a summary of the experimental methods. The authors wish to maintain the table as it is. Some modifications have been made in the text in how the

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table is referred to so that it limits the expectation that data will be included including expectations for significant Arctic Ocean work. For instance: a. The title of section 3.3 was changed to “Aqueous Hg measurement techniques employed in the Arctic”; b. The descriptive sentence in the text was changed to “Error! Reference source not found. provides a summary of aqueous measurements that have been made at various locations in the Arctic, including a brief overview of the analytical method used for each study”; c. The title of the table was changed to “Summary of aqueous mercury measurement methods in the Arctic”. Further, the authors wish to clarify that this is a methods section and makes no claim for saying anything about the geochemical cycling of mercury in the Arctic Ocean at this point in the text.

3. The focus of this paper has been adjusted to not include the link to the oceans and thus focuses mostly on AMDEs and the deposition to the surface. While the authors do not feel that AMDEs are an “academic phenomenon with unknown relevance to Hg trends in wildlife” we understand that the purpose of this review is not to assess this link. 4. In this sentence the authors wanted to recognise that work in the arctic on Hg didn’t start when AMDEs were discovered yet wanted to recognise the wealth of other work. This sentence has been modified from “While the discovery of AMDEs initiated almost a decade of intense study of atmospheric Hg processes, studies of Hg in snow, ice and water have a long and rich history” to “While the discovery of AMDEs in 1995 initiated almost a decade of intense study of atmospheric Hg processes, there have been many studies of Hg Polar Regions prior to this discovery”. 5. The intention of this sentence was to recognise that much work on Hg in polar regions has been undertaken and is not limited to only work surrounding AMDEs. The sentence was thus changed from “While the discovery of AMDEs initiated almost a decade of intense study of atmospheric Hg processes, studies of Hg in snow, ice and water have a long and rich history.” To “While the discovery of AMDEs initiated almost a decade of intense study of atmospheric Hg processes, there have been many studies of Hg polar

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regions prior to this discovery.” 6. See comment #4 of response to reviewer #2. The wording of the sentence “has little industrial activity (except select areas in the Russian Arctic (Bard, 1999) and mining in Svalbard)” was changed to “has, relative to temporate regions, little industrial activity (except select areas in the Russian Arctic (Bard, 1999) and mining in Svalbard)”. 7. The sentence was changed to include this point of view as follows “In the Arctic, Hg levels are shown to be higher in the upper layers of marine sediment indicating that Hg input to the Arctic is post-industrially driven (Hermanson, 1998). Evidence from ice core samples confirms this. While this is not unique to the Arctic, it is often taken as evidence that industrialization is present in this region although some have suggested that this may not always be the case (Gobeil et al., 1999)”. 8. This sentence was reworded and the “condense out reference” was removed so as to not mislead the reader. The sentence was changed to “POPs and the other semivolatile pollutants mentioned above are known to be transported to the Arctic via the “grasshopper effect. Both POPs and Hg are subject to partitioning onto particles and deposition from the atmosphere, however, unlike POPs much of the deposition of Hg in the Arctic results from photochemical reactions”. 9. The authors feel that the statement and continuation and additional long term measurements is valid in this context. Without long term measurements and only short studies, AMDEs would not have been discovered nor would the strong seasonal trends be recognised on their importance. The authors feel that encouraging the reader to consider the importance of trends. The authors have not suggested in this section or in the recommendations/conclusions that this is THE first priority but the authors feel it is of high priority to access the impact of important factors such as emission changes and changes in climate. This paragraph was thus left as is because this paragraph does not suggest that this is the most important thing to put money into, as was suggested by the reviewer. 10. This paragraph has been edited considerably to reflect more of a justification for long term measurements as follows: “Currently, there are no other long term measurements published of Hg in the atmosphere from Polar Regions. The authors

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encourage more long term measurements of GEM and other atmospheric Hg species in Polar Regions as these measurements can yield critical information to better understand the processes involved in the cycling of Hg in the polar atmosphere. Further, two major drivers of Hg deposition to the Arctic are currently undergoing dramatic change. First, the climate is warming which is changing the timing and extent of sea ice and its coverage (Serreze et al., 2002; Stroeve et al., 2005). The affects of shifts in sea ice on Hg scavenging by snow and ice and on halogen emission from open water and sea ice regions are unknown. Warming is also dramatically affecting the seasons with winter coming later and spring melt coming earlier. Thus the amount of time between Hg deposition during AMDEs and Hg mobilization during spring melt are shrinking. This could affect the amount of reemission of Hg from the snow pack but no models or measurements investigating this have been made. Second, coal and fossil fuel combustion in Asia, a major global source of Hg, is expected to increase up to 350% between 1990 levels and 2020 (van Aardenne et al., 1999). The affects of these increasing emissions on AMDE processes and the long term deposition of Hg to the Polar Regions will only be discernible if long term measurements are collected at numerous locations”. 11. A sentence was added to this text to discuss the meaning of the observations as follows: “These results imply that there is a cycling of mercury that occurs near the surface and the air masses are not well mixed within the boundary layer to be measured at heights of 474 a.s.l.”. 12. To clarify the point that the reviewer addressed, the phrase “higher solubility” was changed to “more hygroscopic”. 13. To answer the question of the author “are these net depositions in an annual context”? The authors feel that the depositions referred to in this part of the text are labelled as a #/year which implies an annual deposition. Further, some of the data presented is also seasonal or simply from the input of AMDEs which is not an annual input but a seasonal or an atmosphere dependent input. 14. the authors agree with the comment by the reviewer and changed the last sentence to more accurately reflect the discussion in this section from “The atmosphere is the first medium in which pollutants are found and this section has de-

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scribed the work undertaken to understand the mechanisms and processes of how Hg transforms in this medium and is subsequently transferred to other compartments of the ecosystem” to “The atmosphere is the first medium in which pollutants are found and this section has described the work undertaken to understand the mechanisms and processes of how Hg transforms in this medium”. 15. To address the question by the reviewer of how did these models compare to DEHM the following text was added : “The models have been compared in Europe in a model intercomparison (Ryaboshapko et al., 2007). There is no direct comparison available in the Arctic region but the published independent studies on these models show (Ariya et al., 2004; Christensen et al., 2004; Travnikov, 2005) that they all capture the springtime depletion to some degree but fail to simulate the above average mercury concentrations observed following the AMDEs at some sites”. 16. The answer to this question is both. Lin and Pekhonen state “The aqueous elemental Hg levels in Henry’s equilibrium with GEM range only from 1.3 to 5.3 x 10-14 M which constitutes a negligible fraction of Hg concentrations in atmospheric waters. The solid- liquid equilibria are governed by the solubility products of solid Hg compounds in water”. Thus the dry deposition of Hg in ice and snow is neglected because GEM has a low solubility in aqueous phase and doesn’t partition from the gas phase to the liquid phase according to its HL constant. The text was modified to clarify this as follows: “Dry deposition of GEM over ice and snow is neglected in the Hg models due to its low solubility characteristic”. 17. To address the reviewers question about deposition to water the following text was added: “Mercury deposition as RGM and PHg to the water is included in all the models. The oceanic emission of Hg(0) is also included in the models which depends on the surface temperature and the distribution of primary production activity in the oceans”. 18. The following sentence was added to the text: “This is considered a large gap in information and future modeling efforts should focus on incorporating re-emission of Hg from snow and ice”. 19. Some of this comment was addressed in response to the previous reviewer’s comments. The following sentence was added to

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emphasise the point of where future models may want to focus effort “Further, future modeling efforts should focus on ensuring deposition and re-emission of Hg from surfaces is incorporated within the models”. 20. The authors agree that Figure 6 is repetitive and adds little value to the paper. Thus, it was removed. 21. The importance of this finding was emphasised in the text. The authors agree that this should be further looked into but perhaps in another publication concentrating on methylation of Hg in the high Arctic. The authors feel that this issue has been demonstrated in the text and recommended that it be a priority for future work. 22. This last paragraph was changed to reflect the comments of the reviewer as follows: “The impact of the springtime pulse of MeHg to the high arctic is an important mechanism to understand because of the toxic effects that MeHg may have on the availability of MeHg for marine mammal uptake. Further, the influence of climate changes (e.g. warming, thinning and melting of sea ice) on net MeHg production, most likely through changes in the organic carbon cycle, must be quantified to fully understand the link to this increase in MeHg production and any connection to the uptake of this pollutant by marine mammals”. 23. The authors recognise the lack of depth to this section but with the refocus of the paper away from the link with the water for AMDEs, the authors feel that this section is important to retain in the paper for the reader to understand that there is not much information about polar oceans available and that this is a significant gap in our current understanding of the cycling of mercury in this environment. The concluding sentence was changed to emphasise the importance of the oceans as follow “The oceans play one of the most significant roles in Polar Regions both in spatial breadth and processes and yet information about dynamics of Hg around these environments is scarce. Considering that the Arctic Ocean contains a large, vulnerable ecosystem exposed to this toxic pollutant, the vast number of processes that occur in the water column, sediments and ice (e.g. concentrating and methylation of Hg) and that changes in climate will primarily affect this ocean, the authors recommend that future research must focus on this area”. 24. The sentence was changed from “During the last decade a great leap in the understanding of Hg transformation

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in the Arctic and the Antarctic has occurred, especially in measurement, laboratory and modeling studies” to “During the last decade a great leap in the understanding of Hg transformation in the Arctic and the Antarctic has occurred, especially in measurement, laboratory and modeling studies”. 25. This section has been rewritten and reordered significantly in an attempt to present the research where priorities are expressed. The most pressing priority- multidisciplinary studies of Polar Regions and ecosystem processes, is presented last as a final synthesis. However it is not our intent to label specific research types, discipline sor areas as more important than the others. One of the most promising aspects of Polar Regions Hg research is that is crosses disciplinary lines and we want to continue to support that rather than to place any specific emphasis on the work of individual groups.

27-38. These typos and text clarifications were made as suggested by the reviewer.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 10837, 2007.