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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.

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The authors wish to thank both reviewers for such exhaustive reviews of this paper. The comments have enriched this publication. The following are comments that address the reviewer’s comments.

Comments from reviewers re: ACPD- 2007-0227 Anonymous reviewer #2. General comments: This paper provides a review of the research on atmospheric mercury depletion events observed in polar regions and on their interaction with the polar environment. It tries quite successfully to bring together the findings of measurements in the atmosphere, snow, and water with model and laboratory studies. The review is generally well written and provides a useful overview of the state of research on the

subject. Because of this, I believe that it is appropriate for publication in ACP. To compile a paper from contributions by different authors poses always difficulties. I therefore recommend following modifications to make the paper more clear and to harmonize it:
1. Page 10839, line 15: Are the authors really reviewing “the history of Hg in Polar Regions” or the research on Hg transport and fate there?

2. Page 10843, line 5: “This will be followed by sections outlining the underlying measurement techniques” – remove underlying

3. Page 10843, line 11: replace “a look into..” by “an outlook of”

4. Page 10844, line 13: The sentence starting with “This is the most stable form. . . ” is grammatically incorrect.

5. Page 10844, line 26: Several millions of inhabitants north of the polar circle are not exactly “few people”. The paragraph should also refer explicitly to the phenomenon called Arctic haze which was extensively studied in the 1980s (papers by Raatz et al.).

6. Page 10845, 2nd paragraph: Higher Hg levels in the upper layers of sediments are not specific to the Arctic but for the entire northern hemisphere. The second sentence thus needs rewording.

7. Page 10846, last paragraph: Low precipitation and consequently low wet deposition is also an important feature of the Arctic troposphere.

8. Page 10848, second and third paragraph: Other elements such as lead are also measured on aerosols without talking about “operationally defined measurements”. There may be measurement artifacts, but that is another matter. I disagree with the authors that the measurement of PHg is operationally defined. It is true the both RGM and PHg have short lifetime. But opposite to RGM, the lifetime of PHg is also well defined by the lifetime of the aerosols that carry mercury.

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9. Page 10848, line 26: Should it not be “industrial activities since 1840’s”?

10. Page 10850, line 23: The “bioavailable” fraction of Hg should be defined.

11. Page 10851, line 20: The methods reviewed in Section 3 were not designed specifically for the polar regions.

12. Page 10852, 2nd paragraph: What does it mean: “AFS instruments, which tend to require more facilities. . . ” and “At times, this advantage is forsaken. . . ” Reword or delete.

13. Page 10852, line 23: Enrichment of mercury by amalgamation was not invented by Fitzgerald and Gill, 1979. It was used already by Williston (JGR 73, 7051 (1968)) and much earlier by Stock and Stock and Cucuel (Naturwissenschaften 19, 499 (1931) and 22, 390 (1934)).

14. Page 10853, last paragraph: When writing about the sampling of RGM only methods that sample specifically RGM without PHg should be mentioned. The techniques by Brosset and by Stratton and Lindberg will collect PHg as well when used without filter. Filter has to be mentioned because it is an essential part of these techniques when RGM only has to be measured.

15. Page 10856, lines 14 and 15: “to measure air-snow GEM flux” and “air-snow RGM flux”.

16. Page 10856, last paragraph: “Micromet”, even if defined, sounds like laboratory jargon and thus should be avoided. The general characterization of the micrometeorological methods in the second paragraph applies to REA and MBR but not to eddy covariance method. The paragraph should be reworded.

17. Page 10857, line 9: “fast” is perhaps better than “instantaneous”.

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18. Page 10857, line 23-25: The limitation mentioned here applies also to MBR technique,since both techniques needs some time to collect mercury needed for accurate analysis.Even the eddy covariance technique does not provide instantaneous fluxes but fluxes integrated over a certain period. Please delete or reword.

19. Page 10858, 2nd paragraph: Chambers are essentially good for process studies but not for measurement of real fluxes because their application involves change of parameters governing the flux such as turbulence, radiation, temperature etc. The word “fetch” is used only in connection with micrometeorological techniques. Please reword.

20. Page 10860, line 13: “elution” instead of “elusion”? Page 10861, line 15: “Few measurements of. . . . have been collected” sounds a little bit strange.

21. Page 10862, last paragraph: “The reactions between Hg(0) and. . . ..but may occur faster in the aqueous phase”. This statement is not correct for three reasons. Firstly, the reaction partners are mostly not dissolved O3 and Cl2 but ions formed during their solution. Secondly, the individual reactions might be faster but they are limited only to the aqueous phase which represents only a small fraction of the air. Thirdly, the transport to the droplets and the dissolution of the gases are both kinetic processes and as such reduce the rate of the overall chemical reaction. Please make this paragraph more clear.

22. Page 10870, last 5 lines: “. . . .RGM present in the air is adsorbed on aerosol but at higher levels. . . .”. “The same hypothesis was also used by. . . .”

23. Page 10871, line 18: Reword the sentence starting with “Results from a study. . . .”

24. Page 10872, line 8: “lack of knowledge of Hg speciation..” instead

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of “lack of speciation of Hg”.

25. Page 10872, line 21: “estimated” instead of “demonstrated”

26. Page 10874, line 22: “targeted and comparison studies” sounds strange, please reword.

27. Page 10877, 1st line: “.. more efficient scavenging of Hg resulting from AMDE..” Page 10877, line 10: Should it not be 25 km as mentioned further below?

28. Page 10880, 1st line: “Modeling of mercury in the Arctic region” I would change the sequence of the chapters 5.1 and 5.2 because at the beginning is the transport of mercury to the Arctic. Only mercury that has been imported to the Arctic can be processed.

29. Page 10881, line 5: High concentrations in air or snow?

30. Page 10883, line 10: What does “dominantly” in brackets refer to? Please reword.

31. Page 10883, line 13: “The that main transport. . . .” Delete “that”

32. Page 10883, line 16: replace “Polar Region” by “Arctic”

33. Page 10883, line 22: Do really models provide “a critical understanding”? Please be more critical.

34. Page 10884, line 12: “the reduction of emissions”

35. Page 10885, line 11: “GEM emissions” instead of “GEM fluxes”. The entire paragraph should clearly distinguish between emission and

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deposition, the word “flux” is meaningless in the context of this paragraph.

36. Page 10885, line 23: “have indicated that. . . ”

37. Page 10886, 1st paragraph: This paragraph needs rewording to shorten it and improve its clarity. E,g “snow emitted GEM with a rate of 0 – 50 ng/m3. . . ”. Also more specific “emission” or “deposition” should be used instead of “flux”.

38. Page 10886, line 21: “This is surprising . . . ” does not refer to Fig. 6 but to the first sentence of the paragraph. Please correct.

39. Page 10896, line 8: RGM associated with aerosols is no more RGM but PHg. Please reword.

40. Page 10897, 3rd paragraph: Little is said in many words. One sentence would do.

41. References need generally a homogenization. The titles are sometimes written with all word with capital letters, the journals are sometimes abbreviated sometimes not.

42. Please use consistently the ACP reference format.

43. Page 10900, line 15: 200HgCl2

44. Page 10902, line 29: “pf”?

45. Page 10903, line 29: “transport”

46. Page 10906, line 13-19: The erratum should follow the paper reference.

47. Page 10911, line 32: (HOCl/OCl−)?

48. Page 10913, line 4: Tellus

49. Page 10914, line 25: Hg0

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50. Page 10914, line 32: O3, Hg0

51. Page 10916, line 6: Hg+1

52. Page 10918, Sommar et al. 2004 and 2007: Would not be the final version sufficient?

53. Page 10919, Sumner et al 2005: The title of the book is missing.

54. Page 10920, line 8: Subscripts!

55. Page 10921, line 3: experimental

56. Table 2: The table is confusing for two reasons. The entries in column “analytical method” are not in the line pertinent to column “analyte”. The references are not given specifically for the appropriate line. Please correct even at a cost of the larger length.

57. Table 4: The unit “Torr” is not in use any more.

58. Fig. 5: Text inserted into the figure is garbled.

Response of the authors to comments from reviewer #2: 1. The wording of this sentence was changed from: In this article we review the history of Hg in Polar Regions to “In this article we review the history of Hg research in Polar Regions pertaining to AMDEs.” 2. As suggested, removed the word underlying 3. As suggested, changed the wording from “ a look into” to “an outlook of potential” 4. The wording of this sentence “This is the most stable form of Hg is most dominant species to undergo long range transport” was changed to “Of the Hg species found in the atmosphere, Hg(0) is the most stable and dominant and is subject to undergo long range transport.” 5. The wording of the sentence “The Arctic, for example, is populated by few people and has” was changed to “The Arctic, for example, is not densely populated and has”. The second comment in regards to the numerous arc-

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tic haze studies is not necessary in this paragraph because the following sentence says that the Arctic is perceived to be unaffected by human activity. The Raatz et al. papers were added in at the last sentence of this paragraph when referring to long range transport of anthropogenic contaminants to the Polar Regions. 6. Added “While this is not unique to the Arctic, it indicates that evidence of industrialization is present in this region.” 7. The authors agree that the Arctic troposphere is also characterised by low precipitation and low wet deposition however but feel that this information is not pertinent to the discussion of the transport of mercury to the Arctic. This is more related to the local processes referred to at the end of the paragraph. 8. The authors disagree with the reviewer’s comment that: because the lifetime of aerosols are well understood that we should thus be able to consider the Hg on those particles as well defined. In the context of this paper, because we do not know what species of Hg are on these particles and there are no techniques currently employed to identify these species in polar regions of the Hg on the particles, we consider PHg and RGM operationally defined (work done by Lu et al showed some of this but have not published to the knowledge of the authors). To clarify this position the sentence “As a consequence, RGM and PHg are considered operationally defined at this time” was changed to “As a consequence, RGM and PHg are considered operationally defined for this publication” 9. This is supposed to be 1940s. This refers to the major increase in fossil fuel burning since the 1940s. 10. The sentence “The “bioavailable” fraction of Hg in Arctic snow” was changed to “The fraction of mercury that is detected by a luminescent bioreporter, also known as the “bioavailable” fraction of Hg, in…” 11. The reviewer commented that the methods outlined in section 3 were not designed for Polar Regions. That is correct however, in the introduction to this section, it is stated that “The following section outlines the many different methodologies that are employed to investigate Hg specifically in Polar Regions”. To clarify this point the title of Section 3 was changed from Methodology to “Methodology employed to measure mercury in Polar Regions”. 12.

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The reviewer requested clarification on the statements “AFS instruments, which tend to require more facilities” and “At times, this advantage in sensitivity is forsaken for applicability and practicality when sampling in Polar Regions”. The authors have reworded the first sentence to “AFS instruments, which tend to require more facilities (e.g. AC power and argon carrier gas)”. The authors feel that the latter sentence adequately reflects operational decisions made when making field measurements in Polar Regions and thus retained this sentence in the text. For instance an AAS is used when only power from batteries is available at the sampling location. 13. The reviewers have suggested that additional references are included to the sentence “Elemental mercury’s ability to form alloys, especially amalgams, with noble metals offers a convenient way to collect air samples (Fitzgerald and Gill, 1979)”. The suggested Stock reference is in German and the author could not verify that it can be applied to this context and thus the Williston reference was included. 14. This paragraph was changed so as to include only the methods that are currently employed to measure RGM in Polar Regions. The references to the others techniques were maintained. The methods described in this section now reflect only the methods employed in Polar Regions which include RGM trapped onto KCl. The methods the reviewer is referring to where a filter may be required are bubbling and mist chambers and are not used in Polar Regions. Our current understanding of RGM sampling is that the RGM is first removed from the air using a KCL denuder and then PHg is removed using a filter. Should a filter be installed in front of the RGM sampling an unknown fraction of the RGM will adhere to this filter and lead to inaccurate measurements of RGM. The paragraph has been reworded to consider the comment of the reviewer. 15. The text was changed from “micro meteorological techniques to measure air-snow GEM and air-snow RGM” to “meteorological techniques to measure air-snow surface exchange of GEM and air-snow surface exchange of RGM” as suggested by the reviewer. 16. The terminology of “micromet” is commonly used in the field of research and has been employed in numerous publications. The authors feel that the use of this ter-

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minology is appropriate in this publication and will keep it in the text. In regards to the second comment; the paragraph was reworded and changed around as suggested by the reviewer. 17. The sentence “This is not possible for Hg given the lack of instantaneous measurement methods” was replaced with “This is not possible for Hg given the lack of fast or high frequency measurement methods”. 18. The wording describing the eddy covariance method was changed from instantaneous to fast or high frequency. The authors feel that while this method is not used to measure Hg in Polar Regions (PRs) it is used for other measurements in PRs and thus is informative to the reader to round out the discussion of micromet techniques in PRs. The text was modified to include the comments of the reviewer by changing the sentence “The limitation of the REA method is that Hg is accumulated over time and thus instantaneous information of the species is forsaken” to “The limitation of the REA and the MBR methods is that Hg is accumulated over time and thus fast or high frequency information of the species is forsaken”. 19. The sentence “The use of chambers to measure the flux of Hg in Polar Regions” was changed to “The use of chambers to measure the flux processes of Hg in Polar Regions”. The word fetch was changed to chamber footprint (the area that the chamber covers). 20. The word “elusion” was changed to “elution”. The sentence “Few measurements of air-water exchange” was changed to “There has been only a small number of air-water exchange studies of Hg conducted in Polar Regions.” 21. The comments from the reviewer were considered and the paragraph was clarified as follows “Other mechanistic reaction kinetic studies have also been performed in order to discriminate between oxidation and reduction reactions that may occur simultaneously in this. Reactions between Hg(0) and O3(aq), as well as Br2(aq) and Cl2(aq), have been studied in the laboratory by relative rate (scavenger) hydrolysis titration. Finally, Hg(0) photoradical aqueous reactions between Hg(0) + OH have been studied under laboratory conditions and are reported to be fast” 22. The text was changed to reflect the reviewers comment to “This hypothesis was

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later used by Sprovieri et al. (2005a) and found the same results at Ny-Ålesund in 2003”. 23. As recommended by the reviewer, the sentence was reworded to “In Svalbard, Ferrari et al. (2005) demonstrated that of seven AMDEs recorded, no increase in the concentration of Hg in the surface snow was observed”. 24. Changed the sentence “Such limitations include the lack of speciation of Hg in the atmosphere” to “Such limitations include the lack of knowledge of Hg speciation in the atmosphere”. 25. Changed the word “demonstrated” to “estimated”. 26. Reworded the sentence “it is recommended that further targeted and comparison studies for these reactions be made to provide more information on reaction kinetics” to “it is recommended that future studies are targeted to these reactions and that an intercomparison between experimental studies be made to provide more information on reaction kinetics”. 27. This has been edited by replacing this statement and the following one with the following sentences: “Snow on sea ice generally contains a higher halogen ion content than terrestrial snow (Simpson et al., 2005) and this may promote AMDE chemistry on sea ice but this hypothesis has never been tested. More work needs to be done to address the differences in AMDE Hg deposition to snow on sea ice or land as these two ecosystems may promote different processes in the polar biochemical cycle of Hg”. The paragraph on mercury scavenging by snow and ice has been clarified and strengthened by adding the results of a study that is currently in press as follows: “Douglas et al., (2005) collected surface hoar crystals formed near leads that yielded Hg concentrations up to 820 ng/L. These values are greater than previously reported maximum values for snow collected following AMDEs that typically range between 80 and 100 ng/L (Lu et al., 2001; Lindberg et al., 2002). Douglas et al. (2005) proposed two hypotheses to explain the reported high Hg concentrations near leads: 1) convective processes promoted halogen transfer to the air above the leads and this led to enhanced AMDE chemistry, and/or 2) the convection process and supersaturated air above the lead promoted enhanced active growth of snow and ice crystals from the vapour phase that readily scavenged available RGM.

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Results from a recent study investigating mercury deposition to a range of snow and ice crystal types (Douglas et al., 2007 (in press)) suggest that enhanced scavenging of Hg by condensing ice crystals is the most likely source of elevated Hg near leads. Ice crystals grown from the vapor phase like surface hoar (up to 975 ng/L) and diamond dust (92 to 1370 ng/L) yield the highest mercury concentrations reported to date. Frost flowers are formed from a combination of brine and vapor condensation and they yield mercury concentrations ranging from 140 to 180 ng/L (Douglas et al., 2005; Douglas et al., 2007 (in press)). More work needs to bee done to investigate how unique crystal forms may scavenge Hg differently. Of most importance is a better understanding of the ultimate fate of Hg scavenged by snow and ice crystals following spring melt. Stable mercury isotopes provide a potentially promising tool to track Hg from deposition to melt and into ecosystem pools”.

28. As suggested by the reviewer, the order of Section 5 was changed to reflect first the transport of Hg into the Arctic and then the processes within the Arctic 29. The sentence was clarified by adding the word “in air” after high Hg concentrations to indicated that this model did not reflect Hg in air in the summer and post AMDEs (when applicable). 30. The text was changed from “dominantly” to “predominantly”. 31. “That” was deleted. 32. “Polar Region” was replaced with “Arctic”. 33. The sentence “Models provide a critical understanding of the current and future transport of Hg globally and within Polar Regions. Currently, the largest challenge facing these models is the gaps in the processes of Hg and how it is transferred from the atmosphere to ecosystems” was changed to “While models play a crucial role in understanding the present and predicting the future transport of Hg to the Arctic, their current limitations lie with our knowledge gaps about Hg processes in this region”. 34. The reviewers comment suggests that this is not a clear sentence, thus the sentence “have been used to determine the reduction emissions of GEM” was changed to “have been used to determine the emission of photo-reduced GEM”. 35. P 10885 line 12:

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Changed “GEM fluxes” to “GEM emissions”. P 10885 line 14: Changed “GEM flux” to “GEM emission flux”. P 10885 line 22: Changed “i.e. GEM fluxes” to “GEM emission fluxes”. P 10886 line 2: Changed “GEM fluxes” to “GEM emission fluxes”. 36. The sentence “have indicated roughly” was changed to “have indicated that roughly”. 37. This paragraph was rewritten for clarity as follows: “Emission of Hg(0) from snow surfaces appears to be enhanced by sunlight and temperature. In 2003, at Ny-Ålesund, Hg emission fluxes were reported to range between 0 to 50 ng/m^{2}h using flux chamber techniques. The peak GEM emission flux was recorded after an AMDE but surprisingly, this peak in GEM did not correspond to any commensurate change in Hg concentration in the surface snow. During periods when AMDEs were not active Ferrari et al. reported that the GEM emission fluxes resulted from the production of GEM within the interstitial snow pack air (between 15–50 ng/m2h in the surface and 0.3–6.5 ng/m^{2}h in the deeper snow layers). During a short field campaign in 2002 in Ny-Ålesund, emission fluxes of GEM were observed around AMDE's. The average flux was 8 ng/m2h and a high mid-day peak was reported as 70 ng/m2h”. 38. The text was switched to follow the first sentence rather than the second, as suggested by the reviewer. 39. The text was changed from “during AMDEs and this RGM is either associated with aerosols” to “during AMDEs and this RGM is either associated with aerosols (termed PHg)” for clarity. 40. This paragraph was re-written as follows: “While there has been a tremendous amount of research undertaken since the discovery of AMDEs, several key questions remain that limit a complete understanding Hg cycling in Polar Regions. In the following paragraphs, the authors present suggestions on where future research should be directed in order to gain this desired comprehensive understanding of Hg cycling in this region”. 41. The references were cleaned up. 42. The correct ACP format was employed for the references. 43. The reference was changed from “200HgCl2” to “200HgCl2” 44. The reference was changed from “pf”

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to “of” 45. The reference was changed from “trsnport” to “transport”. 46. corrected 47. corrected 48. corrected 49. corrected 50. corrected 51. corrected 52. yes – 2004 publication was removed and replaced with 2007 53. corrected 54. corrected 55. corrected 56. The text in Table 2 was adjusted so that the analytical method and the analyte match up. The suggestion by the reviewer that each reference refer to the analyte measured should be included, even at the expense of a longer table. The authors feel that this would cause a lot of repetition in the table because several of the references discuss more than one measurement per location. Therefore, the authors did not feel that this was a critical change to make for this publication and that the reader can determine from the table the references that pertain to the analytes without much trouble. Thus, the table was left as is. 57. The authors recognise that the current IUPAC terminology unit is pascal. The unit Torr was used in this table because some of the older references use this unit and in order to calculate to the new units, the necessary information is not available (i.e. the uncertainties are not given in the publications. Thus, for clarity the authors will retain the unit Torr in this table. 58. The authors are unsure of what the reviewer is referring to because the text is fine in the downloaded copy that they have. Perhaps the editor can look into a problem – as this is not a function of the figure submitted by the authors.

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