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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Understanding atmospheric mercury speciation and mercury in snow over time at Alert, Canada" *by* A. Steffen et al.

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Response interactive comments by anonymous Reviewer 1 on "Understanding atmospheric mercury speciation and mercury in snow over time at Alert, Canada" by A. Steffen et al.

Anonymous Referee #1 General Comment: This is a well written, informative, and innovative study that makes use of the detailed data set from Alert to investigate the timing and sources of atmospheric mercury that is deposited to the area. This study will be of interest to atmospheric chemists, climatologists, and Polar and cryospheric

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scientists. I suggest publishing this paper with minimal changes. Some comments and suggests to this end are presented below.

Response: The authors thank the reviewers for the positive and thoughtful comments.

Comment #1: Abstract Line 8: “concentration” Line 14: “decreases” instead of “drops down”

Response: Change line 8 was made in the text as suggested; change to whole sentence was made for line 14, the latter half was dropped as follows “The higher RGM concentration continues into June”

Comment #2: Page 17024 Line 24: “period and were”

Response: Several sentences including this modification were removed from the text as it was felt this belongs in methods. The removed sentences are as follows: Analysis methods for RGM and PHg include separation of the species and quantification as GEM. While there are reasonably reliable reference standards for GEM (Temme et al., 2007), since their chemical identity is not known there exist none to accurately quantify and elucidate RGM and PHg (Temme et al., 2007; Gustin and Jaffe, 2010). The data set used for the current study was obtained using strict sampling protocols, quality control and analysis as described by Steffen et al. (2012). The data were collected over a 10 year period and were compared from year to year to observe recurring patterns and potential processes.

Comment #3: Page 17025 Lines 3-5: elaborate a bit more by stating the measurements done and the statistical analyses done. Maybe one more sentence in total?

Response: The text was modified as follows “This study reports on an analysis of 10 years of mercury sampling in air and 14 years of mercury sampling of the snow coupled with atmospheric local meteorological and particle measurements collected from Alert. Monthly statistics on this unique data set are presented and an investigation into the distribution of atmospheric mercury speciation at Alert through the spring and what

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affects mercury deposition is reported. ”

Comment #4: Page 17025 Line 17: “using a Tekran”

Response: Changes were made in the text as suggested

Comment #5: Page 17026 Line 3: I am not sure what it means to “break all PHg to GEM.” Is this slang or perhaps a term that is not commonly used?

Response: The text was modified as follows: “The quartz filter is then heated to desorb the PHg which is sent through the pyrolyzer to thermally decompose all PHg species into GEM. This GEM is then analysed by the 2537A instrument.”

Comment #6: Page 17027 Line 9: “, the particle at” appears awkward as written

Response: The text was modified as follows: “The average total residence time of a particle from when it is collected outside to its measurement point inside is approximately 3 seconds. Once the particle reaches the analyser it is approximately at room temperature and has a relative humidity (RH) of less than 50%.”

Comment #7: Page 17028 Line 2: Here it is present tense and elsewhere past tense. I recommend going through the manuscript and making past tense any measurements done for this specific study and present tense for the types of ongoing measurements at Alert that the study utilizes. Or at least making sure all the tenses are the same and make sense.

Response: The past tense was only used in the text when referring to past activities that are not related to this work. The present tense is used when presenting data for this study. However, on page 17028 line 2, the past tense was used because we used to use certain lids at the beginning until a certain point but then we switched. It’s a challenge here to use the same tense in this instance. The authors thank the reviewer for this comment and we have reviewed the text and modified tense as required.

Comment #8: The snow sampling in general: Were specific storms targeted? It is hard

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to tell why or when a given snow sample was collected. Was there any correlation between the amounts of snow deposited in a storm versus the Hg concentration? Was there any relationship between the timing of the snow fall and the Hg concentrations and/or the snow storm amount? I realize these questions are a bit off the main intended aspects of the paper but the authors may have data to present in this regard that could strengthen the applicability of the paper. With climate warming some areas may receive more or less snow and this relationship to the Hg cycle warrants a further look.

Response: The authors thank the reviewer for the good insight and suggestion. Unfortunately, the data is collected only on occasions when there is snow on the table and when no storms are occurring. Given the location of the sampling set up and the frequency with which the site is visited, the only method that could be employed consistently, is as follows: when the operator is at the site, he checks if there is snow on the table and if so, then it is sampled at that point. If there is a storm occurring, there tend to be high winds and the snow is blown from the table surface. We have tried to use an automated system that gets covered when the wind picks up but results from this experiment yielded very high blanks and the system did not function well in the harsh arctic conditions. The authors recognize the limitations collecting the samples and thus in interpreting this data with regards to storm events, but we feel that the quantity of data over time and repetitive nature of the results provide a valid set of information.

Comment #9: Page 17029 Lines 19-22: The words “run” and “running” are used three times to represent “measured” or “analyzed” or “quantified.” I recommend against using the word “run” for any of these instances anywhere. It is slang.

Response: The text was modified as follows: “Standard reference water is analyzed alongside samples during analyses. All samples are pre-screened with 10 mL single samples to determine general THg concentrations. The samples are split into low and high samples to fit calibration standards with equivalent concentration ranges. The final analytical measurements determined samples as duplicates or triplicates and spike recoveries were determined every 8 to 10 samples.”

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Comment #10: Page 17035 Line 2: “onto snow and ice” Line: 9: I thought GEM was not deposited to snow but had to be converted to RGM first. This may have been explained earlier but please clarify. I also thought the RGM could be photochemically reduced to GEM and re-emitted so again this is confusing for me.

Response: Changes were made in the text as suggested

Response: GEM has a slower deposition velocity than RGM and PHg. However, GEM is 1000 times higher in concentration in the air than RGM and PHg, thus there may be some GEM that is deposited and accounted for in the snow samples. With that said, most of the GEM in the air has been converted to RGM and PHg thus we only look at the impact of these species for the purposes of this paper and it was shown that, once deposited, GEM is immediately reemitted. The text was modified as follows to clarify this “All 3 forms of mercury can be removed from the atmosphere and deposited onto snow and ice. While the deposition velocity of GEM is much lower than that of RGM and PHg (Zhang et al., 2009), the concentration of GEM in the air is quite high in comparison to other two species and, as a result, GEM could be present in the snow samples (Lin, 2006). However, a review of mercury behaviour in snow concluded that any deposited GEM would immediately be re-emitted (Durnford and Dastoor, 2011) and thus we do not consider GEM to be a significant portion of mercury in the snow samples. Further, most of the GEM in the air during this study is converted to RGM and PHg and thus we only consider these mercury species for the purposes of this analysis of the impact of AMDEs on the mercury levels in the snow at Alert.”.

Yes, RGM can be photoreduced to GEM and reemitted but this is not always the case. The behaviour of all three species, GEM, PHg and RGM, is described in the paper as per the Durnford and Dsatoor paper where GEM immediately is released once deposited, PHg remains in the snow and RGM can undergo several processes including both reduction and oxidation so it is less clear as to its fate, once deposited. The text was modified to reflect this more clearly as follows “In an analysis of the fate of deposited mercury in the snow pack, Durnford and Dastoor (2011) suggested that the

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PHg deposited to snow is likely to remain in the snow pack and that the deposited RGM can undergo several processes including photo reduction and emission and oxidation in the snow and thus its fate is in the snow is uncertain."

Comment #11: Any idea as to the back trajectories of the snow storms in terms of where they came from and their Hg concentrations? I do not expect this paper to address this but am curious.

Response: That is an interesting question. We have not looked into storm events in any detail and their impact on the Hg concentrations for this location. We will come back to this question in a subsequent study, thank you for the idea.

Comment #12: Page 17036 and the Conclusions page 17038: The results of this study suggest that the Hg in snow is predominantly present as RGM and that particles or pHg are not a major factor or component in the snow Hg cycle. This is an important result that should be stressed with greater emphasis. It supports findings of AMDE chemistry and elevated Hg in Antarctic snow where the elevated aerosol component from Arctic haze is not present. It also suggests that cleaning up aerosol emissions will not reduce Arctic Hg deposition?

Response: We would like to clarify the conclusions for the reader because while the highest snow concentrations are reflected when RGM is the predominant species; we do not want to completely negate PHg contribution within the transition period. We conclude that the predominant form of mercury in the air is PHg when there are particles present. When the particles decrease, the predominance of RGM increases but there are still particles and PHg present until at least mid may. During this time period we report elevated Hg in the snow. Thus, it is a combination of PHg and RGM at the beginning where some increase in Hg in the snow is seen followed by the RGM that causes the elevated Hg in the snow.

The text in Section 3.3.1 (now 3.3) was changed as follows for clarification: "During the beginning of the transition period, when both PHg and RGM are present, the levels

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of mercury in the snow begin to increase considerably. Subsequently, the levels of mercury in snow keep rising (and falling) concurrently with [RGM]. We conclude that the highest deposition of mercury to the snow in the Arctic depends on what form of mercury is present in the atmosphere. As shown in Figure 8, mercury levels in the snow begin to significantly increase around day 113 (towards the end of April) where [PHg] and [RGM] are ∼150 and 40 pg m-3, respectively. The highest mercury in snow was reported from days 128-131 where [PHg] and [RGM] were ∼70 and ∼150 pg m-3, respectively. The decrease in PHg, and drop in particle numbers, in May coincide with the initial increase of Hg in the snow. Even though PHg is scavenged more efficiently by snow than RGM (Amos et al., 2012), it appears that the highest levels of mercury in the snow are when [RGM] dominates the atmospheric mercury levels. RGM has a higher dry deposition velocity than PHg (Zhang et al., 2009) and can readily deposit onto the snow surfaces. Thus, when the atmospheric conditions favour RGM, higher levels of mercury in the snow should be expected. Overall, this data show that the highest deposition of mercury to the snow in the spring at Alert is during and after the transition of [PHg] to [RGM] in the atmosphere."

The authors do not suggest that cleaning aerosol emissions will have no effect on Hg deposition in the Arctic. We recommend that the next step is to elucidate the particles during the springtime so see which are related to haze, sea salts and biogenic particles.

We have modified the conclusions as follows for clarification: "Ten years of data from the snow and atmospheric measurements are combined to show that during the transition from a high [PHg] to a high [RGM] domain there is a concurrent increase in the concentration of mercury in the snow. It was concluded that when the atmospheric conditions favour high [RGM], higher levels of mercury in the snow are reported. Therefore, the conditions in the atmosphere directly impact when the highest amount of mercury will be deposited to the snow during the Arctic Spring."

Comment #13: The total Hg is sensitive to the presence of RGM whereby the instance the pHg increases the RGM does and as soon as pHg decreases the Hg in snow

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decreases. This is an intriguing dataset. It is worth adding a few more references that have similar data or research questions but not the large sample dataset available here.

Response: Please see the slight modifications made for comment #12 above.

Several references have been added into the text that address similar research questions and the text was modified and moved to the introduction section as follows: “While atmospheric mercury speciation data in the Arctic air have been collected at several sites (Aspmo et al., 2005; Sprovieri et al., 2005; Kirk et al., 2006; Skov et al., 2006; Cobbett et al., 2007; Steen et al., 2011; Moore et al., 2012; Cole et al., 2013; Steffen et al., 2013; Brooks et al., 2006), few long term (more than 5 years) mercury speciation measurements at temperate regions have been published and the Alert dataset is the only such Arctic dataset (Cole et al., 2013)” and

“Several researchers have previously investigated the deposition and fate of mercury the snow and ice surfaces (Boutron et al., 1998; Lu et al., 2001; Lalonde et al., 2002; Dommergue et al., 2003a; Dommergue et al., 2003b; Ariya et al., 2004; Douglas and Sturm, 2004; Ferrari et al., 2004a; Ferrari et al., 2004b; Douglas et al., 2005; Ferrari et al., 2005; Fitzgerald et al., 2005; Lahoutifard et al., 2005; St. Louis et al., 2005; Kirk et al., 2006; Constant et al., 2007; Poulain et al., 2007; Douglas et al., 2008; Outridge et al., 2008; Poissant et al., 2008; Steffen et al., 2008; Dommergue et al., 2009; Carignan and Sonke, 2010; Durnford and Dastoor, 2011; Douglas et al., 2012; Durnford et al., 2012) but none have used the type of long term snow data set presented here.”

Comment #14: Figure 4: Present the datapoints in the legend in chronological order with 2011 last.

Response: Modifications were made as requested

Comment #15: Figure 5: another random question/comment: are there any trends in the monthly backscattering values over time? IE has the Arctic haze aerosol amount

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changed at all over the past decade? Also I am curious that January has as much backscatter as March and April when I thought the Arctic haze aerosols were at their maximum concentration.

Response: There have not been any monthly scattering data published for time trends at Alert but there have been reported black carbon trends in the combined data from three Arctic sites such as Alert, Barrow and Ny-Alesund that showed a 40% decline in the equivalent black carbon between 1990 and 2009 (Sharma et al, 2013) and by 70% at Alert alone. As well, Gong et al (2010) and Quinn et al (2007) showed that there was a decreasing trend in the non sea salt sulphate from 1990-2004 which is also a scatterer. Scattering is max in Jan and Feb (from long range transport of scattering components and no local production). In March/April you have both long range transport and local photoproduction.

Gong, S. L., T. L. Zhao, S. Sharma, D. Toom-Sauntry, D. Lavoué, X. B. Zhang, W. R. Leaitch, and L. A. Barrie (2010), Identification of trends and interannual variability of sulfate and black carbon in the Canadian High Arctic: 1981-2007,J. Geophys. Res., 115, D07305, doi:10.1029/2009JD012943

Quinn, P. K., Shaw, G. E., Andrews, E., Dutton, E.G., Ruhoh-Airola, T., and Gong, S.: Arctic Haze: current trends and knowledge gaps, Tellus, 59B, 99-111, 10.1111/j.1600-0889.2006.00238.x, 2007.

Sharma, S., Ishizawa, M., Chan, D., Lavoue, D., Andrews, E., Eleftheriadis, K., and Maksyutov, S.: 16-year simulation of Acrtic black carboL transport, source, contribution and sensitivity analysis on deposition, Journal of Geophysical Research, 118, 1-22, 10.1029/2012JD017774, 2013.

Comment #16: Figure 8: “The atmospheric data have been” Interactive comment on Atmos. Chem. Phys. Discuss., 13, 17021, 2013.

Response: Modifications were made as requested

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Temperature versus Particulate Hg Fraction for March
PHg]/([PHg]+[RGM])).

Slopes: **2002**: -27.7; **2004**: -29.4; **2005**: -29.4; **2008**: -16.5; **2009**: -26.7; **2011**: -32.4
R^2 values: **2002**: 0.56; **2004**: 0.64; **2005**:0.45; **2008**: 0.12; **2009**: 0.58; **2011**: 0.72
Years 2003, 2006, 2007 and 2010 are not included due to large data gaps

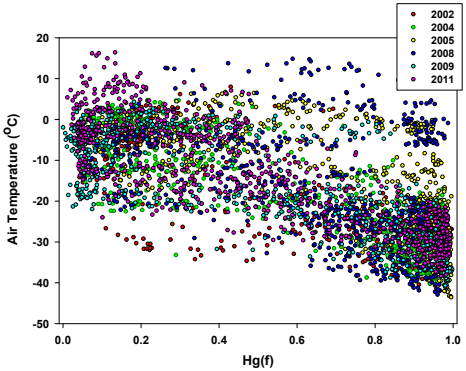

Fig. 1.

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