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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The variability in Gaseous Elemental Mercury at Villum Research Station, Station Nord in North Greenland from 1999 to 2017" *by* Henrik Skov et al.

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Reply to referee 2 All replies to referee questions and comments are in plain text and all changes to the text of the manuscript are in inverted commas (""). Furthermore, the graphs have been updated using Origin instead of Excel. We thank the reviewer for a thorough review of the article. We have answered all questions, added, and modified text when deemed necessary. Especially, we have modified the Material & Methods section and the Results and Discussion section to make them more straightforward to understand and explain better the data interpretation. More references have been added as well. The indicated lines are referring to the revised manuscript and the

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numbers in parenthesis are referring to lines in the ACPD version.

1. Line 91 (Line 89): We have rechecked, which instruments were in use during the period of the measurements. From, 1999 to 2002 only A model instruments were in use and they were applied again from 2009 to 1st Dec. 2016, where they were replaced by a B model that was used until 3rd Dec. 2017. The last month of 2017 and in 2018 X models were used. The referee states that the 20% uncertainty should be included into the uncertainty especially in the trend analyses. This uncertainty is a random uncertainty. All instruments are calibrated towards the same standard (vapour pressure of Hg using instrument Tekran 2505 calibration unit) and this preclude a systematic error. An explanation is added in line 90. We do trend analysis of yearly or seasonally averaged values and thus the random uncertainty is minimized. If there is a systematic error, we correct for it following ISO Guide 98-3:2008 Uncertainty of measurement âĂŤ Part 3: Guide to the expression of uncertainty in measurement (GUM:1995) and include this correction into the uncertainty. In Kamp et al. 2019, we used a separate setup based on two Tekran 2537X instruments and the measurements were independent of our monitoring activities that provide the result for this article.

Line (91-93): The sentence has been modified to make it clearer: “Several generations of the instrument have been used (A, B and X versions) but we estimate that the uncertainty of measuring GEM has remained unchanged during the years as they are all calibrated towards the same standard based on the vapour pressure of Hg0 using Tekran 2505 calibration unit.”

2. The first years 1999-2015 we used 5 minutes sampling. Thereafter we changed to 15 minutes sampling in order to decrease the consumption of Ar.

Trend analysis In the trend analysis, we used yearly and seasonal mean values (3 months). Following the advice of Referee 2, in the revised version of the manuscript we have used the non-parametric Mann-Kendahl test and Sen’s slope calculation, instead of the classical regression analysis that we applied in the manuscript under review,

because of the advantages of this approach (no assumptions about the distribution of the measurements, low sensitivity to outlier values). The following text has been added to the Experimental Section: Line 116-117 (108-109): “The calculation of inter annual trends were performed applying the non-parametric Mann-Kendahl test and Sens slope calculation, using the program developed by Salmi et al. (2002).”

The new trend analysis, including the GEM measurements from 2018 that have now been quality assured, show significant negative trends (at a 90% confidence level) of the autumn and winter (SON, DJF) average values but no significant trend of the annual averages (as in the previous analysis). We have decided not to report non-significant trends, thus we have omitted the previous Table 1. The initial part of the discussion of trends, starting by the beginning of Section 3 has been revised and is now the following:

Line 184-202 (180-193): “The measurements of GEM and ozone from 1996 to 2018 are shown in Figure 3. A seasonal pattern is observed for each year. In January and February, the level of ozone and GEM is rather stable. After the polar sunrise, the concentration starts to fluctuate strongly and ozone and GEM are depleted fast (during 2 to 10 hours). Figure 4 shows the variations of the yearly average GEM concentration and the average for the winter season between 1999 and 2018, where only periods with more than 50% data coverage have been included. The annual averages show a negative trend, however not significant at a 90% confidence level. The autumn (September-October-November) and the winter (December-January-February) season show both negative trends that are significant at a 90% confidence level (annual and winter data are shown in Figure 5). The trends, in percentage of the average GEM concentrations during these periods, are -1.7%/yr for the winter period and -1.4%/yr for the autumn. The annual trend remains non-significant also when excluding the years 1999 and 2000 or the extreme value in 2017. The lack of a significant annual trend seems to be explained by the high variability of the concentrations during the spring period as well as the fact that the GEM concentration during the summer period shows no evidence of a decreasing trend. This result is similar to the result. . . . . ”

Modelling section 1. The focus on this paper is the direct transport of GEM from sources to the measurements site. Therefore, we used simple first order chemistry as written in line 156-157. 2. The emission inventories applied have been clarified in the text, see line 131-137 (126-130): "The global historical AMAP Hg emissions inventories for 1990-2010 have been used as the anthropogenic emissions (UNEP 2013) for the model run with variable emissions. The 1990 emissions have been used for the model calculations for the period 1990-1992, 1995 emissions for the years 1993-1997, 2000 emissions for 1998-2002, 2005 emissions for 2003-2007 and finally the 2010 emission for 2008-2017. The emissions for 2005 were used for the model run with constant emissions. Emissions of mercury from biomass burning were based on CO emissions obtained from Global Fire Emissions Database, Version 3, (van der Werf et al. 2006; Van der Werf et al., 2003), where a fixed Hg0/CO ratio of 8$\times$10-7 kg Hg0/kg CO was applied. Emissions from oceans are based on calculated fluxes from the GEOS-Chem model (Soerensen et al. 2010)."

3. Line 146-161 (133): The text have been modified in order to clarify the meaning of boundary condition. The model calculations is actually a sensitivity study, where the contributions from different sources as function of first order lifetime of GEM are estimated. Moreover, because it is a linear first order lifetime, it is quite easy to scale the different source areas including boundary conditions. The direct anthropogenic influence will be changed (be larger in percent) if the prescribed boundary conditions are decreased.

"The system has been set up with 11 different GEM tracers, which represent eight different anthropogenic source areas (Russia, Eastern Europe, Western Europe, China, North America, Rest of Asia, Africa and South America), biomass burning, ocean sources and the prescribed boundary conditions of 1.5 ng/m3 for the entire period. The latter is introduced because of the long lifetime of Hg0 and accounts for the transport across equator with the exchange velocity between the two hemispheres of about 1 year. The boundary condition concentration of 1.5 ng/m3 represents the typical global

background concentrations, which account for all emissions in both hemispheres, and are close to the concentrations at equator as given in Selin et al (2008). The boundary conditions were kept constant during the period covered by the model. There have been made 2x3 different model runs covering the period from 1990 to 2017, with two main emissions setup, which are with either constant anthropogenic missions (using the emissions in 2005 for all years) or the variable emissions for 1990-2010. Each emissions setup is run with a simple fixed first order reaction lifetime for Hg0 of 1 month, 6 months and 1 year, respectively. The model does not include Arctic mercury depletion in the runs presented here; it focuses only on the direct long-range transported mercury contribution to the GEM concentration at Villum. For each model run the contributions of the 11 different tracers are estimated in order to investigate this contribution as function of the fixed first order reaction lifetime for Hg0, changing meteorology and changing emissions."

Lines 43-48 (43-51): An update of the text has been made and inserted "The sources of mercury in the environment can be divided into natural, anthropogenic, and reemission, accounting for 2.1, 2.5 and 3.4 ktonnes of the emissions, respectively (Outridge et al. 2018). This is in good agreement with other estimates. The global anthropogenic emissions of mercury were estimated as 2.5 ktonnes in 2010 (UNEP 2013; AMAP/UNEP 2013) and including the large uncertainty on these numbers, they are not significantly different. According to an estimate by (Pirrone et al. 2010) natural sources and reemission processes (hereafter referred to as 'background sources'), accounted for 5207 Mg per year in 2005 while the amount of new anthropogenic inputs is 2320 Mg per year also close to the latest emission estimate (Outridge et al. 2018)." Lines (225-226): (Previous Figure 7 and 8 now) Figure 8 and 9. Both Figure 8 and Figure 9 show decreasing concentrations but it more clearly seen in Fig 9. In the first draft (in ACPD) the model output with constant emissions were shown. This is now corrected and the model results presented in Figure 8 and 9 are with variable emissions. As reply to reviewer, the use of variable emissions has been clarified in the figure captions:

"Figure 8: Model calculation with variable emissions of the source apportionment of the direct anthropogenic contribution to the annual average GEM concentrations at Villum. The DEHM model used two years (1990 and 1991) to spin up the model. Source regions: Russia = Russia; EEU = East Europe; WEu = West Europe; China = China; Africa = Africa; Sam = South America. Unit: ng m-3."

"Figure 9: Model calculation with variable emissions of the source apportionment of annual average GEM at Villum. The DEHM model used two years (1990 and 1991) to spin up the model. In the model reemission from ocean and contribution from boundary conditions at equator included. Source regions: Russia = Russia; EEU = East Europe; WEu = West Europe; China = China; Africa = Africa; Sam = South America; Bound = Boundary Condition; Ocean = Ocean; Fire = Wildfire. Unit: ng m-3."

Line 283 (242): It was not a separate calculation. The text has been corrected for this: "In the model calculations with DEHM, it was found that emissions from China had larger relative importance during the summer than in the winter season."

Lines 283-291 (259-264): We have included a comparison with the results from Dastoor et al (2015) in the new version of the text: New text: "Results obtained by applying the DEHM model to simulate GEM concentrations at Villum indicate that changes in the direct atmospheric transport from source areas to Villum cannot explain the observed trend. We have found that the simulated yearly and seasonal GEM values show very little variability and no significant trend over the years 2000-2015, when the emission sources are kept constant at the 2005 level while the meteorology is varying and treated as described above. That is opposite to results by Dastoor et al. (2015) for model run with constant emissions. The main reason for that is perhaps that processes as chemistry and surface exchanges in Dastoor et al. (2015), are more depending on the atmosphere and surface conditions than the simple setup in the present version of DEHM. There are better agreement between our results and Dastoor et al (2015) for the model setup with variable emissions. We see a decrease of 0.08 ng/m3 between 1992 and 2005 for Villum, while Dastoor et al. found approximately 0.1 ng/m3.

The study by Hirdman et al. (2010) of long term trends of sulfate and BC in the Arctic also concludes that changes in atmospheric transport only can explain a small fraction (0.3-7.2%) of the observed trends."

Line-by-line comments.

Lines (42-43): An update of the text has been made see the answer above.

Lines (43-51): We were not aware of the Outridge et al. paper. We are referring to this one as primary reference for the discussion of Hg0 emissions to the atmosphere. See earlier

Line 59-66 (59): The sentence is replaced by: "The atmospheric lifetime of GEM has earlier been estimated to be in the range of about one year (Steffen et al. 2008), while those of oxidized forms of mercury are shorter. Theoretical and laboratory studies showed that the lifetime of GEM towards Br initiated oxidation is much shorter than 1 year (Goodsite et al. 2004, 2012, Donohoue et al. 2006, Dibble et al. 2012, Balabanov et al. 2005, Jiao and Dibble 2017; Donohoue et al. 2005). Applying the latest kinetic data, Horowitch et al. (2017) found a lifetime in the atmosphere of GEM against oxidation of 2.7 months using the GEOS-CHEM model cobbled to an ocean general circulation model (MITgcm). Including photoreduction, the lifetime of total gaseous mercury (TGM) was found to be 5.2 months close to the value 6.1 months of Holmes et al. 2010 but applying a much higher Br concentration and thus also a faster photoreduction."

Line 79 (68-69): The references have been changed from Jiska et al. 2018 to Streets et al. (2019, 2018, 2017).

Line 80 (70): The references have been changed from Obrist et al. (2018) to Zhang et al. (2016).

Line 94 (84): Correction in the text has been made as it was in 2014 that the monitors were moved.

Lines (93-95): The 20% were determined in Skov et al. 2004 and confirmed in the

present work.

Lines 185 (154-156): A new figure (Figure 4 shown suplement) is added showing the seasonal variation: Figure Caption: “Figure 4 Monthly averages of GEM for the years 1999 to 2002 and 2008 to 2018. The whiskers show the $\pm$ 1 std. dev. of the monthly averages.”

Line (163): We have added results from 2018 as the final quality control is finished Line 205 (169): Corrected

Lines 228-231 (192-194): Sentence is now completed. “An important point for the parameterization of GEM depletion is that bromine induced atmospheric mercury depletion event (AMDE) often was observed under stagnant wind conditions and not only during situations with strong wind that may cause bromine release as proposed earlier (see Yang et al. 2020).”

Lines 241-245 (202-204): The discussion has been extended: “In fact, the analyses indicate that AMDE is a net sink for mercury, which is in agreement with direct flux measurements (Brooks et al. 2006). Interestingly, (Angot et al. (2016) found a positive feedback between AMDE in spring and the concentration of GEM in summer at Alert that was attributed to reemission of mercury. Contrary to this result, even the annual mean value at Villum had a negative correlation with AMDE hours. Though this correlation is weak, it is an indication that AMDEs affect the GEM concentration level at Villum and represent a net sink for GEM.”

Line 247-251 (208): The sentence has been changed: “The present study indicates that there is an atmospheric input as well. The significance of this source depends on its chemical form. Previously atmospheric deposited mercury has been identified to be bioavailable (Moller et al. 2011) and thus might still be dominant for the mercury found in the Arctic foodweb?”

Line 263 (223): No the yearly average is higher in 2013 than in 2014. The average

concentration during winter is highest in 2013. This is now specified in the text.

Lines 267 (225-226): See corrections above where Figure captions have been extended to explain that Figure 7 shows only the direct contribution from anthropogenic sources, whereas Figure 8 shows the total contribution to GEM .

Line 275 (234): Missing parenthesis is added

Line 283 (242): The word “separate” has been deleted in sentence

Lines 283 (242-257): The following paragraph has been extended: “In the calculations with DEHM, it was found that emissions from China had larger relative importance during the summer than in the winter season; however, this difference was only significant for relatively short (less than 1 year) atmospheric lifetimes of GEM. The calculations for Villum were performed for the year 2001. This result agrees with Chen et al. (2018), who found that East Asia is the main source for mercury deposition in Arctic. Similar result is also reported by AMAP (AMAP 2018). Durnford et al. (2010), applying the GRAHM model, investigated the contribution of different source regions to total mercury as well as GEM concentrations at several Arctic monitoring stations at different seasons of the year. They found that for the yearly concentration averages and their variability at the Arctic stations, including Villum, Asian emissions were the most important, accounting for more than the sum of the contributions from Europe, Russia and North America.”

Lines (259-264): This point was addressed in the model section above

Lines 325-337 (265-278): The missing Table is inserted and discussion checked.

Line (278): It does not give any meaning to compare measurements and modelled results with the current version of DEHM looking at shorter time scales. DEHM ran with a constant first order lifetime and thus the short-term variation of modelled GEM concentrations are only due to transport, whereas measured GEM is dependent on transport, chemistry and other processes. DEHM can thus only be applied here to

say something about yearly average concentration and trends based on the lifetime, emissions and transport. The discussion of seasonality in measurements and model results has been removed

Lines (279-281): The sentence has been deleted, as it is confusing.

Line (288): The decreasing trend of -0.7% is as written in the text for the model run with variable emissions, while this paragraph is for the model run with fixed emissions as also explained in the text, e.g. the variability of the transport patterns does not give any significant trend.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2019-912/acp-2019-912-AC1-supplement.pdf

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