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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Effects of temperature and other atmospheric conditions on long-term gaseous mercury observations in the Arctic" *by* A. S. Cole and A. Steffen

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Reply to Anonymous Referee #2

"This paper presents an analysis of trends in atmospheric elemental mercury at two Arctic sites - from a 12 year record at Alert, Nunavut, and a 6 year record at Amderma, Russia. The paper reports several very interesting findings, specifically that there is a trend of decreasing GEM concentrations at Alert, that mercury depletion event frequencies are moving to earlier in the year, and that the depletion events generally increase in frequency with lower temperature. The authors examine the correlation of mercury depletion events (AMDEs) and emission events (AMEEs) with climate variables, e.g.

local temperature, wind speed and direction, condition of the sea ice, etc. I think the data sets, while raising as many new questions as are answered, are very interesting, and the paper is very well written. The observations in Figures 1-3 are indeed quite fascinating and important. I have some technical issues with the analysis and interpretation, but overall, I think this is an interesting paper that should be published after attention to a number of minor issues, which I list below in the order the issues appear in the paper.

"A relatively large issue with me is that the paper shows that AMDEs increase in frequency with decreasing temperature, and says that this is consistent with the literature, but the paper doesn't explain this in any quantitative way, or present a hypothesis. While the paper seems to imply (e.g. in reference to the Goodsite et al. work) that the temperature dependence can be explained by the temperature dependence of the gas phase kinetics, it glosses over the possibility, which has been raised in the literature, that ozone and mercury depletions could exhibit a temperature dependence strictly because of the temperature dependence of the release of Br2 from the snowpack, and the associated availability of Br atoms to react with Hg, and not at all because of gas phase kinetics. Specifically, as discussed in Koop et al., 2000; Cho et al., 2002, and Tarasick and Bottenheim, 2002, there could be a discontinuity in the temperature dependence because when NaClâ′NEËĞ 2ÎU° 2Î§precipitates out (e.g. from the QLL) at -21oC, Br- is effectively concentrated at the surface, and thus the rate of bromine activation may increase. I am not suggesting that we know this is the answer, but the possibility that the temperature dependence results from the temperature dependence of Br2 release from the condensed phase should be mentioned. The Abstract should be less definitive on this issue. Additionally, while the Conclusions recommends studies of the temperature dependence of gas phase reactions, it again seems to ignore the need for study of the temperature dependence of the processes that liberate bromine. In this regard, I think overall the paper could give the reader the wrong impression about what is important, and what things are unknown. For example, for the last sentence in the Conclusions, you might mention that we still don't know for sure the relative importance of Br and BrO as oxidants for Hg. "

– Thank you for your thorough review. Your major point regarding the insufficient discussion of halogen chemistry as a mechanism for our observations is very much appreciated. It was not our intention to dismiss this mechanism by limiting its discussion to the introduction, or to imply that it is well understood. We did highlight the need for experimental data on mercury oxidation temperature effects simply because there is essentially no data on these temperature effects, while there is some information about bromine kinetics and temperature in the literature (as you mention). We see how this would be misleading and we have included more discussion about bromine chemistry in the Discussion and Conclusions sections.

"I think the paper should also discuss more the fact that, as shown in Figure 2, the temperature for AMDEs needs to be colder earlier in the season. Why do you suppose that is?"

– It may be due to the low levels of radiative flux early in the season leading to slower generation of halogen radicals. Favourable AMDE conditions may then be a balance between high radiation levels and low temperatures. Alternately, or in addition, there may be more open water or leads later in the season, such that freezing temperatures result in more fresh ice and/or frost flowers that seem to lead to bromine production. We've added these points to the discussion.

" The paper could also mention that the very interesting temperature trend shown in Figure 6 for March is not likely to continue in the long term? "

– We've added a note about longer-term warming at the beginning of section 3.3.

"Additionally, I am not at all convinced that the explanation proposed for the temperature and wind direction dependence of AMEEs at Alert is right. While it is suggested that the sea ice acts as a barrier to Hg emission from the ocean, this statement implies that a local 0oC temperature correlates with the time of maximum sea ice breakup. Is

that true? I am not sure. In addition, the wind direction dependence of AMEEs at Alert could be because the maximum in the RGM and aerosol Hg deposition occurs over the Arctic Ocean in turn because that is where halogen atom concentrations are highest. Then Hg could be re-released in a temperature dependent photochemical process on the surface of the sea ice. Is there any information regarding total Hg in snow on sea ice vs inland? These issues should be discussed in more detail. "

– These are very good points and we agree that sea ice breakup is unlikely to be a cause of the AMEE correlation with temperature, though it may contribute to the wind direction correlation. That said, snow Hg levels are definitely elevated on sea ice as shown by Douglas et al. (2005), and likely are the major reason for the wind direction correlation – a point that we overlooked in the manuscript and have now incorporated, thank you.

"Minor issues are listed below.

"1. The text referring to equation 1 confuses me. While it indicates that it is the "integrated AMDE frequency", equation 1 is the average magnitude of the depletion, in concentration units. The text and perhaps an additional equation to explain how the frequency numbers were obtained should be improved. "

– The calculation is not exactly the average magnitude of the depletions (since the denominator includes all AMDE and non-AMDE measurements). We had initially looked at the AMDE frequency by counting AMDE points and dividing by total points, but then added the concentration term to account for the magnitude of the events – essentially integrating the area between the measurement curve and the cutoff value on a concentration vs. x plot, then normalizing to the size of x. We've improved the text to clarify what the calculation represents.

"2. I consider the observation of a shift in the timing of AMDEs to be big news indeed; in this light, I think it should be discussed in even more detail. In particular, since this is likely to be caused by a shift in the timing of the surface concentrations of bromine atoms, we should see the same change in the frequency of ODEs. The paper would be even higher impact if the authors provided a little information about changes in the behavior of ozone over this period. Climate change is known to impact transport patterns in the Arctic, e.g. related to the change in the dipolar pressure pattern. Could this have any impact in AMDEs at Alert, where both AMDEs and ODEs are transport related? There should be a bit more reference to the literature in general. "

– We've added some additional discussion about the importance of the shift in AMDE timing to Section 3.1. The ozone data do show some evidence of a shift (fewer May ODEs), but it is not of the same magnitude as for mercury (though we have not done the complete statistical analysis yet). We are continuing to explore the ozone and mercury relationship in more detail in the light of our findings here, so that will be a focus of another paper in the future. In terms of the impact of transport patterns, as reported in the paper we only saw a link in March to the NAO and PET indices, so if there is an impact it may be limited to the time of the polar vortex. Or perhaps the influence of transport patterns may be multi-pronged; wind patterns affect the ice dynamics over the ocean as well as the transport of air masses to these sites. There is probably a lot more to explore on that topic that could be a focus of future work.

"2. Page 27171: There should be a general reference provided that describes the measurement method, for both sites. Was there radiation data after 2003 for Alert? "

– The measurement method was the same at both sites. We've added more detail and a reference. Unfortunately, as far as we can find there is no radiation data publicly available.

"3. Sometimes the wording in the paper is unclear; as examples, on page 27174, it says "there was a significant decrease in the total springtime integrated AMDEs at Alert". Do you mean the total mass of Hg consumed, or the frequency of the defined AMDEs? Does the sentence on the next page, "While springtime depletion events do not appear to have increased at Alert..." contradict the earlier statement? "

– We have changed the text on p. 27174 to refer to the quantity defined in Eq. 1, and the wording of the second sentence to specify that depletion events decreased (rather than "not increased").

"4. Page 27177: regarding the lack of dependence on wind speed, the paper should at least cite the Yang et al 2008 blowing snow paper in GRL, which hypothesized that blowing snow liberates sea salt aerosol which could then be converted to active bromine. Your results could be taken as lack of support for that mechanism."

– This reference has been added. If the bromine activation (and mercury depletion) is happening far upwind of the sites, though, we would not necessarily expect the wind speed at Alert or Amderma to correlate with levels of sea salt aerosol over the ocean.

"5. Bottom of page 27178: while it isn't absolutely necessary, a simple trajectory analysis for Amderma might be useful for this paper? "

– We had considered this as well, but decided it would be best left for a future paper.

"6. The statement on page 27180 about the frequency of AMDEs correlates with a strong circumpolar vortex seems to be contradicted by an opposite statement in the Conclusions. "

– The wording was correct but confusing and has been clarified.

"7. Top page 27182: clearly the fact that your two-parameter fit predicts the timing of fluctuations in GEM is a function only of the temperature variable, since the day of year is a smooth variable. Isn't it likely that such a multivariate fit could be improved by adding a simple stability variable, like _T(10m) or something like that? Perhaps you could suggest specifically how to improve such a simple parameterized fit? It should also be noted that while your fit in Figure 5 shows a temporal trend toward of increasing "baseline" concentration with month, the observations do not show that, they show a relatively constant baseline GEM of 1.5-1.7, punctuated by AMDEs. So, really, I don't think the day of year variable is very robust. "

– It is true that the 2008 data don't show a seasonal cycle, but that is actually unusual. Generally there is a GEM minimum in mid-April, but in 2008 there is a long period around April 1 where GEM concentrations were high for a long period. I do feel that we need to account for the day of year for a couple of reasons: (a) for whatever reason, the chemistry is happening in the springtime, not other seasons when meteorological conditions are similar; (b) the temperature dependence does have a temporal component, as seen in Figs. 2 and 3. Your suggestion of a stability variable is interesting, although I would expect if that is a large component it would be reflected in a correlation with wind speed as well. Ideally, local BrO measurements would be available to include in the parameterization. But really, if the chemistry is occurring upwind of the site, looking at local variables is never going to tell the whole story. We did not intend to suggest that GEM concentrations could be predicted in any robust way based on local temperature, but just that the correlation is significant enough that it should be included in mercury models. After careful consideration of the comments of three reviewers, we have chosen to remove Figure 5 from the paper as it is somewhat misleading in that respect.

"8. Figure 1 - could the large apparent shift in timing of AMDEs be influenced in any way by binning the data? Is the shift statistically significant on the date axis?"

–The timing shift is significant. If we used smoothed GEM vs. date and look at the date that the minimum GEM value occurs, the trend in this date is -1.2 +/- 0.8 days per year (95% CL). We have added this result to Section 3.1 as well.

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