Atmos. Chem. Phys. Discuss., 9, C9779–C9782, 2010
www.atmos-chem-phys-discuss.net/9/C9779/2010/

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

Anonymous Referee #2

Received and published: 17 January 2010

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 NaClâŃĚ2ÎŮ2Î§ 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. 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? 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? 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. 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.

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.

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?

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?

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.

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

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 ΔT(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.

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?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 27167, 2009.