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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Natural and anthropogenic atmospheric mercury in the European Arctic: a speciation study" *by* A. O. Steen et al.

A. O. Steen et al.

anne.steen@chem.ntnu.no

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The authors are grateful for the anonymous referee's comments on the manuscript, which improved the manuscript. Our comments are given below. Corrections are made in the revised manuscript.

The paper by Steen et al. presents observations of GEM, RGM, and PHg from Ny-Alesund over a period of more than one year. The data should be published as it is important and will be useful to researchers. However, there are many conclusions, statements, etc. in the paper that are not well founded or at best confusing. For this reason, I believe the paper needs to be revised with an eye towards simplification and

a focus on the observations. More detailed comments are listed below.

1) First sentence of the abstract “It is agreed: : :.” Should be deleted if something is well founded in the literature it shouldn’t be in the abstract.

The authors agree. “It is agreed” is deleted in the revised manuscript.

2) Line 10 of abstract and later in the text. The authors state that a new seasonal pattern of GEM, etc. I honestly don’t know what this seasonal pattern is – I think they mean that you RGM throughout the summer and that PHg is only in spring. I am not sure this is a “new” seasonal pattern. There are observations of RGM outside of Spring ODE/AMDEs. For example see the work of Brooks at Summit, Greenland or work by Jaffe group, etc.. So I highly encourage the authors to state specifically what the important observations instead of couching it in these terms which are vague at best.

The authors agree that the sentence starting with “The study revealed a clear seasonal distribution. . .” can be misleading. Corrections are made in the revised manuscript: Significant concentrations of RGM were observed from March through August, while increased PHg concentrations occurred exclusively from March through April. Corresponding corrections are also made in the introduction. Increased RGM concentrations during summer have been observed by Brooks et al. (2011) at Summit, Greenland. However, Brooks et al. (2011) was published in ACPD two months after our paper and it is therefore not natural to refer to their work. In the paper we have changed for claiming seasonality in general to seasonality in the Arctic. Unfortunately, we found no work by the Jaffe group dealing with RGM in the Arctic.

3) The authors state that BrO oxides GEM this is not the case. Br atoms are much more likely to the be the oxidant of GEM than BrO. This is misleading and the authors should review the likely oxidants of GEM and revise the paper accordingly. This is incorrectly stated in the introduction and abstract and should be changed.

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According to Goodsite et al. (2004) Br atoms are suggested as oxidants for GEM. Holmes et al. (2009) support this and suggest that oxidation of GEM by Br accounts for 35-60% of the RGM (for details see comments by referee #1). Corrections are made in the revised manuscript (abstract, introduction, section 3.3 and section 4).

4) The conclusions about the origin i.e. local vs. non-local AMDEs are really not supported by any data in this work. Or at least I don't understand the arguments. I really don't think that it is the origin or oxidant of GEM in this study is well understood. So conclusions along these lines are really speculative and should be minimized or at least softened.

The possibility of so-called non-local AMDEs are supported by the low RGM and PHg concentrations during the events. This means that the deposition of RGM and PHg mainly occurred elsewhere, and the reactive mercury observed in Ny-Ålesund reflects a "residue" after the oxidation of GEM outsite the study site. Supported by the elevated PHg concentration with respect to RGM and no meteorological regime associated with the AMDEs would all suggest the AMDEs to be of non-local origin. However, as mentioned in the response to the comments posted by the anonymous referee#1 caveats associated with Tekran may affect the RGM and PHg measurements. This may in turn result in incorrect concentrations. For this reason discussing local vs non-local AMDEs becomes speculative.

5) The authors state in the last paragraph of the introduction that the EC model supplements the results of the study. I would say that it is used to analyze or understand the results of the study. The way it is phrased makes it seem that emissions from the model are providing the date in this work.

Agreed. The following replaces the last paragraph in the introduction: Natural and anthropogenic emissions of GEM, RGM and PHg seen by the Environment Canada's Global/ Regional Atmospheric Heavy Metal model (GRAHM) is used to better understand the results in this study.

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Interactive Comment

6) What are composite RGM and PHg measurements? A reference to an owner's manual is not appropriate. Please define the timing of these measurements more clearly.

Composite RGM and PHg measurements refer to the semi-continuous measurements performed by the speciation system. RGM and PHg were collected for one hour, while the preconcentrated RGM and PHg were determined in the following hour. Please see comment 8 for more details.

7) Bro columns from SCHIAMACHY were used to investigate BrO. However, the work by Salawitch et al., 2010 in a recent GRL demonstrate that much of the BrO column labeled as tropospheric is due to stratospheric variation. Has this been taken into account?

The work by Salawitch et al. (2010) is included in the revised manuscript (section 2.3) as the paper discusses important aspects related to the monthly vertical BrO densities.

8) The experimental details are sketchy – e.g. is stated that the soda lime is replaced every week again consistent with the Tekran manual. Either provide more details or reference a work that does. Also stating that a constant i.e. 8.33 is used to scale the data has no physical significance. This needs to be rewritten for clarity.

The authors believe that referring to the papers by Landis et al. (2002) and Cobbett et al. (2007) are satisfactory for further details concerning the method, as the Hg speciation measurements make us of a more or less standardised method used by several researchers. Scaling by a user entered constant is deleted from the Quality control, section 2.4. Please see the revised manuscript for detailed corrections.

9) The argument on page 27262 that observed RGM is somewhat too low because it is a factor of 3 lower than the EC model is not a statement that I would make. There are many reasons for such a discrepancy including model resolution, uncertainty in oxidation pathways.

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Since we do not know even theoretically the exact emissions, the exact chemical reaction rates, the nature of the oxidised mercury produced, the conversion between RGM and PHg, or deposition rates, we can't say that the model is absolutely accurate. What we can say is that the model is able to reproduce observations of GEM concentrations. It is possible that multiple errors in the model cancel each other out so that we get the right GEM concentrations by mistake. For this reason, the simulated GEM observations can only be called an estimate. However, since our deposition estimates, which are extremely difficult to simulate, tend to be fairly accurate, it is likely that GRAHM is doing well overall.

Concerning the model resolution comparing a model estimate to a point source is problematic, as the model estimate represents the entire grid cell. Since the resolution used was 1 degree by 1 degree, the grid cell is approximately 110 km (latitudinal) by 21 km (longitudinal) at 78.9 N. Even though we interpolate the model concentrations to the point source, some smoothing is unavoidable. Thus, if the RGM was produced within a very small region of the grid cell, a simulated lower value and an observed higher value can both be correct. Another consequence of the smoothing is that a model time series is never expected to reproduce the high-frequency variability in observed time series.

10) Page 27262 line 12 should be "shorter" atmospheric residence time. "Shorter" replaces "lower".

11) The reference to the "hump" in GEM in spring in figure 2 is very hard to support by looking at the figure. So the ensuing discussion of GEM fluxes is hard to justify. Either Figure 2 data need to be shown with more resolution or a running seasonal average needs to be show to support his statement. I highly encourage breaking up figure 2 into a couple of plots that allowed the data to be show with more resolution. This is the heart of the paper and it is very hard to make out. Other figures can be deleted to make up the space.

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The authors acknowledge the referee's comment. A so-called "hump" (i.e. increased GEM concentration) was observed both during polar spring and following springmelt in Ny-Ålesund. This could be seen in April through July 2007 and 2008 (Fig 2). The figure is improved in the revised manuscript according to the referee's comment. Emission from surface snow (Steen et al. (2009), efflux from surface waters (Sommar et al. (2007) and mercury transport would all encourage the increased GEM concentrations. The work by Steen et al. (2009) and Sommar et al. (2007) are both performed in Ny-Ålesund. Please see section 3.1 in the revised manuscript.

12) During polar night GEM concentrations are probably constant due to lack of chemistry as well as transport conditions (p. 27262 line 26)

The authors agree and corrections are made in accordance with referee #1 comments: During polar night the GEM concentration remains at background concentration, due to the absence of atmospheric oxidants for the conversion of GEM to occur and transport conditions. The ozone concentration remains high (average 36 ppb) and the average BrO vertical densities were below 4.0x10-13 moleculescm-2 during polar night, i.e. absence of atmospheric oxidants for the conversion of GEM to occur. The importance of transport of mercury is also valid in summer explaining the fluctuating GEM concentrations from June through August. For details see section 3.1 in the revised manuscript.

13) I am not sure what Global Radiation means. I also think it is not surprising that RGM (which is short lived in the boundary layer) correlations with actinic flux? This is driven by photochemistry so this conclusion which is stated several times in the paper is not that surprising and could be stated once.

Global radiation" refers by definition to the sum of direct and diffuse solar radiation. In the revised manuscript correlations are made with met variables measured at Zeppelin. UVB data therefore replaces the Global Radiation data. Measurements of UV erythemal hourly doserates (Dahlback, 1996) were obtained from the ground-based Ultraviolet Radiometer (GUV Biospherical Instruments Inc.) on top of the Sverdrup Station

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in the Ny-Ålesund village at 25 m above sea level. Applying the libRadtran simulation package (Mayer et al., 2005), the erythemal UV measurements were transformed to UV quantities which are more relevant for the Hg measurements at Zeppelin, i.e. UVB hourly doserates at 474 m above sea level. Being just about two km apart, the ambient cloud and surface conditions were assumed to be identical for both sites. However, the attenuation of air between 25 m and 474 m above sea level were corrected for, and the erythemally-effective UV doserates were converted to UVB doserates. Unfortunately, photolysis rates could not be estimated because we found no applicable absorption cross sections and quantum yields. Furthermore, the conversion of measured irradiances to actinic fluxes remains uncertain and nontrivial (Kylling et al., 2003).

We agree that RGM formation is photo chemically mediated. We therefore removed all but one of the statements about RGM and radiation.

For further details please see the revised manuscript (section 2.3 and 3.1).

14) The statement that (p. 27263) that RGM was observed for the first time beyond spring time is simply not true.

Please see our response to comment 2 above. We have changed from claiming seasonality in general to seasonality in the Arctic. This study reports the first summertime RGM increase in the Arctic.

15) Section 3.2 argues that spring RGM is due bromine – this may be true but satellite data is at best uncertain. A better argument would be to include ozone data (this should probably go in Figure 2) as ozone should also be reduced if bromine is present. Even this wouldn't be definitive but it would be a much better argument.

According to comment 7 a large uncertainty exists in the BrO vertical densities used to identify so-called bromine explosions. Ozone concentrations were above 20 ppb throughout the study except for a near zero concentration drop in April 2008. Although not definitive, this observation is in agreement with the highest monthly BrO vertical

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densities above Svalbard. Corrections are made in the revised manuscript (section 2.3, 3.2 and Fig 2). The formation of RGM during non-AMDEs could neither be linked to BrO "hotspots", nor to decreased ozone concentrations.

16) The whole discussion of AMDE origin is confusing and in my mind at best speculative. I don't see how any conclusions can be made from the observations and the model. The oxidants and there distribution are too uncertain. The emissions map – Figure 5 – is not useful as far as I can tell. This discussion should be curtailed.

The authors agree that the AMDE discussion is speculative. However, the revised manuscript lists several observations favouring the presence of non-local AMDEs (i.e. depletion of GEM occurred outside Ny-Ålesund: RGM and PHg accounted for on average 10% of the depleted GEM. This means that the formation and subsequent deposition of reactive mercury mainly occurred before the air masses arrived at Ny-Ålesund. The observed RGM and PHg at fairly low concentrations denote "leftovers" after the oxidation of GEM outside the sampling location. The predominance of PHg with respect to RGM, as PHg deposits at a faster rate than RGM, as well as no clear meteorological regime associated with the AMDEs would all suggest the AMDEs to be of non-local origin.

As discussed in more detail in the revised manuscript, limitations with the sampling system may also affect the RGM and PHg concentrations presented in this paper.

We find the emissions shown useful as GEM emission is significant over the Arctic. RGM and PHg are not expected to be emitted in the Arctic. Please see our response to referee #2.

Corrections are made in section 3.2 and 3.3 in the revised manuscript.

17) The correlation plot and analysis is not that useful. I would much rather the authors focus on some periods where the correlation coefficient is large and show this. As it is presented now in the figure it is very hard to follow.

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Corrections are made in the revised manuscript using met variables measured at Zeppelin, according to referee #1 comments. As stated in the current paper, periods with correlations coefficients above ± 0.5 form the basis for the discussion. This means that the authors focus on distinct periods. The authors agree the figure can be hard to follow. However we found it important to include the small correlation coefficients as they are important to the complete understanding of the met variables influence on the Hg chemistry. The shaded area in the figure, expressing correlation coefficients below ± 0.5, is more clearly and dotted lines represent low Hg concentrations while solid line represent high Hg concentrations in the revised figure. The authors hope this will make the figure easier to follow.

18) I don't understand the third further research direction nor how it relates to the results in this paper.

The authors agree that the third research direction can be misleading. Since increased RGM concentrations was observed from March through August the formation mechanism for RGM, which is still not known, may be different in spring and summer. The following corrections are made in accordance with the third research direction: - Formation mechanism for RGM: RGM was observed at increased concentrations during spring and summer in the duration of this study. The formation mechanism which still remains less clear should be more carefully evaluated and it may even differ throughout the year.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 27255, 2010.