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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.

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We acknowledge the comments from the anonymous referee. Please see the revised manuscript for detailed corrections based on the three referee reports.

Our comments are given below the referee's comments:

This paper presents a long term data set of air Hg speciation from a European Arctic site. I found that despite having an interesting data set the paper does not present a sufficient detailed data assessment and because of this has many statements that are conjecture and not supported by the data or data analyses presented. The paper is also hard to read. The authors should separate the results and data analyses and

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then provide discussion and interpretation. The authors need to go back and do a more detailed assessment of their observations as well as a more complete statistical analyses and then place their work within the context of others work and data collected.

The manuscript is revised based on comments from three anonymous referees with a focus on simplifications and observations. Many statements are now more carefully discussed and supported by ancillary data and placed within the context of previous observations.

The paper should be checked for significant figures, there should only be one decimal place for GEM and none for RGM and PHg (i.e. Table 1).

The authors agree about the decimal places and significant figures. Please see corrections made in the revised manuscript.

In the abstract they state their data shows an undiscovered seasonal trend. However this trend is not clear from the data presented or as discussed.

The authors agree that this "seasonal trend" can be misleading. The revised manuscript state specifically what the important observations are, i.e. increased concentrations of RGM was observed from March through August, while increased PHg concentrations occurred exclusively in March and April. This study reports the first summertime increase of reactive mercury from an Arctic site.

Also some graphical presentation is needed to show how RGM trends correlate with sunrise. It would be good to show some plot that shows this and how this differs from data collected at other sites.

As UVB is thought to be of importance according to the photo chemically mediated GEM oxidation and subsequent RGM formation, correlations of RGM concentrations with UVB were performed. Please see section 3.4 in the revised manuscript.

Also in the abstract they state that high PM constituted 75% of the reactive Hg. I am not sure they know this.

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The authors agree and figure 4 presenting the PHg: RGM relationship is not included in the revised manuscript. The PHg: RGM relationship is still assessed in the revised manuscript as it indicates the age of an air parcel. Please see corrections made in the revised manuscript (section 3.2).

They show in fairly poor graphs that there is elevated RGM that is anticorrelated with GEM however the trends are hard to see and the details not clear. It might be best for the authors to develop a graph that shows the daily mean or median GOM and GEM rather than the hourly data. Statistical analyses should be done using daily mean data and then also hourly data for each month. This might better show trends.

Figure 2 shows that during AMDE periods (i.e. sufficient GEM decrease) the concentrations of RGM and PHg is increasing. On average the increase in RGM and PHg concentrations account for 10% of the depleted GEM during these events. The situation is somewhat different in summer with GEM concentrations in the range $\sim$1.0 - 2.8 ngm-3 and RGM concentrations periodically elevated with respect to the spring RGM concentrations. When presenting daily mean GEM concentration important information is lost, as the GEM concentration is a strong indication of AMDEs with a lifetime of less than 10 hours (Goodsite et al. 2004). The resolution of figure 2 is improved in the revised manuscript.

A table with correlation coefficients may be more useful than as show in figure 6 that is fairly busy and a bit hard to understand.

The authors agree that the figure can be hard to read. Please see our response to referee#3 and the revised manuscript for further details.

Also what are the correlations between GEM and GOM are they well anticorrelated on a daily and hourly time step? It is really hard to see this as they have presented the data.

Please see over comments above addressing this issue.

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Also what about ozone and GEM and GOM correlations on a daily time step and hourly? In the abstract they suggest that reactions with ozone are responsible and in the next sentence they suggest reactions with BrO are responsible.

Possible mechanisms for the oxidation of GEM are carefully discussed in the revised manuscript. Based on the paper by Goodsite et al. (2004) Br was suggested as the predominant oxidant for GEM. According to Salawitch et al. (2010), the satellite BrO "hotspots" are under the influence of both tropospheric and stratospheric BrO. To account for the uncertainty, ozone concentrations were included in the revised figure 2, as the ozone concentration should be reduced if bromine is present. Although ozone depletions events and AMDEs are well correlated in the spring, no such clear trend was observed throughout the rest of the year. This issue is discussed in section 3.3. Please see sections 3.1 and 3.2 for further details.

What exactly does their data suggest based on clearly shown relationships. So they think that the AMDE were occurring outside of the area and then RGM being advected in? It is not clear how they came to this conclusion.

The AMDEs were believed to be of non local origin as the reactive mercury concentrations were fairly low (i.e. indicating "leftovers" after oxidation of GEM and formations of RGM and PHg before the arrival in Ny-Ålesund), the PHg concentration was mainly elevated compared to the RGM concentration and the correlations made for GEM, RGM and PHg showed mainly less significant correlations coefficients. For details, this paper refers to Gauchard et al. 2005. Advection from emission sources outside Ny-Ålesund could, however, not be excluded.

In the introduction –line 30 how does the relative distribution indicate the age of a parcel?

Both RGM and PHg are readily scavenged or deposited and have atmospheric residence times on the order of days, where the residence time of PHg depends on particle mass and size distribution (Schroeder and Munthe 1998; Lyman et al. 2007; Steffen et

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al. 2008). Observations show that PHg deposits at a faster rate than GEM, but not as fast as RGM (Zhang et al. 2009). This means that the relative distribution of RGM and PHg may indicate the age of an air parcel: a high PHg concentration relative to RGM refer to “older” air masses as RGM is deposited at a faster rate than PHg. For details this study refers to papers discussing this issue.

Are the GRAHM results published?

Dastoor et al. (2008) discusses how AMDEs and the subsequent emissions are calculated. Emission fields are not presented in this paper. However, global emission as seen by GRAHM are published in Durnford et al. (2010).

Some discussion of the emission sources in pristine areas needs to be discussed. Is this due to evasion from snow? Could down slope and upslope air movement off the mountains and then land – oceans air movement influence the data as shown?

Emission sources are discussed in the introduction in the revised manuscript. The possible contribution from surface waters and the influence of arrival of new air masses is discussed in section 3.3. Aspmo et al (2005) discusses Hg measured at 25 meters above sea level and 474 meters above sea level (i.e. Zeppelin) in Ny-Ålesund. The GEM concentrations were comparable, while the reactive mercury concentrations (i.e. RGM and PHg) were significantly different. This difference is however not exclusively related to the different sampling locations used as caveats associated with the Tekran may introduce a considerable uncertainty. Please see the revised manuscript for further details (section 3.2).

Methods- They describe the site as having two Tekran systems operating one to measure GOM/ GEM/PHg and one to measure TGM. Is there anything to be better understood from the data with both systems? This is not really discussed in the paper.

The authors agree and corrections are made in the revised manuscript: Two Tekrans were used both to increase the time resolution for the GEM measurements as well as

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reduce the possibility of erroneous values. Observations indicate that GEM measured by the speciation system is periodically somewhat lower than the GEM measured at a five minutes time resolution. According to this issue it is also important to mention that the use of two Tekran 2537 units is also suggested by Gustin et al. (2010) due to artefacts associated with collection and determination of GEM, RGM and PHg. Caveats associated the speciation system is carefully evaluated in the revised manuscript.

Results and discussion First paragraph- they do not know that the larger standard deviation reflects faster reactivity and lower atmospheric residence time. Please see Junge 1972 and Poissant et al. 2005 for details concerning the standard deviations for RGM and PHg, which may in turn reflect faster reactivity.

Second paragraph they discuss a GEM spring emission increase from snow. They should quantify this. Could the emission expected account for the increase in air concentration? They say this needs to be investigated. So what do they have that supports this? Based on their data analyses they cannot really state that efflux from water and arrival of air parcels explains the fluctuating GEM. There are no really detailed data analyses that have been done to support what they are saying. Some time series showing polar night versus then average daily light would be useful here.

The GEM emission from both surface snow and soils are to be published. Please see Steen et al. (2009) for GEM exchange in the air-snow boundary, where GEM emissions from snow are measured by a GEM flux gradient method. The fluctuating concentrations of GEM with respect to possible local emission are carefully discussed based on earlier findings in section 3.1. Emission of dissolved gaseous mercury from the water surface in Kongsfjorden is addressed in Sommar et al. 2007. Although the fluxes measured were likely overestimated, a significant efflux from the fjord was observed. It is therefore reasonable to believe that the fluctuating GEM concentrations observed in summer could (partly) be explained by volatilisation from water surfaces. This issue is discussed in section 3.1 in the revised manuscript.

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The best way to deal with this rambling paper is to clearly present the data and the correlation analyses and then discuss the implications. More detailed statistical analyses are needed.

Please see our detailed comments below.

Does RGM correlate with wind speed and direction if so how?

RGM correlation with met variables measured at Zeppelin is shown in figure 6 and discussed in section 3.4: RGM was only significantly correlated with ozone in this study.

How could low PHg be attributed to short lived RGM species?

The low PHg concentrations during non-AMDEs could be attributed to short lived RGM species which are easily reduced to GEM as RGM is considered a precursor for PHg existence, i.e. short atmospheric residence time means that RGM is removed before PHg formation occurs. Please see section 3.1 in the revised manuscript.

They describe March through April as having the highest BrO vertical densities. Was this measured for the year of the study? And where is the data?

Monthly BrO vertical densities are available (Sciamachy instrument, University of Bremen) throughout the year. The data is available to public online and not shown in this paper. Please see section 3.1 in the revised manuscript for further details.

In section 3.2 a more detailed investigation of their data may provide more robust statement for the RGM being advected. They only now have a speculative discussion rather than quantitative support.

A more detailed investigation of the data which supports that the RGM formation occurred outside Ny-Ålesund in the spring is given in the revised manuscript (section 3.2).

Then in 3.3 they describe it as forming locally? What do does the meteorological and

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air chemistry show to support this?

This is an important issue and section 3.3 is revised accordingly. The observed RGM in spring was attributed to a possible “residue” after the depletion of GEM outside Ny-Ålesund. The increased RGM concentration in summer could be due to in situ oxidation of GEM. This is supported by the GRAHM which is able to reproduce the elevated concentrations.

Figures 1 B is not very useful.

The authors find the figure useful as it shows the location of Zeppelin on the Vest coast of Spitsbergen. Additionally, the distance to the Mainland of Norway is also shown.

Figure 2. What are the units on the x axis?

Corrections are made in the revised manuscript. The unit on the x-axis (month) is shown in the revised figure.

It would be useful to have a time series of light and perhaps other parameters. Mean daily value might be more useful than hourly average.

As the meteorological variables of importance to the GEM, RGM and PHg concentrations are included in figure 6, the authors chose not to include a figure with time series of the respective meteorological parameters. As previously mentioned, ozone is included in the revised figure 2.

Figure 3 is not very useful nor is figure 4

We prefer to use figure 3 as it clearly shows the monthly distribution of the different Hg forms throughout the year. Such a graphical presentation illustrates the seasonal trends as well as important values becomes available to other authors for comparison in prospective work. Figure 4 is not included in the revised manuscript.

Figure 5 has this data been published elsewhere? How good is this GEM emission estimate over North Pole?

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The emission data were published in Durnford et al. (2010), and GRAHM was seen to perform well in the Arctic in Dastoor et al. (2008) and Durnford et al. (2010). This indicates that the emissions are accurate according to the current state of knowledge on mercury processes, based on observations. Anthropogenic emissions are of GEM, RGM and PHg. However, all other emissions of mercury (from soils, water and snow) are of GEM only. In the figure, GEM emissions are significant over the Arctic. These emissions represent the revolatilisation of mercury deposited onto the cryosphere during AMDEs, and also at other times, by both dry and wet processes. RGM and PHg are not expected to be emitted in the Arctic.

Figure 6. A correlation analyses table may be more useful here.

Please see our comments above concerning this issue.

Figure 7.The back trajectory data is small and hard to see. This figure has been saved directly as pdf from Matlab. Unfortunately, we see no way to improve the resolution.

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