

## ***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 appreciate the detailed and helpful comments from the reviewer. Please find our responses below. The changes that we have made to address the issues are listed in response to the reviewer's specific comments. Corrections based on the three anonymous referees are made in the revised manuscript.

Anonymous Referee #1 General Comments This is a valuable and an interesting contribution, and I hope that the editor will chose to accept this work for publication. There are some issues that I think need to be pursued further by the authors, but I think that the authors will be able to deal with them fairly easily.

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My main comments are: 1) The abstract of the paper communicates well the trends in the GEM, PHg and RGM species observed, but does not communicate well the authors' discussion of what factors control the relationship between RGM and PHg, or the seasonal variation in the relative importances of the BrO and ozone oxidation reactions.

2) Recent work which investigates the importance of the BrO reaction chemistry in marine environments vs the ozone oxidation reaction (Jacob, Harvard), and laboratory and field based gas-particle partitioning work (Schauer, U. Wisc-Madison) are not utilized.

3) The study does not adequately evaluate caveats associated with the Tekran. For example, the impact of ozone concentrations on RGM collection efficiency by the KCl coated denuder is not adequately addressed (Gustin, U. Nevada-Reno). Furthermore, the study does not discuss the consequences of keeping the particulate matter/PHg sample heated to 50°C during the collection period. This may be an important as some of the suggested species of PHg are semi-volatile, and RGM may become PHg by partitioning to airborne snow in the sample location being discussed.

Specific Comments P27256 L9: Give RGM and PHg concentration summaries as ranges followed by a mean or median; as 8+/- 13 pg m<sup>-3</sup> taken literally means that negative concentrations were observed, and is therefore distracting.

We agree that negative concentration can be distracting. An explanation for the concentrations reported in the manuscript is given below: In this study concentrations below MDL (method detection limit) were set to MDL/2. Calculating the mean ± 1 SD (standard deviation) of the complete dataset (including concentrations below MDL, i.e. MDL/2) gives the concentrations given in the manuscript. The median GEM concentration equalled the mean GEM concentration. The median RGM and PHg concentrations (3.5 pgm<sup>-3</sup>) reflect the majority of fairly low concentrations. The large difference between the maximum and minimum concentrations explain the large SD used in the manuscript. Please see section 3.1 in the revised manuscript for corrections.

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L11: Seasonality of these species has been observed at other latitudes. Extend sentence to restrict this claim to the arctic.

We are aware that high concentrations of RGM during summer have been reported from lower latitudes. We have changed this phrase as recommended. Please see the revised manuscript for corrections (abstract).

L11: Put the “For the complete: : .<1%” sentence after the concentration summaries, and before the discussion of seasonality in concentrations”.

The authors agree and corrections are made in the revised manuscript. The sentences now read: For the complete dataset the atmospheric mercury distribution was 99% GEM, whereas RGM and PHg constituted <1%.

L14: “RGM was suggested as the precursor of PHg ...” The measurements in Fig 2 suggest that RGM may not always lead to the same concentrations of PHg from year to year which may cause some readers to question this claim. This statement should be modified to acknowledge the uncertainties in our knowledge of how RGM and PHg are related in the environment.

We agree that RGM may not always lead to the same concentrations of PHg. The sentence is modified to acknowledge the uncertainties in the knowledge of how RGM and PHg are related in the environment. For corrections, please see section 3.1 and 3.2 in the revised manuscript.

L16 Remove “surprisingly” Surprisingly is removed in the revised manuscript.

L17-21 Suggest reversing discussion of BrO and ozone, or at least state why you are discounting ozone as an oxidative source. It may be that both sources are important at different times of the year. It should be recognized that the Jacob (Harvard) modeling work which looks at marine RGM formation uses the Hall et al 1995 ozone rate coefficient, which is an order of magnitude slower than more recent measurements. This is not to say that the bromine reaction is not important and certainly the Jacob results

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remain a very important contribution, but the ozone oxidation reaction may be more important than the Jacob study might suggest.

We agree that possible oxidants for GEM must be carefully discussed due to the uncertainty related to possible oxidative sources. According to Goodsite et al. 2004 and Holmes et al. 2009 Br is considered the predominant oxidant for GEM. The importance of Br for the oxidation of GEM in this study is supported by monthly BrO vertical densities retrieved from the Sciamachy instrument and hourly ozone concentrations measured by the Norwegian Institute for Air Research at the Zeppelin station.

L21-23. Mention the evidence/analysis that brought you to this conclusion to give the conclusion more weight.

RGM and PHg accounted for on average only 10% of the depleted GEM during the AMDEs. The fairly low RGM and PHg concentrations reflect a “residue” after the oxidation of GEM outside Ny-Ålesund. Supported by the predominance of PHg in respect to RGM and no clear meteorological regime associated with the AMDE would all suggest the AMDEs to be of non-local origin. However, due to both uncertainties related to the BrO plumes and the Hg speciation measurements discussing local vs. non-local AMDEs becomes rather speculative. Corrections are made in the revised manuscript.

P27257 L9-10. Modify sentence by changing “to occur” to something like “to be an important influence on RGM and PHg concentrations”. At present the sentence may suggest to some readers that partitioning will not occur if aerosol concentrations fall below a certain concentration, which is not scientifically accurate.

The sentence is deleted in the revised manuscript (abstract and introduction) since several factors control the gas-particle partitioning of reactive mercury. The factors are discussed in more detail in section 3.1.

L10-15. Since you compare the ozone and halogen oxidation pathways in the abstract, the ozone reaction studies should be added in this paragraph. I also suggest adding

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the aforementioned Holmes modeling study to give an idea of the relative importances of the halogen and ozone reactions.

Please see the authors comment above discussing the possible oxidative sources.

L15. Halogens may also be released by nitric acid replacement in sea salt aerosol.

We have added the following to reflect the possibility: A summary of possible mechanisms for the release of reactive halogens from sea salt particles is given in George et al. (2007). Halogen formation may also depend on nitric acid being the precursor for OH (Abbat et al. 2010). Please see section 1 for corrections.

P27258 L5-10. More recent work has shown that other factors also impact PHg and RGM distributions. See general comments for more details.

We agree that several factors, including caveats associated with the Tekran, may impact the PHg and RGM distributions (section 1, 3.1 and 3.2).

L25. Ny-Alesund and Zeppelin names are used inconsistently between here and Fig 1b, as Ny-Alesund does not appear in Fig 1b itself as indicated by the text. To avoid confusion, perhaps present the mercury monitoring site as "Zeppelin" in the text and figure caption and then explain its geographic and functional relationship to Ny-Alesund.

The following correction is made in section 2.1 in the revised manuscript. Composite RGM and PHg determinations were performed at the Zeppelin air monitoring station (henceforth named Zeppelin) from 27 April 2007. Zeppelin is located 2 km from the settlement in Ny-Ålesund at an elevation of 474 meters above sea level. Zeppelin is used consistently in the revised manuscript. Corrections are made in section 2.1.

P27260 L4 Explicitly state SCIAMACHY is a satellite for readers who are unfamiliar with BrO measurement methods.

"... on board the satellite ENVISAT" is added to the sentence "Monthly average BrO vertical densities were retrieved from the Sciamachy instrument...".

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L9. Met data from Zeppelin should be used in parallel analyses as they may be different enough to Ny-Alesund to cause errors in interpretations. If the authors know that the differences between the met data at both sites are negligible this should be explicitly stated, to assure the readers that this practice is acceptable.

The authors agree that met data from Zeppelin may be different enough to Ny-Ålesund to cause errors. In the revised manuscript correlations are made with met data measured at Zeppelin. Corrections are made in section 2.3 and in the correlation analysis (section 3.4). With the use of UVB hourly doses Ola Engelsen at NILU were added as a co-author.

L15 Were ozone concentrations ever high enough to see reduced RGM collection efficiencies in the denuders as seen by Gustin (U. Nevada-Reno)?

Lyman et al. (2010) reported a 12-30% decrease in collection efficiency for denuders exposed to 50 ppb. Ozone concentrations exceeded 50 ppb 13 April 2007, 29 April - 1 May 2008, 19 May 2008 and 26 May 2008. The importance of the ozone concentration on the collection of RGM is discussed in section 3.2.

P27261 L23. See comment about concentration summary ranges made in Abstract. Please see our comments above.

P27262 L26. Also prolonged darkness means that known GEM oxidants would be very low in concentration by the time spring insolation starts. You state this later in the paragraph, but I would bring first mention of it forward to here. What were ozone concentrations during the dark period? Are model predictions of BrO concentrations available during the polar night? If these are available you might consider mentioning them here.

This is an important issue which is included in the revised manuscript (section 3.1) During polar night (October – February) the minimum, maximum and average ozone concentrations were 21, 45 and 36 ppb, respectively. For comparison, the ozone con-

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centration decreased to 0.3 ppb during an AMDE in April 2008 (22 April). Monthly average BrO vertical densities are available (Sciamachy instrument, University of Bremen) throughout the year. The monthly average BrO vertical densities remain low ( $<4.0 \times 10^{-13}$  molecules  $\text{cm}^{-2}$ ) during the polar night. High ozone concentrations and low BrO concentrations reflect the absence of atmospheric oxidants for the conversion of GEM to occur. The ozone and BrO concentrations are discussed in section 3.1 in the revised manuscript.

P27263 Importance of radiation to RGM formation and the explanation of why large increases in RGM were observed in the absence of significant concentrations of PHg are valuable information which I think are under-represented in the abstract. Please also see comments made in General section about relationship between RGM and PHg, and limitations of using Tekran for understanding this relationship.

The RGM: PHg relationship is more carefully discussed in the revised manuscript as it appears really important to the understanding of mercury within the Arctic. The following is added to the abstract: Increased concentrations of RGM were observed during the insolation period from March through August, while increased PHg concentrations occurred exclusively during the spring AMDE period in March and April. The elevated RGM concentrations suggest that atmospheric RGM deposition also occurs during the Polar summer. RGM was suggested as the precursor for the PHg existence, but long range transportation of PHg has to be taken into consideration. Still there remain gaps in the knowledge of how RGM and PHg are related in the environment. Please see comments above concerning the uncertainty related to the RGM and PHg concentrations due to limitations using Tekran.

P27264 L12. Has this been demonstrated with models? What are feasible possibilities for the other 90% of the depleted GEM. It seems that there could be other possibilities beyond those the authors have presented. Having read a bit further on P27265 it seems as though you observe AMDEs which have occurred elsewhere, and much of the produced RGM and PHg has deposited before it reached the sampling site. Please

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explain this more clearly on P27264.

During AMDEs the GEM concentration was found to decrease below 1 ngm<sup>-3</sup>. A 1 ngm<sup>-3</sup> decrease in GEM concentration could principally be converted to 1 ngm<sup>-3</sup> RGM and/or PHg. The RGM and PHg concentrations observed during this study did not account for the decrease in GEM concentration observed during AMDEs. Lyman et al. (2010) indicated that KCl coated denuders for collection of RGM may not be as robust as previously thought when exposed to 50 ppb ozone during sample collection. Ozone concentrations above 50 ppb were periodically observed during spring 2007 and 2008. The possibility of less efficient sample collected for RGM therefore has to be taken into consideration. Other possibilities that may influence the concentrations of RGM and PHg is the consequence of keeping the RPF heated at 50°C during sample collection (Rutter et al. 2007). Some PHg species may be semi volatile and evaporate before collection on the RPF. The possibility that RGM may partition to airborne snow and particles should also be taken into consideration. Additionally, no standardized calibration method exists to determine RGM and PHg. According to caveats associated with the Tekran it is important to note that a 1 ngm<sup>-3</sup> difference in GEM concentration is observed at Zeppelin for GEM measured by a Tekran 2537 and GEM measured by the speciation system (Tekran 2537, 1130 and 1135). This is the reason why a second Tekran 2537 was used to collect GEM at a five- minute resolution.

P27267 L15. As PHg concentrations were shown to be anti-correlated with temperature, were RGM concentrations positively correlated with temperature? Why is this analysis not shown in Fig 6?

It was decided that we needed to tidy up the correlation figure. We did that by eliminating any variable that did not have a correlation coefficient smaller than -0.5 or greater than 0.5. So, the reason why Fig. 6 does not show temperature for RGM is simply that RGM was not sufficiently strongly correlated with temperature. As long as either high or low RGM concentrations are sufficiently correlated (R smaller than -0.5 or greater than 0.5) with the respective meteorological variable, the correlation coefficients for

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both high and low concentrations for the entire correlation period are shown in Fig. 6 ( i.e. if the low concentrations are strongly correlated but the high concentrations are not, we still show correlations for both the low and high concentrations). Corrections are made in the revised manuscript (section 3.4).

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