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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric mercury over sea ice during the OASIS-2009 campaign" *by* A. Steffen et al.

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General comments The manuscript presents novel measurements of atmospheric mercury species collected on the sea ice close to open leads during springtime near Barrow, Alaska. At the same time measurements were also performed over the tundra, and it is obviously very tragic that the tundra experiment suffered from instrument problems. The results presented are very interesting and add new insight to our understanding about the mercury cycling in the Arctic. For those who have hands on experience with this type of mercury instrumentation and have been working in the Arctic knows how challenging, not to say difficult, it can be to achieve reliable data, so therefore applaud the effort undertaken in this study. However, the results as presented are lengthy, in

particular the factors, and I would suggest to tone down this part. The comparison of GEM data from the sea ice and over the tundra, and the finding that more mercury is retained in sea ice snow is the most interesting finding and also most important in terms of the Arctic mercury cycle, so this should get more attention in your discussion. The manuscript certainly merits publications but need some revisions.

General response to reviewer 2: The authors thank Reviewer 2 for their insightful comments about the manuscript which have improved it significantly. The authors realize that it is disappointing that the second speciation instrument was not fully working during the study and we have removed the reference to this as it appears to be highlighted as a disappointment to both reviewers. The discussion about the meteorological factors has been toned down and shortened (Figures 4 and 8 and Table 1b were removed) as suggested and the latter discussion about the emission of GEM has been highlighted to a greater degree. Below are the authors responses to the specific comments identified in the review.

Specific comments 1. Page 5690, line 15-21: The Jacobi et al., 2006 (JGR) should also be included here.

Response: This reference was added and referred to in the text as follows: Strengthening the argument that this chemistry is initiated over the sea ice, near-complete O3 depletion was observed over Arctic Ocean sea ice on a German icebreaker in 2003 and on a sailboat expedition in 2008 (Jacobi et al., 2006; Bottenheim et al., 2009)..

2. Page 5692, site descriptions: When the authors describe the OOTI sites, it would be great for the reader to know the distances from the sites to the shoreline and the distance between the sites to be able to put things into perspective.

Response: This information was added to the logistics and sites section in the methods as follows: Sites 1, 2 and 3 were located 1.4, 2.9 and 2.2 km from the shoreline, respectively. The distance between sites 1 and 2, and sites 2 and 3 was approximately 10 and 1km, respectively. This "tundra" site was 1.2 km inland and 7.6 km from site 1,

4.6 km from site 2 and 4.5 km from site 3.

3. Page 5696, line 7: The authors apply the same AMDE limit as defined for Alert. How applicable is this limit for Barrow?

Response: This point is appreciated by the authors and a similar calculation for data collected by the authors from Barrow 2007-2009 was employed to calculate such a limit for this site. The information in the text was adjusted as follows: A GEM concentration of less than 0.77 ng m-3 was calculated as the upper limit indicating that an AMDE is occurring. This value is two standard deviations below the September to December mean GEM concentration for Barrow (from 2007-2009). In this study, the GEM concentrations were below this threshold for 63% of the total number of hourly averages with a mean concentration of 0.59 $\pm$ 0.40 ng m-3.

4. Page 5696, line 15: The authors list two GEM means; 1,54 and 1.70 ng/m3. What do these means refer to? Please clarify.

Response: This was changed in the text to use the annual mean at Barrow from 3 years of GEM measurements and the reference to Alert here was removed. The text was changed as follows: Annual average GEM concentrations for Barrow (2007-2009) are 1.15 ng m-3 and are lower than the northern hemispheric average ($\sim$1.70 ng m-3) (Slemr et al., 2003).

5. Page 5696, line 17-18: The sentence: "The average concentration reported on the sea ice in this study is lower than the lower spring time average for Alert". This is an interesting observation. Can the authors please provide some thoughts on why this is the case, as I cannot find this anywhere in the manuscript.

Response: The authors changed the comparison from Alert concentration to the Barrow concentrations because the overall concentrations at Barrow are lower than those reported at Alert. Therefore, the comparison with the shorter Barrow data (3 years) was used as a reference point.

7. Page 5696, line 21-22: The presented concentrations of RGM are much lower than those presented by Lindberg et al., 2002 (ES&T). Any thoughts on why this may be the case?

Response: There can be several reasons for this difference. Firstly, the measurements were collected in 2 different locations. We suspect that there are higher levels of PHg over the sea ice than more inland where the Lindberg measurements were made. Secondly, at Alert we see a switch from PHg to RGM as the main component in the speciated Hg and that happens at a later time in the spring when Lindberg et al saw their highest numbers in the RGM. Thirdly, the concentration of RGM varies from year to year based on the sea ice and weather conditions so a comparison of concentrations without other parameters is not that useful.

Response: To address this comment the following sentence was added into the text: These RGM concentrations are lower than others reported from Barrow (Lindberg et al., 2002a) and we attribute the differences to spatial, seasonal and inter-annual variability

8. Page 5706, line 12-13: Referring to the average Hg content in the sea ice snow and the tundra snow. How many samples are these numbers based on and perhaps median would be a more reliable number as Hg content in snow tends to be very inhomogeneous, as also presented by the standard deviations.

Response: The authors agree and have added in the number of samples and the range of the data to provide the reader more information rather than only expressing the concentrations as median values. The text has been changed as follows: The overall results showed that the average concentration of mercury in the surface snow over land (16 samples) and sea ice (13 samples) averaged 66 $\pm$ 30 (range 25-136) ng L-1 and 75 $\pm$47 (range 34-212) ng L-1, respectively. These results indicate that there is somewhat more Hg in snow over the ice than over the tundra although there is high variability in this data. While a Mann-Whitney U-test showed that these concentrations

are not statistically different (95% confidence), they do follow the pattern of previously reported results where concentrations of mercury in the snow are lower further inland from the coast (Douglas et al., 2008). Samples of brine around sea ice measurement sites averaged Hg concentrations of 83.1 $\pm$ 58.4 (range 38-164) ng L-1 and samples of frost flowers averaged 93.7 $\pm$ 60.8 (range 11 -200) ng L-1.

9. Page 5726, figure 6: The figure presents BrO and PHg/RGM measurements over sea ice and BrO and GEM over tundra. The BrO data looks equal in the two panels, is it the same data? This is a bit confusing. The figure caption states the different events are marked yellow, purple and blue, however the purple and blue looks the same my printout so it may be advisable to choose different colors.

Response: Yes it is the same BrO data. This was done so that the illustration of BrO can be seen in comparison with the RGM and PHg data and the GEM over ice and land data. The Figure caption has been modified to the following:

Response: Figure 6: BrO and PHg/RGM measurements over the sea ice and BrO and GEM measurements over both tundra and sea ice. The BrO data displayed is the same in both panels. Events 1, 2 and 3 are marked as yellow, red and blue, respectively Thank you for bringing the colour issue to the attention of the authors, it was changed as follows: Event 1- yellow Event 2 – red Event 3- blue

Technical comments

10. Page 5691, line 10-11: The sentence starting with “Currently, modelers use a number of roughly 50% : : :”. It is not clear from the text whether the number in this sentence refers to the fractions of retained or re-emitted mercury. Please clarify.

Response: The text refers to re-emitted mercury and has been clarified as follows: Currently, modelers have assessed the amount of GEM re-emitted from the snow surface in their simulation models. Fisher et al. (2012) use 60% re-emission in their standard simulation while others use 59% and 60 % as the estimates (Dastoor et al., 2008;

Holmes et al., 2010). In an in depth study, Durnford et al. (2012), determined modelled re-emission rates of 67% between 60oN and 66.5oN and 75% from 66.50N to 90oN as a result of the mechanisms discussed above. In a general review, Douglas et al. (2012b) estimated an overall re-emission of between 60 and 80% of deposited Hg.

11. Page 5694, line 24-25: There seem to be a grammatical error in this sentence.

Response: The text was changed to the following: Liao et al. (2011) concluded that BrO is often distributed homogeneously on spatial scales of up to at least 4 km. Since the measurements from the LP-DOAS were collected within this distance, they are considered representative at the OOTI site.

12. Page 5695, line 5: The melted snow was filtered through acid washed polypropylene filters, however it is not mentioned which acid was used. I believe the reader would like to know what acid was used as the type of acid can influence the results depending on which ions are of interest.

Response: The text was modified as follows: Samples were stored frozen until arrival at the laboratory where they were allowed to melt to room temperature and were filtered through trace metal grade nitric acid acid washed 0.45 mm polypropylene filters.

13. Page 5695, line 6: 18 MW water? Should it be 18 MâËĞD ËŻe? Is there perhaps some conversion problem.

Response: Thank you for bringing that to our attention. The text should read Megaohm. We have changed it in the text as such.

14. Page 5702, line 23-24: There seem to be a grammatical error in this sentence. Response: The sentence was changed to: March 22-24 shows a weak depletion of GEM (Figure 2) and the open leads are between 18 and 45 km away and the nearest refrozen lead was also further away than during previous days.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 5687, 2013.

Figure 1a: Field experimental sites around Barrow located near the northernmost tip of Alaska. OOTI Site 1 at 71.29°N; 156.85°W, OOTI Site 2 at 71.36°N;156.69°W, OOTI Site 3 at 71.36°N;156.66°W and Tundra at 71.32°N;156.66°W. The MODIS Aqua satellite is translucently overlain to show sea ice conditions in the Chukchi Sea on March 19, 2009.

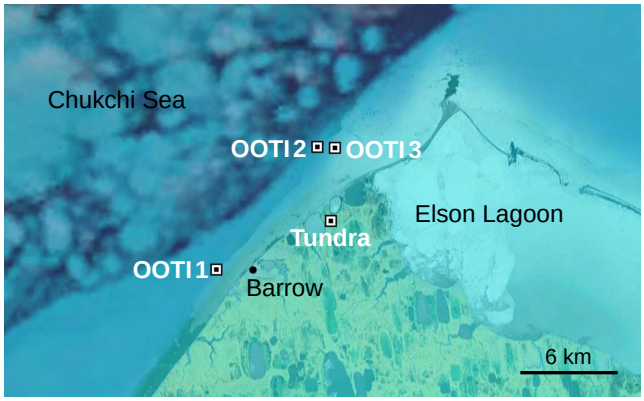

Fig. 1.

Figure 1b: Experimental set up of the Out On The Ice (OOTI) System. Box 1 housed the meteorological, MAX-DOAS and ozone instrumentation. Box 2 housed the mercury instrumentation. The inlet for the atmospheric mercury measurement is shown.

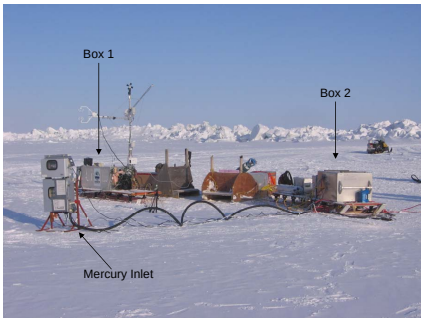

Fig. 2.

Figure 2: Hourly speciation and air temperature data from over the ice. Gaseous elemental mercury (top) is reported in ng m^{-3} and Reactive gaseous mercury (RGM – bottom) and Particulate mercury (PHg – middle) are reported in pg m^{-3}. Air temperature is reported in ^{o}C. The gaps in data indicate when the system was moved to a new site or when the power failed.

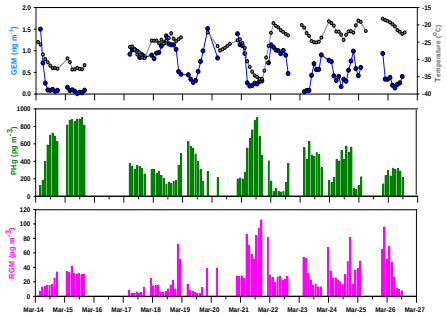

Fig. 3.

Figure 3: Modis satellite images of the sea ice Sea ice conditions for March 14- 25, 2009. March 14-16; March 20-22 and March 23-15 are from when samples were collected over the sea ice at Sites 1, 2 and 3, respectively. March 14-16 represents Event 1; March 20, 21 and 24 represent Event 2 and March 25 represents Event 3.

The black dot indicates the sampling location. The colours represent as follows: very light blue (lake ice or ice lagoon); light blue (first-year or older sea ice); darker blue (thinner and younger sea ice) and black (open water or thin new/nilas ice)

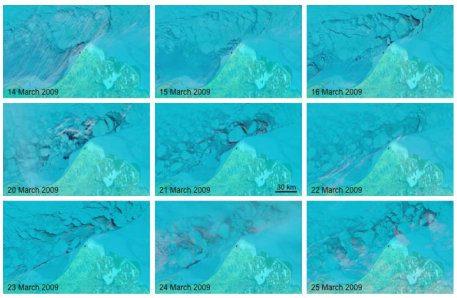

Fig. 4.

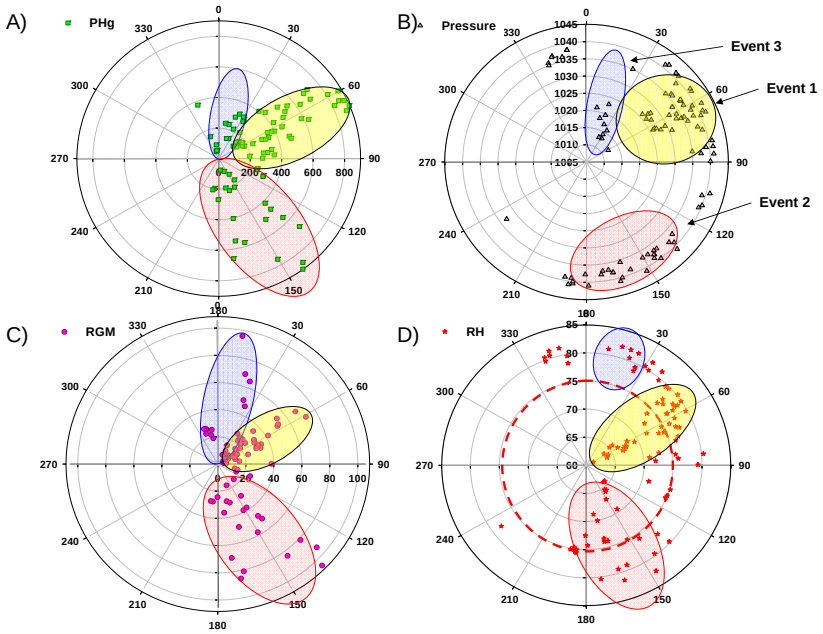

Fig. 5.

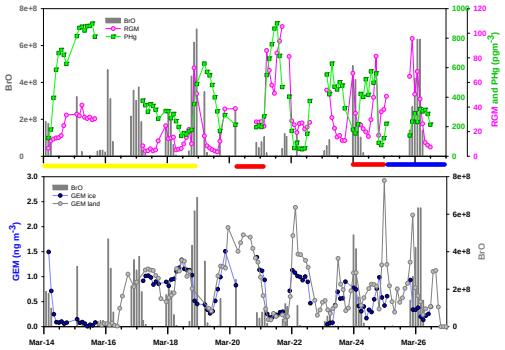

Figure 5 –BrO and PHg/RGM measurements over the sea ice and BrO and GEM measurements over both tundra and sea ice. Events 1, 2 and 3 are marked as yellow, red and blue, respectively

Fig. 6.

Figure 6 – GEM measurements over tundra inland (grey circles), over the sea ice (blue circles), solar radiation (orange) and the defined threshold for mercury depletions (1.063 ng m^{-3}) (dashed grey line)

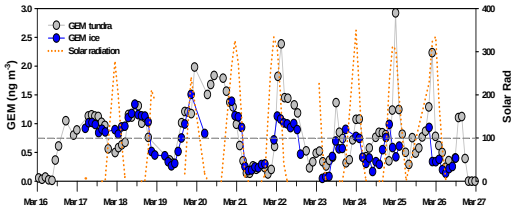

Fig. 7.