

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

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This article presents the results of measurements of atmospheric mercury species and compounds believed to be linked to the elemental mercury oxidation, within the Arctic Circle at the time of year when Hg depletion events occur. The results are interesting because the measurements were made simultaneously over tundra and sea-ice, and give an insight into the different behaviour of deposited oxidised Hg compounds in the snow over sea-ice and land. The link between the retention of deposited HgII and the salinity of the underlying snow is, as the authors point out, important for modeling studies, and also in the context of a changing Arctic climate. It is obviously a great shame that the authors had problems with the Hg speciation unit which was at the

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inland site, however the sea-ice measurements make this a very valuable data set worthy of publication. The aspect that lets this manuscript down is the rather tortuous, and at times long winded and confused discussion. This section really does need to be rewritten before publication, and I have made some suggestions below. There are also a few places in which the descriptions / language seem imprecise, I have tried to highlight the most obvious of these as well.

Response: The authors thank Reviewer 1 for their insightful comments about the manuscript which have improved it significantly. It was a shame that the inland speciation system failed during the experiment and we have removed that statement to not disappoint the reader. The experiments were repeated in 2012 with 2 fully functioning instruments on the ice and inland (stay tuned!). The text has been significantly tightened up based on the reviewer's suggestions.

Introduction 1. The discussion of AMDEs, and the fact that O₃ depletion is observed at the same time, and that both are believed to be the result of boundary layer bromine chemistry is unclear. The use of 'conversion' rather than 'oxidation' doesn't help the reader make the link between HgII and RGM. (p5689 line 18 onwards)

Response: The writing has been cleaned up and made more concise as follows: The Arctic atmosphere plays a key role in controlling mercury deposition to snow and ice surfaces. In the spring, through a series of photochemically initiated reactions, mercury is oxidized from its predominant form GEM (Hg(0)) in the air to inorganic Hg(II) species, either as a gas or associated to particles. These gaseous or particle-bound Hg (II) species are termed reactive gaseous mercury (RGM) or particulate mercury (PHg), respectively. This oxidation process is called an atmospheric mercury depletion event (AMDE) and is concurrent with the depletion of marine boundary layer ozone (O₃) (Steffen et al., 2008). Ozone is destroyed by bromine atoms that are produced through a series of photochemically initiated reactions from sea salts and GEM is oxidized by bromine atoms either as Br or BrO (Simpson et al., 2007; Steffen et al., 2008). Both GEM and O₃ depletions require the presence of sea salts, sunlight, stable boundary

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conditions and cold temperatures.

2. The comment on line 22, These reactions have been shown to be in direct relation to the depletion of ozone, could be changed to be more precise. There is a correlation? Still on p5689 line 27), it is not the Hg that is collected on particles, but rather the particles that are collected on filters and then the Hg associated with the particles that is determined.

Response: The text was revised as follows: Both GEM and O3 depletions require the presence of sea salts, sunlight, stable boundary conditions and cold temperatures. At this time, RGM and PHg are operationally defined as mercury that adsorbs to a KCl denuder (gas phase) and mercury that is associated to particles <2.5µm and collected on quartz filters, respectively.

3. The sentence that follows seems unnecessary.

Response: As suggested, the sentence was removed

4. p5690 It is believed that the majority of the O3 depletion events occur over the Arctic Ocean and are meteorologically modulated to coastal measurement sites, meteorologically modulated?

Response: Meteorological modulation is a term in weather to describe meteorological forcing or change. In this case we refer to the air masses containing depleted Hg and O3 are meteorologically brought to the sampling site rather than the depletion chemistry being at the measurement site. The text was changed so that all readers understand the description to: It is believed that the majority of the O3 depletion events occur over the Arctic Ocean and those reported at coastal measurement sites are a result of depleted air masses that have travelled from the ocean to the site and not from local chemistry (Bottenheim and Chan, 2006).

5. On page 5690 line 17 sailboat? Really?

Response: Yes, please see the link below for details. <http://www.damocles-C3451>

eu.org/research/TARA_ARCTIC_2007-2008_The_Great_Arctic_drift_54.shtml

6. And line 22; it is speciation data that is collected I would have thought, rather than speciation itself. This section does not explain that RGM is assumed to be HgII, or that RGM is comprised of gas phase oxidised Hg species.

Response: The word data was added into the sentence. The terminology has been cleaned up and we use GEM, RGM and PHg after defining them at the beginning of the paragraph

7. The rest of the paragraph uses both HgII and RGM, perhaps it would be more clear to the reader not familiar with atmospheric Hg chemistry to use one or the other.

Response: The terminology has been cleaned up and we use GEM, RGM and PHg after defining them at the beginning of the paragraph

8. p5691 line 6 the level of mercury drops off ? line 10. Looking at the cited articles I find the following:

Our simulation includes an improved treatment for the fate of HgII deposited to snow. Photo-reduction of deposited HgII followed by Hg0 re-emission is known to take place but not all deposited HgII is easily reduced. Observational estimates of the reducible component of HgII range from less than 10% to more than 90%. Here we assume that 60% of deposited HgII is reducible, but test the sensitivity to this assumption. from Fisher et al. The text says roughly 50% for some reason.

Response: The reason for saying approximately 50% was because they varied the assumption for the several model runs. The reviewer is correct that 60% is the amount used in the standard model and we will use that number. The text has been changed as follows: Currently, modelers have assessed the amount of GEM re-emitted from the snow surface in their simulation models.

9. Simulations by GRAHM and its new snowpack/meltwater model for mercury suggest that, on an annual basis, the average fraction of mercury deposited onto snowpacks

that is revolatilized increases with latitude from 39% between 30 and 45_N, to 57% from 45 to 60_N, 67% from 60 to 66.5_N, and 75% polewards of 66.5_N. from Durnford et al., which does not correspond to the values in the manuscript.

Response: I had averaged the numbers over larger latitude sections. The text was modified as follows: Currently, modelers have made assumptions on 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 66.5oN 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.

10. In the section on Max-DOAS it is stated that a radiative transfer model was used to simulate aerosol vertical profiles. As the authors refer to the results from this model in a later section it would be useful if the model used was described or named and a reference given.

Response: The text was modified as follows and includes the reference to the model used: A mini-Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) was used to record the aerosol extinction vertical profiles. This instrument is based on the Ocean Optics Inc. USB2000 miniature spectrometer (Hoffmann Messtechnik GmbH) (Hönninger and Platt, 2002; Frieß et al., 2004; Wagner et al., 2004; Frieß et al., 2006; Frieß et al., 2011) with a spectral resolution of 0.7 nm. Scattered sun light was collected by rotating telescope from a series of elevation angles: 2°, 5°, 10° and 20° and 90° (zenith orientation). Differential slant column densities (DSCDs) are directly measured from the instrument and represent the integrated concentrations of the absorbers along the scattered light path relative to the absorbers in measured reference spectrum selected from zenith observations. The vertical column density (VCD) is the vertically integrated trace gas concentration and is independent from the line of sight

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and the observed light path. DSCD and VCD are linked through an air mass factor $AMF = DSCD/VCD$ which reflects the radiative transfer within the atmosphere and is determined through radiative transfer models (RTM). Various aerosol scenarios were simulated using the radiative transfer model McArtim (Deutchmann, 2009) at 361 nm. Aerosol extinction values between 0.02 and 1 km⁻¹ were used in the simulations with different profiles (with variable thickness) closely confined in a narrow layer over the surface and extending up to 2500 m in the atmosphere from the surface.

11. Section 3.1 There are a few sentences which are a little unclear here: Frost flowers are intricate ice crystals formed from brine wicked through the sea ice that is subsequently coated with air vapour deposition (Simpson et al., 2007; Douglas et al., 2012a) and have an appearance of a flower on the surface., air vapour deposition?

Response: The text was modified to be clearer as follows: Frost flowers are formed from water vapour above the sea ice into intricate ice crystal clusters (Simpson et al., 2007; Douglas et al., 2012a) that have the appearance of flowers on the surface. Brine enriched in sea salts are wicked up through the ice into these crystals.

12. Using Max-DOAS, the position of the particle load and the thickness of the aerosol layer at the surface layer of the study site can be modeled to confirm the presence of aerosols.

Response: We have modified the sentence to read: Using mini-Max-DOAS, the position and thickness of the aerosol layer close to the study site can be modeled to confirm the presence or absence of aerosols, the position and thickness of the layer in the atmosphere

13. The comment on the particle sizes that the instrument collects is not very well worded. This confirms that there is a measured concentration of particles present in the measurement area at the lower surface air.

Response: The text was clarified as follows: The sizes of the aerosols measured with

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the Max-DOAS are not limited to the size of particles measured by the mercury instrument (<2.5 μm).

14. page 5698, line 16; emerged?

Response: The authors feel that emerged is the best word to use for this sentence. The word emerge can mean "become evident" and in this case we are referring to an air mass containing an increased aerosol load that "emerged" or became evident after a wind shift. The authors do not feel a change is necessary in this sentence.

15. This small crystal forms in the air on clear, cold days and has a relatively large surface area onto which reactions can occur. They have been reported to have a length between 1 and 1000 μm , onto which reactions can occur? length?

Response: Ice crystals are crystalline structures formed through sublimation of the water vapour in the air at very cold temperatures. They are long crystals and are often cited as length rather than diameter because of this shape. The references cited in the text are in length. The text was changed to clarify as follows: These small needle-like crystals form in the air on clear, cold days and have a relatively large surface area on which reactions can occur. They have been reported to have a length between 1 and 1000 μm (Ohtake et al., 1982; Walden et al., 2003; Intrieri and Shupe, 2004).

16. The discussion regarding the possible contribution of Hg adsorbed on diamond dust is divided into two parts, one in section 3.1 (p5699) where it is described as 'likely minor'. Then again in section 3.2 (p5700) where the hypothesis that diamond dust causes a peak in PHg is presented. So it a minor peak?

Response: The comment from the reviewer is a valid one. The text has been changed as follows: The contribution from diamond dust to the total particle load is likely minor but cannot be ruled out as a contributor to PHg levels because the Hg concentration in them is so high.

Response: We have changed the text in section 3.2 on the discussion of the large PHg

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peak on March 21-22 as follows and clarified the discussion about this peak in PHg: Further, direct observations of diamond dust events were made on March 21 and 22, 2009 (Domine et al., 2011b) raising the interesting hypothesis that RGM partitioning onto these crystals is the cause for the peak in PHg. March 21-22, the RGM and PHg data differ from the other times in that they both peak during low solar radiation. The authors suggest that at the beginning of this time period an increase in RGM is reported, but as diamond dust crystals begin to form, some of this RGM associates to the crystals and is then detected as PHg. This shift could explain the atypical near-concurrent PHg and RGM peaks at this time. It should be noted that, on March 20/21, fractures and leads opened up to the north of the measurement site approximately five to eight kilometres away and nilas ice formed on the 22nd (Figure 3) and may be a source of moisture for ice crystal formation.

17. Section 3.2 The fact that PHg 'lags behind by a few hours' (how many?) does not indicate that this fraction of Hg is not photochemically derived, only that it is perhaps not directly formed by photochemical processes.

Response: The sentence "The results in this figure also show that PHg concentrations do not peak with solar radiation but lags behind by a few hours suggesting that this fraction of Hg is not photochemically derived" was changed to the following: "The results in this figure also show that PHg concentrations do not peak with solar radiation but lags behind by a few hours suggesting that this fraction of Hg is not directly formed by photochemical processes"

18. The following sentences are not very clear: Interestingly, Event 3, where %RH is above 75%, is the warmest event may also decrease the potential of RGM to partition onto particles.

Response: The following sentences were removed from the text as they were not clear and did not add significant value to the discussion: "Interestingly, Event 3, where %RH is above 75%, is the warmest event may also decrease the potential of RGM to partition

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onto particles. We suggest that when %RH is below 75%, the PHg concentration data would include more sea salt particles in the air than when it is above 75%.”

This close refrozen surface can reflect a strong depletion of GEM and elevated PHg (potentially a source of fresh sea salts). On 25 March the measurement site was further from the refrozen sea ice and but a closer distance from the open water (12.5 km); however, the air mass is coming from a different direction at this time and thus the northern sea ice may not be the biggest driver in activities during this event.

Response: This paragraph was changed to be clearer as follows: The distances between the sample locations and the nearest refrozen ice/open water or nilas ice are estimated using MODIS satellite images. These estimates are summarized in Table 3 and are separated into Events 1, 2 and 3 to assess if there are links between the proximity of certain sea ice and mercury concentrations. During Event 1, a strong depletion of GEM and elevation in PHg are reported when the sampling site was located close to refrozen sea ice (1.2 -1.8 km). At this time, the air measured is directly from the direction of this refrozen lead and is concurrent with the low GEM and high PHg concentrations. At the beginning of Event 2, the refrozen sea ice is further away from the sampling site (4-5 km) but an open lead is within 8 km. The proximity of the open lead may explain the increase the %RH if the air mass with moisture from the lead came near the study site; however the wind direction during this event is predominately from the south and thus the chemistry is not likely impacted from this lead. On March 25, during Event 3, open leads are closer at 12.5 km to the measurement and GEM is again depleted. These results suggest that both open leads and recently frozen sea ice are associated with GEM loss and with differences RGM and PHg concentration levels.

19. Section 3.4 It was also observed that after the spike in GEM concentrations at both locations the GEM is again oxidized and depleted from the air. How can this be true if no measurements of oxidised Hg were made at the inland site? Can transport of already Hg depleted air be ruled out?

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Response: The assumption is that when GEM is depleted, it has been oxidized and thus when the reemission spike occurs and then rapidly decreases, we assume that oxidation of the GEM continues. It is unlikely that the depleted air mass would cause this at such a regular daily pace.

10. The measurements are suggestive of higher Hg retention in the snow over sea-ice than the snow over land, and this is an extremely important finding in terms of the Hg cycle in the Arctic. However I am unsure that it can be considered as a definite fact as the result of one 12 day experimental campaign in one are of the Arctic, especially as the supporting speciation measurements over land were not performed successfully. The discussion of AMDEs, ODEs and the atmospheric chemistry of Bromine containing compounds during Springtime in the Arctic boundary layer is rather convoluted, repetitive and at times confusing.

Response: We are confident in the results from this experiment. It does not matter that the data for RGM and PHg collected over the tundra were not included because this discussion is exclusively about GEM. The GEM measurements are very clear at all 3 different locations on the sea ice when compared to the tundra site. The 2 instruments were run side by side after the experiment and showed excellent agreement in their GEM concentrations. The experiment was also repeated in 2012 and we found the same result, thus we have great confidence in the conclusions we have drawn. This 2012 data was not included in this text as it is part of another paper being prepared. The discussion about AMDEs, ODEs and the bromine chemistry were revised.

21. The interplay between RGM (HgII) and Hg associated with particulates is also tortuous at times.

Response: All the HgII and Hg0 have been changed to be consistent throughout the text.

The manuscript as whole is rather difficult to follow, and this is a shame given how interesting the results are. The manuscript requires significant revision (and shorten-

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ing) in order to present clearly and concisely the results obtained and the conclusions reached.

Response: The manuscript has been shortened and made more concise, the text has been clarified in many cases to make the read less problematic for the reader.

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

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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.

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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.

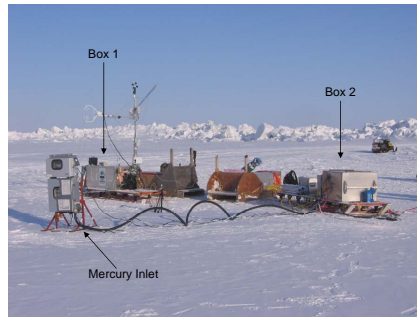


Fig. 2.

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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 $^{\circ}\text{C}$. The gaps in data indicate when the system was moved to a new site or when the power failed.

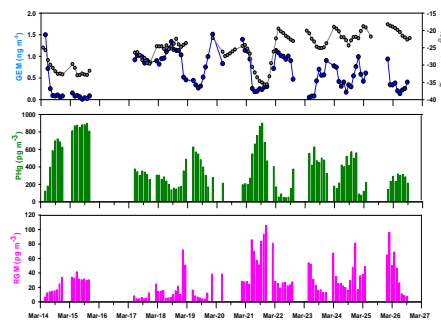


Fig. 3.

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Figure 3: Modis satellite images of the 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)

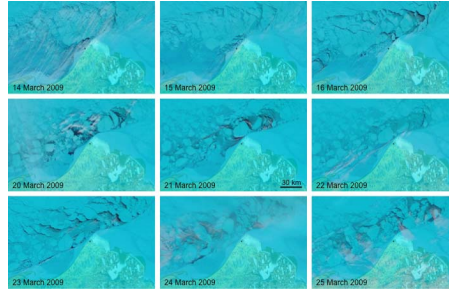


Fig. 4.

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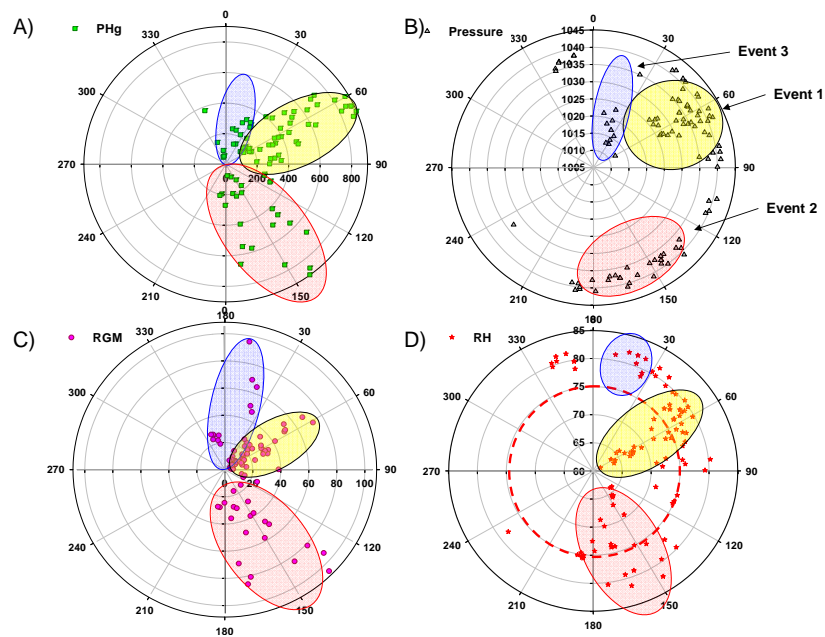


Fig. 5.

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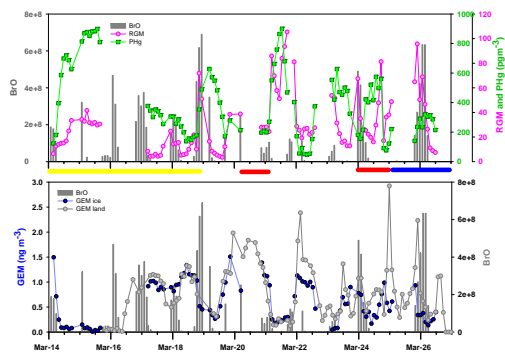


Figure 5 – BrO and PHg RGM measurements over the sea ice and BrO and GEM measurements over both tundra and sea ice. Events 1, 2 and 3 are marked as yellow, red and blue, respectively

Fig. 6.

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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)

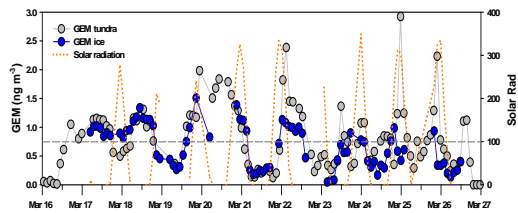


Fig. 7.

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