

Author's comment

The comments presented by the two referees are generally sound and most relevant. The authors are most thankful for the interest and time they dedicated to screen the paper. The authors' reply to comments/questions/suggestions is in red font colour.

Referee #1

General Comments:

This manuscript presents data from a circumpolar cruise in the Arctic Ocean during summer covering 60 – 90 °N. The dataset is unique yet I was disappointed in its presentation. There was too much emphasis on reporting mean values rather an in-depth analysis of interesting events that occurred during the cruise. Looking at figure 2, many events are evident, but not even mentioned in the text. Certainly boreal wildfires must have influenced the data, but it's not even mentioned.

Analysis of backward trajectories ending at IB Oden during the ship's circumpolar cruise revealed almost exclusively (>95%) a marine origin (cf. draft figure 1). Only along the Chukchi Peninsula, air masses crossing over land were prevalent. The land crossed consists mainly of treeless tundra. Moreover, Hg⁰, TGM and CO were generally not correlated as one will expect in smoke plumes from boreal wildfires (Friedli et al., 2003). It was only during the first week of August in a port and along the coast of the Chukchi Peninsula that two distinguished events of correlated elevated Hg⁰&CO concentrations were measured. We have now analyzed Hg/CO ratios during these events by linear fits. Hg/CO ratios of (5 - 8) x 10⁻⁵ mol/mol were measured (duration of episodes in total 15 h), which is well above the narrow range of (0.67 - 2.4) x 10⁻⁷ mol/mol hitherto reported for biomass burning (Ebinghaus et al., 2007) and also significantly higher than East Asian industrial emission ratios of ~ (5±2) x 10⁻⁶ mol/mol reported by Weiss-Penzias et al. (2007). A highly tentative source appointment could be non-ferrous ore smelting activities. We think the referee could be misled by Figure 2, where the raw data are not easy to distinguish from the data screened from local pollution. This figure will be remade to improve its clarity. In order to strengthen our argument, we will in our re-submission add a Figure (such as draft Figure 1) displaying relevant back-trajectories in addition to an analysis of the elevated Hg+CO events.

The focus of the manuscript apperas to be on mercury, yet I believe there is more discussion of O3 and CO. The text would be improved greatly by infiltration of more discussion directly on mercury. Most of the figures presenting time series information are hard to read, and need improvement.

Agreeable! Figures will be improved in the re-submission.

The discussion on ship plume impact needs to be brought together in one place, and made more succinct.

Agreeable!

Although trajectory analysis was conducted, it is hardly utilized in the text. In summary, the authors need to conduct more in-depth analysis of the mercury data, and improve its presence in the manuscript. For example, why is mercury not shown in figure 5?

Figure 5 is naturally included in order to visualize simultaneous CO&O₃ data from Barrow and Alert coinciding with the Oden expedition. Corresponding TGM, Hg⁰ data from these coastal stations have to the best of our knowledge not been published in detail. We know that such measurements were actually been performed at Alert, however we have been in contact with the sampling manager but not yet get reply.

In general, the discussion needs to follow the key figures more closely and in more detailed discussion. The discussion jumps immediately to impact of ship plumes, instead of presenting the large-scale picture first. There is almost no discussion of this, and it's a main point of the manuscript. The authors have a very nice data set; they just need to focus more on the mercury data.

Specific Comments:

Abstract:

p. 20914, “strong Hg(0)pulse in the water was spilled with some time-delay. . .” The use of the word “spilled” here is puzzling.

The verb release will be used as replacement.

p. 20915, “suggesting that atmospheric mercury deposition to the Arctic basin is low during summer and autumn.” I would expect the deposition to be continuous year-round, and actually highest in summer due to open water. The fact that high mixing ratios of mercury were not encountered does not imply any information about its down-ward flux.

We are very puzzled by the referee’s comment here. There is no evidence presented in the literature that the highest deposition to the Arctic basin should occur during summer. Rather the contrary case, Dastoor et al. (2008) estimated for 2002-4 depositional fluxes of 240-247 tons and 68-74 during Mar-May and Jun-Aug respectively. The presence of open water should promote evasion flux to air due to supersaturation levels of DGM. In summer, air transported with strong surface contact over the Arctic Ocean show high concentrations of TGM (Hirdman et al., 2009). Given the low RGM, Hg-p concentrations measured during leg 3 and the restricted importance of scavenging processes in the desert-like conditions prevailing in the high Arctic imply indeed low atmospheric Hg depositional fluxes during this period of time.

p. 20915, elevated levels (how much?) were episodically observed . . . indicating regional pollution. Were trajectories run to confirm this? Why could it not be from long range transport. What type of pollution sources could account for these events? Wild-fires?

As stated above backward trajectories calculated will be visualized in a new figure (cf. draft Figure 1)

Mercury Measurements:

If the gold cartridges were changed frequently (how often? Every two weeks), was the instrument recalibrated each time? Naturally, the instrument was re-calibrated. It appears so, what was the change in response? Traps were never passivated when replaced for treatment. The action was always preventive. Responses were very similar before and after treatment with respect to spans (within the reproducibility of the internal Hg source) and air samples. I’m amazed that the washing procedure used actually cleaned the gold surfaces. According to our experience, marine air in general tends to passivate gold trap relatively quick and eventually seriously (permanent passivation). The treatment used here is not contained Tekran recommendations. However, in our lab and some other lab it has been found to significantly extend the life-time of Au traps if the treatment is applied regularly after initial exposure.

p. 20191, Was this a custom fabricated sampling system, or a modified Tekran?

In house built system, described in more detail in the references given.

Ozone and CO measurements:

p. 20920, line 14 – the 150C temperature to oxidize CO seems low. Most use at least 250 °C. Did you test this to see if all CO was oxidized to CO₂? I am surprised if it was.

A temperature of 150 °C corresponds to the standard setting of the CO trap recommended by the manufacturer of the commercial CO detector. Tests performed by the manufacturer indicate that the used CO trap removes the CO very efficiently already at room temperature: For example, the CO concentration in a CO standard containing 1036 ppbV was reduced to below the detection limit. During the measurements, ambient air with much lower CO concentrations were used to generate the CO-free air. In summary, we are confident that the applied set-up of the CO trap successfully produced CO-free air throughout the trip.

p. 20920, line 14 – why did you select FEP tubing? Most researches use PFA. What type of tests were conducted on the tubing to ensure high passing efficiencies?

We have used FEP tubing for Hg measurements during more than 10 years. We have no indication that such tubing should give losses. Injections of saturated Hg⁰ vapour from a thermostatted source (4 °C) at the inlet (>4 °C) have showed unity recoveries. In the literature, we can not find any support that PFA- and FEP-tubing should differ in high passing efficiency. Rather the opposite (cf. Edwards et al., 2005)

p. 20920, line 15 – what material was the protective housing constructed out of?

PFA (Savillex Corp. column components)

Data Analysis:

p. 20921 – I assume since you used the O₃/CO to detect the ship plume that no other direct measurements of it such as NO, SO₂, or CN were available? I now see you actually used CO/O₃ to screen, so I would revise line 18.

OK!

p. 20922 – Delete the two sentences at the top of the page that describes the software used to generate the plots. It is unnecessary information.

OK!

p. 20922 – the authors have used Hg(0)/TGM in the manuscript, but this is misleading since it implies that you divided Hg(0) by the TGM values. It doesn't appear that this is the case. I would use a comma between them instead to avoid confusion.

OK, we will use TGM, Hg⁰.

Figure 2 – I can not distinguish the open from colored symbols on this figure. It needs to be improved to show these better.

This figure will be revised.

p. 20924, line 12 – Any idea what caused the decreased O₃ values?

Note that similar ozone decreases were observed during the same period at Alert and Barrow (Fig. 5). In fact, fast ozone depletions (so-called ozone depletion events ODE) are regularly observed at arctic coastal stations or over the Arctic Ocean. However, they occur in springtime and are related to active halogen chemistry. We refer to these specific springtime conditions on page 20916 - 20917 and 20929. Therefore, it is tempting to explain the observed O₃ decreases in summer by the same mechanism. Nevertheless, we refrained from doing so because we feel that the available data is not sufficient to claim that we observed ODEs during the summer season. One reason is also that we do not observe simultaneous mercury depletion, which always accompany the ODEs observed in springtime. Further observations are needed to elucidate the responsible processes.

Figure 5 – this figure is also very hard to read. It should be improved. Why is there not a panel showing mercury? After all, this is the focus of the manuscript.

Table 5 is included to display the comparison between IB Oden and Alert & Barrow. No TGM data have been retrieved from these coastal stations (no publications of detailed observations, See above)

p. 20925, lines 7-8 – “which appear not to be inferior over . . .” This needs to be re-written, as inferior is not a correct word here and I don't understand what your trying to say.

Could be replaced by “which appear not be lower over...”

p. 20926 – what does DGM refer to? Define it.

Dissolved Gaseous Mercury, will be defined accordingly in the re-submission.

p. 20926 – To me, much of the discussion on this page should be in the Introduction Section, as its background information.

We will move part of it to the introduction

p. 20926, line 23 – what does this sentence mean, the number of hours sampled each day was 22? The sentence will be changed in

“The day length during the expedition was at least 22 h”.

p. 20927 – why would Hg(0) evasion from seawater follow a diurnal cycle?

Imbalances between production by photo-reduction in the surface water and loss to the atmosphere.

p. 20927 – I assume that dissolved mercury was measured on the cruise by Anderson et al.? This should be more clearly stated in the methods section. OK!

p. 20928 – The discussion on future predictions uses almost no data from this manuscript, so I would

reduce it substantially. It appears to have been already published by Anderson. **Agreeable!**

Oxidation Capacity:

The first paragraph is not the focus of this manuscript. The second paragraph deals with mercury, but does not add any new information. I would consider cutting this section of the manuscript.

We will consider to put the discussion on Hg before the other trace gases here and revise it.

Referee #2

The paper presents valuable measurements of gaseous mercury (Hg^0), reactive gaseous mercury (RGM), particulate mercury (PHg), CO and O_3 in the marine boundary layer of the Arctic Ocean during a cruise in summer of 2005. The data are unique because they cover a large part of the Arctic Ocean for which data from only a few land based stations are available. The analysis of the data is comprehensive, apart from a few suggestions listed below. The paper is clearly written, although, it would profit at times from editing by a native English speaker. Therefore, I recommend the publication of the paper with minor modification suggested below:

Factual remarks:

Page 20916, line 17: In fact the maximum Hg concentrations in the Southern Hemisphere reported by Slemr et al. (2008) occur in austral summer, not austral winter.

Please correct. **Page 20915, line 17 This mistake will be corrected.**

Page 20916, line 21: The sweeping statement about ozone maximum in summer might be true for continental boundary layer and northern midlatitudes. However, in remote marine boundary with low NO_x concentrations ozone is photochemically destroyed, which might compensate for the summer maximum of the advected ozone. The statement should be confined to what is being reported for the Arctic stations which sample marine boundary layer.

The mentioned paragraph describes the behavior of ozone during polar mercury depletion events in springtime. However, there is no statement about ozone in summertime in this paragraph. In contrast, paragraph 3.2.2 briefly describes the ozone in the marine boundary layer in summertime. In fact, this paragraph summarizes reasons why the observed ozone is lower than expected, for example connected to the low NO_x concentrations as mentioned by the referee: page 20929, l. 5: "The low NO_x -environment of the Arctic can also contribute to a more efficient chemical O_3 destruction during summer (Helmig et al., 2007)." In our opinion, no changes necessary.

In the section "Data Analysis" the authors mention the investigation of the 10 min averaged data for abnormally high and low concentrations. Thereafter, they are discussing only the high concentrations, mostly of CO, caused by the ship exhausts. But no specifications are being made in respect to "abnormally low" concentrations. **As mentioned local pollution cause peaks in CO and correlated dips in O_3 . Local pollution was found not to influence Hg^0 (TGM) .** Were there any "abnormally low" mercury concentrations screened out of the data, and if so what criteria were used for it? **No!** In view of the summer Antarctic mercury depletion episode described by Temme et al. (Environ. Sci. Technol. 37, 22-31, 2003) and depletion episodes in marine boundary layer reported recently by Brunke et al. (ACPD 9, 20979-21009, 2009) there might be nothing like "abnormally low" mercury concentrations, at least not in the marine boundary layer. Therefore, no "abnormally low" mercury concentrations should be deleted out of the data set.

We agree! No "low" mercury data were screened out.

In the section 3.1.2 the authors report the occurrence of the pollution plumes with elevated Hg and CO concentrations near to the Chukchi Peninsula. What was the Hg/CO (emission) ratio in these plumes? **See above (Page 1)** In this paragraph the authors also refer to Sect. 5 which does not exist. **This mistake will be corrected.**

In the section 3.2 the authors mention a diurnal variation of TGM concentrations during the crossing of the North Atlantic and they refer to Fig. 1, which does not provide any information about its timing, and to Fig. 2 with such a highly compressed time scale, that the timing of the maxima and minima cannot be found out either. An additional figure for this section of the cruise with an expanded time scale could solve this problem. **We will supply an extra figure or an addition to figure 2.**

In the last paragraph of section 3.2.1 the authors conclude that the observed low RGM and PHg concentrations suggest "that the Arctic Ocean MBL during summer does not promote significant chemical conversion of Hg^0 . . .". At the end of the same paragraph they mention the increased removal of RGM and

PHg by frequently occurring fog and high relative humidity. In the latter case only a rapid chemical conversion would be able to sustain the observed RGM and PHg concentrations, which is at odds with the initial statement. Perhaps some insight could be gained from the statistics of the RGM and PHg concentrations binned according to the fog and fog-free episodes.

Good point. Additional time-resolved information will be added to figure 3 (cf. draft Figure 2) and corresponding text to strength argument (together w/ draft Figure 2).

Page 20916, line 21: The sweeping statement about ozone maximum in summer might be true for continental boundary layer and northern midlatitudes. However, in remote marine boundary with low NO_x concentrations ozone is photochemically destroyed, which might compensate for the summer maximum of the advected ozone. The statement should be confined to what is being reported for the Arctic stations which sample marine boundary layer. See above!

Editorial remarks:

As already mentioned, the paper would substantially profit from editing by a native English speaker. The following suggestions represent only a few examples where a more precise and pertinent wording could improve the readability:

Page 20916, line 26: In view of our limited knowledge about the origin of high levels of neurotoxic mercury in the Arctic ecosystems the wording “It has been elucidated” is too presumptuous.

OK, the sentence will be revised.

Page 20917, line 15: The sentence starting with “We. . .” is neither grammatically correct nor understandable. “eligible candidate” - for what?

We have already pointed out that the regimes of O₃ are similar with that of Hg⁰ during MDEs, in addition O₃ is produced from degradation of CO by OH radicals, so the addition of O₃ measurements to the sampling programme was a matter of course.

Page 20918, line 22: The cleaning of the cartridges can regenerate them, but it cannot prevent their deactivation. “To prevent deactivation...” changed into “To regenerate..., they...”

Page 20921, line 18: A reference to a refinery processing might improve the readability of the sentence starting with “Mercury in crude oil..”

We will add a reference to Hg in the refining process (Wilhelm and Spitz, 2003)

Page 20926, line 3: When reading the sentence starting with “However, concerning the corresponding DGM data. . .” the reader tries vainly to find the DGM data in Table 3.

OK, DGM data will be added

Table 3: As medians provide additional information about the distribution of the data, they should be added to this table. The authors should keep in mind that the statistical tests for difference of averages assume the normal distribution of the data. Added medians can help to justify the application of such tests.

OK, medians will be supplied.

Fig. 3: For convenience of the readers the figure should contain the TGM/Hg⁰ concentrations as well.

OK, a draft figure is added below:

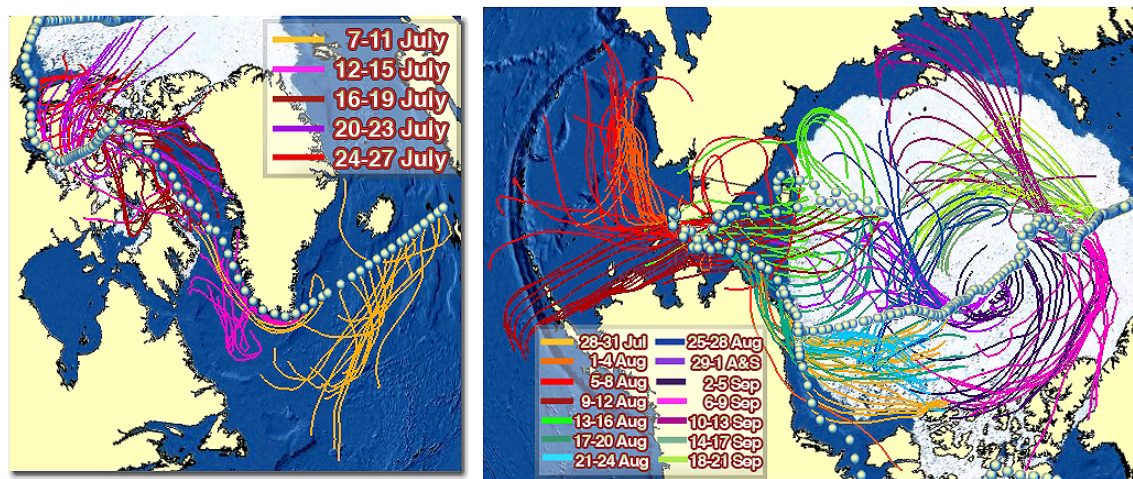


Figure 1. Visualization of 3-days backward trajectories (final version 5-days trajectories !?).

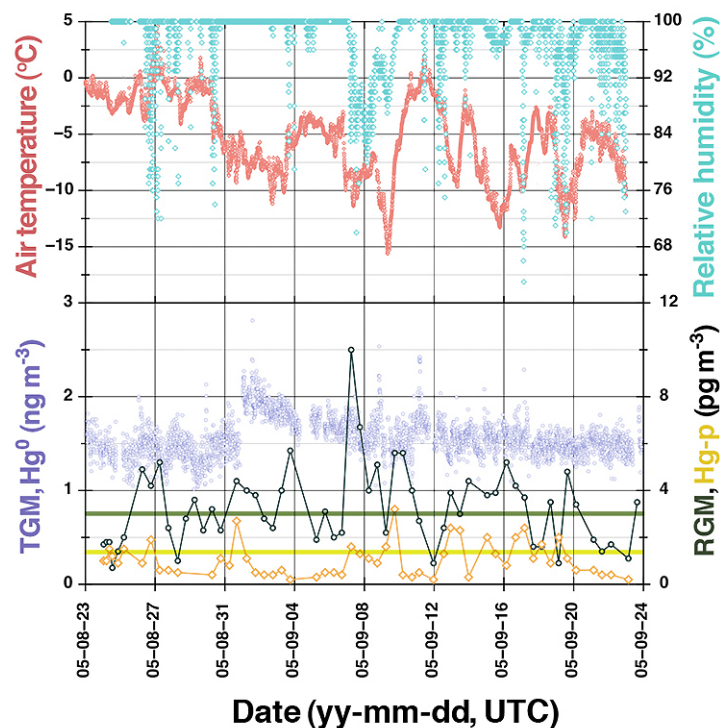


Figure 2. Draft revision of original Figure 3.

References

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