Reply to Anonymous Referee # 4 Comment on 'Dynamics of gaseous oxidized mercury at Villum Research Station during the High Arctic summer'

The authors present data from two summer measurement campaigns at a high Arctic station. The presentation and discussion of the data is focused on the origin of the gaseous oxidized mercury (GOM). They arrive at the conclusion that high GOM concentrations during all 5 events are due to the transport from the free troposphere. At a very remote site this is almost always the case and, as such, too unspecific. This is a pity because the observed events display different patterns which would enable more specific conclusions.

The data are valuable and worth of detailed analysis. Unfortunately, the manuscript is difficult to read because GEM, GOM, PHg, O_3, BC, H_2O, and N_{coarse} are all discussed in different chapters. A change of perspective in O_3 chapter from the analysis of individual events to the whole campaign analysis does not make the understanding easier. Ideally, the air mass of each event would be characterised by all of the available data, including backward trajectories (the consideration of the latter would probably result in splitting the event 1 into two events). This would be followed by detailed discussion of GOM origin in each of the characterised events separately before making final conclusions. I recommend the publication of the manuscript after a thorough reorganisation of the text along the lines proposed above. Some of the comments below are also to be considered:

We thank Referee # 4 for their careful review of our manuscript. Their comments and suggestions will improve the clarity, presentation, and discussion of the results. We have addressed the referee's concerns and corrected errors below with the author's responses in blue. The line numbers refer to the text in the clean version of the revised manuscript. New references are highlighted in yellow.

We regret the referee found the manuscript difficult to read and agree a detailed discussion of each event is warranted. Therefore, we have made substantial changes to the organization of the text, we have split the Results and Discussion section into two separate sections. In the new Results section, we present the results of each parameter for each campaign. We also agree that the criteria for defining an event should include considerations for specific air masses. We have also recalculated the trajectory length for 240 hours. Using these new trajectories and the new criteria, we have split Event 1 into Events 1a and 1b, per the referee's suggestion, this also made us re-evaluate other events, resulting in Event 5 being split into 5a and 5b. These two events occurred sequentially therefore the naming convention using the same number and different letters. In the new Discussion section, we discuss factors influencing event vs non-event periods and factors influencing individual events, per the referee's suggestion. We feel this is a compromise between addressing the referee's concerns and completely rewriting the manuscript.

Lines 12-13: „we performed measurements of ……air mass history"?

This is a good catch by the referee, we did not measure air mass history but utilized modeled air mass history. The text has been amended accordingly.

Lines 11-14: "Therefore, to further our understanding of the dynamics of gaseous oxidized mercury in the High Arctic during the late summer, we performed measurements of GEM and GOM along with meteorological parameters, atmospheric constituents, and utilized modeled air mass history during two summer campaigns in 2019 and 2020 at Villum Research Station (Villum) in Northeastern Greenland."

Line 24: Biomass burning is partly natural and partly man-made.

We have included 'biomass combustion' in the list of anthropogenic sources of mercury.

Lines 31-33: Wording: During depletion events… GOM and PHg can constitute large fractions of… In contrast,….. GOM and PHg can constitute large fractions of. ??

We have amended the text to delineate when the authors refer to the distribution of atmospheric mercury in the polar regions and the mid-latitudes.

Lines 41-44: "However, during depletion events in the spring, GOM and PHg can constitute large fractions of total atmospheric mercury (Steffen et al., 2014). In contrast to the polar regions, the mid-latitudes, and especially locations close to anthropogenic emission point sources, GOM and PHg can be emitted directly to the atmosphere and represent significant fractions of the atmospheric mercury burden (Muntean et al., 2018)"

Steffen, A., Bottenheim, J., Cole, A., Ebinghaus, R., Lawson, G., and Leaitch, W. R.: Atmospheric mercury speciation and mercury in snow over time at Alert, Canada, Atmos Chem Phys, 14, 2219-2231, 10.5194/acp-14-2219-2014, 2014.

Line 41: "oxidation" instead of "oxidization"

We have corrected this embarrassing spelling mistake.

Line 51: What does it mean "liable halogen reservoir species"?

We have corrected 'liable' to 'labile'.

Lines 56-57: Uptake by vegetation and soil in the high Arctic? Is there enough vegetation and soil not covered with snow for that in the high Arctic?

We have similar questions about how the results of these studies would translate to the High Arctic as indicated in the text, however, we thought this information relevant to the reader since it shows GEM dry deposition to be the main source of mercury input even though this has yet to be demonstrated in the High Arctic.

Line 65: "important" instead of "pertinent"?

We have made this change in the text.

Line 80: CA stands usually for California, not Canada.

The ISO 3166-1 alpha-2 code for Canada is CA. To avoid further confusion for the reader, we have specified, throughout the text, the full location for Alert as 'Alert, Nunavut, Canada'.

Section 2.2: Duration of GOM and PHg sampling time should be given. This is important because the usual 2h sampling at 10 L/min usually provides too small Hg amounts for analysis unbiased by the internal Tekran signal integration routine (Slemr et al., Atmos. Meas. Tech., 9, 2291-2302, 2016; Ambrose, Atmos. Meas. Tech., 10, 5063-5073, 2017). This artefact applies also for 5 min GEM sampling time which probably leads to a small underreporting of the GEM concentrations.

We acknowledge the internal integration routine may be biased low. We are aware of the problem at low mercury values since 2017, therefore we use 15 minutes average in

our monitoring program (Skov et al. 2020). Furthermore, we have taken the results into account in estimating the overall uncertainty. In the present study, GEM is always above 0.5 ng m^{-3} and thus the uncertainty is 20% (95% confidence interval). For measurements of mercury using the speciation monitors from Tekran, the use of 15 minutes time resolution for a single measurement cycle would result in too coarse of a time resolution (~6 hours), therefore we have opted for the 5 min cycles.

Skov, H., Hjorth, J., Nordstrøm, C., Jensen, B., Christoffersen, C., Bech Poulsen, M., Baldtzer Liisberg, J., Beddows, D., Dall'Osto, M., and Christensen, J. H.: Variability in gaseous elemental mercury at Villum Research Station, Station Nord, in North Greenland from 1999 to 2017, Atmos. Chem. Phys., 20, 13253-13265, 10.5194/acp-20-13253-2020, 2020.

The sampling times for the campaigns are listed on lines 141-142: "For the 2019 campaign, the sampling time was 80 minutes, while for the 2020 campaign the sampling time was 60 minutes.".

We have added the following sentence, commenting on the quality of the GOM measurements.

Lines 145-148: "With the KCl denuders being prone to unequal collection efficiencies for different GOM species and artifacts (Gustin et al., 2015) and the internal signal integration routine biasing the concentrations low (Slemr et al., 2016; Ambrose, 2017), the GEM and GOM concentrations are likely a lower limit (Huang and Gustin, 2015; Huang et al., 2017; Marusczak et al., 2017)."

Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B., and Heidecorn, K.: Measuring and modeling mercury in the atmosphere: a critical review, Atmos. Chem. Phys., 15, 5697-5713, 10.5194/acp-15-5697-2015, 2015.

Slemr, F., Weigelt, A., Ebinghaus, R., Kock, H. H., Bödewadt, J., Brenninkmeijer, C. A. M., Rauthe-Schöch, A., Weber, S., Hermann, M., Becker, J., Zahn, A., and Martinsson, B.: Atmospheric mercury measurements onboard the CARIBIC passenger aircraft, Atmos. Meas. Tech., 9, 2291-2302, 10.5194/amt-9-2291-2016, 2016.

Ambrose, J. L.: Improved methods for signal processing in measurements of mercury by Tekran® 2537A and 2537B instruments, Atmos. Meas. Tech., 10, 5063-5073, 10.5194/amt-10-5063-2017, 2017.

Huang, J., and Gustin, M. S.: Uncertainties of Gaseous Oxidized Mercury Measurements Using KCl-Coated Denuders, Cation-Exchange Membranes, and Nylon Membranes: Humidity Influences, Environmental Science & Technology, 49, 6102-6108, 10.1021/acs.est.5b00098, 2015.

Huang, J., Miller, M. B., Edgerton, E., and Sexauer Gustin, M.: Deciphering potential chemical compounds of gaseous oxidized mercury in Florida, USA, Atmos. Chem. Phys., 17, 1689-1698, 10.5194/acp-17-1689-2017, 2017.

Marusczak, N., Sonke, J. E., Fu, X., and Jiskra, M.: Tropospheric GOM at the Pic du Midi Observatory—Correcting Bias in Denuder Based Observations, Environmental Science & Technology, 51, 863-869, 10.1021/acs.est.6b04999, 2017.

Line 181: RH at a given H_2O content of air is inversely related to temperature and as such provides a redundant information on temperature (as can be clearly seen in Figures 1 and 2). Consequently, it is not a suitable variable for the characterisation of the air mass. H_2O content of

air, as shown in Figure S5 and discussed elsewhere in the manuscript, should be used mostly through the paper. The use of RH makes sense only when discussing the GOM attachment to particles.

> We agree with the referee and have calculated an H_2O mixing using ground-level measurements of temperature, RH, and pressure. We have included H_2O mixing ratios in Figures 1 and 2 and have discussed the results concerning this parameter.
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> Lines 151-152: "Ground-level H_2O mixing ratios were calculated using ambient temperature, RH, and pressure (Bolton, 1980; Weiss-Penzias et al., 2015).
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> Bolton, D.: The Computation of Equivalent Potential Temperature, Monthly Weather Review, 108, 1046-1053, 10.1175/1520-0493(1980)108<1046:Tcoept>2.0.Co;2, 1980.
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> Weiss-Penzias, P., Amos, H. M., Selin, N. E., Gustin, M. S., Jaffe, D. A., Obrist, D., Sheu, G. R., and Giang, A.: Use of a global model to understand speciated atmospheric mercury observations at five high-elevation sites, Atmos. Chem. Phys., 15, 1161-1173, 10.5194/acp-15-1161-2015, 2015.

Section 3.1: Figures S1 and S3 show that local meteorological parameters essentially do not matter. What matters are the times of the air mass exchanges, characterized more clearly by their specific chemical fingerprints, and the question where they come from. As already mentioned, RH should be replaced by H_2O content of the air.

> We agree with the referee's suggestion and have re-evaluated our criteria for the event definition. We have also recalculated the trajectory length, which revealed a synoptic view of the air mass history this enabled us to define each event considering air mass history. This resulted in the splitting of Event 1 into Event 1a and 1b as well as the splitting of Event 5 into 5a and 5b. These two events occurred sequentially therefore the naming convention using the same number and different letters. We have examined each event based on all the parameters in the section 'Factors influencing individual events'. We have included the H_2O mixing ratio in our revised manuscript as indicated above.

Figures 1 and 2: I think that these figures should include all measured parameters, i.e. additionally O_3, BC and N_{coarse} . Measurements of BC and N_{coarse} shown in Figure 7 are especially important because these species are specific tracers for anthropogenic activities and biomass burning. GOM and PHg below detection limit are plotted as zero concentration which is misleading because "below detection limit" does not mean zero. As mentioned above, their concentrations are underreported due to the internal Tekran integration procedure. I would plot only the measured GOM and PHg concentrations above the detection limit.

> We have remade Figures 1 and 2 to include all parameters and have added H_2O mixing ratios and accumulated precipitation along the trajectory path.
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> We have not plotted values <LOD as zero. All measurements as recorded by the instrument are plotted as is. Readings of zero GOM concentrations were included in the figures to reflect the inability to detect a GOM signal during the non-event periods.
>
> We have excluded values <LOD in the revised versions of Figures 1 and 2.

Figure 3: RH in panel b provides hardly any additional information to T in panel a. Water content could be more useful because it would reveal the precipitation along the trajectory as discussed in the related text. A comparison of panel a (T) with panel d (altitude) shows an inverse relationship which is not mentioned in the text.

We have also remade Figures 3 and 4 to include H_2O mixing ratios and precipitation. We have also commented on the relationship between altitude and temperature.

Lines 465-466: "The temperature and altitude parameters are interconnected since with increasing altitude the temperature will decrease as the air becomes less dense."

Figures 1, 5a and S2 show that event 1 consists essentially of two events with different trajectories which should be perhaps treated separately.

Following the referee's suggestion about evaluating events based on air mass characterization, we have split Event 1 and 5 into two events as described above.

Figure 5: The addition of trajectory altitudes, as in Figure S4, could provide support for the claim of GOM arriving from the free troposphere.

We have remade Figure 5 with trajectories colored-coded by arrival date at Villum and added a boxplot showing the distribution of trajectories altitudes binned in increments of ten hours. This shows the temporal evolution of trajectories and the distribution of trajectories' altitudes.

Line 325: "Influence of the troposphere on mercury concentrations" sounds like "water has influence on fish". Please reword.

We have reworded to:

Line 480-481: "Previous studies have demonstrated the influence of the free troposphere on mercury concentrations within the boundary layer."

Lines 328-332: Measurements of GEM by Talbot et al. (2007) are subject to two experimental artefacts: a) with their specific inlet system they measured most likely GEM + GOM, not only GEM as they claim, and b) their reported concentrations are too low because they relied on internal Tekran signal integration procedure which was demonstrated to underreport Hg concentrations leading to numerous zero concentrations in the paper which are incorrect. With these problems, Talbot et al. does not provide any usable information about GOM. A reference to Lyman and Jaffe (Nature Geosci., 5, 114-117, 2012) and Slemr et al. (Atmos. Meas. Tech., 9, 2291-2302, 2016; Atmos. Chem. Phys., 18, 12329-12343, 2018) would be more appropriate.

We have removed reference to Talbot et al., 2007 since they measure in altitudes that are outside of the range in this study. We appreciate the two references the referee suggested and will keep them for future reference.

Line 355: Do you mean O_3 median at Villum station?

Yes, we have amended the text to reflect this.

Section 3.4: Elevated O_3 mixing ratios could be due to a transport from free troposphere but also due to O_3 formation in polluted air masses. The latter applies clearly due to anthropogenic pollution during the events 1 and 3 and to a smaller degree to event 2 as indicated by BC and N_{coarse}. A discussion of the elevated GOM concentrations during these events in terms of anthropogenic pollution would be more appropriate.

We agree elevated ozone could arise from other sources such as pollution from either anthropogenic sources or biomass burning. We have updated our interpretations of the trajectories and discussed these sources of ozone accordingly.

Figure 6: Putting all data for 2019 and 2020 campaigns into each GEM vs O_3 and GOM vs O_3 diagrams is inconsistent with the discussion of individual events 1-5 in other chapters and obscures the origin of GEM instead of revealing it. What would be the GEM vs O_3 and GOM vs O_3 correlations for each of the individual events 1 – 5?

> We agree with the referee's suggestion. We have removed Figure 6 in the previous version of the manuscript and replaced it with one including a scatter plot for important parameters for each event. We have included a discussion on the correlations between GOM and these parameters in the discussion section.

Section 3.5: This discussion is muddled. GOM correlates well with BC and N_{coarse} during the events 1, 2, and 3 but not during the events 4 and 5. Despite the different patterns, the authors conclude that emissions from biomass burning and combustion have little to no influence on GOM levels at Villum station. That may be true for events 4 and 5 but obviously not for events 1, 2, and 3. The discussion in lines 445 – 454 may be used as an argument against biomass burning being the source of GOM in some of the events but not in all.

> We agree that grouping ozone during all the event periods can muddle the interpretation of individual events. We have replaced Fig. 6 in the previous version of the manuscript with a figure detailing the correlations between GOM and important parameters for individual events (Fig. 7 in the revised manuscript. With the new trajectory analysis, we have indicated which events could have been influenced by active fires.

Section 3.6: This section is highly speculative and confusing. As in the discussion of GOM vs O_3 the different pattern of each of the five events is not mentioned. Especially that of event 5 with no relation between GOM and N_{coarse} and BC, whatsoever. A weak correlation with of GOM with O_3 in this event could be interpreted as transport from the free troposphere. A general problem is that the authors attribute high GOM to free troposphere in all events while the halogens claimed for GEM oxidation are produced more likely in the boundary layer. I would skip this section.

> We agree with the referee that we should remove this section. We have made changes to the analysis methods and criteria for event classification and therefore changed our conclusions based on the new discussion.

Line 491: The statement about "the positive correlation between GOM and N_{coarse} observed in our study (Figure 7).." is valid only for events 1, 2, and 3, not for the events 4 and 5. The statement is thus wrong without a qualifier.

> We agree this statement is not valid for all events and have removed this sentence in the revised manuscript. We have recalculated the correlation between GOM and important parameters for individual events, see comment above. We have discussed these correlations for individual events in the revised manuscript.

Section 4: The conclusions are too unspecificl, they do not reflect on the different patterns of the individual events.

> We thank the referee for challenging us in this manner. Our new analysis reveals the unique origins of each event in the revised manuscript.

Figure S4: I could not find a reference to it in the manuscript.

> We reference Fig. S4a-c on Line 204 of the original manuscript.

Ambrose, J. L.: Improved methods for signal processing in measurements of mercury by Tekran® 2537A and 2537B instruments, Atmos. Meas. Tech., 10, 5063-5073, 10.5194/amt-10-5063-2017, 2017.

Bolton, D.: The Computation of Equivalent Potential Temperature, Monthly Weather Review, 108, 1046-1053, 10.1175/1520-0493(1980)108<1046:Tcoept>2.0.Co;2, 1980.

Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B., and Heidecorn, K.: Measuring and modeling mercury in the atmosphere: a critical review, Atmos. Chem. Phys., 15, 5697-5713, 10.5194/acp-15-5697-2015, 2015.

Huang, J., and Gustin, M. S.: Uncertainties of Gaseous Oxidized Mercury Measurements Using KCl-Coated Denuders, Cation-Exchange Membranes, and Nylon Membranes: Humidity Influences, Environmental Science & Technology, 49, 6102-6108, 10.1021/acs.est.5b00098, 2015.

Huang, J., Miller, M. B., Edgerton, E., and Sexauer Gustin, M.: Deciphering potential chemical compounds of gaseous oxidized mercury in Florida, USA, Atmos. Chem. Phys., 17, 1689-1698, 10.5194/acp-17-1689-2017, 2017.

Marusczak, N., Sonke, J. E., Fu, X., and Jiskra, M.: Tropospheric GOM at the Pic du Midi Observatory—Correcting Bias in Denuder Based Observations, Environmental Science & Technology, 51, 863-869, 10.1021/acs.est.6b04999, 2017.

Slemr, F., Weigelt, A., Ebinghaus, R., Kock, H. H., Bödewadt, J., Brenninkmeijer, C. A. M., Rauthe-Schöch, A., Weber, S., Hermann, M., Becker, J., Zahn, A., and Martinsson, B.: Atmospheric mercury measurements onboard the CARIBIC passenger aircraft, Atmos. Meas. Tech., 9, 2291-2302, 10.5194/amt-9-2291-2016, 2016.

Steffen, A., Bottenheim, J., Cole, A., Ebinghaus, R., Lawson, G., and Leaitch, W. R.: Atmospheric mercury speciation and mercury in snow over time at Alert, Canada, Atmos Chem Phys, 14, 2219-2231, 10.5194/acp-14-2219-2014, 2014.

Weiss-Penzias, P., Amos, H. M., Selin, N. E., Gustin, M. S., Jaffe, D. A., Obrist, D., Sheu, G. R., and Giang, A.: Use of a global model to understand speciated atmospheric mercury observations at five high-elevation sites, Atmos. Chem. Phys., 15, 1161-1173, 10.5194/acp-15-1161-2015, 2015.