Review of Dynamics of gaseous oxidized mercury at Villum Research Station during the High Arctic summer by Jakob Boyd Pernov et al.

This manuscript presents original data regarding atmospheric Hg species during summertime in the high Arctic. The authors suggest that the GOM peaks (so called " events") that are measured are explained by the influence of free tropospheric production of GOM and transport to the sea-level site.

The scientific reasoning that is conducted here is presented in backwards order. The authors conclude on the influence of air masses from the free troposphere on GOM measurements. To my opinion, the supplementary data are not robust enough to support this very original but debatable hypothesis. Then the authors examine additional data to further explore the GOM origin including other GOM sources. From the data they show, it appears to me that the hypothesis of alternative GOM sources remain still valid awhile the authors clearly reject these sources since they do not support their initial idea. I think this is a biased way of discussing their data set, and that their initial hypothesis is not supported by clear evidence and data.

Demonstrating the direct influence of the free troposphere at an ocean-front site requires solid multiparameter measurements, on-site knowledge of the vertical structure of the atmosphere and probably vertical concentration profiles (aircraft). Although the hypothesis is attractive, there are many other possibilities to explain these peaks of GOM , which have been only partially studied in this manuscript, including local pollution sources (ships, airplanes), biomass fires, anthropogenic influence of European pollution, and transport of GOM species from the Greenland ice cap. The back-trajectory analysis is not deep enough and the statistics are not convincing.

Moreover, the introductory part contains too many approximations and requires an obvious reformulation work.

For these reasons, this work cannot be published in ACP . It could at least be requalified as a "measurement report" with however an important work on the formulation of the different hypotheses.

> We would like to thank Referee # 1 for their review of our manuscript. Some of their comments and suggestions will improve the clarity, presentation, and discussion of the work. We will have to respectfully disagree with the main conclusion of the review. We acknowledge the reviewer's viewpoint that we focused on the parameters first and then analyzed the events from the viewpoint of these parameters and that might lead to confusion. Therefore, we have redone the structure of the article as suggested by another review so we now focus on the general pattern observed during event vs non-event periods as well as each individual event. In this way, we make clear what conclusions can be extracted from all event and non-event periods and which events deviate from this general pattern. Thus, we will offer our rebuttal on the overall conclusion of Referee 1. We have addressed the referee's concerns and corrected errors in the manuscript below with the author's responses in blue. Due to the large amounts of changes in the manuscript, line numbers refer to the clean version of the manuscript which has no track changes present. New references are highlighted in yellow.

They state that our hypothesis is very original but debatable, however, this process has been repeatedly demonstrated to occur throughout the global atmosphere both through in situ measurements and modeling studies as we indicate in the text. While we are the first to propose this process is occurring in the High Arctic, it has been widely demonstrated at lower latitudes, and so the hypothesis is not unreasonable nor is it a far stretch beyond current scientific understanding. They go on to state that we reject alternative sources of GOM. While we explore possible sources of GOM oxidation, at no point in the manuscript do we use such language as reject. We assessed the data, weighed the likelihood of all possibilities, and adjusted our hypothesis accordingly. We respectfully, yet firmly, disagree with their assessment that we discuss our data set in a biased way and that our initial hypothesis is not supported by clear evidence and data.

The referee argues that the demonstration of our hypothesis at an oceanfront site (while Villum is located near the coast the surrounding waters are ice-covered throughout the year making it a cryosphere station and not an oceanfront site) requires solid multiparameter measurements (which we have attempted to provide although we are limited by the instrumentation available), on-site knowledge of the vertical structure of the atmosphere, and probably vertical concentration profiles (aircraft). We have attempted to address the verticality issue by using back trajectory modeling. Adding vertical measurements would require a completely different project, which is outside of the scope of the current project.

The referee concludes by stating many other possibilities that explain the GOM events, such as local anthropogenic pollution (ships and airplanes), biomass burning, anthropogenic influence of European pollution, and transport of GOM species from the Greenland ice cap. To counter their alternative possibilities, we offer the following response. All datasets have been extensively quality controlled to remove the influence of local pollution from the Station Nord military base including all airplane activity and ship traffic is minimal in this part of the Arctic (due to ice-covered sea surfaces in the surrounding waters) and would not produce the long, gradual increases in GOM over several days. We have recalculated the trajectories for a length of 240 hours as suggested by the referee and indicated where necessary if active fires are influencing individual events. Finally, the transport of GOM species from aloft the Greenland ice cap is shown in Event 5b, the two studies cited by the referee concerning this matter both deal with boundary layer processes involving the snowpack and not air mass arriving from aloft. We fail to see how these alternative possibilities could explain our observations given the supporting evidence. In our reorganization of the text, we have indicated where alternative processes could in influencing GOM concentrations.

Details comments.

Line 9: « GOM, once introduced into the ecosystem, »- GOM are not really introduced in ecosystems, these species are deposited. The link with « threat to human and wildlife » is exaggerated since there is no proven direct link between GOM and wildlife contamination. This need to be rephrased

While it has been shown that mercury in the snow is bioavailable at Station Nord (Moller et al. 2011), we have rephrased the sentence to remove any exaggeration.

Lines 9-11: “GOM, once deposited and incorporated into the ecosystem, can pose a threat to human and wildlife health, though there remain large uncertainties regarding the transformation, deposition, and assimilation of mercury into the food web.”

Moller, A. K., T. Barkay, W. Abu Al-Soud, S. J. Sorensen, H. Skov and N. Kroer (2011). "Diversity and characterization of mercury-resistant bacteria in snow, freshwater and sea-ice brine from the High Arctic." Fems Microbiology Ecology **75**(3): 390-401.

Line 11 : « the ecosystem » is not appropriate.

We have replaced ‘ecosystem’ with ‘food web’

Line 21 « an »

While ubiquitous starts with a vowel, the spoken word starts with a ‘y’ sound which is a consonant sound therefore not warranting the preceding ‘an’.

Line 21 : what is « relaxation time » ?

The relaxation time of GEM is the time delay between emission reductions and the effect on actual concentrations (Skov et al., 2020), this term is frequently used for CO_2. We have included this definition in the text to aid the reader.

Line 31: “relaxation time refers to the time delay between emission reductions and effect on ambient concentrations”.

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.

Line 24 : artisanal small-scale gold mining

We have amended the text to read “artisanal small-scale gold mining”.

Line 28 : atmospheric particles or aerosol, not a combination of both

From Table 2.18 in Seinfeld and Pandis (2016), an aerosol is defined as “tiny particles dispersed in gases” and a particle is defined as “an aerosol particle may consist of a single continuous unit of solid or liquid containing many molecules held together by intermolecular forces and primarily larger than molecular dimensions (> 0.001 μm); a particle may also consist of two or more such unit structures held together by interparticle adhesive forces such that it behaves as a single unit in suspension or on deposit”.

This is a common term used widely in the atmospheric community, for example, see Kulmala et al. (2012).

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 3 ed., John Wiley & Sons, 1152 pp., 2016.

Kulmala, M., Petaja, T., Nieminen, T., Sipila, M., Manninen, H. E., Lehtipalo, K., Dal Maso, M., Aalto, P. P., Junninen, H., Paasonen, P., Riipinen, I., Lehtinen, K. E., Laaksonen, A., and Kerminen, V. M.: Measurement of the nucleation of atmospheric aerosol particles, Nat Protoc, 7, 1651-1667, 10.1038/nprot.2012.091, 2012.

Line 31. A reference is missing for « depletion events », at least you should cite Schroeder et al 1998.

We have added the references Steffen et a. (2014) and Steen et al. (2011) since these studies specifically deal with Hg speciation. Schroeder et al. (1998) only measures TGM and not GOM nor PHg. When we discuss AMDEs we cite Schroeder et al. (1998).

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.

Steen, A. O., Berg, T., Dastoor, A. P., Durnford, D. A., Engelsen, O., Hole, L. R., and Pfaffhuber, K. A.: Natural and anthropogenic atmospheric mercury in the European Arctic: a fractionation study, Atmos Chem Phys, 11, 6273-6284, 10.5194/acp-11-6273-2011, 2011.

Line 31 PHg is not a fraction of total gaseous mercury.

We have replaced ‘gaseous’ with ‘atmospheric’; we thank the referee for this good catch.

Line 32. The link with the previous sentence is not straightforward. « in contrast » is not appropriate here.

We have revised the text to connect these two sentences.

Lines 42-44: “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).

Line 34 – reactive halogens would be better. And especially bromine radicals. There is no real evidence for other halogens reactivity. Why coastal regions? There are many coastal sites where no reactivity is observed (e.g Mace Head in Ireland).

We have modified the text to reflect the presence of elevated reactive halogen concentrations and especially bromine radicals and replaced “coastal regions” with “the marine boundary layer” to be more precise. We thank the referee for pointing out this necessary distinction.

Lines 45-47: “In locations with elevated reactive halogen concentrations (e.g., polar environments, the marine boundary layer, volcanic plumes, and salt lakes) and especially bromine radicals, GEM is quickly transformed into GOM (Obrist et al., 2010; von Glasow, 2010; Angot et al., 2016; Ye et al., 2016; Wang et al., 2019).”

von Glasow, R.: Atmospheric chemistry in volcanic plumes, Proceedings of the National Academy of Sciences, 107, 6594-6599, 10.1073/pnas.0913164107, 2010.

Obrist, D., Tas, E., Peleg, M., Matveev, V., Faïn, X., Asaf, D., and Luria, M.: Bromine-induced oxidation of mercury in the mid-latitude atmosphere, Nature Geoscience, 4, 22-26, 10.1038/ngeo1018, 2010.

Ye, Z., Mao, H., Lin, C. J., and Kim, S. Y.: Investigation of processes controlling summertime gaseous elemental mercury oxidation at midlatitudinal marine, coastal, and inland sites, Atmos. Chem. Phys., 16, 8461-8478, 10.5194/acp-16-8461-2016, 2016.

Wang, S. Y., S. M. McNamara, C. W. Moore, D. Obrist, A. Steffen, P. B. Shepson, R. M. Staebler, A. R. W. Raso and K. A. Pratt (2019). "Direct detection of atmospheric atomic bromine leading to mercury and ozone depletion." Proceedings of the National Academy of Sciences of the United States of America 116(29): 14479-14484.

Line 38-39 : This statement is only valid for Alert in Canada. Has it been observed elsewhere?

The referee is correct that this only applies to Alert, NU, which is the only site where long-term Hg speciation is available. Although, the Arctic Haze phenomenon and AMDEs are observed at locations across the Arctic (Steffen et al., 2008; Freud et al., 2017) so this is not an unreasonable assumption.

Steffen, A., Douglas, T., Amyot, M., Ariya, P., Aspmo, K., Berg, T., Bottenheim, J., Brooks, S., Cobbett, F., Dastoor, A., Dommergue, A., Ebinghaus, R., Ferrari, C., Gardfeldt, K., Goodsite, M. E., Lean, D., Poulain, A. J., Scherz, C., Skov, H., Sommar, J., and Temme, C.: A synthesis of atmospheric mercury depletion event chemistry in the atmosphere and snow, Atmos Chem Phys, 8, 1445-1482, 10.5194/acp-8-1445-2008, 2008.

To be concise, we have amended the text to reflect that this has only been demonstrated at Alert, NU.

Lines 50-53: “In the early spring at Alert, Nunavut, Canada, it has been demonstrated that GOM is converted to PHg (through condensational processes due to the cold temperatures and high aerosol surface area concentration (Freud et al., 2017)) while in the late spring oxidized mercury is mainly present as GOM (due to reduced surface area and increased temperatures) (Steffen et al., 2014).”

Freud, E., Krejci, R., Tunved, P., Leaitch, R., Nguyen, Q. T., Massling, A., Skov, H., and Barrie, L.: Pan-Arctic aerosol number size distributions: seasonality and transport patterns, Atmos Chem Phys, 17, 8101-8128, 10.5194/acp-17-8101-2017, 2017.

Line 40 : the peak of Hg in snow – This should be clarified. What kind of peak ? is it totalHg in surface snow ? « GOM is the main deposition pathway » does not mean anything.

We have specified that this is the peak of total Hg in surface snow and amended the text to specify that dry deposition is a major pathway of mercury into the ecosystem.

Lines 53-55: "Late spring is also the peak of total Hg in surface snow at Alert, Nunavut, Canada and Utqiagvik, Alaska, USA (formerly Barrow), indicating that dry deposition of GOM is a major pathway of mercury into the ecosystem (Lu et al., 2001; Lindberg et al., 2002; Steffen et al., 2002; Steffen et al., 2014)."

Steffen, A., Schroeder, W., Bottenheim, J., Narayan, J., and Fuentes, J. D.: Atmospheric mercury concentrations: measurements and profiles near snow and ice surfaces in the Canadian Arctic during Alert 2000, Atmospheric Environment, 36, 2653-2661, https://doi.org/10.1016/S1352-2310(02)00112-7, 2002.

Lindberg, S. E., Brooks, S., Lin, C. J., Scott, K. J., Landis, M. S., Stevens, R. K., Goodsite, M., and Richter, A.: Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise, Environmental Science & Technology, 36, 1245-1256, 10.1021/es0111941, 2002.

Line 60 : Do Ariya et al really mention a ionic pulse ? there are better references for this .

Aryia et al. (2004) does not specifically mention an ionic pulse, but it does give the reader more context into the removal processes and the fate of atmospheric and deposited mercury in the Arctic. We have included more references that deal with the ionic pulse.

Lines 74-76: "The snowpack will retain a fraction of this mercury and release it with the ionic pulse during the melt season, introducing mercury into the ecosystem (Lu et al., 2001; Ariya et al., 2004; Durnford and Dastoor, 2011; Douglas et al., 2017)."

Lu, J. Y., Schroeder, W. H., Barrie, L. A., Steffen, A., Welch, H. E., Martin, K., Lockhart, L., Hunt, R. V., Boila, G., and Richter, A.: Magnification of atmospheric mercury deposition to polar regions in springtime: The link to tropospheric ozone depletion chemistry, Geophysical Research Letters, 28, 3219-3222, 10.1029/2000gl012603, 2001.

Douglas, T. A., Sturm, M., Blum, J. D., Polashenski, C., Stuefer, S., Hiemstra, C., Steffen, A., Filhol, S., and Prevost, R.: A Pulse of Mercury and Major Ions in Snowmelt Runoff from a Small Arctic Alaska Watershed, Environmental Science & Technology, 51, 11145-11155, 10.1021/acs.est.7b03683, 2017.

Line 61. Are you sure that GEM can be directly methylated ? PHG ? Methylation does not occur at the « earth's surface, this should be better explained.

We have removed ‘onto the Earth’s surface’, ‘GEM’, and ‘PHg’ to be more concise.

Lines 79-80: “After deposition, GOM can be methylated through biotic and abiotic processes to organic mercury (methyl- and dimethylmercury) (Macdonald and Loseto, 2010; Møller et al., 2011).”

Line 65. I do not understand why « it is pertinent to understand mercury oxidation in response to a changing climate » . There is no link with the preceding sentences.

In this paragraph, we describe how mercury, once methylated, can be detrimental to human and ecosystem health and why it is important to research this pollutant at high latitudes. We have amended the text to make this link clearer.

Lines 82-84: “Therefore, as the Arctic becomes more populated and continues to change it is important to understand mercury oxidation in response to a changing climate, especially in high latitude regions (AMAP, 2011; Durnford and Dastoor, 2011; Stern et al., 2012).”

AMAP: AMAP Assessment 2011: Mercury in the Arctic, Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway, xiv + 193 pp., 2011.

Line 71 : GOM deposition does exist outside of AMDE since this is a major removal pathway for Hg on a global scale

We have added ‘in the Arctic’ at the end of this sentence to indicate that we are specifically referring to the Arctic here.

Line 88-89: “This study revealed a pattern of GOM previously unknown to the Arctic, with elevated GOM concentrations during the summer, which postulates GOM deposition occurs outside of AMDEs in the Arctic.”

Line 82-83 : I do not agree with this conclusion. Most of the studies report low GOM/PHG values.

Studies utilizing short shipborne campaigns found relatively low levels of GOM/PHg, although a year-long campaign found high levels of GOM during the Arctic summer (Steen et al., 2011). We have rephrased the last sentence in the paragraph to indicate that while the levels are relatively low, they do show mercury oxidation and deposition is occurring.

Lines 101-102: “While these latter studies found relatively low levels of GOM, the presence of GOM at all indicates that mercury oxidation and deposition are occurring outside of AMDEs in the Arctic.”

Line 84-86 : this sentence is difficult to understand.

We have rewritten the beginning of this paragraph and made additions to the paragraph above to increase the readability and flow of this part of the introduction.

> Lines 103-105: “With only limited measurements of GOM performed in the High Arctic summertime, there are many questions still unanswered. The dynamics of GOM in the Arctic are extremely complex; uncertainties in its spatiotemporal variability, annual cycle, and formation mechanisms emphasize the need for further examination.”

Line 87 – I don’t understand what « will help to infer the response of mercury in the context of a changing climate » mean

> Climate change in the Arctic is proceeding at a rapid rate, twice the global average, a term called ‘Arctic Amplification’. This change is manifesting as changes in temperature, RH, precipitation, and sea ice extent/concentration/age. All of which can affect mercury dynamics, which is poorly understood during the Arctic summer. Therefore, resolving these dynamics can provide knowledge that will help predict mercury oxidation in a changing climate. We have rephrased the sentence to convey this.
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> Lines 105-108: “The Arctic region is undergoing rapid changes due to anthropogenic climate change and the dynamics of mercury oxidation are poorly resolved, especially in summer. Understanding these dynamics can offer insight into the general chemistry during Arctic summer and atmospheric mercury will respond to future changes in the Arctic climate.”

Line 88 : It does not make sense “is also important to understand the dynamics of mercury to assess the effects of abatement strategies on atmospheric concentrations in the framework of the Minamata Convention (UNEP, 2013) »

What is the link between abatement strategy and Hg dynamic in the Arctic ?

> Due to the complex nature of mercury cycling in the environment, it is important to have spatiotemporal measurements of mercury speciation from around the globe to assess any changes in concentrations levels. We have rephrased the sentence to make this link clearer.
>
> Lines 108-109: “It is also important to understand the changes of mercury concentrations in the Arctic to assess the effects of abatement strategies of the Minamata Convention (UNEP, 2013) globally.”

Line 125. You should be consistent with the numbers.

> We have added the trailing zero for 0.180 on Line 145 so the number of significant figures is consistent between the two LOD values. We thank the referee for this good catch.

Line 128 : How is snow depth measured ?

> Snow depth is measured with one Campbell SR50A sonic sensor. The sensor is placed at 3 m in height. The sensor is based on a 50 kHz (Ultrasonic) electrostatic transducer. The SR50A determines the distance to a target by sending out ultrasonic pulses. The time from transmissions to the return of an echo is the basis for obtaining the distance measurement. Since the speed of sound in air varies with temperature, an independent

temperature measurement is required to compensate for the distance reading for the SR50A. A simple calculation is applied to initial readings for this purpose. The SR50A projects an ultrasonic beam that can pick up objects in its field of view that is 30° or less. The closest object to the sensor will be detected if it is within this field of view.

Line 129 : What does « averaged to 30 - minute means » mean?

We have amended the text to indicate that we refer to arithmetic mean here.

Line 151-153: "Ozone (O_3) was measured at Villum using a photometric O_3 analyzer (API M400) at 1 Hz, averaged to a 30-minute arithmetic mean."

GOM data

Is the use of the GOM detection limit appropriate? Why not using the Quantification limit since we all know that these speciation instruments are quite difficult to manage? Event 2 is very closed to the detection limit and the first days of Event 1 and may be excluded.

We have opted to use the limit of detection and not the limit of quantification since we are investigating events of GOM enhancements. These events involve the presence of GOM in elevated concentrations over background levels. Therefore, we choose the limit of detection as a lower analytical limit since we are largely interested in distinguishing the presence of GOM from the noise of blank measurements. For the sake of argument, we calculated the limit of quantification (LOQ) as 10 times the standard deviation of blank measurements. This resulted in LOQs of 0.300 and 2.28 for the 2019 and 2020 campaigns, respectively. For the 2019 campaign, there were no non-zero values <LOD or <LOQ. For the 2020 campaign, the number of GOM measurements <LOD or <LOQ was 17 and 80, respectively, although none of the measurements <LOQ occurred during the GOM enhancement events. The use of LOQ would not affect the timing of the events nor our interpretation of them since no event measurements were <LOQ.

There is no discussion on the quality of GOM data obtained with denuders while the authors may know that Tekran speciation unit underestimate GOM value as shown in recent studies (Marusczak et al 2017 – Gustin et al 2015 – Huang et al 2015, 2017)

We have added the following sentences to comment on the quality of the data.

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.

Are the raw data available for all these events ? This is critical to make sure that all the blanks where correctly made.

All data required to reproduce this study, in its fully processed and quality-controlled form, will be made available before publication.

Blanks were calculated according strictly to Model 1130/1135 Mercury Speciation Unit User Manuals. We are confident all measurements included in this manuscript were calculated correctly.

Line 204 : yes but there is no evidence that there are open leads on the way ?

The sentence indicates that the elevated GEM concentrations *could* be the result of oceanic evasion as previously observed by the references given. To further support this statement, we have added a link to satellite images of sea ice in the surrounding areas of Villum. While these images only show the sea ice conditions on a scale of 100s of kilometers and not over the central Arctic Ocean, they give an idea of the conditions that *could* lead to oceanic evasion of mercury.

Line 244-247: “These elevated concentrations could be the result of oceanic evasion through open leads and fissures in the consolidated pack ice (Aspmo et al., 2006; DiMento et al., 2019), as air masses experienced extensive surface contact with sea ice on July 19–21 (Fig. S4a–c). Satellite images, which show fractured sea ice surrounding Villum are available at http://ocean.dmi.dk/arctic/nord.uk.php.”

Line 218 : snow cover is not displayed in figure S2

We thank the referee for catching this error, this sentence has been corrected to refer to Fig. S3.

By the way the color scale for the contour is quite difficult to read.

Contour plots are always rather difficult to read, especially when values cover a wide range. We have tested the figures on people with unimpaired vision and with colorblind people and found this color scheme to be an appropriate compromise between clarity and detail.

Line 230 : What is considered as high radiation and low RH ? How are those thresholds defined ? Event 1 had some low radiation too (<200). Was there a snow/rain fall ? on august 21st ?

We have amended the text to make these thresholds relative when compared to the non-event periods.

What is the dynamic of the boundary layer ? This is an important factor that can explain some variation in your concentrations.

We have added a short statistical description of the modeled mixed layer depth from HYSPLIT during each campaign in the Methods and Materials sections. Our analysis revealed no connection between the modeled mixed layer height and GOM concentrations.

Line 230 : your suggestion that cold temperatures are associated to mercury oxidation is not valid in volcanic plumes or in salt lake regions. To me, the temperatures are not a solid argument to reject in situ production. Halogen measurements could give a major evidence to demonstrate this -although I do not believe that this is likely to happen at this time of the year.

The state of the knowledge indicates that the oxidation of GEM is temperature-dependent and dominated by Br initiated oxidation. In volcanic plumes and salt lake regions, the Br concentration is orders of magnitude higher than in the Arctic and is not representatively for the air masses at Villum. We have indicated that the observations were performed in the Arctic to clarify this. Preliminary measurements of BrO show a U-shaped concentration profile with peaks in the spring and autumn and minima during the summer (personal communication Alfonso Saiz-Lopez). Therefore, the statement is correct, and too high temperatures is a logical argument.

Line 249-253 : How are calculated those averages ? on the whole trajectory duration ?

Given the uncertainties of all these measurements and of the average, are these air masses statistically different ? Given the shown interval, I do not see any evidence of a robust difference. The Wicoxon test is used for comparing independant populations. Here you have an overlap on « event » and « non-event » trajectorie : for example the 28/08 -120h trajectories overlap and are supposed to be included with the one from the 26/08.

Where the test conducted on each separate observation? (ie RH in « event » with RH in « non event »). Btw, water mixing ratio if a function of temperature and RH ?

The Wilcoxon rank sum test is a nonparametric test for two independent populations. The distribution of the trajectory-derived meteorological parameters is non-normal and the high sample size adds confidence to the power of the test statistic. For our research, we have assumed independent populations given the variability of the geographic location (latitude, longitude, and altitude) for each step along the trajectory path. Using meteorological data at each step of each trajectory for event vs. non-event periods, which covers a range of altitudes and geographic locations, is the likely cause for the slight differences. Our goal was to test for statistically significant differences, not the absolute differences, between these periods which the Wilcoxon rank sum test has accomplished. Given the new analysis of the revised manuscript, we have opted to remove the use of this test since we focus more on the general pattern observed during event periods relative to non-event periods as well as individual events.

Line 276 : The meaning of this sentence is not clear. What does « these air masses » refer to ?

'These air masses' refers to event period air masses. Although we have removed this sentence from the revised manuscript.

Line 280 : Figure 3d and 4d With this figure the author suggest that GOM event air masses spent more time at high altitude. The overall picture is not that clear. Event 3 and 4 are not very different from the non-event period (27/07-31/07). Regarding the strongest event in 2020 (on the 23/07) these air masses are not different from the day before and the altitude is close to what one can expect as a marine boundary layer. In summer time it can be several hundreds of meters thick, even more when passing over turbulent and convective areas.

The exact wording used in the text is 'aloft' and not 'high altitude', in this context aloft is referring to above the mixed layer. As indicated in Table S2, air masses that arrived during event periods were consistently above the mixed layer height compared to air masses that arrived during non-event periods. This demonstrates numerically what the figure is displaying and supports our statement.

Air masses spending time above the mixed layer is not the only condition conducive for GOM formation but also cold temperatures, low RH, low H_2O mixing ratios, and intense radiation along the trajectory path. So, while these altitudes might be similar, favorable conditions for GOM formation (cold and dry air masses from aloft with intense radiation) were only present during the event periods as shown in Fig. 4.

Line 282 : for the 2019 campaign : what is the value show with the median height ? 1sigma ? min-max ? For this campaign, there are important overlap between « event » and « non event » periods.

The variance stated after the median altitude is the median absolute deviation (m.a.d.), for an overview of the trajectory derived parameters see Table S2.

Line 285 : how is retrieved the mixed layer height ? How robust is it in Hysplit ? Why is it no plotted on your figures ?

Overall with the presented data, I do not come to the same conclusion (line 286-289).

The HYSPLIT model uses the mixed layer depth value from the meteorological model, in this case, Global Data Assimilation System (GDAS) meteorological data on a 1° spatial resolution and 3-hour time resolution. We have updated Fig. S5 to include the mixed layer height for the 2019 and 2020 campaigns. We have systematically analyzed the altitudes and trajectory-derived meteorological parameters for event vs. non-event periods and this is our interpretation of the general pattern observed in the data.

Line 295 : you mentioned earlier than cold temperature below -15°C are likely needed.

Looking at temperature along the BT ways, it is not the case here ?

In the free troposphere what could cause the formation of GOM is mainly the supposed abundance of Br concentrations ?

We gave this value as a literature example of field observations that indicates cold temperature are required for the oxidation of mercury to proceed in the Arctic region. In one of the campaigns presented in Brooks et al. (2011), the temperature exceeded their threshold during observations of oxidized mercury, indicating this is not an absolute threshold. We have updated the text to indicate this as well as including other references which show a frozen heterogeneous surface is required for halogen propagation. The trajectory-derived temperatures were frequently below 0°C.

Lines 436-442: "Lower temperatures aid in the formation of GOM from HgBr, for example, Skov et al. (2004) and Christensen et al. (2004) modeled a surface temperature below -4 °C for mercury depletion to occur in the Arctic, while Brooks et al. (2011) observed a temperature threshold of -15 °C for mercury oxidation to occur at Summit Station, atop the Greenlandic ice sheet. It should be noted that Brooks et al. (2011) detected oxidized mercury at temperatures above this threshold but not above 0 °C. Tarasick and Bottenheim (2002) analyzed ozonesonde records and observed surface temperatures below -20 °C were required for the occurrence of ozone depletion events. Furthermore, Halfacre et al. (2019) and Burd et al. (2017) demonstrated that a frozen heterogeneous surface is required for the propagation of halogen explosion events."

Halfacre, J. W., Shepson, P. B., and Pratt, K. A.: pH-dependent production of molecular chlorine, bromine, and iodine from frozen saline surfaces, Atmos. Chem. Phys., 19, 4917-4931, 10.5194/acp-19-4917-2019, 2019.

Burd, J. A., Peterson, P. K., Nghiem, S. V., Perovich, D. K., and Simpson, W. R.: Snowmelt onset hinders bromine monoxide heterogeneous recycling in the Arctic, Journal of Geophysical Research: Atmospheres, 122, 8297-8309, 10.1002/2017jd026906, 2017.

Tarasick, D. W., and Bottenheim, J. W.: Surface ozone depletion episodes in the Arctic and Antarctic from historical ozonesonde records, Atmos. Chem. Phys., 2, 197-205, 10.5194/acp-2-197-2002, 2002.

Line 298 what is the low surface resistance ?

The surface resistant is commonly used in description of fluxes F

F = vC where $v = (r_a + r_b + r_c)^{-1}$, where C is the concentration, v is the flux velocity and r_a and r_b are atmospheric resistances and r_c is aerodynamic resistance, see Seinfeld and Pandis, 2016.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 3 ed., John Wiley & Sons, 1152 pp., 2016.

We have amended the text to give the estimate of the surface resistance of GOM given by Skov et al. (2006).

Lines 469-472: "Additionally, given the low surface resistance of GOM over snowpack (Skov et al. (2006) estimated a surface resistance of GOM close to zero), the occurrence of dry (and possibly wet) deposition will increase when air masses come in close contact with the surface layer (i.e., below the mixed layer), resulting in decreased concentrations."

Line 299 There are two verbs in the sentence.

Please see the amended text in our reply to the comment above. We thank the referee for catching this error.

Line 301 : survival is not appropriate for a chemical species

In this context, we feel survival is appropriate as it explains the ability of GOM to overcome removal by deposition, although this sentence was removed in the revised manuscript.

Line 31 – 5 days backtrajectories are clearly not long enough. For BC studies or aerosols 10 days are usually used (see Thomas et al 2017 in GRL). The life time of GOM is poorly known and could be of several days to weeks in dry conditions?

This approach is not relevant. CO data and BC may be a more straightforward approach to track fires. This whole paragraph does not bring any relevant information and fires may contribute to these GOM events, and/or GEM.

The original length of back trajectories was chosen as a compromise between information gained and associated uncertainty, which is estimated to be around 20 % of the distance traveled by the trajectory (Stohl, 1998). We decided for a limited length of 120 hours as uncertainties rise with the distance back in time and this is especially the case where meteorological fields are based on a limited number of meteorological measurements, as in the Arctic. Therefore, we have erred on the side of caution with our original analysis.

We acknowledge 120 hours might have been too short, therefore, we doubled the length of the trajectories and thus doubled our criteria for intersections between trajectories and active fires to account for any added uncertainty in the locations of the trajectory endpoints and active fires. We have incorporated our interpretation of the new air mass history analysis and interactions with active fires in the revised manuscript.

Our analysis indicates interaction between active fires and air mass trajectories. We, therefore, disagree with the referee's statement that this approach is not relevant. The section of air mass history details the geospatial extent of air masses during each event period, which highlights how they are heterogeneously distributed, which we find highly relevant. While back trajectory modeling is not a perfect representation and has its document uncertainties/drawbacks, we feel its use in this study is warranted and appropriate.

Stohl, A.: Computation, accuracy and applications of trajectories - A review and bibliography, Atmospheric Environment, 32, 947-966, 10.1016/s1352-2310(97)00457-3, 1998.

Line 325 : this first sentence has no meaning in atmospheric chemistry.

We have amended the text to make the meaning of this sentence clearer.

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

The Shah and Jaeglé study point sub-tropical areas and this is an important difference from mid-latitudes.

We have removed 'in the mid-latitudes' from this sentence to indicate this is occurring over the entire Northern Hemisphere and not just the mid-latitudes.

Line 340 : Why not using aerosols (check Uge et al in GRL 2017). The paragraph 3.3 is only a short review of FT measurements and is of no interest for the discussion.

In their initial assessment of the manuscript, the referee states that our hypothesis is very original but debatable. While this paragraph is a short review, it details how the free troposphere has been repeatedly demonstrated to be a source of GOM throughout the global atmosphere both through in situ measurements and modeling studies. While we are the first to propose this process is occurring in the High Arctic, it has been widely and repeatedly demonstrated at lower latitudes, and so the hypothesis is not unreasonable nor is it a far stretch beyond current scientific understanding.

The authors were unable to find Uge et al. in GRL 2017. The authors will kindly ask the referee to at least give a digital object identifier (DOI) when referencing articles, this will ensure unambiguous identification and save time in the future.

In our reorganization of the text, we have moved this text to a location where it supports our findings.

Line 390 – and after. The authors make a confusion between the influence of free troposphere and a stratosphere intrusion Stratospheric intrusion would bring very dry air masses and very high ozone. It is likely that the Biomass burning may have an influence on ozone.

We agree the text could be confusing. While we observe a correlation between ozone, GOM, and hydrological-related parameters during event periods, they are not to the extreme that would be representative of stratospheric air masses. We have removed

parts of this text in the revised manuscript to avoid any confusion. We have also acknowledged the influence of active fires on ozone levels during the event periods, due to the new analysis of air mass history.

There is not ozone data presented in Jacob et al 2010. I don't understand what do the authors find in Monks et al 2015 to support their statements. Monks et al suggest that European anthropogenic emissions may be important for lower tropospheric summertime ozone and that PAN reactivity may be a source of ozone.

The Jacob et al. (2010) reference is in relation to the ARCTAS campaigns and the Monks et al. (2015) reference was incorrectly inserted as Monks et al published another article in the same year which was mistaken for the article listed below. Figure 7 in Monks et al. (2015) shows increasing ozone mixing ratios with increasing altitude. We thank the referee for this good catch and have corrected the mistake in the bibliography.

Monks, S. A., Arnold, S. R., Emmons, L. K., Law, K. S., Turquety, S., Duncan, B. N., Flemming, J., Huijnen, V., Tilmes, S., Langner, J., Mao, J., Long, Y., Thomas, J. L., Steenrod, S. D., Raut, J. C., Wilson, C., Chipperfield, M. P., Diskin, G. S., Weinheimer, A., Schlager, H., and Ancellet, G.: Multi-model study of chemical and physical controls on transport of anthropogenic and biomass burning pollution to the Arctic, Atmos. Chem. Phys., 15, 3575-3603, 10.5194/acp-15-3575-2015, 2015.

In the reorganization of the text, we have however removed these references.

Paragraph 435 – 444 . The correlation of GOM and BC looks very interesting in 2019 so I do not understand why the conclusion is that combustion sources has no influence – As said earlier the 5 days trajectories are too short to reach this conclusion. For year 2020, event 3 and 4 may be as well related to combustion sources (the scale is different on figure 7a and b). Event 5 could be due to production of GOM over the Greenland ice cap (as mentioned in Brooks et al 2011 – although earlier in the season), or as proposed in Angot et al 2016 10.5194/acp-16-8265-201. This hypothesis would also lead to low BC.

Then I do not agree that this airmasses comes from the upper troposphere. The GOM peak on August 1st show trajectories around 1000-2000 m ? This could only be air masses leaching the Greenland icecap before arriving to VRS.

Given our previous length of the trajectories, no influence of active fires and trajectories could be observed. We have recalculated the length of the trajectories and expanded the criteria for intersections between trajectories and active fires, as mentioned above. We have updated the manuscript to reflect this new analysis and our interpretation of the results, in which we found active fires to likely be contributing the coarse mode aerosol needed for halogen propagation. For Event 3, the new trajectory length revealed only one intersection between trajectories and active fires, and none for Event 4 (Fig. 5). We have recharacterized the events, as suggested by another referee, in which we have split Event 5 into 5a and 5b. Event 5a appears to be the results of emissions in Northern Scandinavia, either from active fires or anthropogenic sources. For Event 5b, we observe air masses arriving from over the Greenland Ice Sheet. We have offered

hypotheses in the revised manuscript about the similarities in the levels of BC for these two events, however, a definitive conclusion is unavailable.

Brooks et al. (2011) detected GOM during Arctic springtime depletion events at Summit, their analysis showed that during periods of large GOM concentrations air masses had largely resided near the surface, void of marine and upper troposphere influence, and the GOM formation likely occurred because of surface-related processes (Thomas et al., 2012). This is contrary to Event 5b, from which air masses arrived over the Greenland Ice Sheet from high altitudes under cold, dry, and sunlit conditions (Fig. 4 and 5).

Thomas, J. L., Dibb, J. E., Huey, L. G., Liao, J., Tanner, D., Lefer, B., von Glasow, R., and Stutz, J.: Modeling chemistry in and above snow at Summit, Greenland – Part 2: Impact of snowpack chemistry on the oxidation capacity of the boundary layer, Atmos. Chem. Phys., 12, 6537-6554, 10.5194/acp-12-6537-2012, 2012.

453-454 – This is not because a high BC is observed without GOM for a single event that biomass burning cannot influence artic GOM concentration. This is too speculative.

We acknowledge this is speculation. Given the new trajectory analysis, we have added to our interpretation of the interaction between event periods and active fire emissions.

508-511 – This is a very vague speculation.

We have re-evaluated our interpretations and conclusions based on new knowledge and removed this section in the revised manuscript.

Angot, H., Dastoor, A., De Simone, F., Gårdfeldt, K., Gencarelli, C. N., Hedgecock, I. M., Langer, S., Magand, O., Mastromonaco, M. N., Nordstrøm, C., Pfaffhuber, K. A., Pirrone, N., Ryjkov, A., Selin, N. E., Skov, H., Song, S., Sprovieri, F., Steffen, A., Toyota, K., Travnikov, O., Yang, X., and Dommergue, A.: Chemical cycling and deposition of atmospheric mercury in polar regions: review of recent measurements and comparison with models, Atmos Chem Phys, 16, 10735-10763, 10.5194/acp-16-10735-2016, 2016.

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Lindberg, S. E., Brooks, S., Lin, C. J., Scott, K. J., Landis, M. S., Stevens, R. K., Goodsite, M., and Richter, A.: Dynamic oxidation of gaseous mercury in the Arctic troposphere at polar sunrise, Environmental Science & Technology, 36, 1245-1256, 10.1021/es0111941, 2002.

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