

Reply to referee 1

All replies to referee questions and comments are in plain text and all changes to the text of the manuscript are in inverted commas (""). For clarity, we list the question in *italics*. Furthermore, the graphs have been updated using Origin instead of Excel, following a comment by both referee 1 and 2.

We thank the reviewer for a precise review of the article. We have answered the questions, added, and modified text when necessary. More references have been added as well.

There are substantial advances in the knowledge of Arctic Hg cycling using stable isotopes.

- *An example is that dry deposited Hg⁰ rather than AMDE-sourced Hg comprises the majority (~76–91%) of snowmelt HgII in the coastal Arctic [1, 2].*

The two references have been added in the discussion and the following text added:

New Lines 249-252 “From studies of mercury isotopes at Utqiagvik at the North coast of Alaska (Douglas et al., 2019) and Toolik Research Station in central Alaska (Jiskra et al. 2019), it was found that most mercury in melt water was from deposition of GEM and that a large majority of deposited oxidised mercury during AMDE was reduced and reemitted. Further studies are needed to determine if these results are valid also for more northern Arctic locations as Alert, Villum or Zeppelin.”

Figure 5 old version, now Figure 6, has been updates to include also deposition of GEM.

There has also been a progression in the assessment of Br-induced GEM oxidation.

- *The authors should consider responding and citing e. g. the following paper: Wang S, McNamara SM, Moore CW, Obrist D, Steffen A, Shepson PB, et al. Direct detection of atmospheric atomic bromine leading to mercury and ozone depletion. *Proceedings of the National Academy of Sciences* 2019; 116: 14479-14484.*

The article has been included in the discussion as follows:

New Lines 232-235 “Recently, the Br induced oxidation of Hg⁰ has been proven directly in a study, where Br, BrO, O₃, GEM and RGM were measured simultaneously during AMDE and ODE and using a multiphase box model to study the complex set of processes (Wang et al., 2019).”

The variability in Gaseous Elemental Mercury at Villum Research Station, Station Nord in North Greenland from 1999 to 2017

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Abstract. Mercury is ubiquitous in the atmosphere and atmospheric transport is an important source for this element in the Arctic. Measurements of gaseous elemental mercury (GEM) have been carried out at the Villum Research Station (Villum) at Station Nord, situated in north Greenland. The measurements cover the period 1999-2017 with a gap in the data for the period 2003-2008 (for a total of 11 years). The measurements were compared with model results from the Danish Eulerian Hemispheric Model (DEHM) model that describes the contribution from direct anthropogenic transport, marine emission and general background concentration. The percentage of time spent over different surfaces was calculated by back-trajectory analysis and the reaction kinetics was determined by comparison with ozone.

The GEM measurements were analysed for trends, both seasonal and annually. The only significant trends found were negative ones for the winter and autumn months. Comparison of the measurements to simulations using the Danish Eulerian Hemispheric Model (DEHM) indicated that direct transport of anthropogenic emissions of mercury accounts for between 14 and 17% of the measured mercury. Analysis of the kinetics of the observed Atmospheric Mercury Depletion Events (AMDEs) confirms the results of a previous study at Villum of the competing reactions of GEM and ozone with Br, which suggests a lifetime of GEM of on the order of about a month. However, a GEM lifetime of 12 months gave the best agreement between model and measurements. The chemical lifetime is shorter and thus the apparent lifetime appears to be the result of deposition followed by reduction and reemission; for this reason the term 'relaxation time' is preferred to 'lifetime' for GEM. The relaxation time for GEM causes a delay between emission reductions and the effect on actual concentrations.

No significant annual trend was found for the measured concentrations of GEM over the measurement period despite emission reductions. This is interesting and together with low direct transport of GEM to Villum, as found by the DEHM model, it shows that the dynamics of GEM is very complex. Therefore, in the coming years: intensive measurement networks are highly much needed to describe the global distribution of mercury in the environment as the use of models to predict future levels will still be highly uncertain. The situation is increasingly complex due to global change that most likely will change the transport patterns of mercury not only in the atmosphere but also between matrixes.

1 Introduction

35 The effects of long-range atmospheric transport of anthropogenic pollutants into the Arctic are well documented: contaminants are affecting the Arctic by contamination of food chains, and by altering the radiation budget, ~~thus and by that~~ contributing to climate change (UNEP 2013a; AMAP/UNEP 2013, Heidam et al. 2004, [Breider et al. 2017](#)). ~~Until now, T~~there are still only few local sources of pollutants in the Arctic and long-range transport mainly from mid latitudes represent the main source. Mercury (Hg) is one of the first substances that have been identified as a pollutant in the food web worldwide, causing adverse effects to human health and wildlife. On this background the Minamata Convention, aiming at reducing the exposure of human beings and the environment to mercury, was ~~decided established~~ in 2013 ([UNEP 2013b](#)); the convention entered into force in 2017.

The sources of mercury in the environment can be divided into natural, anthropogenic, and reemission, accounting for ~~roughly 2.140, 39-2.5 and 3.460 ktonnes%~~ of the emissions, respectively ([Outridge et al. 2018](#)). ~~This is in good agreement with other estimates.~~ The global anthropogenic emissions of mercury were estimated as ~~1960-2.5 ktonnes~~ in 2010, ~~however with large uncertainties~~ (UNEP 2013a; AMAP/UNEP 2013) ~~and including the large uncertainty in these numbers, they are not significantly different.~~ According to an estimate by (Pirrone et al. 2010) natural sources and reemission processes (hereafter referred to as 'background sources'), accounted for 5207 Mg per year in 2005 while the amount of new anthropogenic inputs is 2320 Mg per year, ~~also close to the latest emission estimate~~ ([Outridge et al. 2018](#)). According to recent assessments (Pacyna et al. 2010; Pirrone et al. 2010; AMAP/UNEP 2013; UNEP 2013; Muntean et al. 2014), main anthropogenic sources of atmospheric mercury are coal combustion and artisanal/small gold mining, with relevant contributions from non-ferrous metal/steel combustion along with several other industrial/residential sources such as waste incineration. The main background source is evasion from ocean surfaces, accounting for about half of the sum of the natural and reemission contributions (Pirrone et al. 2010). Reemission of deposited atmospheric mercury of anthropogenic origin gives a major contribution to the reemission budget, e.g. it has been found that the accumulation of mercury inputs from anthropogenic sources to oceans have led to an increase ~~in the~~ mercury concentration in surface waters of about a factor of three (Lamborg et al. 2014)). Mercury is transported by rivers, sea currents, and in the troposphere. Mercury in air is mainly found in the gas phase, where the major part is gaseous elemental mercury (GEM), covering more than 90%, while a minor part is oxidized mercury as well as ~~in~~ particle bound mercurys. The share of oxidized mercury of the overall global emissions of mercury has been estimated to be around 25%, based on speciation factors from the Arctic Monitoring and Assessment Program (Muntean et al. 2018). The atmospheric lifetime of GEM has earlier been estimated to be in the range of about one year (Steffen et al. 2008), while those of oxidized forms of mercury are shorter. Theoretical and laboratory studies showed that the lifetime of GEM towards Br initiated oxidation is much shorter than 1 year (Balabanov et al. 2005; Dibble et al. 2012; Donohoue et al. 2005; [Donohoue et al. 2006; Goodsite et al. 2004, 2012; Jiao and Dibble 2017](#)). ~~Applying the latest kinetic data, Horowitz et al. (2017) found a lifetime in the atmosphere of GEM towards gaseous oxidized mercury (GOM) oxidation of 2.7 months using the GEOS-CHEM model cobbled to an ocean general circulation model (MITgcm). Including photoreduction, the lifetime of total~~

gaseous mercury (TGM) was found to be 5.2 months close to the value 6.1 months of Holmes et al. 2010 but applying a much higher Br concentration and thus also a faster photoreduction. The atmospheric lifetime of GEM has been estimated to be in the range of about one year while those of oxidized forms of mercury are shorter (Steffen et al. 2008). The lifetime is however under dispute and evidence has been obtained from experimental and theoretical studies for a much shorter lifetime of GEM (Skov et al. 2004; Goodsite, Plane, and Skov 2004; Holmes et al. 2010; Soerensen et al. 2010; Goodsite, Plane, and Skov 2012a). The deposition rate depends on the chemical processes that transform GEM into the less volatile Hg^{II} species; these processes are only partially understood (Angot et al. 2016). Chemical conversion of GEM to Hg^{II} seems to be particularly important in the Arctic area where ozone and mercury chemistry have been found to be coupled during events where both are observed at ground level to be depleted from the air. There is strong evidence that these depletion episodes are caused by the photochemical formation of bromine atoms (Skov et al. 2004; Goodsite, Plane, and Skov 2004, 2012a; Skov et al. 2006; Kamp et al. 2018) and recently direct evidence was found for Br initiated AMDEs and ODEs (Wang et al. 2019).

The geographical distribution of the emissions have changed in the last decades, where Asian countries have gained importance compared to emissions in Europe, North America, and Japan. Today China accounts for about 40% of the global Hg emission (Muntean et al. 2014; Streets et al. 2019, 2017, 2018; Jiskra et al. 2018). In North America, Europe and on the North Atlantic Ocean there is seen a decline in the GEM concentration of between -1.5 and -2.2% yr⁻¹ (Zhang et al. 2016; Obrist et al. 2018). In the Arctic the decline is zero at Svalbard (Berg et al. 2013) and -0.9% at Alert (Cole et al. 2013).

The aim of the present article is to present and discuss the long time series of GEM measurements at Villum Research Station at Station Nord in North Greenland with a focus on observed inter-annual and seasonal trends as well as the likely explanations for these in terms of sources, transport patterns and dynamics.

2 Experimental section

2.1 Measurements

Villum Research Station (Villum) at Station Nord in North Greenland is the second most northerly, permanently open station in the Arctic, only preceded by Alert, Canada. The station has all the logistic requirements and infrastructures that are necessary for being a major international platform for scientific studies focused on the Arctic cryosphere, nature and interaction with humans. It is located in the farthest north-eastern corner of Greenland on the north-south oriented peninsula Prinsesse Ingeborgs Halvø (a small Peninsula, 81°36' N 16°40' W) which northern end is a 20 x 15 km² Arctic lowland plain (see Figure 1). Villum is an important logistic site for many scientific research activities in the Greenlandic National Park, in North Greenland, see www.villumresearchstation.dk. Ozone and GEM were measured at Flygers Hut from 1996 and 1999, respectively, to 2014 when the measurements were moved to the newly built Air Observatory (Figure 2), and they continue to this day.

Since 1999, GEM has been measured by a TEKRAN 2537 mercury analyser. In the first years, funding was only available for six month per year of observations and thus the data coverage over the entire year is limited to spring, summer and early

100 autumn except for the very first year. There are no measurements available for the years 2003-2008 as the research station was closed. Several generations of the instrument have been used (A, B and X versions) but we estimate that the uncertainty of measuring GEM has remained unchanged during the years [as they are all calibrated towards the same standard based on the vapour pressure of Hg⁰ using Tekran 2505 calibration unit](#). The principle of the instruments is as follows: a measured volume of sample air is drawn through a gold trap that quantitatively retains elemental mercury. The collected mercury is desorbed thermally from the gold trap and is transferred by argon into the detection chamber, where the amount of mercury is detected by cold vapour atomic fluorescence spectroscopy. The detection limit is 0.1 ng m⁻³ and the reproducibility for concentrations above 0.5 ng m⁻³ is within 20 % based on parallel measurements with two TEKRAN 2537A mercury analysers (at a 95 % confidence interval) [using the principle described in ISO Guide 98-3:2008 Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement \(GUM:1995\)](#). The calibration of the instrument is checked every 25 hours by adding known quantities of elemental mercury to the detection system from an internal permeation source. The sample air was either taken through a sample tube heated to 50°C or by drawing sample air from a 20 cm i.d. stainless sample tube. The flow rate in the stainless tube was > 1 m³ min⁻¹. Comparison of measurements from the two different sample lines did not reveal any difference within the uncertainty of the instruments. Prior to entering the instrument air passes a soda lime trap to avoid passivation of the gold traps.

110 Ozone has been measured since 1996. Though different instruments have been applied, the measurement uncertainty is unchanged as the basic principle in all instruments is absorption of UV light at 254 nm. The stability of the instruments is ensured by addition of known concentrations of ozone from an internal ozone generator traceable to a primary standard. The uncertainty at a 95 % confidence level is <7% for concentrations above 20 ppbv and 1.4 ppbv for concentrations below 20 ppbv.

120 [The calculation of inter annual trends were performed applying the non-parametric Mann-Kendahl test and Sens slope calculation, using the program developed by Salmi et al. \(2002\).](#)

~~We have applied the Danish Eulerian Hemispheric Model (DEHM) to calculate the concentrations and direct contributions from different source areas to the concentrations levels at Villum as a function of a prescribed chemical lifetime of Hg⁰ and the meteorological variability of the atmospheric transport from source areas.~~

2.2 Model calculations

125 [We have applied the Danish Eulerian Hemispheric Model \(DEHM\) to calculate the concentrations and direct contributions from different source areas to the concentrations levels at Villum as a function of a prescribed chemical lifetime of Hg⁰ and the meteorological variability of the atmospheric transport from source areas.](#)

130 DEHM is a three-dimensional, offline, large-scale, Eulerian, atmospheric chemistry transport model (CTM) developed to study long-range transport of air pollution in the Northern Hemisphere with focus on [the Arctic](#) or Europe. The model domain used in previous studies covers most of the Northern Hemisphere, discretized on a polar stereographic projection, and includes a

two-way nesting procedure with several nests with higher resolution over Europe, Northern Europe and Denmark or the Arctic (Frohn, Christensen, and Brandt 2002; Brandt et al. 2012).

DEHM was originally developed in the early 1990's to study the atmospheric transport of sulphur and sulphate into the Arctic (Christensen 1997; Heidam, Wählén, and Christensen 1999; Heidam et al. 2004) and has also been used to study transport of Mercury to the Arctic (Christensen et al. 2004, Skov et al. 2004).

The model system has been setup with one model domain with 150x150 grid points. The domain covers the northern hemisphere with a grid resolution on 150 km at 60°N. The vertical grid is defined using the σ -coordinate system, with 29 vertical layers extending up to a height of 100 hPa.

The DEHM model is driven by meteorological data from the Advanced Research WRF version 3.6 (WRF ARW) (Skamarock et al., 2008). This WRF model simulation was driven by global meteorological ERA-Interim data, which is a global atmospheric reanalysis data set from the European Centre for Medium-Range Weather Forecasts (ECMWF) starting from 1979 and continuously updated in real time. These data have been nudged every 6 hour into the WRF model. The WRF model has been run in a climate mode setup, e.g. continuously updating Sea Surface Temperature and deep soil temperature (both from the ERA interim).

The global historical AMAP Hg emissions inventories for 1990-2010 have been used as the anthropogenic emissions (UNEP 2013) for the model run with variable emissions. The 1990 emissions have been used for the model calculations for the period 1990-1992, 1995 emissions for the years 1993-1997, 2000 emissions for 1998-2002, 2005 emissions for 2003-2007 and finally the 2010 emission for 2008-2017. The emissions for 2005 were used for the model run with constant emissions.

Emissions of mercury from biomass burning were based on CO emissions obtained from the Global Fire Emissions Database, Version 3, (van der Werf et al. 2006; Van der Werf et al., 2003), where a fixed Hg⁰/CO ratio of 8×10⁻⁷ kg Hg⁰/kg CO was applied. Emissions from oceans are based on calculated fluxes from the GEOS-Chem model (Soerensen et al. 2010). The global historical AMAP Hg emissions inventories 1990-2010 have been used as for the anthropogenic emissions (UNEP 2013) for the model run with variable emissions, where 1990 emissions have been used for the model calculations for the period 1990-1992, 1995 emissions for 1993-1997, 2000 emissions for 1998-2002, 2005 emissions for 2003-2007 and finally the 2010 emission for 2008-2017. The Emissions for 2005 have used for the model run with constant emissions. Emissions of mercury from biomass burning was based on CO emissions obtained from Global Fire Emissions Database, Version 3, (van der Werf et al. 2006; Van der Werf et al., 2003) where a fixed Hg⁰/CO ratio of 8×10⁻⁷ kg Hg/kg CO. Emissions from oceans are based on calculated fluxes from the GEOS-Chem model (Soerensen et al. 2010). The anthropogenic emissions are variable up to 2010 where after they are constant.

The system has been set up with 11 different GEM tracers, which represent eight different anthropogenic source areas (Russia, Eastern Europe, Western Europe, China, North America, Rest of Asia, Africa and South America), biomass burning, ocean sources and the prescribed boundary conditions on 1.5 ng/m³ for the entire period. The latter is introduced because of the long lifetime of Hg⁰ and accounts for the transport across equator with the exchange velocity between the two hemispheres of about 1 year. The boundary condition concentration of 1.5 ng/m³ represents the typical global background concentrations, which

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165 account for all emissions in both hemispheres, and are close to the concentrations at eEquator as given in Selin et al (2008).
The boundary conditions were kept constant during the period covered by the model. ~~The boundary condition is also introduced~~
~~to account for all emissions in both hemispheres.~~

There have been made ~~three 2x3~~ different model runs covering the period from 1990 to 2017, ~~with two main emissions setup,~~
~~which are with either constant anthropogenic missions (using the emissions in 2005 for all years) or the variable emissions for~~
170 1990-2010. Each emissions setup is run with a simple has a fixed first order reaction lifetime for Hg⁰ of 1 month, 6 months
and 1 year, respectively. ~~The boundary conditions were kept constant during the period covered by the model.~~ The model does
not include Arctic mercury depletion in the runs presented here; it focuses only on the direct long-range transported mercury
contribution to the GEM concentration at Villum. For each model run the contributions offer the 11 different tracers are
estimated in order to investigate this contribution as function of the fixed first order reaction lifetime for Hg⁰, changing
175 meteorology and changing emissions.

2.3 Trajectory model

In order to investigate the influence of different surfaces on GEM concentration, 120 hours back trajectories for air masses
arriving at 100 m altitude at Villum were calculated with hourly resolution using the BADC (British Atmospheric Data Centre)
Trajectory Service. For each of the trajectories the time spent over different surfaces was calculated using a polar stereographic
180 map of the Northern Hemisphere, where each of the 1024x1024 24 km grid cells were classified as -land, sea, snow or sea ice,
and thus the percentage of the total transport time spent over these four types of surfaces could be calculated. The snow and
ice coverage values were generated by the NOAA/NESDIS Interactive Multisensor Snow and Ice Mapping System (IMS)
developed by the Interactive Processing Branch of the Satellite Services Division. For what concerns the sea ice coverage, a
similar calculation was performed using daily stereographic maps of sea ice concentration with a resolution of 12.5 km,
185 available also from NOAA/NESDIS. This calculation allowed ~~to establish~~ establishing the percentage of time where the air
mass of the back trajectory was passing over sea ice as done earlier in studies of atmospheric particle dynamics (Dall'Osto et
al. 2018). Combining these calculations for the periods where GEM measurements were carried out at Villum, the percentages
of the 120 hour duration of the trajectory, where the air masses passed over land, sea, snow and sea ice surfaces could be
established.

190 3 Results and discussion

The measurements of GEM and ozone from 1996 to 2017 are shown in Figure 3. A seasonal pattern is observed for each year,
see Figure 4. In January and February, the level of ozone and GEM is rather stable. After the polar sunrise, the concentration
starts to fluctuate strongly and ozone and GEM are depleted fast (during 2 to 10 hours). Figure 54 shows the variations of the
yearly average GEM concentration and the average for the winter season between 1999 and 20187, where only periods with
195 more than 50% data coverage have been included. ~~The yearly and seasonal averages and their trends as well as their uncertainty~~

limits (assuming a normal distribution of the measurement data around the regression line) are shown in Table 1. The annual averages do not show a negative trend, however not significant any significant trend at a 90% confidence level [95% confidence interval (Table 1)]. The autumn (September-October-November) and the winter months show both negative trends that are significant at a 90% confidence level. The trends, in percentage of the average GEM concentrations during these periods, are -1.7%/yr for the winter period and -1.4%/yr for the autumn. The annual trend remains non-significant also when excluding the years 1999 and 2000 or the extreme value in 2017. The lack of a significant annual trend seems to be explained by the high variability of the concentrations during the spring period as well as the fact that the GEM concentration during the summer period show no evidence of a decreasing trend. This lack of yearly trend is the result of a combination of rather different seasonal trends: in the autumn (September-October-November) there is an insignificant decrease (-0.87%/yr), whereas in winter (December-January-February) a pronounced decrease of -1.56%/yr is observed (significant on 95% confident interval). A test of the importance of the value in 2000 showed that the decrease is almost unchanged removing the point but R^2 falls to 0.29 though the trend is still significant. In the spring (March-April-May) there is not any significant trend, though a small positive trend is seen (0.35%/yr). For the summer (June-July-August) there is a positive trend of 0.75%/yr that however is not significant. This result is similar to the result obtained at Zeppelin Station on Svalbard for the period 2000 to 2008 (Berg et al. 2013) and, as previously mentioned, at Alert, Canada, where a negative trend of -0.009 ng/m^3 (-0.58%/yr) is seen for the period between 1995 and 2008 (Steffen et al. 2015). ~~In a~~ study of GEM in firm snow from the Greenlandic inland ice at about 3 km altitude, ~~Dommergue~~ Dommergue et al. (2016) showed that there is a positive trend or no trend during the period 2000-2010, though the authors pointed out that nothing conclusively can be said about the concentration trends based on their results. The behaviour of the trends may in principle be explained by changes in the emissions in the source regions, in transport patterns, in deposition, re-emission as well as atmospheric chemistry. The seasonal differences in the trends must be explained by a different influence of these factors during the different seasons. Finally, it has been suggested that decreasing GEM concentrations in the Northern Hemisphere over the last 20 years may be partially explained by increased uptake by vegetation due to increased net primary productivity (Jiskra, 2018). ~~Our data set does not permit to evaluate this hypothesis. In the following section, we will discuss these possible explanations for the observed trends separately.~~

3.1 Changes in atmospheric chemistry

The strongest concentration trend is found during the winter, where photochemically driven chemistry obviously does not take place in the area but where long range transport from mid-latitudes is at its maximum. The main influence of Arctic atmospheric chemistry on GEM concentrations is expected to be in the spring and summer period, where the fate of GEM is believed to depend on the presence of seasonal sea ice and the presence of air temperatures below -4°C (Christensen et al. 2004). Figure 65 shows a conceptual description of mercury removal in Arctic. Also a regression analysis of the number of hours with depletion events (defined here as $\text{GEM} < 0.5 \text{ ng/m}^3$) did not show any significant change over the years 2000-2017. Neither the ozone data obtained during the period 1999-2017 did show any significant trend for the concentrations in spring or summer. The ozone observations will be the subject of a separate publication.

The data until 2002 were used to investigate reaction kinetics of ozone and GEM with a third reactant. Log – log plots of ozone against GEM gave a straight line as seen earlier (Schroeder et al. 1998; Berg et al. 2003; Steffen et al. 2008; Skov et al. 2004). A reaction rate for Br with Hg⁰ was calculated, which fitted well with a reaction rate determined by theoretical chemistry (Goodsite, Plane, and Skov 2012b; Goodsite, Plane, and Skov 2004; Skov et al. 2004). We made the same analysis on the data from 2007 and onwards. GEM was averaged to a time resolution of 0.5 hour. The new analysis confirmed the previous result, though the data points were more scattered and thus the resulting slope ~~was connected with a larger~~ had a higher uncertainty, mostly due to smaller difference between the initial GEM concentration and the final concentration. An important point ~~for regarding~~ the parameterisation of GEM depletion is that bromine induced atmospheric mercury depletion events (AMDEs) often ~~were~~ observed under stagnant wind conditions and not only during situations with strong wind that may cause generated bromine release as proposed earlier (see latest Yang et al. 2020). Recently, the Br induced oxidation of Hg⁰ has been proven directly in a study, where Br, BrO, O₃, GEM and RGM were measured simultaneously during AMDE and ODE and using a multiphase box model to study the complex set of processes (Wang et al., 2019). As shown in Table 1, the seasonal averaged concentration has a maximum in the summer (June-July-August) and a minimum in the spring (March-April-May). In order to test the hypothesis that the spring minimum is related to the occurrence of the combined mercury and ozone depletion events, an indicator of the duration and frequency of such depletion episodes was created. The number of measured hourly GEM concentrations below 50% of the average value in a previous event free period was compared, as a percentage, to the total number of available hourly measurements during the period of interest. For the March-April-May period, this percentage of AMDE hours was found to be strongly correlated with the average GEM concentrations in the same period (Figure 7). Thus, there is evidence for a strong impact of AMDE on GEM concentrations in the spring period. The frequency of AMDE in spring and GEM concentration in summer showed a poor negative correlation. If the deposited Hg during AMDE should be released again during snowmelt, a positive correlation would have been expected, but this was not observed. In fact, the analyses indicate that AMDE is a net sink for mercury, which is in agreement with direct flux measurements (Brooks et al. 2006). Interestingly, Angot et al. (2016) found a positive feedback ~~of between AMDE in spring and the concentration of GEM in summer at Alert that was attributed to reemission of mercury. Contrary to this result, even the annual mean value at Villum had a significant (99% confidence level) negative correlation with AMDE hours. Though this correlation is weak, it~~ This is an indication that AMDEs affect the GEM concentration level at Villum and represent a net sink. From studies of mercury isotopes at Utqiagvik at the North coast of Alaska (Douglas et al., 2019) and Toolik Research Station in central Alaska (Jiskra et al. 2019), it was found that most mercury in melt water was from deposition of GEM and that a large majority of deposited oxidised mercury during AMDE was reduced and reemitted. Further, studies are needed to determine if these results are valid also for more northern Arctic locations as Alert, Villum or Zeppelin. It has been determined that outflows from rivers are a main source of Hg in the Arctic Ocean (e.g. Outridge et al. 2008, Fischer et al. 2012). The present study indicates that there is an atmospheric input as well can be significant as well. The significance ~~A very important step in the determination of the significance of these sources depends on its chemical form. Previously~~

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atmospheric deposited mercury has been identified to be bioavailable -for understanding Hg accumulation in the food web is to determine the bioavailability of mercury deposited (Moller et al. 2011) compared to that from river discharge and thus might still be dominant for the mercury found in the Arctic food web?-

3.2 Decrease in the emissions in the source regions

Recent studies show that mercury emissions from Europe and North America have been decreasing since 1990, while emissions in Asia have been increasing (UNEP 2013; Muntean et al. 2014). Russian emissions, considered as a separate entity, have been decreasing as well. Concentration data from cruises on the North Atlantic show a declining trend since 1990 with a steep decrease in the surface seawater Hg⁰ concentration between the years 1998-2000 and 2008-2010 of -5.7% per year. It has been found that the corresponding decrease in mercury emissions from the sea can explain the decreasing trend observed over the North Atlantic and adjacent areas (Soerensen et al. 2012). Chen and co-workers (Chen et al. 2015) found that the decline in atmospheric concentrations at north-mid latitudes was significant for the period 2000-2009 but much weaker in the Arctic. They explained this by the fact that declining sea ice cover and increasing temperatures caused a tendency towards higher emissions from the sea that (partially) compensates for the forcing by decreasing surface water Hg⁰ concentrations in the North Atlantic. The observed seasonality with a significant declining tendency in the atmospheric GEM concentration in winter (DJF) and (weaker) in autumn (SON) than in but not in spring (MAM) or summer (JJA) may be explained as suggested by Chen et al. The highest yearly average concentration of GEM was found in 2013, thereafter there has been a continuous decrease and that might be the effect of emission reductions that now is evident also in high Arctic.

The DEHM model, using variable anthropogenic emissions as described above, shows a slightly decreasing concentration trend, -0.7% per year (see Figure 87). However, this direct anthropogenic input, assuming an atmospheric lifetime of GEM of 12 months, does only account for between 14 and 17% of the observed GEM concentrations, (Figure 98). Including the impact of sea emissions and of the boundary conditions, and assuming a GEM atmospheric lifetime of 12 months, the model predicts an annual average GEM concentrations of 1.40-1.43 ng/m³, i.e. in agreement with the measured average in the period of 1.46 ng/m³, although the measured data covers a larger range of values (1.2 - 1.8 ng/m³). When applying longer or shorter GEM lifetimes, the model results deviate more from the measured concentrations. This indicates that the best relaxation time of GEM in the Northern Hemisphere is 12 months. The chemical lifetime of GEM in the atmosphere is most likely shorter according to the theoretical and experimental evidence (e.g. Goodsite et al. 2004, 2012; Ariya et al. 2008, Donohoue et al. 2005, 2006; Dibble et al. 2012). Therefore, the deposition of Hg^{II} species appears to be followed by reduction and reemission of Hg⁰ (e.g. Brooks et al. 2006, Kamp et al. 2018, Soerensen et al. 2012, Steen et al. 2009, Cobbett et al. 2007). Thus, relaxation time seems to be a more appropriate name than lifetime for GEM. This is supported by a study on the photo-reduction of Hg^{II} in cloud droplets, which was found to be much slower than the one used in models leading to the conclusion that deposition and reemission are involved in the dynamics of atmospheric mercury (Saiz-Lopez et al. 2018). The sea emissions were found to account for 20-21% of the GEM concentration at Villum, and the boundary conditions of 1.5 ng/m³ explained 62-65%,

295 while emissions from fires contributed by 1% during the years of the measurements, still assuming a 12 months GEM atmospheric lifetime.

300 ~~In separate~~ the calculations with DEHM, it was found that emissions from China had larger relative importance during the summer than in the winter season; however, this difference was only significant when applying relatively short (less than 1 year) atmospheric lifetimes of GEM. The calculations for Villum were performed for the year 2001. This result agrees with Chen et al. (2018), who found that East Asia is the main source for mercury deposition in Arctic. Similar result is also reported by AMAP (AMAP 2018). Durnford et al. (2010), applying the GRAHM model, investigated the contribution of different source regions to total mercury as well as GEM concentrations at several Arctic monitoring stations at different seasons of the year. They found that for the yearly concentration averages and their variability at the Arctic stations, including Villum, Asian emissions were the most important, accounting for more than the sum of the contributions from Europe, Russia and North America. This result is in agreement with the present study but in contrast to several studies addressing the origin of shorter-lived pollutants such as black carbon and sulphate that point to the northerly part of Eurasia as the main source regions (Nguyen et al. 2016; Freud et al. 2017). Particularly in the case of Station Nord (now named Villum Research Station), Nguyen et al. 2013 found evidence of a strong influence of direct transport of particles from Siberia including results from previous work (Heidam et al. 2004). Heidam et al. identified Russia as the main contribution to sulphate concentrations, followed by East and Western Europe, while Asian contributions appeared to be of minor importance. The explanation for this difference between modelling results regarding mercury and more short-lived air pollutants is likely to be the large difference in atmospheric lifetimes (relaxation time for GEM). The above discussion highlights the importance of assessing the chemistry of GEM and determining the fate of the resulting reaction products, especially the photo-reduction of Hg^{II} compounds in marine waters.

315 3.3 Changing transport patterns

320 Results obtained by applying the DEHM model to simulate GEM concentrations at Villum indicate that changes in the directly atmospheric transport from source areas to Villum cannot explain the observed trend. We have found that the simulated yearly and seasonal GEM values show very little variability and no significant trend over the years 2000-2015, when the emission sources are kept constant at the 2005 level, while the meteorology is varying and treated as described above. That is opposite to results by Dastoor et al. (2015) for model run with constant emissions. The main reason for that is probably that processes as chemistry and surface exchanges in Dastoor et al. (2015) are more depending on the atmosphere and surface conditions than the simple setup in the present version of DEHM. There ~~is~~ are better agreement between our results and Dastoor et al (2015) for the model setup with variable emissions. We see a decrease of 0.08 ng/m³ between 1992 and 2005 for Villum, while Dastoor et al. found approximately 0.1 ng/m³. The study by Hirdman et al. (2010) of long term trends of sulfate and BC in the Arctic also concludes that changes in atmospheric transport only can explain a small fraction (0.3-7.2%) of the observed trends. Results obtained by applying the DEHM model to simulate GEM concentrations at Villum Research Station indicate that changes in directly atmospheric transport from source areas to VRS cannot explain the observed trend. We have found that the

330 simulated yearly and seasonal GEM values show very little variability and no significant trend over the years 2000–2015, when
the emission sources are kept constant at the 2005 level while the meteorology is varying and treated as described above. That
is opposite to results by Dastoor et al (2015) for the model run with constant emissions. The main reason for that is perhaps
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surface conditions than the simple setup in with DEHM in this work. There are better agreement between our results and
Dastoor et al (2015) for the model setup with variable emissions. We see a decrease of 0.08ng/m³ between 1992 and 2005 for
VRS while Dastoor et al (2015) got approximately 0.1ng/m³ for the same period. The study by Hirdman et al. (2010) of long
335 term trends of sulphate and BC in the Arctic also concludes that changes in atmospheric transport can only explain a small
fraction (0.3–7.2%) of the observed trends.

In an earlier paper on particle formation in Arctic atmosphere, important results have been obtained correlating the time air
masses spent over different surfaces and measured concentration (Dall'Osto et al. 2018). We did the same calculations for
GEM data. The correlations between the time that air masses passed over different surfaces and the measured GEM
340 concentrations at Villum are shown in Table 12. Relatively strong negative correlations ($R^2 > 0.3$) were found only with land
and sea area in the autumn. Performing a two-tailed t-test it was found that the only significant correlation at a 90% confidence
was the anticorrelation in the autumn with land ($R^2 = 0.44$) while the anticorrelation with sea area was significant only at an
85% confidence level ($R^2 = 0.32$). Different types of surfaces may influence deposition and emission rates for mercury, and
they may have an influence on atmospheric chemistry, e.g. by release of reactive bromine compound. However, the correlations
345 may also not be due to a relationship caused by the impact of the surfaces within the 120 hours' time span of the trajectories
but rather by the longer term histories of the air masses. As the percentage of time passed over land by the air masses in the
autumn months (SON) is very short (1–4% of the 120 hours) it seems most likely that the correlation observed is not due to a
direct influence of land. It can thus be concluded from the results shown in Table 12 that no statistically significant impact of
surfaces on GEM concentrations within the range of the 120 hours back trajectories could be observed.

350 The DEHM model predicts that there is a maximum in GEM concentration during late winter and spring (data not shown) due
to long range transport. Such a behaviour is not observed in the measurements (Figure 3). In fact, the highest concentration of
GEM is observed during summer and is attributed to release of GEM from the melting snow and ice pack from mercury
deposited during AMDEs in spring. However, emission from open sea may also be a plausible explanation (Chen et al. 2015).

4 Conclusion

355 In this paper, we present measurements of GEM concentrations in air at Villum Research Station from 1999 to 2017 with a
break in the dataset from July 2002 until 2007. The large fraction of GEM assigned to background contribution and from sea
emissions makes it difficult to assess a trend from the otherwise predicted emission reduction in the immediate source areas
for direct anthropogenic emissions of mercury. A decreasing trend in the concentration of GEM was found during autumn
and winter at a 90% confidence level but it was counteracted by a weak increase during the rest of the year summer and a high

360 variability during spring. Therefore, there was not any significant trend in the yearly average concentrations at the 905% confidence level.

Simulations of the concentrations at Villum using the DEHM model using fixed emission inventory show no significant trends and thus it is concluded that the observed trends are not caused by changes in atmospheric transport patterns. The measurement area is known to be strongly influenced by long-range transport of pollutants in the winter and spring period and the only viable explanation of the observed trend in the winter appears to be decreasing emissions in the source regions. However, 365 according to the DEHM simulations the ~~direct anthropogenic~~ transport of direct anthropogenic emissions only accounted for between 14 and 17 % of the GEM concentration and might be counteracted by the hemispheric background on 1.5 ng/m³ that accounts for 62-65 % and was kept constant in the model. The boundary conditions represent contributions from indirect transport from sources on the Northern hemisphere and transport from sources on the southern hemisphere. ~~Similar~~ 370 considerations could be made about sea emission, accounting for 20-21%. Sea emissions account for 20-21%. The emissions from the North Atlantic are likely to be decreasing due to the lower mercury concentrations in the water but a smaller extent of the sea ice cover around Greenland can counteract this tendency.

The seasonal variation confirms the effect of AMDE leading to generally lower concentrations during spring; in fact, a strong anticorrelation between the average GEM concentrations during springtime and the number of hours with AMDE conditions was observed. The analyses indicated that AMDEs are a net sink for mercury in the atmosphere and that it affects the yearly 375 average concentration.

Simulations with the DEHM model showed best agreement with observations applying an atmospheric lifetime of GEM of 12 months; however, it was found that the apparent lifetime is likely to be the result of a shorter chemical lifetime with respect to oxidation, followed by deposition, reduction and reemission. Thus, 'atmospheric relaxation time' seems to be a more 380 appropriate term than 'lifetime' for GEM.

The lack of a trend in the measured concentrations of GEM despite emission reductions is striking but, together with low direct transport of GEM to Villum as found by the DEHM model, it shows that the dynamics of GEM is very complex. Therefore, in the coming years intensive measurement networks are strongly needed to describe the global distribution of mercury in the environment because the use of models to predict future levels will still be highly uncertain. The situation is increasingly 385 complex due to global change that most likely will change the transport patterns of mercury not only in the atmosphere but also between matrixes.

Table

390 **Table 1. Mean values and yearly trends of the seasonal averages of the GEM measurements at Villum. The upper and lower limits are calculated for a 95% confidence limit. The data points and the trend lines are shown in Figure 4.**

	DJF	MAM	JJA	SON	All
Mean value (ng/m ³)	1.48	1.29	1.63	1.42	1.46
Trend (% per year)	-1.56	0.35	0.75	-0.87	-0.42
Lower Limit (% per year)	-2.73	-2.45	-1.33	-2.28	-1.94
Upper limit (% per year)	-0.38	3.14	2.83	0.54	1.10

Table 1 The correlation of the time air masses spent over different surfaces and GEM concentration shown for the different seasons (DJF, MAM, JJA and SON). Values for both R and R² are shown.

R ²	DJF	MAM	JJA	SON		R	DJF	MAM	JJA	SON
Sea ice	0.28	0.01	0.00	0.24		Sea ice	-0.53	0.11	0.04	0.49
Snow	0.17	0.00	0.06	0.03		Snow	0.41	-0.04	-0.25	-0.17
Land	0.03	0.02	0.02	0.44		Land	-0.17	0.17	0.12	-0.66
Sea	0.22	0.03	0.14	0.32		Sea	0.47	-0.17	0.37	-0.56

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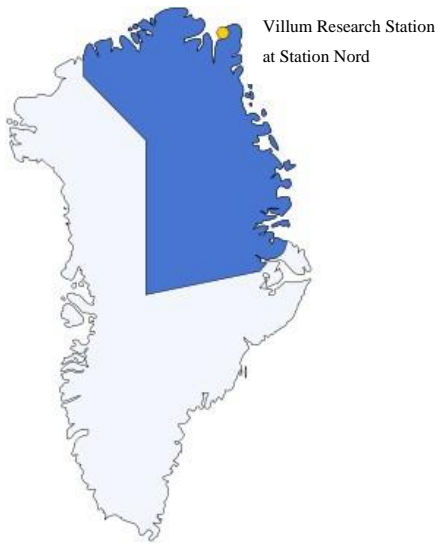
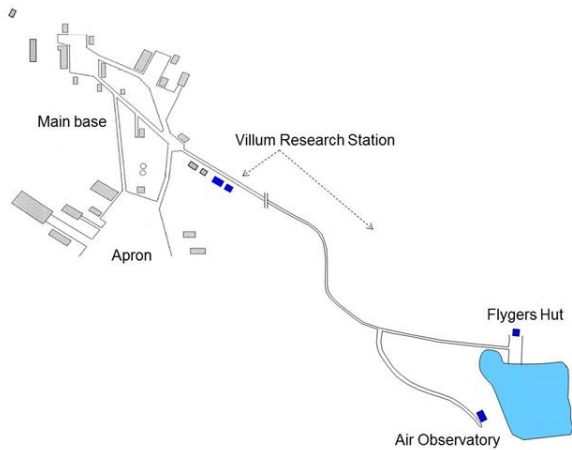
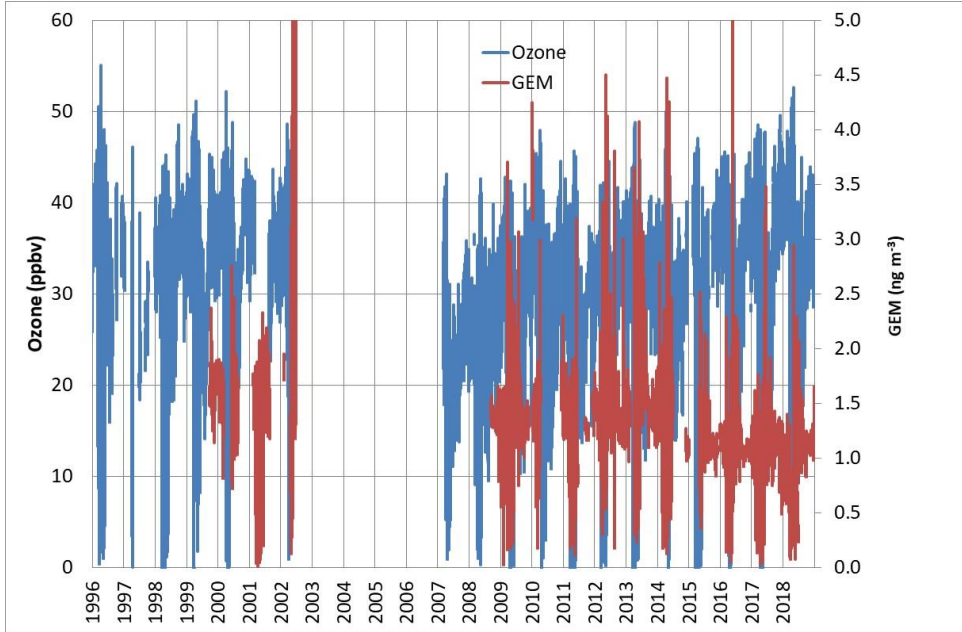


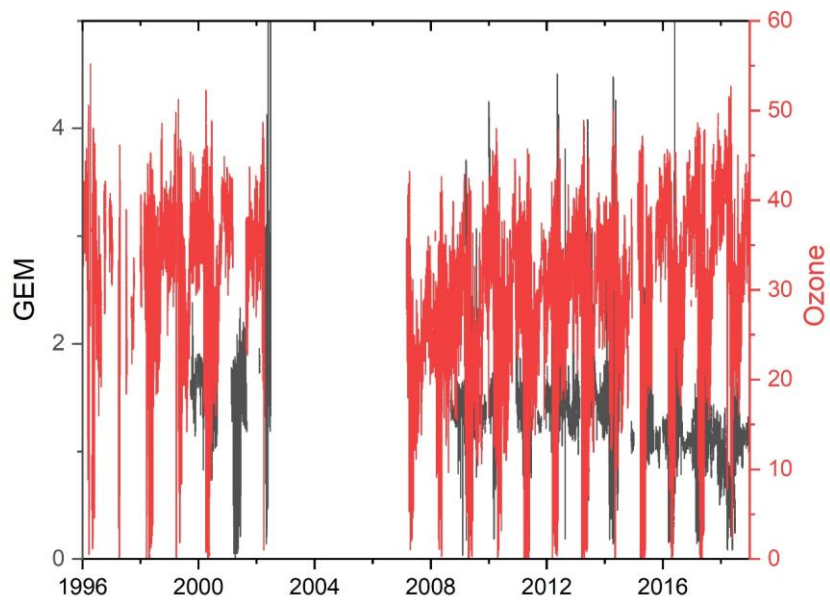
Figure 1: The position of Villum Research Station at Station Nord in North Greenland. The blue area represents the Greenlandic National Park.

400



405 **Figure 2: Map of Villum Research Station with its buildings (blue) relative to Station Nord military outpost. Flygers Hut and Air Observatory are located about 2 km outside main base of Station Nord. Until 2014 all measurements were performed in Flygers Hut, thereafter they were moved to Air Observatory.**





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Figure 3: Time series of the concentration of GEM and the mixing ratio of ozone at Villum Research Station

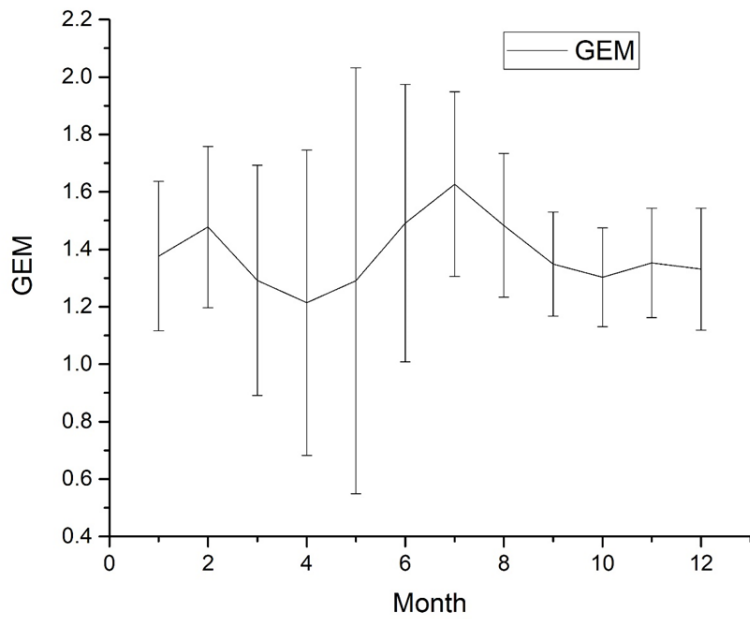
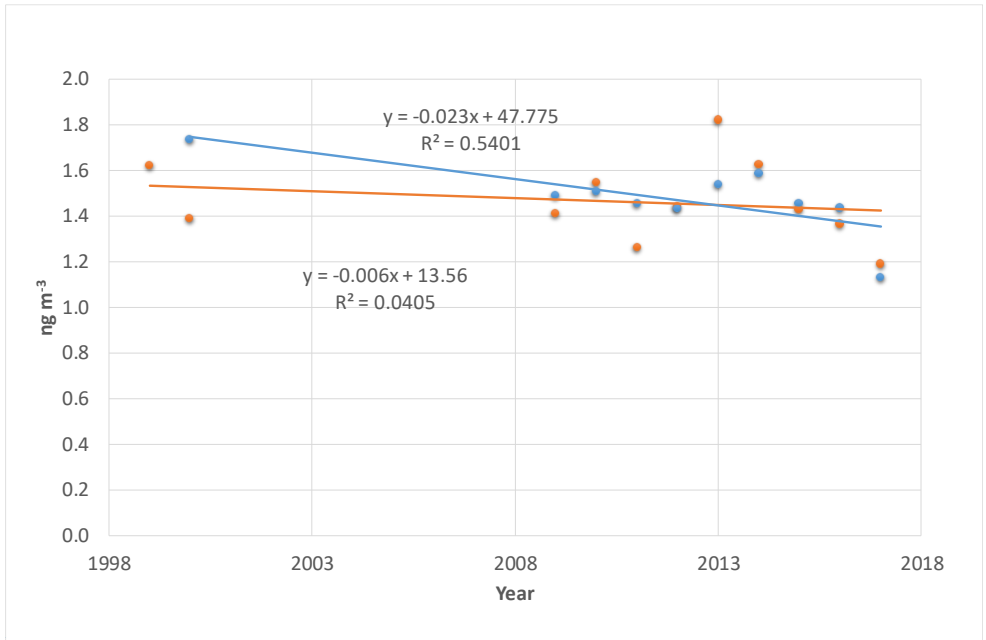


Figure 4 Monthly averages of GEM for the years 1999 to 2002 and 2008 to 2018 at Villum Research Station. [The spread in monthly mean value is shown as plus/minus one std. dev.](#)

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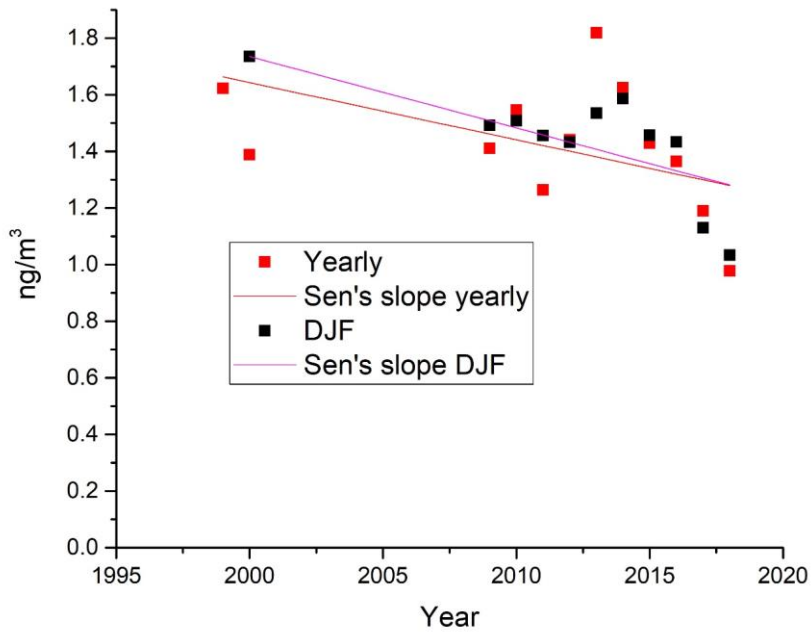


Figure 54: Yearly (Orange) and winter season (December-January-February, Blue) average values of measured GEM concentrations at Villum with trend lines.

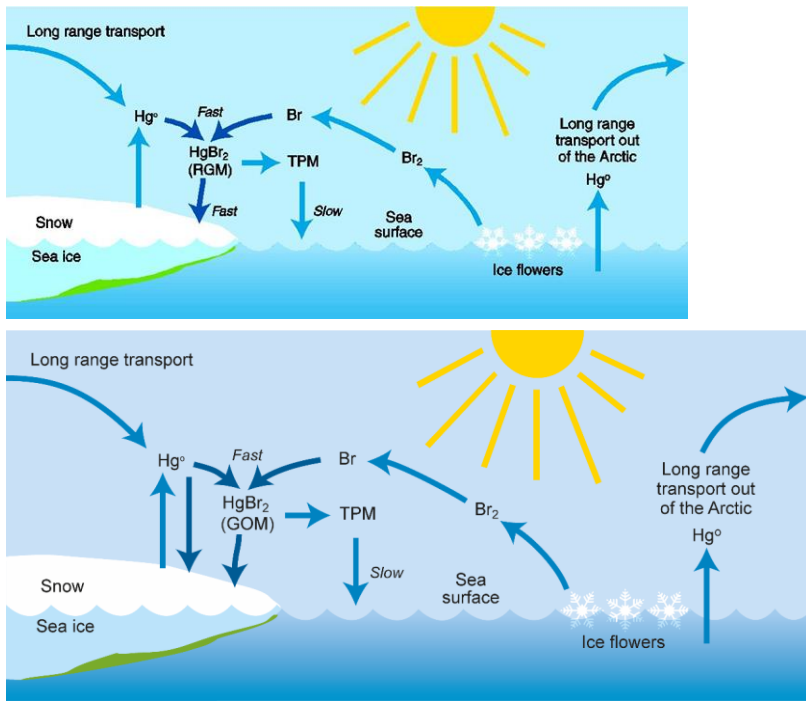
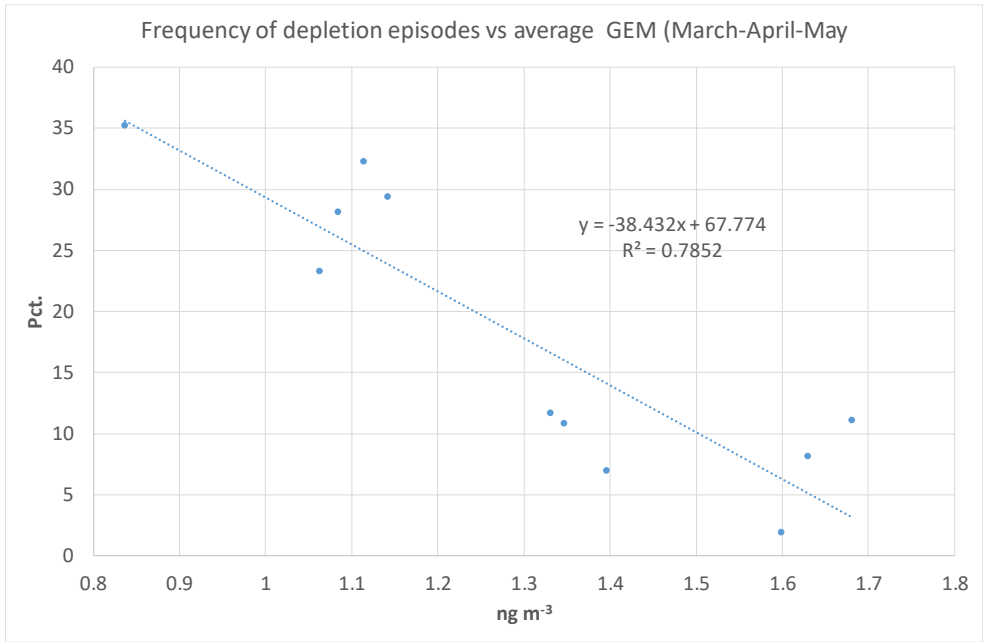


Figure 65: The mercury cycle in the Arctic atmosphere where gaseous elemental mercury (Hg^0) is converted to reactive gaseous oxidized mercury (RGM) that is fast either deposited or converted into total particulate mercury (TPM). The chemical composition of RGM is unknown and $HgBr_2$ is one suggestion among many. (From Henrik Skov in AMAP report 2013).

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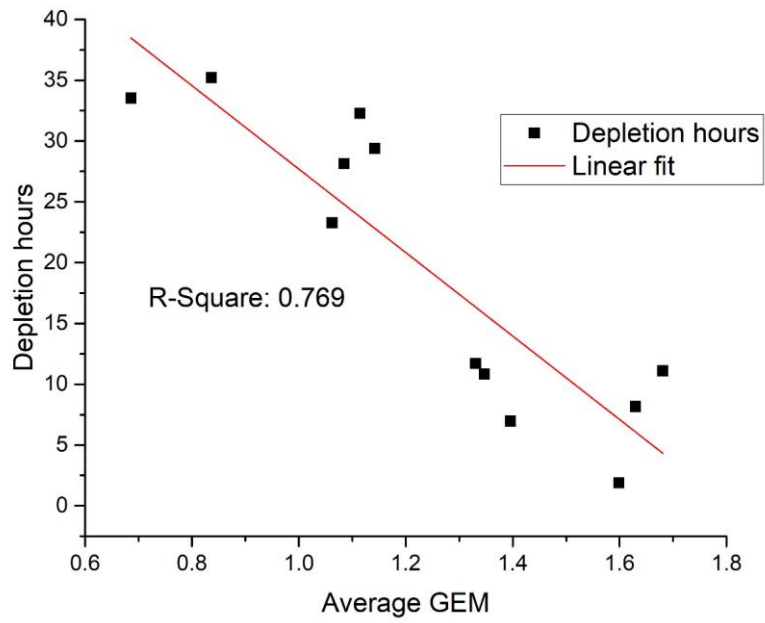
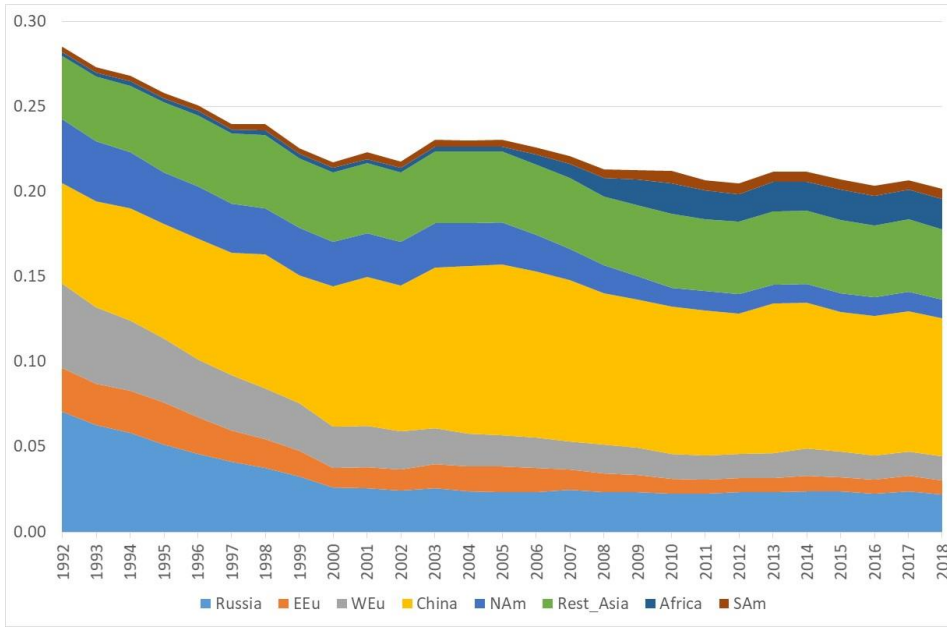
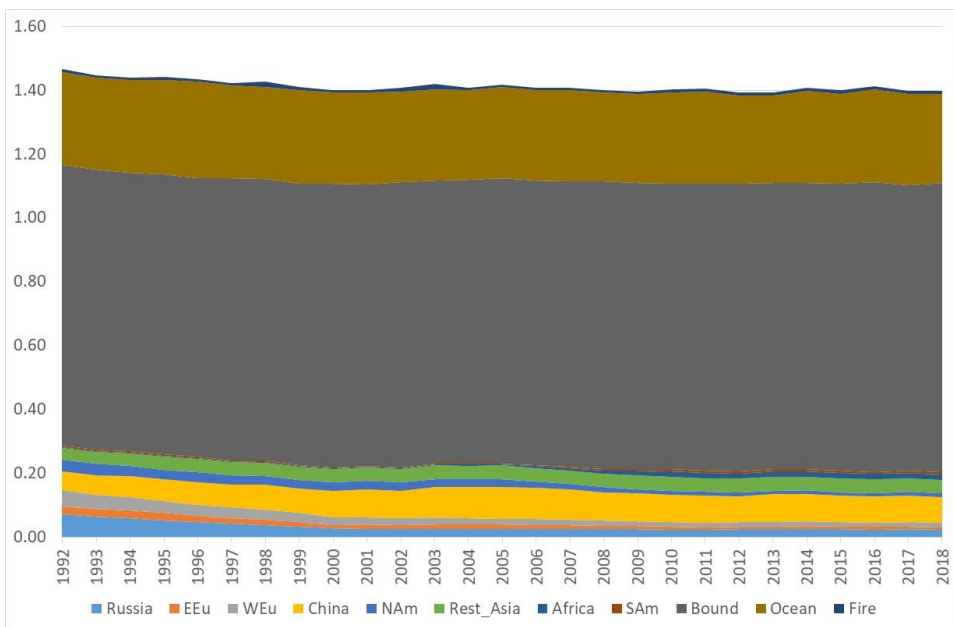


Figure 76: Frequency of depletion episodes versus average GEM concentration in March, April and May.



440 **Figure 8: Model calculation with variable emissions of the source apportionment of the direct anthropogenic contribution to the annual average GEM concentrations at Villum. The DEHM model used two years (1990 and 1991) to spin up the model. Source regions: Russia = Russia; EEU = East Europe; WEU = West Europe; China = China; Africa = Africa; Sam = South America. Unit: ng m^{-3} .** **Figure 7: Model calculation with variable emissions of the source apportionment of the direct anthropogenic contribution to the annual average GEM concentrations at Villum. The DEHM model used two years (1990 and 1991) to spin up the model. Source regions: Russia = Russia; EEU = East Europe; WEU = West Europe; China = China; Africa = Africa; Sam = South America. Unit: ng m^{-3} .**



445 **Figure 9: Model calculation with variable emissions of the source apportionment of annual average GEM at Villum. The DEHM model used two years (1990 and 1991) to spin up the model. In the model reemission from ocean and contribution from boundary conditions at equator included. Source regions: Russia = Russia; EEU = East Europe; WEU = West Europe; China = China; Africa = Africa; Sam = South America; Bound = Boundary Condition; Ocean = Ocean; Fire = Wildfire. Unit: ng m⁻³.**
 450 **Figure 8: Model calculation with variable emissions of the source apportionment of annual average GEM at VILLUM. The DEHM model used two years (1990 and 1991) to spin up the model. In the model reemission from ocean and contribution from boundary conditions at equator included. Source regions: Russia = Russia; EEU = East Europe; WEU = West Europe; China = China; Africa = Africa; Sam = South America; Bound = Boundary Condition; Ocean = Ocean; Fire = Wildfire. Unit: ng m⁻³.**

455 **Author Contribution**

- All co-authors were involved in the scientific discussions of the paper
- Henrik Skov: Project leader and principal writer
- Jens Hjorth: Co-writer, coordination of statistical analysis
- Bjarne Jensen: Calibration, tests and setup of instruments
- 460 Christel Christoffersen: Calibration, tests and setup of instruments
- Maria Bech Poulsen: Trend analysis and analysis of the relation between ozone and GEM

Jesper Baldtzer Liisberg: Analysis of depletion events

David Beddows: Trajectory clustering analysis and K-statistics.

Manual Dall'Osto: Trajectory clustering analysis and K-statistics as well as overall design of article

465 Jesper Heile Christensen: Model calculations by DEHM.

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