Interactive comment on "Fluxes of gaseous elemental mercury (GEM) in the High Arctic during atmospheric mercury depletion events (AMDEs)" by Jesper Kamp et al.

Anonymous Referee #2
Received and published: 13 September 2017

General comments:
The authors present a first paper using the relaxed eddy accumulation (REA) method to measure flux over an Arctic snow covered surface, providing useful results for those looking to undertake similar Arctic mercury flux studies in the future. However, thorough editing of the text for grammar and clarity should be undertaken; in many areas, sentence fragments are present (see technical corrections for examples), and this should be corrected prior to publication, to increase the comprehensibility of the text. In addition, I would also caution that the authors appear to be extrapolating their conclusions from a relatively limited data set, and many of the conclusions drawn from their results do not appear to be adequately supported by the presented results. In their Fig. 7a, GEM fluxes appear to be predominantly near 0, which means that any derivation of relationships based on this data set must be approached with caution, and broad sweeping statements about the importance of various factors should be avoided (see specific comments below).

Specific comments:
1. *Use of the REA method*:
The manuscript presents a study using a technique (REA) which had not previously been used for this type of Arctic GEM flux work; however, the authors fail to explain why they have chosen this technique. In a "first use" study such as this it is important to explicitly outline the benefits of this technique over more traditionally used or other available methods, as well as the potential short-comings. In its present state, it is unclear why this work using the REA method is a benefit to the Arctic Hg flux literature, or why one may choose to do a REA based Hg flux study rather than use a chamber or AGM type method.
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We agree that a more detailed argument for choice of measurement method is needed. Therefore following text has been inserted into the manuscript at page 3 line 5:
Chamber methods are attractive methods for measuring fluxes because of their low cost and simplicity but suffers from a number of weaknesses. They only capture the flux over a small area, the chamber affects the surface over which the measurement is taken and they can modify physical properties such as light and temperature (Bowling et al., 1998, Fowler et al., 2001). This implies that the measured flux will differ from the natural flux. The AGM is not altering the surface; however, it requires a homogeneous surface several hundred meters upstream the measurement site. Furthermore, it is assumed that the vertical profile is only a product of the vertical turbulent transport; nevertheless fast chemical reactions can affect the profile. The most direct flux measurement technique is the eddy covariance (EC) technique (Buzorius et al., 1998) but close to the surface this technique only works for fast responding monitors (sampling frequency >5 Hz), which is not available for Hg. Therefore, we chose to employ the relaxed eddy accumulation (REA) method (Businger and Oncley, 1990) which is based on EC and the method does not affect the surface. Oncley et al. (1993) reported results with agreement within 20% for EC and

REA and a study by Hensen et al. (1996) shows agreement between EC and REA within 10%, a difference that is reported not to be significant because the main error for REA is the determination of the concentration difference.

2. *Exclusion of data (primarily CO_2 flux to determine b section, and one Results reference)*:
It is not immediately clear how the limits were chosen for various parameters to allow for inclusion or exclusion of data (in "CO_2 flux to determine b" section). In total, the authors state that they excluded 74% of the collected data, which seems rather extreme, especially lacking adequate justification for the exclusion criteria. The authors state that they have estimated an uncertainty for b (<<10%), and state that the uncertainty is then assumed to be insignificant, but provide no methodology for that estimation, or justification for the assumption of insignificance. In this section, the authors also include a "z/L" criteria as a means by which data were included/excluded from the presented results, but this "z/L" is neither defined, nor described. Various parameters are given, however the choice to discard data should be more thoroughly explained and justified, especially when it means that very little of the originally collected data is included and used to derive the final relationships presented in this work. In the Results and Discussion (pg. 7, line 18 – 19), the authors propose a means by which some data may be falsely interpreted as outliers, but it is unclear whether this was a problem in the presented data set, and, if so, how was this dealt with?
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We agree it is unclear how the various parameters to exclude data is chosen. A more detailed explanation for the choice of the limits of b and the uncertainty is needed, as well as an explanation of z/L. Furthermore we have made further studies of the uncertainty of b and have adjusted our estimates and the discussion of uncertainty. Therefor the section 2.5 has been changed to the following text:

We determine the proportionality factor b used to calculate fluxes of GEM from CO_2 fluxes assuming fluxes of all gases are transported by the turbulence in a similar way. CO_2 flux can oppose to GEM be measured using the more direct EC method, thus b can be estimated from the measured CO_2 flux and CO_2 concentrations using Eq. 1.
Close to the REA flux system, an enclosed CO_2 gas analyzer (LI-7200, LI-COR Inc.) was mounted on the boom with the inlet directly below the ultrasonic anemometer 6.08 m above ground and above the GEM sample inlets. The gas analyzer measures CO_2 and H_2O concentration at 10 Hz to derive the EC flux of CO_2 and H_2O. The CompactRIO compiles all data from the gas analyzer, valve positions and meteorological data from the REA system. The flux of CO_2 was measured in order to determine b from the CO_2 flux and back-calculations of CO_2 concentration in updrafts and downdrafts in each measuring interval (Gao, 1995;Ruppert et al., 2006). For each interval, b is used to determine the REA flux of GEM.
Meteorological conditions or parameters, such as temperature, wind direction and speed, heat fluxes, relative humidity, pressure, and water vapor were measured for further analysis of the GEM fluxes. The Monin-Obukhov length (L) was calculated in order to estimate stability, as atmospheric stratification is expected to affect the surface exchange. In order to ensure data from a well-developed turbulent flow field and a reasonably constant wind direction, wind speeds below two m s^{-1} were discarded.
For an ideal Gaussian joint probability distribution of the vertical wind speed and the scalar concentration, b has a well-defined value of 0.627 (Wyngaard and Moeng, 1992). However, experimentally determined b's for fluxes of heat, moisture and CO_2 typically

range from 0.5 to 0.7 (e.g. (Katul et al., 1996), Ammann and Meixner, 2002, Sakabe et al., 2014).
As mentioned a fixed "dead band" of 0.076 m/s is introduced. Adding a "dead band" will affect the magnitude of b. In many applications, a dynamic dead band scaled with standard deviation of the vertical velocity w (σ_w) is used, which gives a smaller but relatively constant b (Hansen et al.2013) according to Eq. 3:

$$b = b_0 exp \frac{-0.75 \cdot \omega_0}{\sigma_w} \qquad (3)$$

Where b_0 is b without the dead band and ω_0 is the dynamic dead band. However, for practical reasons (limitation on processing time for data control and data collection) we used a fixed dead band causing a b, which varies with σ_w. The standard deviation of w measured in present study varied between 0.03 and 0.4 m/s. According to eq. 3, this will cause a variation of b (~ 0.2-0.8) depending on the size of b_0. Several researchers have studied the dependence of b_0 on the atmospheric dimensionless stability parameter z/L (L is the Monin-Obukhov length and z is the measurement height, $z/L < 0$ indicates unstable, $z/L > 0$ stable and $z/L = 0$ neutral conditions). The majority of the studies (Andreas et al, 1998; Ammann and Meixner 2002 and Salkabe et al., 2014) showed an increase in b_0 with increasing z/L, however for the most part they refer to a limited stability range ($-1.5 < z/L < 1.5$). In the high Arctic, we often find very stable as well as neutral and slightly unstable stratification. In order to keep the estimated b values within a well-investigated stability range, data are discarded if they fall out site the stability range ($-1.5 < z/L < 1.5$). If b in a given experiment differs too much from the expected value, the probability distribution is likely to differ from the Gaussian distribution, thus in the present experiment, data was discarded in periods where b derived from T or CO_2 was below 0.2 and above 0.8.
After data filtration, only 26% of the total 1653 measurements were approved during the campaign. We are aware that this is a very strict filtration; however, this ensures that the data used for the analysis are solid.
Several studies have been dedicated to investigate the implications on the flux related to b (e.g. Andreas et al., 1998; Ruppert et al., 2006; Sakabe et al., 2014) and the standard deviation of b is often estimated to be around 10% (e.g. Amman and Meixner, 2002; Sommar et al., 2013; Zhu et al., 2015). However, b is calculated based on measurements of CO_2 fluxes, thus the uncertainty of b must be related to the uncertainty of the measured flux. It is not trivial to estimate the uncertainty of EC fluxes. Finkelstein & Sims (2001) suggested to use direct calculation of the variance of the covariance for calculating the random sampling error in EC measurements. They tested measurements at several type of surfaces and found the relative error to be approximately 25-30% for trace gas fluxes. However, one could argue that this method is only revealing how constant the flux measurement is and not how accurate the measured flux is. A more correct way to estimate the error is to measure the flux in parallel towers (Post et al., 2015). This is very expensive and very rarely carried out. Hence, here we use the general relative standard deviation of CO_2 fluxes on 25-30% estimated by Finkelstein &Sims (2001). Using error propagation theory on eq.1 the uncertainty of b (u_b) can be estimated as the combined relative uncertainty of the measured flux (25%) and the relative uncertainty of the measured concentration of CO_2 (1%, (Li-Cor)) from following equation:

$$u_b(y) = \sqrt{\sum_{i=1}^{n} u(x_i)^2}$$

Where $u(x_i)$ is the standard uncertainty. The uncertainty of b is ≈ 25%. To estimate the total uncertainty of the GEM flux we also have to consider the uncertainty of the measurements of the GEM concentration. This was found to be 10% by Skov et al. 2004, which used same type of instrument for GEM measurements. The uncertainty of the GEM flux can now be determined from the combined uncertainty of the concentration measurements and uncertainty of the estimated b: $\sqrt{0.1^2 + 0.1^2 + 0.25^2} \approx 0.30$ *and the uncertainty of the flux becomes ≈ 60% at 95% confidence level.*

3. *Uncertainty in presented data (pg. 6, lines 12 – 14)*:
The authors provide an estimate of the uncertainty "of the two concentration determinations", but it is unclear what precisely they mean by "the two concentration determinations"; is this the uncertainty of Hg flux based on the instrumental detection limit of 0.1 ng/m3? If so, this needs to be clarified (and units should be included with the appropriate numbers). In addition, it is stated that the uncertainty of the flux (which is given as 0.14) becomes 28% at the 95% confidence interval (unclear how this was derived), and then in the following sentence the authors give a GEM uncertainty of 10% above 0.5 ng/m3, but this is attributed to another study, so it is unclear how this fits in with any of their data, or uncertainty in their data, and precisely what the uncertainty on any of the provided results would be. In addition, no factors besides flux and b are given any consideration with respect to uncertainty, which makes it impossible to know how robust any of the presented results/relationships are.
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The section of uncertainty has been revised (see text under section 2 above)

4. *Results and Discussion*:
I believe that this section of the manuscript should be thoroughly reviewed by the authors, and revised prior to publication, as many conclusions/relationships appear to have been drawn from GEM flux results that, as presented, typically seem to be approximately zero (Fig. 7a). In instances where the authors are calling on certain events (eg/increases in flux) these events should be explicitly stated, for clarity.
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We have changed figure 7, so it becomes more clear. We have added numbers to Fig. 7 to refer to the events and refers to the numbers in the discussion. Furthermore, we have added an extra figure showing the relation between the fluxes and temperature.
The whole section has been thoroughly revised and rewritten.

5. *The importance of heat/temperature changes*:
On pg. 2 (lines 30 – 31) the authors propose that a correlation between solar radiation induced heat flux/temp change and GEM production/flux exists, due to the observed relationship between solar radiation and GEM concentration increases in surface snow, and then again in the results/discussion (pg. 8, lines 9 – 12) they propose a temperature dependence in their observed results, and in the conclusions (pg. 9, lines 29 – 31) state that their data support the hypothesis that heating of the surface is influencing GEM formation/emission; however, this ignores the generally accepted idea that GEM production in snow (and many other media) is the result of photochemical reduction of Hg^{2+} to produce Hg^0. It is possible that this process (Hg^{2+} reduction or subsequent Hg^0 emission) from snow may be influenced by heat, but the primary reason for an increase in Hg^0 production with increased solar radiation intensity

will most likely be due to increases in the extent of Hg^{2+} photoreduction, not as a result of heat induced processes in the snowpack.
In addition, in the results/discussion section, the authors state "After deposition, we speculate that GOM is reduced photolytically to GEM." (pg. 6, line 23 – 24), but then later state "GOM is reduced at the snow surface when temperature increases (Ferrari et al., 2008)." (pg. 6, line 26). GOM in the snow will most likely be reduced by some manner of photochemical reduction reaction (whether this be photolytic, or as a result of some other photochemically driven process), and while temperature may influence the extent of this reaction, or movement of GEM from the snowpack, radiation (sunlight) is required for the reaction to proceed. As it is used in the aforementioned statement, the Ferrari et al. (2008) reference is somewhat misleading, and this should be revised. In addition, the authors are using air temperature rather than the snowpack surface temperature to derive relationships with flux, and these will differ. Since the surface snow temperature may be significantly different than the ambient air temperature, it is difficult to make compelling conclusions about temperature dependence on snowpack Hg flux without these snowpack temperatures.
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We are aware of the reduction of GOM and possible subsequent emission of GEM and this was also our initial hypothesis. We investigated the relation between solar radiation and GEM emission but found no clear relation. However we found a possible correlation between temperature and GEM emission, which we think could be an important information to the scientific society measuring Hg fluxes in the Arctic, and we did not think it would be right to ignore this. We have inserted a figure showing the relation between GEM flux and radiation and the GEM flux and temperature, stating we are aware that this is the temperature in the atmosphere, since we unfortunately did not measure the snow temperature. We have changed the text in the discussion so it becomes more clear that the relation between GEM flux and temperature as well as radiation was investigated. Also we now refer more clear to other studies which also found a (reduction/emission???) temperature relation. Furthermore, we have changed the text on page 2 line 30-31 to:

This is most likely due to photoreduction of GOM and subsequent emission of GEM; however, it is also possible that a correlation between solar radiation-induced parameters such as heat flux or temperature change and GEM fluxes exists, making it relevant to look into temperature and heat flux as well as radiation in relation to GEM flux.

In addition, the authors state that "The highest temperatures were found during events with the largest emissions…" (pg. 7, line 32 – 33), but these events have not been explicitly pointed out to the reader using the dates provided in the figures. From the data, I can see three easily observable GEM flux increase events (April 27, 28, 30); however, in one of these three easily observable emission events (April 28) increasing GEM fluxes occur before temperatures begin to increase, and, at least at the beginning of the GEM flux increase event, temperature is actually decreasing, and this is counter to what the authors have stated in their text. As a result, the text should be revised to explain this divergence from what they are stating to be typical behaviour (if more than the three observable events are being invoked).
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We have added a figure (Fig. 9) showing the relation between GEM flux and atmospheric temperature. We found no clear correlation between GEM flux and radiation, but we are aware of the relation. It is true that the relation between GEM and temperature and latent and

sensible heat flux is not straightforward. This is because other parameters are also affecting the size of the flux. This has been written more clearly in the text now.

The authors use an instance of an upward latent heat flux (presumably indicated as a positive number in Fig. 7e?) on April 27 which coincided with a GEM emission event as evidence to support their GEM flux temperature/water dependence hypothesis; however, this increase in LH flux appears to be quite small, and while it does coincide with an increase in GEM flux, other increases in LH flux which appear to be comparable in magnitude (eg/April 25 – 26) did not result in increased GEM fluxes. Further, the second observed increase in GEM flux (April 28) appears to have occurred with no significant change in LH flux, and the largest observed increase in GEM flux (April 30) occurred with a LH flux decrease (negative value) that was much more significant than any of the LH flux increases observed in the data set. At best, it would appear that the data presented by this work appears to neither support nor dispute the hypothesis of temperature dependence of Hg flux based on LH flux information, but it supplies no compelling evidence to support it. If the latent heat flux argument is to be included, other incidents which were counter to the authors' hypothesis must also be discussed in the text, and adequate reasoning provided as to why these do not give evidence to disprove the proposed hypothesis.
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The event on April 30 is an extreme event caused by a strong change in the meteorological conditions (possible a front passing) and as we have pointed out in the text this should not be a part of the general analyses. We have tried to make it more clearly in the text.
It is true that many other parameters are influencing the flux and concentration of GEM. We have tried to make this more clear in the result and discussion.

6. *The effects of wind speed on GEM flux*:
The authors state that all large emission events occurred when wind speeds increased (pg. 7 line 10), but it is unclear how wind speed effects and temperature effects are distinguished, or whether the proposed temperature effect on flux (see above) is simply the result of greater wind speeds appearing to coincide with increases in temperature (Fig. 6). With so many variables changing (potentially independently) at the same time, it is not possible to tease apart the relative importance of these on GEM flux by visual observation alone, which is how the proposed relationships appear to have been derived.
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It is true many parameters are affecting the flux and we have tried to show that especially for GEM the temperature is special since we don't see the same relation between CO2 and temperature, however the relation between CO2 and wind speed is the same as for GEM and wind speed.

7. *Conclusions based on flux data trends*:
The authors attempt to determine relationships and draw conclusions regarding the effects of various factors on GEM flux; however, in looking at the data in Fig. 7a, it appears that in most instances, GEM flux is at or very near 0 ng/m3; while this may be a function of the scale being used, there simply does not appear to be adequate data to support strong conclusions, with the data presented, especially with no inclusion of the uncertainty on these data. Further, if the authors plan to make conclusions regarding the dependence of flux on the various factors that they measured, it would be very helpful to have some manner of statistical test to back up these claims, as without them, the invoked trends are neither clear nor compelling. For example, the authors state that depletion events on April 23 – 25 and May 2 – 5 are

followed by GEM emissions; however, while this may be supported by the April 27 increase in GEM flux that is visible in the results, there does not appear to be a significant increase in GEM flux following May 5, until the small (almost apparently negligible) increase in flux on May 7, when GEM concentrations are higher again. With the data as it has been presented, this does not appear to support GEM emission post-AMDE as the authors have proposed (pg. 6 line 21).
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We have changed part of the conclusion and made it more subtle:
The results of this study supports to some extent the general understanding of the AMDE mechanisms where GEM oxidation is followed by deposition of GOM, which is partly reduced to GEM and reemitted into the atmosphere. Furthermore, the data indicates that heating of the snow surface influences formation of GEM and reemission of GEM.

8. *Correlation between CO_2 and GEM*:
The authors state that there is a correlation between CO_2 and GEM, but offer no methods used to determine this. Was this decided based on mathematical/statistical analysis? Simple observation? Is this GEM concentration, or GEM flux? Based on a quick visual inspection of the results in Fig. 7a/b and 7c, there does not appear to be a compelling case for simple visual observation of such a trend. If this conclusion is to be included in the paper, there should be a more thorough investigation of the claim, or the methods used to draw this conclusion should be explicitly stated, at the very least.

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The relation between CO2 and GEM was suggested by the editor. We have now added figure 10, which shows the co2 and GEM flux in relation to wind speed and it by visual observation we see an anti-correlation between the two fluxes. It is explained more careful in the text

9. *Comparison of study results with literature results (pg. 7 lines 19 – 24, pg. 8 line 15 – pg. 9 line 21)*:
Overall, the authors' discussion of their results as compared to other literature results is somewhat difficult to follow, and should be revised for clarity. This portion of the manuscript would benefit from the inclusion of more concrete results and explicit discussion (eg/ pg. 7 line 23 – 24: how can your results being in opposition to those from the Osterwalder study be explained by the difference in location? How is the GEM dynamic different in these studies? eg/pg. 8 line 21: what was your net emission, exactly? What were the values found by the other works that are referenced?), and from complete discussion of one topic before moving on to another to improve flow and comprehensibility (eg/ stability conditions are discussed in more than one place). Overall, as a discussion paper, comparison with other studies should be much clearer, allowing the reader to easily place the present study with those already existing in the literature (does it agree with other studies using similar method or not, and why?), and at present this is not the case. It is further unclear, in some instances, how certain discussions relate to the present study. For example, when discussing stable conditions/GEM build-up (pg. 9, lines 3 – 10), the authors state that strong stratification with a build-up of GEM near the surface will result in violation of a basic assumption for the flux gradient method; was this phenomenon expected in your study, and if so, how did you deal with it? If this violation of a basic assumption for the flux gradient method was not observed in your study, why have you included it here? The discussion section (and comparison to other studies) might also be easier to follow if a better introduction to the chosen technique was included (see specific comment #1).
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We agree that this could be more clear and the discussion has in general been cleaned so it is follows the recommendation of the reviewer.

The phrase opposite concerning Oswalds observations is changed to: "*On the other hand, Osterwalder et al. (2016) observed emission during unstable conditions, a small deposition during stable conditions and deposition during neutral conditions.*"

Regarding the strong stratification and assumptions for different flux measurement techniques, we expect the reader to be familiar with the basics of the different techniques, but see answer to comment 1 where justification for the method is added. To the introduction the following has been added: "*Furthermore, strong stratification violates the assumption of gradient measurements, thus REA is in our opinion the best possible option to measure GEM flux.*"

10. *Results figures/tables*:
For the results figures (Fig. 6 and 7), the markers/scales chosen make it almost impossible to see differences in the data with time, except where those differences are very large. Since the authors are attempting to use such differences in various measurements over time to derive information regarding factors influencing GEM flux, it is imperative that the reader be able to see the differences the authors appear to be speaking of, and at present, this is not true in most cases. In addition, where uncertainty is known (eg/flux uncertainty = 28%, as stated in the manuscript) error bars should be provided for the data in these figures, as it is unclear whether changes (eg/in flux over time) might be statistically significant, or not. Also, certain events (eg/ AMDEs as in pg. 9 line 26 – 27: "…during which several AMDEs were observed.") should be explicitly marked on your data, or the dates you are proposing they have occurred should be present in the text and/or figure captions.
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We agree that this should be more clear. This has been revised accordingly (see previous comments and text).

In the summary table (Table 1, pg 21) the authors give a flux range of 8 – 190 ng m^{-2} min^{-1} for their data set; however, in looking at the results in Fig. 7a, it is apparent that there were some incidents of negative (depositional) flux (April 27), and there are many instances where the flux appears to be zero. As a result, it appears that the flux range given in the table is either incorrect, or some values were excluded, and if they were excluded, a reason should be given for this, as the table is not particularly informative without it.
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There is an error in table 1. The range should be -8.1 to 179.2 ng m-2 min-1. This is now corrected both in the main text and the table.

Technical corrections:
Pg. 1 line 27 – pg. 2 line 2: These two sentences appear to be contradictory, and it is unclear what the authors are attempting to inform the reader of re: atmospheric lifetime of GEM with the given text.
>>>>> **This sentence is now removed since it confuses the reader instead of enlighten.**

Pg. 1 line 29: What do you mean by "…the relaxation time of mercury in the atmosphere…"? Please clarify/revise.

>>>>> **This sentence is removed as part of the sentence above.**

Pg. 2 line 4 – 5: Sentence fragments; consider adding fragment "These atmospheric mercury depletion events…" to the previous sentence.
>>>>> **Changed as suggested, and made into one sentence.**

Pg. 2 line 8 – 9: "Thus, this is a human health…" sentence fragment.
>>>>> **Changed to one sentence.**

Pg. 2 line 13: Consider revising "…concentration decreases during…" to "…concentration decreases due to…"
>>>>> **Changed as suggested.**

Pg. 2 line 18 – 19: "Vertical gradient…" is repeat of the information presented in previous sentence, consider revising.
>>>>> **We agree, and have removed the sentence**

Pg. 2 line 22 – 24: "This is likely due to…" sentence fragment, consider adding to the previous sentence.
>>>>> **Changed as suggested.**

Pg. 2 line 25: affect, not affects.
>>>>> **Changed as suggested.**

Pg. 2 line 30 – 32: "Thus it is likely that a correlation…" this statement is somewhat misleading, as increases in solar radiation lead to increases in GEM production/emission as a result of an increase in Hg^{2+} reduction, which may have nothing to do with heat!
>>>>> **This statement is changed to: *"This is most likely due to photoreduction of GOM and subsequent emission of GEM; however, it is also possible that a correlation between solar radiation-induced parameters such as heat flux or temperature change and GEM fluxes exists, making it relevant to look into temperature and heat flux as well as radiation in relation to GEM flux."***

Pg. 5 line 19: The detection limit you have given is the literature value for the instrumental detection limit, which may be significantly different than your method detection limit. Consider revising to be the method detection limit.
>>>>> **It is specified, and a section on errors has been added, see above.**

Pg. 5 line 25: "EC" is used without definition in the text (provided in the abstract, but should also be included on first use in the main body of the manuscript).
>>>>> **Changed as suggested.**

Pg. 5 line 26 – 28: "The flux of CO_2…" Sentence is confusing, please revise.
>>>>> **The sentence has been rewritten.**

Pg. 6 line 2: Was b derived based on T (presumably temperature?)? If so, this method has not been described.
>>>>> **A sentence has been added.**

Pg. 6 line 7: What is z/L? This is not defined.
>>>>> **A sentence is added.**

Pg. 6 line 26 – 27: “This leads to increased…” Sentence fragment, please revise.
>>>>> **Rephrased as part of revision of section 3.**

Pg. 6 line 31 – pg.7 line 2: “We observed a clear diurnal pattern…” Did you measure incident solar radiation intensity? If so, this data should be included, and if not, how have you arrived at this conclusion/the timing of max and min sunlight?
>>>>> **A reference to figure 9a is added, which shows no correlation between the flux and solar radiation. We think it is redundant to show a graph with the diurnal pattern, as there is no correlation.**

Pg. 7 line 15 – 18: “This could have occurred…” Sentence fragment, please revise.
>>>>> **Rephrased as part of revision of section 3.**

Pg. 7 line 23 – 24: “These differences can be explained…” Sentence fragment, please revise.
>>>>> **It is specified to differences in emission during different stabilities.**

Pg. 8 line 3: “At low temperature (< -20 C) the flux of GEM was near zero.” GEM flux was also near zero in many cases when the temperature was > -20 C; this should be discussed.
>>>>> **It is true that the GEM flux was near zero in many cases, so the sentence is rephrased as there are only fluxes close to zero < -20 C with a reference to fig 9b.**

Pg. 8 line 24 – 25: “This could be due to higher wind speeds…” Sentence fragment, please revise.
>>>>> **The two sentences are combined.**

Pg. 8 line 31 – 34: The two sentences about the Manca et al. (2013) study should be combined, as the second is mostly redundant.
>>>>> **Rephrased as part of revision of section 3.**

Pg. 9 line 14 – 15: “Differences in locations between research sites…” Please state why this is important and/or how this is expected to influence your study with relation to others, as there is no context for this statement at present.
>>>>> The sentence is coupled to the next and rephrased to specify why the differences are important.

Pg. 9 line 15: “Important parameters are…” Sentence fragment, please revise.
>>>>> **Changed with the previous comment.**

Pg. 9 line 29 – 31: I don’t believe you have provided a compelling case to support the given hypothesis, as the manuscript stands.
>>>>> **We hope the changes made in the manuscript are sufficient to support this sentence.**

Pg. 14 Fig. 1: It’s a little bit difficult to find the yellow dot in your figure, consider giving this dot a dark coloured outline to increase visibility where it overlies the white page.
>>>>> **We think that the position is already pointed out in the caption and by visual contrast, so nothing has been changed here.**

Pg. 15 Fig. 2 caption: Should be “indicates”, not “indicate”.
>>>>> **Changed as suggested.**

Pg. 16 Fig. 3 caption: Should be “shows” not “show”.
>>>>> **Changed as suggested.**

Pg. 19/20 figure labels: authors are not consistent with the way they are writing units in the text vs. the figures (eg/ ng/m^3 in text vs. ng m^{-3} in figures).
>>>>> **All cases have been changed, expect z/L that is a normal term in meteorology.**

Pg. 20 Fig. caption: “mol” not “mole”.
>>>>> **Changed as suggested.**

Pg. 21 Table title: Should be “Summary table of…” rather than “Summary table over…”
>>>>> **Changed as suggested.**

Interactive comment on “Fluxes of gaseous elemental mercury (GEM) in the High Arctic during atmospheric mercury depletion events (AMDEs)” by Jesper Kamp et al.

Anonymous Referee #3
Received and published: 25 October 2017

[Summary]
This study reports the measurements of gaseous elemental mercury (GEM) fluxes over the snow cover at Station Nord, Greenland, from late April to mid-May. The authors employed a relaxed eddy accumulation (REA) technique, which is new for its application to the determination of GEM fluxes in the snow-covered polar region. They observed occasional, large emissions of elemental mercury from the snow surface, which is speculated to have resulted from the prior deposition of gaseous oxidized mercury (GOM). I believe that the data presented here are valuable additions to the literature obtained by a micro-meteorological technique rarely employed to date for the measurements of mercury fluxes over the snow cover. In particular, it is found that the mercury (re-)emissions from the Arctic snow surface could take place, at least occasionally, at substantially greater rates than reported in earlier field studies using other types of methodology. The authors convey well the description of their methodology in sufficient details and yet quite concisely so that readers can understand the scientific background of the method, the instrumental configuration in the field and the data screening criteria. On the other hand, the quality of presenting results and discussion needs some significant improvement in both the presented contents and language to make this paper more compelling than currently is, hence the rating of “fair” for “Scientific Quality” and “Presentation Quality”. I recommend major revisions before the present work is considered for final publication.

[Major comments]

1. Section 3 (Results and discussion) appears to need a thorough re-writing, as there are vague statements and unclear logical flows quite often. In addition, some of the speculative statements are given to sound as if they were evidenced in the present study. Since there were no measurements of GOM conducted in this study, any discussions related to the involvement of bromine chemistry leading to the oxidation of GEM to GOM and its temperature dependence as well as the deposition of GOM as a source of GEM re-emitted from the surface snow are all no more than speculations based on prior knowledge of AMDEs. In this regard, the illustration in figure 8 is not really based on evidence from this study and therefore should be dropped. On the same ground, the occurrence of very shallow surface inversions that did not reach the height of instruments for the field data acquisition and its connection to the temporal variations of measured GEM concentrations and fluxes remain speculative, although quite plausible. In my opinion, the sentences in section 3 must be composed more clearly to distinguish between facts and speculations. I also suggest the authors to cut back on the amount of speculative discussions and to increase fact-based and/or quantitative arguments such as those suggested below.

>>>>>
>>>>>

Figure 8 has been removed. We have changed figure 7, so it becomes more clear. We have added numbers to Fig. 7 to refer to the events and refers to the numbers in the discussion. Furthermore, we have added an extra figure showing the relation between the fluxes and temperature.
The whole section has been thoroughly revised and rewritten.

2. One of the major findings reported in this study is that the magnitude and rate of GEM (re-)remissions from the springtime Arctic snow surface can be much larger than previously reported. In addition to difference in time and location of measurements from earlier studies, the flux estimation technique employed here is different and more sophisticated. To increase the value of the present work, the authors could elaborate more on discussions related to the technical advantage of the REA method over the aerodynamic gradient method (AGM) and whether the two methods can result in significantly different data approval/rejection characteristics, for example, under windy conditions such as during April 26-30. I suppose that small vertical concentration gradients under the enhanced turbulent mixing render the AGM more or less inaccurate as you approach the limit of instrument accuracy. Is it not possible to perform some quantitative micro-meteorological (mathematical) arguments by estimating vertical scalar (tracer) diffusion coefficients and the GEM concentration gradients between the two hypothetical heights above the ground using the present field data, by which the authors could demonstrate the potential advantage of the REA method under windy conditions? I mean, hypothetically. In other words, had the authors derived the GEM fluxes by AGM instead of (or in addition to) REA, could the results have been largely the same? Such arguments could also help decrease the amount of speculative and qualitative statements in section 3.

>>>>>
>>>>>

We agree that a more detailed argument for choice of measurement method is needed. Therefore following text has been inserted into the manuscript at page 3 line 5:
"*Chamber methods are attractive methods for measuring fluxes because of their low cost and simplicity but suffers from a number of weaknesses. They only capture the flux over a small area, the chamber affects the surface over which the measurement is taken and they can modify physical properties such as light and temperature (Bowling et al., 1998, Fowler et al., 2001). This implies that the measured flux will differ from the natural flux. The AGM is not altering the surface; however, it requires a homogeneous surface several hundred meters upstream the measurement site. Furthermore, it is assumed that the vertical profile is only a product of the vertical turbulent transport; nevertheless fast chemical reactions can affect the profile. The most direct flux measurement technique is the eddy covariance (EC) technique (Buzorius et al., 1998) but close to the surface this technique only works for fast responding monitors (sampling frequency >5 Hz), which is not available for Hg. Therefore, we chose to employ the relaxed eddy accumulation (REA) method (Businger and Oncley, 1990) which is based on EC and the method does not affect the surface. Oncley et al. (1993) reported results with agreement within 20% for EC and REA and a study by Hensen et al. (1996) shows agreement between EC and REA within 10%, a difference that is reported not to be significant because the main error for REA is the determination of the concentration difference.*"

3. Given the orders of magnitude greater re-emission fluxes of GEM than reported previously, the authors should provide a more detailed description of synoptic meteorology during April 26-30 when the episodes of large GEM emissions occurred. Showing a synoptic weather map or two if available and briefly explaining synoptic conditions around the study site (e.g., passage of cyclones) would be great; even greater if such weather maps could be associated with the time series of meteorological data presented in figure 6 and backward trajectories presented in figure 3. The passage of cyclones could also enhance bromine chemistry and hence the production of GOM in the atmospheric boundary layer, potentially serving as a fresh source of oxidized mercury in the

surface snow (e.g., Zhao et al., ACPD, 2017, https://doi.org/10.5194/acp- 2017-427; Toyota et al., ACP, 2014, https://doi.org/10.5194/acp-14-4135-2014); it may be interesting to check with satellite BrO data if the authors can manage within the time frame of manuscript revision.

>>>>>
>>>>>

The event on April 30 is an extreme event caused by a strong change in the meteorological conditions (possible a front passing) and as we have pointed out in the text this should not be a part of the general analyses. We have tried to make it more clearly in the text, thus we do not thing synoptic weather maps for this period is relevant.

[Minor comments]

1. Equation (2): Something seems to be missing in these equations; as currently formulated, $C_{up} = C_{zero\ air}$ and $C_{down} = C_{zero;}$. I guess C_{up} and C_{down} on RHS must be multiplied by $_{up}$ and $_{down}$, respectively. Please double check.
>>>>> **The equation is as it should be.**

2. Throughout section 3, the authors use the term "GOM" to refer to oxidized mercury retained in the snow after its deposition from the atmosphere. It should have been referred to differently, perhaps simply by "oxidized mercury".
>>>>> **We agree, and have changed the use of GOM to oxidized mercury when it is retained in the snow.**

[Technical suggestions]
P1, L29: inexplicit -> uncertain
>>>>> **Sentence removed**

P1, L29: relaxation -> residence
>>>>> **Sentence removed**

P2, L1: the sea -> seawater
>>>>> **Changed as suggested.**

P3, L30: backwards -> backward
>>>>> **Changed as suggested.**

P4, L9: the vertical turbulent flux of transported quantity is
>>>>> **Changed as suggested.**

P4, L23: must be larger than this threshold FOR AIR SAMPLES to be collected.
>>>>> **Changed as suggested.**

P9, L3: strongLY stable
>>>>> **Changed as suggested.**

P10, L6: extant -> of mercury chemistry and transport dynamics
>>>>> **Changed as suggested.**

P16-17, Figure 3: Add (a), (b), (c) and (d) on top of the trajectories maps.
>>>>> **Changed as suggested.**

P18, Figure 4: Add (a) and (b) on top of the trajectory frequency maps.
>>>>> **Changed as suggested.**

P21, Table 1: The range of GEM fluxes reported in the present study should be -8.0 to 190 ng m^{-2} min^{-1}. Also, it seems useful to include the time (season) of data collection for each study.
>>>>> **There is an error in the table, which has been corrected.**

Fluxes of gaseous elemental mercury (GEM) in the High Arctic during atmospheric mercury depletion events (AMDEs)

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Abstract. Measurements of gaseous elemental mercury (GEM) fluxes over snow surfaces using a relaxed eddy accumulation (REA) system are carried out at the High Arctic site Villum Research Station, Station Nord in North Greenland. Simultaneously, CO_2 fluxes are determined using the eddy covariance (EC) technique. The REA system with a dual-inlets and dual-analyzers are used to measure fluxes directly over the snow. The measurements were carried out from April 23 to May 12 during spring 2016, where atmospheric mercury depletion events (AMDEs) took place. The measurements showed a net emission of 8.9 ng m^{-2} min^{-1}, with only a few depositional fluxes, a maximum deposition of 8.1~~0~~ ng m^{-2} min^{-1} and a maximum emission of 179.2~~190~~ ng m^{-2} min^{-1}. The data support the theory that gaseous oxidized mercury (GOM) is deposited during AMDEs followed by formation of GEM on surface snow and is reemitted as GEM shortly after the AMDEs. The measurements also indicate GEM emission is increasing with increasing temperature, supporting that surface heating controls GOM reduction in the surface layer of the snow.

1 Introduction

Mercury (Hg) is a toxic element found in the atmosphere primarily as elemental mercury. Airborne Hg can have several forms: gaseous oxidized mercury (GOM), particulate bound mercury (PBM) or gaseous elemental mercury (GEM). PBM and GOM are removed faster from the atmosphere than GEM and have atmospheric lifetimes on the order of days (Sørensen et al., 2010;Goodsite et al., 2004, 2012;Valente et al., 2007). Thus, GOM and PBM generally deposit near emission sources. The lifetime of GEM, ~~is~~ determined by the reaction between GEM and Br (Goodsite et al., 2012, 2004), ~~and~~ spans from one to two months (Holmes et al., 2006;Sørensen et al., 2010). Thus, GEM can be transported over longer distances to areas with low natural and anthropogenic emissions. GEM concentrations in the Arctic are mainly due to long-range transportation from lower latitude sources (Dastoor et al., 2008;Pandey et al., 2011;Christensen et al., 2004). ~~However, in the Arctic, during polar spring, the lifetime of GEM can be as short as roughly 10 hours (Berg et al., 2013;Steffen et al., 2008;Skov et al., 2004). Furthermore, the oxidation chemistry of Hg^0 is still inexplicit and the relaxation time of mercury in the atmosphere could be longer due to reduction of Hg^{II} in cloud droplets and/or in the sea, e.g. Angot et al. (2016) and Travnikov et al. (2017).~~

In the Arctic, sub-Arctic and Antarctic ~~rapid decrease in GEM concentration in coastal areas has been observed during spring (Ebinghaus et al., 2002;Berg et al., 2013;Skov et al., 2004;Schroeder et al., 1998;Steffen et al., 2008). These~~ atmospheric mercury depletion events (AMDEs) have been observed in coastal areas during spring ~~cause significant Hg deposition in Polar Regions~~ (Steffen et al., 2008;Dastoor et al., 2008) causing significant Hg deposition in Polar Regions (Steffen et al., 2008;Dastoor et al., 2008). During AMDEs, GEM is depleted from the atmosphere by oxidation to GOM (Skov et al., 2004;Toyota et al., 2014), which is then deposited locally due to fast deposition limited only by aerodynamic resistance (Skov et al., 2006). Mercury bio-accumulates in Arctic marine wildlife through the food web~~. Thus,~~ this is a human health concern in Arctic communities due to high mercury exposure through the traditional indigenous diet (AMAP, 2011).~~(AMAP, 2011).~~

Typical Arctic spring conditions such as low temperatures, sunlight and reactive halogens favor AMDEs (Brooks et al., 2006;Steffen et al., 2015;Goodsite et al., 2004, 2012;Berg et al., 2003). In earlier studies (Skov et al., 2004;Schroeder et al., 1998), depletion of ozone during AMDEs revealed a correlation between ozone and GEM concentration. Ozone concentration decreases due to~~during~~ reaction with bromine: $O_3 + Br \rightarrow O_2 + BrO$ (Hausmann and Platt, 1994). Data from Villum Research Station (VRS), Station Nord in North Greenland suggests a mutual reactant responsible for the removal of GEM and ozone that agreed with Br reactions during AMDEs (Skov et al., 2004).

Following AMDEs, elevated concentrations of GEM have been observed (Lalonde et al., 2002;Steffen et al., 2008), and it is suggested that photochemical processes in the snow reduce deposited Hg back to GEM, which is then reemitted into the atmosphere (Ferrari et al., 2004;Lalonde et al., 2002). ~~Vertical gradient measurements and measurements from interstitial air in snow indicate GEM emission at the snow surface (Ferrari et al., 2004;Steffen et al., 2002).~~ The reduction to GEM is assumed to take place in the aqueous phase and potentially in particles with significant water content (Steffen et al., 2015).

Knowledge of the dynamics of Hg in snow during AMDEs is important in order to understand the fate of GEM. Studies of Hg in snow evince an increase from February and peak in May (Steffen et al., 2014)~~. This is~~ likely due to the accumulation of deposited GOM, and this finding corresponds well with the peak occurrence of AMDEs in April and May (Steffen et al., 2015). A number of specific conditions and parameters, such as temperature, radiation and chemical composition of the snow affect~~s~~ the dynamics of Hg in the snowpack (Lalonde et al., 2002), but Hg in snow is mainly found in oxidized forms (Steffen et al., 2008).

The dynamics of Hg in snowpack have been studied previously, e.g. by Faïn et al. (2013) who observed complex GEM variations at a mid-latitude site in Colorado, USA. They found that GEM concentration in the top layers of the snowpack increased with increasing solar radiation, suggesting GEM production in the snowpack (Faïn et al., 2013) and that GEM production follows AMDE (Brooks et al., 2006). This is most likely due to photoreduction of GOM and subsequent emission of GEM; however~~Thus~~, it is also possible~~likely~~ that a correlation between solar radiation-induced parameters such as heat flux or temperature change and GEM ~~production and GEM~~ fluxes exists, making it relevant to look into temperature~~, radiation~~ and heat flux as well as radiation in relation to GEM flux.

A recent non-Arctic study with a similar setup to measure GEM flux during snowmelt in Degerö, Sweden revealed diurnal variations of fluxes showing deposition from midnight to noon and emissions from noon to midnight with a mean of 3.0 ± 3.8

ng m^{-2} h^{-1} (Osterwalder et al., 2016). Furthermore, Osterwalder et al. (2016) found significant difference between GEM fluxes during unstable, stable, and neutral conditions with a near-zero flux during stable conditions, emission during unstable conditions and deposition during neutral conditions.

Previous GEM flux studies in the Arctic were mainly performed using chamber methods (e.g. Ferrari et al. (2008)) and the aerodynamic gradient method (AGM) (e.g. (Brooks et al., 2006;Cobbett et al., 2007)). The overview in Table 1 clearly shows the large variations in GEM fluxes found by studies performed in the Arctic. Chamber methods are attractive methods for measuring fluxes because of their low cost and simplicity but they suffer from a number of weaknesses. They only capture the flux over a small area, the chamber affects the surface over which the measurement is taken and they can modify physical properties such as light and temperature (Bowling et al., 1998;Fowler et al., 2001). This implies that the measured flux will differ from the natural flux. The AGM is not altering the surface; however, it requires a homogeneous surface several hundred meters upstream from the measurement site. Furthermore, it is assumed that the vertical profile is only a product of the vertical turbulent transport; nevertheless fast chemical reactions can affect the profile. Strong stratification violates the assumption of gradient measurements, thus REA is in our opinion the best possible option to measure GEM flux. The most direct flux measurement technique is the eddy covariance (EC) technique (Buzorius et al., 1998) but close to the surface this technique only works for fast responding monitors (sampling frequency >5 Hz), which is not available for Hg. Therefore, we chose to employ the relaxed eddy accumulation (REA) method (Businger and Oncley, 1990) which is based on EC and the method does not affect the surface. Oncley et al. (1993) reported results with agreement within 20% for EC and REA and a study by Hensen et al. (1996) shows agreement between EC and REA within 10%, a difference that is reported not to be significant because the main error for REA is the determination of the concentration difference. ~~in the Arctic.~~

The aim of the study presented here is to enhance the understanding of the processes controlling the fluxes of GEM over snow-covered surfaces during the Arctic spring, where AMDEs take place. The relaxed eddy accumulation (REA) method (Businger and Oncley, 1990) is used for the flux measurement in a setup with a dual inlet (Cobos et al., 2002;Osterwalder et al., 2016) and dual detectors. GEM fluxes have been determined with REA previously over agricultural soil (Cobos et al., 2002), in a winter wheat cropland (Sommar et al., 2013;Zhu et al., 2015a), in an urban environment, and in boreal peatland (Osterwalder et al., 2016), but never in the Arctic.

2 Materials and methods

2.1 Measurement site

From April 23 to May 12 of 2016, measurements of GEM flux, CO_2 flux, GEM concentration, wind speed, wind direction, atmospheric stability and temperature were carried out at “Flyger’s hut”, a part of Villum Research Station, Station Nord (VRS). The hut is located 2.5 km southeast of the central complex of the Danish military base Station Nord in North Greenland (81°36’ N, 16°40’ W) (Figure 1). The station is located in the world’s largest national park (Rasch et al., 2015). Flyger’s hut is located at 81°34.90’ N, 16°37.19’ W southeast of Station Nord to minimize influence from local air pollution. The hut has been

used as a monitoring site for the Arctic Monitoring and Assessment Programme (AMAP, 2011), since 1994. At this latitude, the polar day lasts from mid-April to September and the polar night lasts from mid-October until the end of February. The dominant wind directions measured locally are from the southwest, potentially with katabatic winds from the Greenlandic ice cap southwest of Flyger's hut. The wind distribution during the campaign is shown in Figure 2.

At the beginning of the measuring period at the end of April, the snow depth was 1.02-1.03 m. Little precipitation was observed and the snow depth varied between 0.94 m and 1.09 m during the campaign. When we ended the measurements, the depth was 1.00-1.03 m. The changes in snow depth are due to blowing snow or sublimation as the temperature never rose above -1.7℃, with a mean temperature of -16.7℃. Snowmelt did not remove the snow until mid-July.

2.2 Air mass trajectories

To evaluate the origin of the air masses, backward~~s~~ trajectories were calculated using the NOAA HYSPLIT model (Rolph et al., 2017;Stein et al., 2015). Trajectories are calculated every six hours as 24-hour backwards trajectories from a starting point at VRS at 20 meter<u>s</u> above ground level. Four examples of trajectory plots of single trajectories and trajectory frequency are shown in Figures 3 and 4.

2.3 Local meteorological measurements

An ultrasonic anemometer (METEK, uSonic-3 Scientific), installed at 6.40 m above ground level, was used to measure the wind components in x-, y- and z-directions at 10 Hz (see Figure 5). Fifteen-minute averaged values were calculated for wind speed, wind direction, friction velocity, temperature, stability and turbulence intensity.

2.4 Measurement of GEM flux

Atmosphere-surface fluxes of GEM were measured using the REA technique proposed by Businger and Oncley (1990), where the vertical turbulent transported flux is estimated from:

$$F = b\,\sigma_w\left(\overline{c_{up}} - \overline{c_{down}}\right), \quad (1)$$

When applying the REA technique, slower responding sensors can be used<u>, in contrast to the</u> ~~instead of an~~ eddy covariance technique where faster responding sensors are required. In eq. (1), b is a proportionality factor (the Businger coefficient) which can be experimentally determined from sensible heat or another scalar flux; σ_w is the standard deviation of the vertical wind speed; the overbar denotes a mean; and c_{up} and c_{down} are gas concentration in updrafts and downdrafts, respectively. Separation of updrafts (c_{up}) and downdrafts (c_{down}) is obtained by the sonic anemometer and fast shifting valves, which separates the airstream according to the direction of fluctuations in the vertical wind velocity.

The REA technique proposed by Businger and Oncley (1990) uses a constant flow rate accounted for by the addition of the Businger coefficient, discussed extensively elsewhere(e.g. (Gao, 1995;Gronholm et al., 2008;Tsai et al., 2012)). A constant

value for b can be used, but it is preferable to determine b from site to site from other scalars like CO_2 or temperature under the assumption of scalar similarity (Gao, 1995).

Often a wind-controlled "deadband" is introduced to avoid sampling of eddies with a vertical velocity close to zero. A threshold above or below zero indicates this deadband, and the magnitude of the fluctuations of the vertical wind velocity must be larger than this threshold to be collected. This also decreases the switching frequency of the valves by removing many small fluctuations. As a consequence, the deadband will increase the concentration difference between updrafts and downdrafts, hence b is reduced to compensate for the increased difference (Ammann and Meixner, 2002).

The overall system is shown in Figure 5, the system consists of two automated Hg vapor analyzers (Tekran, model 2537X) are used to measure the GEM concentrations in updrafts and downdrafts, respectively. Data from the two Hg analyzers was compiled on a PC inside Flyger's hut. The sampling inlets are located 5.69 m above ground. Osterwalder et al. (2016) and Zhu et al. (2015a)~~Zhu et al. (2015b)~~ describe the advantages of using dual inlets, where temporally synchronous concentration determination of updrafts and downdrafts is the most obvious advantage. The Teflon tubes were heated to 50°C and each tube is connected to a three-way valve, which can either collect sample air or zero air. The zero air was delivered from a zero air generator in excess to the valves when not sampling. A CompactRIO processor (cRIO-9033, National Instruments) sets the position of the valves according to the vertical wind velocity measured with the ultrasonic anemometer. The software LabVIEW (National Instruments) was embedded on the CompactRIO processor with a real time module and a programmable FPGA for high-speed control directly in the hardware. This allowed control of valve positions and collection of data from the ultrasonic anemometer.

The REA system was mounted on a boom on top of Flyger's hut. The boom was placed at the edge of the roof and directed towards the prevailing wind direction in order to minimize flow distortion from the hut.

The standard deviation of the vertical wind speed was obtained from previous wind measurements at Station Nord and used for selection of the deadband range to yield a robust b (Held et al., 2008;Ruppert et al., 2006). Thus, a fixed deadband of $\pm$0.076 m /s~~$^{-1}$~~ is applied to all the data. Correction for dilution according to the opening times of the valves is performed according to (Sommar et al., 2013):

$$C_{up} = \frac{[c_{up} - c_{zero\ air}(1-\alpha_{up})]}{\alpha_{up}} \ and \ C_{down} = \frac{[c_{down} - c_{zero\ air}(1-\alpha_{down})]}{\alpha_{down}}, \quad (2)$$

where c_{up} and c_{down} refers to the GEM concentration in updrafts (c_{up}) or downdrafts (c_{down}); $c_{zero\ air}$ is the GEM concentration in the zero air delivered to the valves. α_{up} and α_{down} refers to the fraction of time where the updrafts (α_{up}) or downdrafts (α_{down}) are collected.

Tekran 2537 models are based on pre-concentration of Hg on gold cartridges followed by thermal desorption in a flow of inert argon gas, and Hg detection by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS). UV light (253.7 nm) excites Hg atoms, which emit the absorbed energy by fluorescence. Collection on gold traps, thermal desorption and CVAFS is an accurate method to measure Hg content in the air. The detection limit is 0.1 ng m^{-3} for the Tekran 2537 (Ma et al., 2015). The sampling

interval is 15 minutes with a flow rate of 1.5 L min^{-1} and auto calibration every 25 hours. Skov et al. (2004) estimate the reproducibility to be within 20% (95% confidence interval) for two Tekran mercury analyzers measuring above 0.5 ng m^{-3}.

2.5 CO_2 flux determination for calculation of b

We determine the proportionality factor b used to calculate fluxes of GEM from CO_2 fluxes assuming fluxes of all gases are transported by the turbulence in a similar way. CO_2 flux can oppose to GEM be measured using the more direct EC method, thus b can be estimated from the measured CO_2 flux and CO_2 concentrations using Eq. 1.

Close to the REA flux system, an enclosed CO_2 gas analyzer (LI-7200, LI-COR Inc.) was mounted on the boom with the inlet directly below the ultrasonic anemometer 6.08 m above ground and above the GEM sample inlets. The gas analyzer measures CO_2 and H_2O concentration at 10 Hz to derive the eddy covariance (EC)~~EC~~ flux of CO_2 and H_2O. The CompactRIO compiles all data from the gas analyzer, valve positions and meteorological data from the REA system. The flux of CO_2 was measured in order to determine b from the EC CO_2 flux and back-calculations of CO_2 concentration in updrafts and downdrafts compared to the valve positions~~in each measuring interval~~ (Gao, 1995;Ruppert et al., 2006). Similarly, b was determined from temperature flux measurements. For each interval, b is used to determine the REA flux of GEM.

Meteorological conditions or parameters, such as temperature, wind direction and speed, heat fluxes, relative humidity, pressure, and water vapor were measured for further analysis of the GEM fluxes. The Monin-Obukhov length (L) was calculated in order to estimate stability, as atmospheric stratification is expected to affect the surface exchange. Stability is often described as z/L, where z is the measurement height. In order to ensure data from a well-developed turbulent flow field and a reasonably constant wind direction, wind speeds below two m s^{-1} were discarded.

For an ideal Gaussian joint probability distribution of the vertical wind speed and the scalar concentration, b has a well-defined value of 0.627 (Wyngaard and Moeng, 1992). However, experimentally determined b's for fluxes of heat, moisture and CO_2 typically range from 0.5~~51~~ to 0.7~~62~~ (e.g. Katul et al. (1996), Ammann and Meixner (2002), Sakabe et al. (2014)).

As mentioned a fixed "dead band" of 0.076 m s^{-1} is introduced. Adding a "dead band" will affect the magnitude of b. In many applications, a dynamic dead band scaled with standard deviation of the vertical velocity w (σ_w) is used, which gives a smaller but relatively constant b (Hansen et al., 2013) according to Eq.3:

$$b = b_0 \exp\frac{-0.75 \cdot \omega_0}{\sigma_w} \quad (3)$$

Where b_0 is b without the dead band and ω_0 is the dynamic dead band. However, for practical reasons (limitation on processing time for data control and data collection) we used a fixed dead band causing a b, which varies with σ_w. The standard deviation of w measured in present study varied between 0.03 and 0.4 m s^{-1}. According to eq. 3, this will cause a variation of b (~ 0.2-0.8) depending on the size of b_0. Several researchers have studied the dependence of b_0 on the atmospheric dimensionless

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stability parameter z/L (L is the Monin-Obukhov length and z is the measurement height, z/L < 0 indicates unstable, z/L >0 stable and z/L= 0 neutral conditions). The majority of the studies (Andreas et al., 1998;Ammann and Meixner, 2002;Sakabe et al., 2014) showed an increase in b_0 with increasing z/L, however for the most part they refer to a limited stability range (-1.5< z/L <1.5). In the high Arctic, we often find very stable as well as neutral and slightly unstable stratification. In order to keep the estimated b values within a well-investigated stability range, data are discarded if they fall out site the stability range (-1.5< z/L <1.5). ~~(Katul et al., 1996)).~~ If b in a given experiment differs too much from the expected value, the probability distribution is likely to differ from the Gaussian distribution, thus in the present experiment, data was discarded in periods where b derived from T or CO_2 was below 0.2 and ~~4 or~~ above 0.8.

~~Meteorological conditions or parameters, such as temperature, wind direction and speed, heat fluxes, relative humidity, pressure, and water vapor were measured for further analysis of the GEM fluxes. The Monin-Obukhov length (L) was calculated in order to estimate stability, as atmospheric stratification is expected to affect the surface exchange. The shape of the theoretical co-spectra (Kaimal et al., 1972), is a function of stability, where the uncertainties are smaller for neutral conditions (z/L ≈ 0). Therefore, data was discarded if z/L was below -1.5 or above 1.5 in order to remove ambiguous data. Furthermore, wind speeds below two m s^{-1} were discarded in order to have a well-developed turbulence flow. After data filtration, 26% of the total 1653 measurements were approved during the campaign.~~

~~The b values are derived from EC and REA flux of CO_2. For each interval, b is used to determine the REA flux of GEM.~~ After data filtration, only 26% of the total 1653 measurements were approved during the campaign. We are aware that this is a very strict filtration; however, this ensures that the data used for the analysis are solid.

Several studies have been dedicated to investigate the implications on the flux related to b (e.g. Andreas et al. (1998), Ruppert et al. (2006) and Sakabe et al. (2014)) and the standard deviation of b is often estimated to be around 10% (e.g. Ammann and Meixner (2002), Sommar et al. (2013) and Zhu et al. (2015a)). However, b is calculated based on measurements of CO_2 fluxes, thus the uncertainty of b must be related to the uncertainty of the measured flux. It is not trivial to estimate the uncertainty of EC fluxes. Finkelstein and Sims (2001) suggested to use direct calculation of the variance of the covariance for calculating the random sampling error in EC measurements. They tested measurements at several types of surfaces and found the relative error to be approximately 25-30% for trace gas fluxes. However, one could argue that this method is only revealing how constant the flux measurement is and not how accurate the measured flux is. A more correct way to estimate the error is to measure the flux in parallel towers (Post et al., 2015). This is very expensive and very rarely carried out. Hence, here we use the general relative standard deviation of CO_2 fluxes on 25-30% estimated by Finkelstein and Sims (2001). Using error propagation theory on eq.1 the uncertainty of b (u_b) can be estimated as the combined relative uncertainty of the measured flux (25%) and the relative uncertainty of the measured concentration of CO_2 (1% (Li-Cor)) from following equation:

$$u_b(y) = \sqrt{\sum_{i=1}^{n} u(x_i)^2} \quad (4)$$

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Where $u(x_i)$ is the standard uncertainty. The uncertainty of b is ≈ 25%. To estimate the total uncertainty of the GEM flux we also have to consider the uncertainty of the measurements of the GEM concentration. This was found to be 10% by Skov et al. 2004, which used same type of instrument for GEM measurements. The uncertainty of the GEM flux can now be determined from the combined uncertainty of the concentration measurements and uncertainty of the estimated b: $\sqrt{0.1^2 + 0.1^2 + 0.25^2} \approx 0.30$ and the uncertainty of the flux becomes ≈ 60% at 95% confidence level.

~~This correction is anchored in statistical assumptions of zero mean of the fluctuations from EC. We estimate that the uncertainty of b is << 10% and is thus assumed to be insignificant. Hence, the flux estimate is determined from the uncertainty of the two concentration determinations $\sqrt{0.1^2 + 0.1^2} = 0.14$ and the uncertainty of the flux becomes 28% at a 95% confidence interval. The uncertainty of the GEM concentrations is 10% above 0.5 ng m^{-3} (Skov et al., 2004).~~

3 Results and discussion

Fluxes of GEM and GEM concentrations are shown in Figures 8a~~7a~~ and 8b~~7b~~. Principally, we found GEM emission (positive fluxes) and a net mean emission of 8.9 ng m^{-2} min^{-1} over the 20 days. The largest measured deposition (negative flux) was 8.0 ng m^{-2} min^{-1}, whereas the largest emission was 190.0 ng m^{-2} min^{-1}. As expected the large emission events were connected to increased wind speed, while increased wind speeds causes an increase in turbulence transport (Figure 9).

A rapid increase in GEM flux was found on April 30. Simultaneously, the pressure dropped rapidly from 1032 hPa to 1013 hPa and increased again to about 1025 hPa. During this abrupt pressure drop, latent and sensible heat fluxes decreased rapidly (Figure 7) and the temperature increased from about -18°C up to -4°C before decreasing to -13°C again. Wind speed reached its maximum-recorded speed for the duration of the campaign during this event. At the same time, stability changed from unstable to stable conditions. The observations above indicate that this sudden increase in GEM flux is most likely explained by a front passing with a sudden change in meteorological conditions and changes in wind flow. We will consider this special case as an outlier. The meteorological parameters are shown in Figure 6.

The measurements were started when depletion was already present and, as seen in Figure 8a~~7a~~ and Figure 8b~~7b~~, depletion (low GEM concentration during April 23-25 (AMDE 1) and May 2-5 (AMDE 2))~~)~~ was followed by GEM emission as observed by Brooks et al. (2006), supporting that GEM is reemitted after AMDEs. The results correspond to the general understanding that GEM is initially removed rapidly from the atmosphere.~~.~~ This removal is most likely due to photolytic oxidation to oxidized mercury~~GOM~~, which, contrary to GEM, has a very low surface resistance (Skov et al., 2006) and thus deposits relatively quickly. It is generally accepted that GEM production in snow is the result of a photochemical reduction of oxidized mercury to produce GEM. Thus, ~~After deposition,~~ we at first hypothesized~~speculate~~ that oxidized mercury~~GOM~~ is reduced photolytically to GEM in the surface snow followed by reemission. However, Ferrari~~In accordance with earlier observations, this implies that a predominant fraction of the downward flux of Hg is in the form of GOM during AMDEs (Skov~~ et al. (2005) found that production of GEM is linked to the snow temperature and according to Steffen et al. (2015), the photochemical reduction of oxidized mercury in snow – and thus the reemission of GEM – is temperature dependent. Therefore, an increase

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in temperature could lead~~2006, Brooks et al. 2006). GOM is reduced at the snow surface when the temperature increases (Ferrari et al., 2008). This leads~~ to increased reemission of GEM causing the concentration of GEM in the atmosphere to ~~again~~ increase. At the present study, the largest emissions were found during events~~This observation is in agreement~~ with the highest temperatures, as seen in Figures 9b. The same behavior is not found for CO_2 flux (Figure 9c),~~observations from Barrow, Alaska (Skov et al. 2006, Brooks et al. 2006)~~ where the~~GOM~~ fluxes are independent of temperature, but does correlate~~were measured together~~ with the wind speed (Figure 10) ~~gradients of GEM~~ and stability, thus we argue that the temperature is a possible driver for the GEM emissions presented here.

At low temperature (< -20 ℃) only fluxes of GEM close to zero were present, see Figure 9b~~ozone.~~. Low temperatures are required for the occurrence of AMDE (< -4 ℃) (Lindberg et al., 2002;Skov et al., 2004), at which point GEM is oxidized to GOM. This indicates that GEM is so easily oxidized to GOM at lower temperatures (< -20 ℃) that GEM falls below the detection limit. Ozone and GEM depletion are correlated during AMDEs possibly due to reactions mainly with Br, and low temperatures favor the reaction between Br and GEM (Goodsite et al., 2004, 2012;Skov et al., 2004;Schroeder et al., 1998). Furthermore, oxidized mercury species are water-soluble, hence it is assumed that reduction of deposited Hg takes place in the water phase (Steffen et al., 2015), which is followed by emission of the more volatile GEM. It is possible that the temperature dependence observed here is due to an increased water content in the snowpack. Heating of the surface (i.e. downward sensible heat flux) and upward latent heat flux (evaporation) occurred on April 27 during the first larger GEM emission event (Event1), supporting the temperature- and water- dependency hypothesis. Similarly, in the sub-arctic Dommergue et al. (2003) showed that melting snow emits more GEM than at lower snow temperatures. Unfortunately, we did not measure temperature or humidity in the snow, to support the hypothesis.

However, a part of the increase in the concentration of GEM can also be explained by long-range transportation. Trajectory calculations of air mass transport show downward mixing from higher elevations (Figure 3a), but in order to obtain an upward surface flux, the concentration in the snow must be higher than in the atmosphere. We observed a clear diurnal pattern for the radiation intensity with the maximum at noon and the minimum at midnight, but these diurnal variations seem not to influence the GEM flux or concentration directly, see Figure 9a.

~~The The rapid increase in GEM flux on April 30 was a unique situation. At that time, the pressure dropped suddenly from 1032 hPa to 1013 hPa and increased again to about 1025 hPa. During this abrupt GEM emission event, latent and sensible heat fluxes decreased rapidly and the temperature increased from about -18℃ up to -4℃ before decreasing to -13℃ again. Wind speed reached its maximum recorded speed for the duration of the campaign during this peak in the GEM flux. At the same time, stability changed from unstable to stable conditions. The observations above indicate that this sudden increase in GEM flux is most likely explained by a sudden change in meteorological conditions and changes in wind flow. All the meteorological parameters are shown in Figure 6a-e and the GEM flux in Figure 7a.~~

~~It is clear from Figures 6a and 7a, that all large emission events were connected to increased wind speed as would be expected. Increased wind speeds cause a rise in turbulence transport, which leads to increased vertical turbulence flux. The~~ GEM emission on April 28 (event 2) was followed by an increase in GEM concentration on April 29. This~~, which~~ occurred as the

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stability rapidly changed from stable (z/L> 0) to unstable (z/L< 0) conditions. The day prior to~~before~~ this event, the GEM concentration was relatively constant~~stable at~~ around 1 ng m^{-3} and increased threefold as the stratification ~~stability~~ changed from stable condition to unstable.~~.~~ According to trajectory calculations, this sudden increase was not caused by mixing from aloft (Figure 3b). However,~~This could have occurred as~~ a formation~~result~~ of an extremely stratified surface layer directly above the ground could be formed, and we speculate that~~where~~ GEM concentration might build~~builds~~ up in this layer directly over the snow surface. This~~, but the~~ buildup concentration would~~is~~ not be detected until the layer at the surface is mixed to a higher elevation when the stratification becomes unstable. This is just a hypothesis, however, if this is a general pattern for very stable conditions, this can be an important effect, which needs to be considered in future measurements of Hg concentrations in the high Arctic.~~Thus, the atmospheric stability might have significant influence on GEM concentration measurements during AMDEs, causing concentration fluctuations to be falsely interpreted as outliers.~~ According to Osterwalder et al. (2016), GEM REA fluxes were significantly different under stable, unstable and neutral conditions over a snow-covered surface. In the present study, GEM was primarily emitted under neutral and slightly stable conditions, and fluxes close to zero were observed under unstable and neutral conditions. On the other hand, ~~The opposite is observed by~~ Osterwalder et al. (2016) observed~~with~~ emission during unstable conditions, a small deposition during stable conditions and deposition during neutral conditions. The~~se~~ differences in emission during certain stabilities can be explained by a non-Arctic location and a very different dynamic of GEM.

On May 6-7~~5~~, a change from stable to unstable conditions occurred simultaneously with an increase in concentration, which could also be explained by inversion of the surface layer as described above. The concentration increase was not as rapid or as large as the previous event, but there was almost no GEM emission in the days leading up to it. The lack of GEM emission~~, which~~ could be explained by the observation that only a small concentration of GEM was build up before the surface layer was inverted. The concentration increase cannot be explained by a mixing from aloft as~~because~~ the trajectory calculations show a constant air mass transport pattern from May 3 to May 6 (Figures 3c and 3d), which should preclude such an event. If a "build up" or "storage" effect exists, the flux measurements are also affected, and evaluation of flux data becomes even more complicated.

~~According to Steffen et al. (2015), the photochemical reduction of GOM in snow and thus the reemission of GEM is temperature dependent. The highest temperatures were found during events with the largest emissions, as seen in Figures 6b and 7a. This behavior is not found for CO_2 flux, where the fluxes are independent of temperature but does correlate with wind and stability, thus we argue that stability and wind variations can be ruled out as the causes of the changes in GEM emissions presented here. Apparently, there is some correlation between CO_2 and GEM, but the reason for this correlation is unknown and we speculate that chemical reactions or bacterial activity in the snow could be partially responsible for this result; further research regarding this is needed. At low temperature (< -20 °C) the flux of GEM was near zero. Low temperatures are required for the occurrence of AMDE (< -4 °C) (Lindberg et al., 2002;Skov et al., 2004), at which point GEM is oxidized to GOM. This indicates that GEM is so easily oxidized to GOM at lower temperatures (< -20 °C) that GEM falls below detection limit. Ozone and GEM depletion are correlated during AMDEs possibly due to reactions with Br, and low temperatures favor the reaction~~

between Br and Hg^0 (Goodsite et al., 2004, 2012;Skov et al., 2004;Schroeder et al., 1998). Further, Hg(II) are water-soluble, hence it is assumed that reduction of deposited Hg takes place in the water phase (Steffen et al., 2015), which is followed by emission of the more volatile GEM. It is possible that the temperature dependence observed here is due to increased water content in the snowpack. Heating of the surface (i.e. downward sensible heat flux) and upward latent heat flux occurred on April 27 during the first larger GEM emission event, supporting the temperature- and water- dependency hypothesis. The temperature dependence of GEM during AMDEs is illustrated in Figure 8. Similarly, in the sub-arctic Dommergue et al. (2003) showed that melting snow emits more GEM than at lower snow temperatures.We observe some (anti)correlation between CO_2 and GEM from Figure 10. The correlation can be a result of the common correlation to wind speed, however, we speculate if chemical reactions or bacterial activity in the snow also could be part of the explanation of a correlation between the two fluxes; further research regarding this is needed.

In the following paragraphs, we compare our results with results found in other studies. We do not compare to studies using chambers since this is a very different approach.

Chamber measurements are enclosure methods, and therefore run the risk of potentially changing temperature, humidity, radiation, etc. (Fowler et al., 2001), furthermore chambers "capture" the exchange with the surface over a very small limited area.. Micrometeorological methods, such as REA and AGM, are non-invasive, and are thus more appropriate for comparing the results of the present study with other non-invasive methods.

Our findings do not agree with Cobbett et al. (2007) and Manca et al. (2013), as we found a few negative fluxes of GEM and a large net emission of GEM during the campaign despite the potential for long-range transported GEM between April 25 and April 28. However, Brooks et al. (2006) report a small reemission of GEM with a net gain of mercury in the snow over a two-week period during March-April 2003 at Barrow, Alaska. A net emission of GEM was found in the present study, as well as in those conducted by Brooks et al. (2006) and Steen et al. (2009), but the net GEM flux evident in the present study is much higher than others have observed. A study by Ferrari et al. (2004) was performed at the same location as the present study, but the range of the fluxes found waswere more than three orders of magnitude lower than presented here, maybe. This could be due to higher wind speeds and concentration levels during the present study. Despite the difference in magnitudes of fluxes, GEM depletion was observed in all three studies. Brooks et al. (2006) estimated the GOM flux from surface resistance models based on results in Skov et al. (2006), while gradient measurements were used to estimate the GEM flux, thus the difference in the estimated fluxes can also be explained by differences in the methods used. Measurements by Cobbett et al. (2007) from April to June in Alert, Canada showed zero net flux. The most significant fluxes observed during polar day were found in early June when and where the soil was visible, which was never the case during the present study's campaign. Manca et al. (2013) found a net deposition at Ny Ålesund, Svalbard from April to May with significant depositions and emissions, which can be explained by the location, since Ny Ålesund is located at open seawater and thus it is not expected that any local AMDEs would take place because AMDEs are related to sea ice and snow surfaces. The measurements by Manca et al. (2013) were carried out over a snow-covered surface, but the processes involved were different due to the location at open water. During

the present study, the air masses recorded derived mainly from sea ice during the depletion events (Figures 4a and 4b) in spite of the local SW winds.

As mentioned earlier, we speculate that strongly stable conditions can result in GEM buildup directly above the surface, similar to CO_2 storage over forested sites (Yang et al., 2007). Surface emission of GEM into a relatively shallow layer of air will result in its higher concentration close to the ground. If the measurement height is above the "ground surface layer" the measured flux will increase when the stability changes and mix the air directly above the surface to higher elevations. Brooks et al. (2006), Cobbett et al. (2007) and Manca et al. (2013) all used the flux gradient method to determine GEM flux, and the different results obtained could be due to the flux measurement techniques used. Using the gradient method, flux is estimated from concentration measurements at different heights. Strong stratification with GEM buildup near the surface will likely result in a non-constant flux layer, violating a basic assumption for the flux gradient method.

The study sites in the present study and in the studies by Brooks et al. (2006), Cobbett et al. (2007) and Manca et al. (2013) differ significantly in terms of orography and meteorology, which have an effect on the fluxes. Theoretical studies by (Goodsite et al., 2012, 2004)~~Theoretical studies by Goodsite et al. (2004) and Goodsite et al. (2012)~~ show that GEM removal is driven by chemical reaction with Br and increases with decreasing temperature. The differences~~Differences~~ in locations, orography and meteorology between research sites ~~undoubtedly~~ affect the concentrations of GEM, because~~. Important~~ parameters such as~~are e.g.~~ temperature, Br concentration and origin of air masses are different for the sites.~~.~~ The wind direction in the present study was primarily from SW, caused by katabatic winds from the local Flade Isblink ice sheet~~glacier~~; however this is merely the source of the local wind and most air masses in the study area overall are derived from sea-ice covered surfaces according to the trajectory calculations (see Figures 3 and 4). As mentioned, atmospheric stability influences the observed GEM fluxes (Osterwalder et al., 2016) and different stability conditions between sites could explain the differences in fluxes found by Cobbett et al. (2007) and Manca et al. (2013). Overall, our results suggest that variations in GEM concentrations and fluxes are much more variable than previously assumed.

4 Conclusion

Mercury is primarily transported in the atmosphere in the form of GEM and it is ubiquitous in the atmosphere. Fluxes of GEM have been measured at Villum Research Station, Station Nord, in the high Arctic of north Greenland over snow-covered surfaces from April 23 to May 12, 2016 with a REA system utilizing dual inlets and dual detectors.

This work showed an average GEM emission of 8.9 ng m^{-2} min^{-1} during the 20-day research campaign, during which several AMDEs were observed. A maximum deposition of 8.0 ng m^{-2} min^{-1} and a maximum emission of 190 ng m^{-2} min^{-1} were recorded. The results of this study support to some extent the general understanding of the AMDE mechanisms where GEM oxidation is followed by deposition of GOM, which is partly reduced to GEM and reemitted into the atmosphere. Furthermore, the data indicate~~supports the hypothesis~~ that ~~temperature (~~heating of the snow surface influences ~~) and water present in the snow is influencing GEM~~ formation of GEM and reemission of GEM~~after depletion~~.

The observed fluxes and concentrations are related to meteorological conditions and comparing concentrations and fluxes found at other high-latitude sites reveals wide variation between sites. However, these comparisons imply that GEM fluxes and concentrations can be rather heterogeneously dispersed in the Arctic atmosphere due to the complex meteorological flows and stratification.

Further studies on this heterogeneity, including potential inversion at the surface and mixing from aloft, are needed, as are studies of fluxes of both GEM and GOM adjacent with measurements of the energy budget and controlling parameters extant in snow pack.

Competing interests

The authors declare that they have no conflict of interest.

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Figures and tables

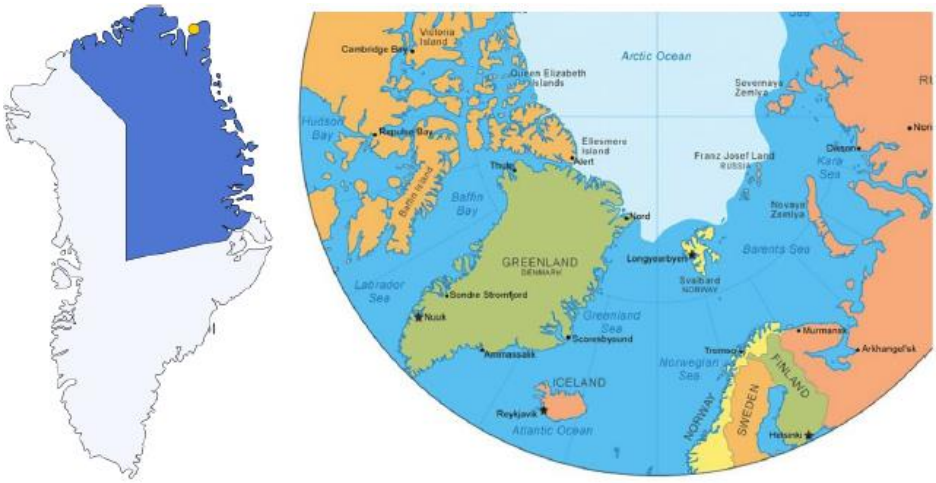


Figure 1: Left: Greenland with indication of the largest Natural Reserve in the world (blue) and the position of Station Nord (yellow dot). Right: The northern hemisphere where Station Nord (Nord) also can be seen.

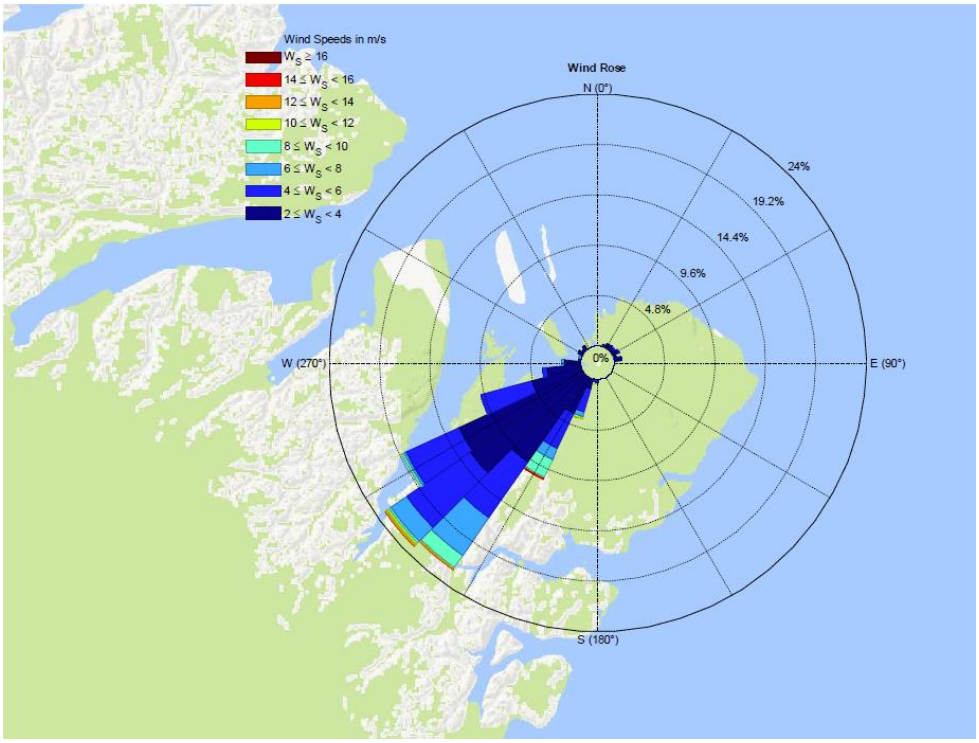
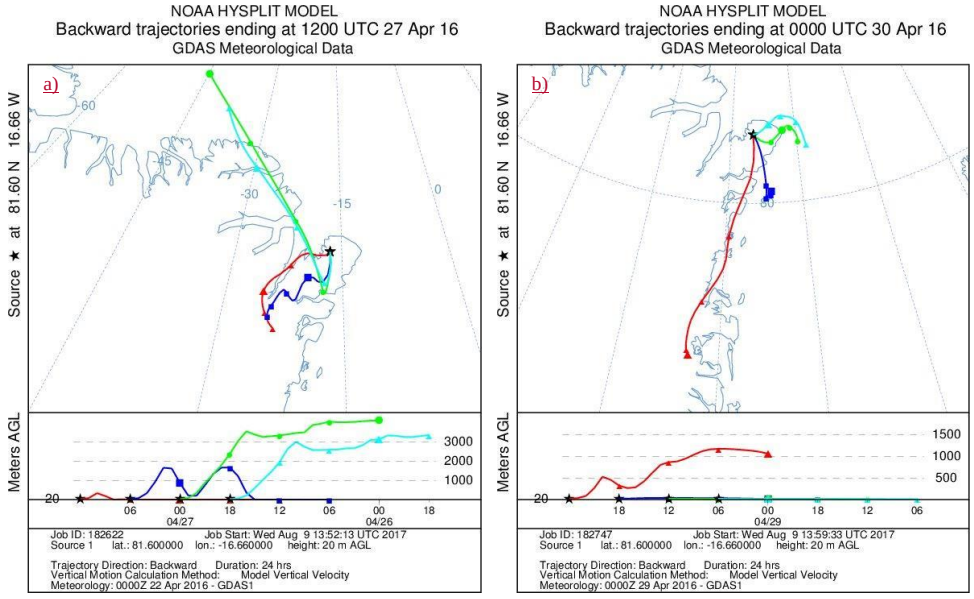


Figure 2: Wind rose centered at Villum Research Station, Station Nord. Length of the bars indicate frequency of the direction and color indicate the wind speed. Units in m s^{-1}.



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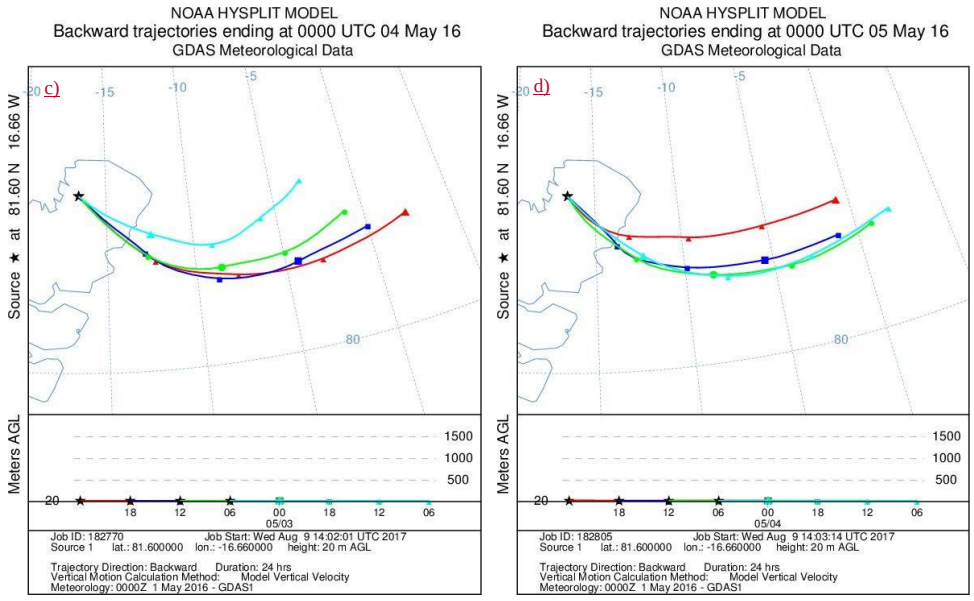

Figure 3: Backward trajectories for four different days showing the origin of the air masses. All trajectories are 24-hour calculations and each figure show a new trajectory for every 6 hour backward. a) Starting~~a) Top left panel, starting~~ April 27, 12:00. b) Starting~~Top right panel, starting~~ April 30, 00:00. c) Starting~~Bottom left panel, starting~~ May 4, 00:00. d) Starting~~Bottom right panel, starting~~ May 5, 00:00.

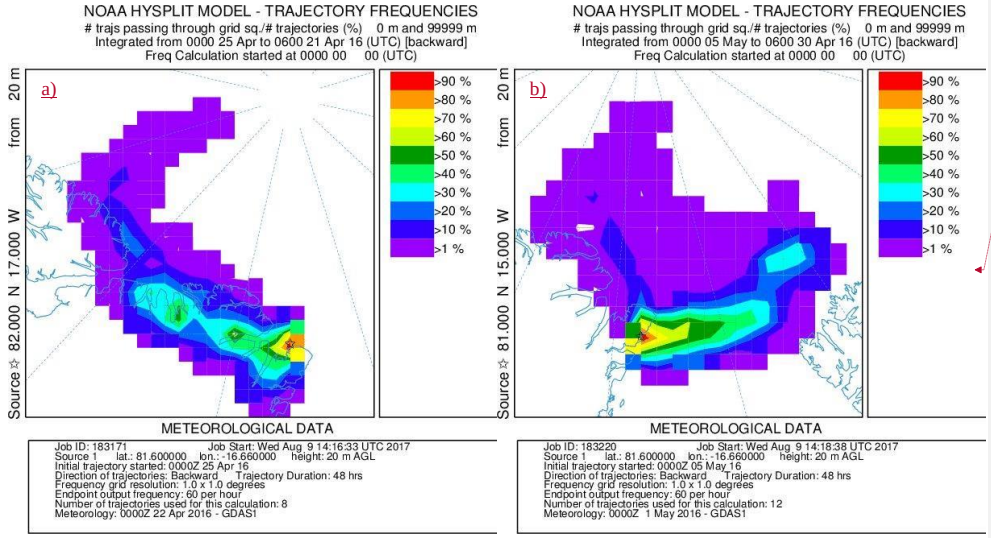

Figure 4: Trajectory frequencies showing the number of trajectories passing through a grid. The resolution is 1 degree. a) ~~Left panel,~~ April 21 to April 25. b) ~~Right panel,~~ April 30 to May 5.

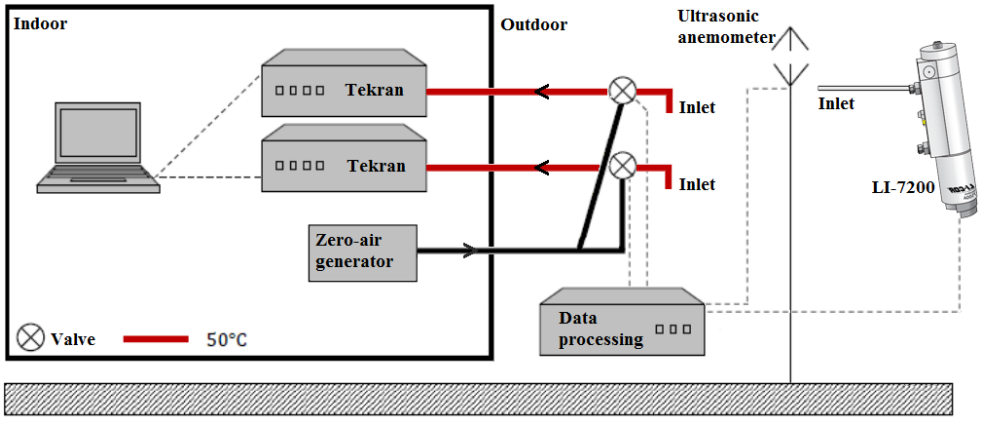

Figure 5: A Schematic representation of the GEM REA system.

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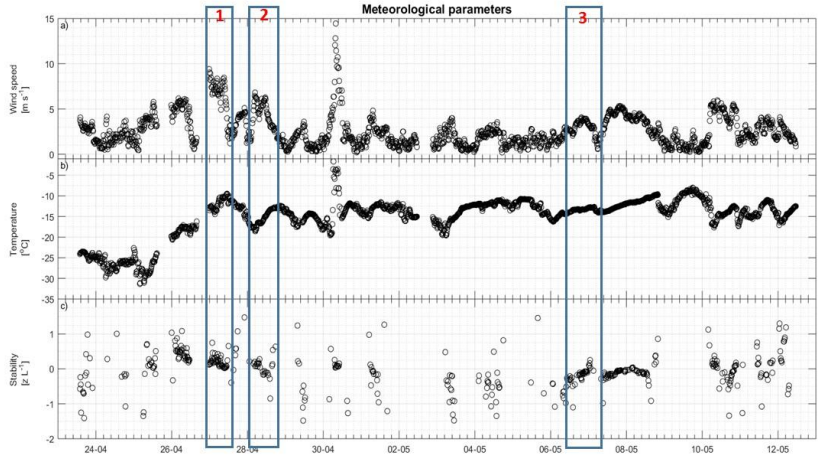

Meteorological parameters
1
2
3
a)
b)
c)
Wind speed [m s⁻¹]
Temperature [°C]
Stability [z L⁻¹]
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
1
0
-1
-2
24-04
26-04
28-04
30-04
02-05
04-05
06-05
08-05
10-05
12-05

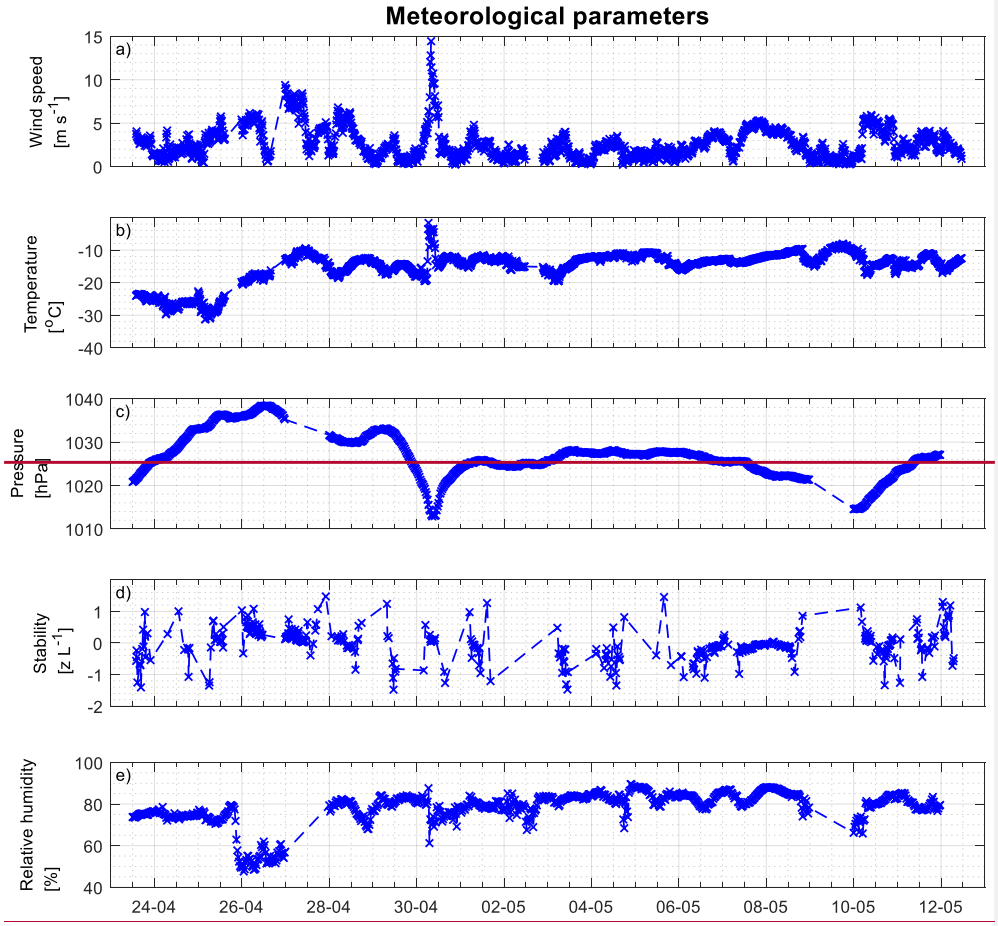
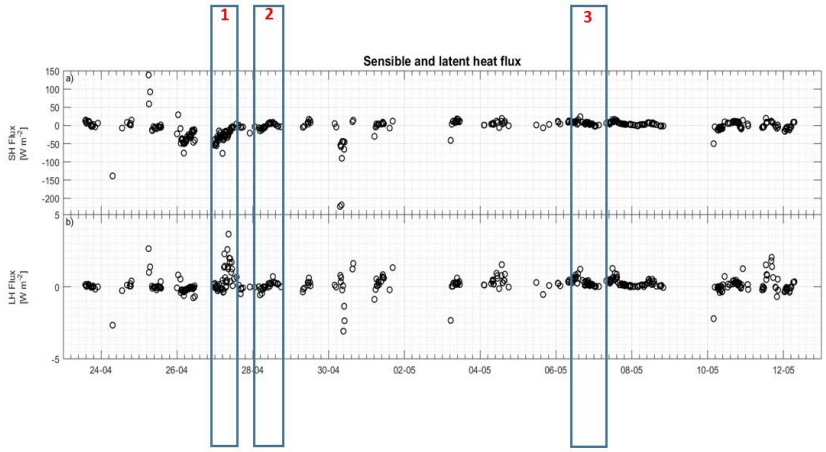


Figure 6: Meteorological parameters over time with three events highlighted. a) Wind speed in m s^{-1}, b) Temperature in °C, and c) Pressure in hPa, d) Stability as z/L, and e) Relative humidity in %.


1
2
3
Sensible and latent heat flux
a)
b)
SH Flux [W m-2]
LH Flux [W m-2]
150
100
50
0
-50
-100
-150
-200
5
0
-5
24-04
26-04
28-04
30-04
02-05
04-05
06-05
08-05
10-05
12-05

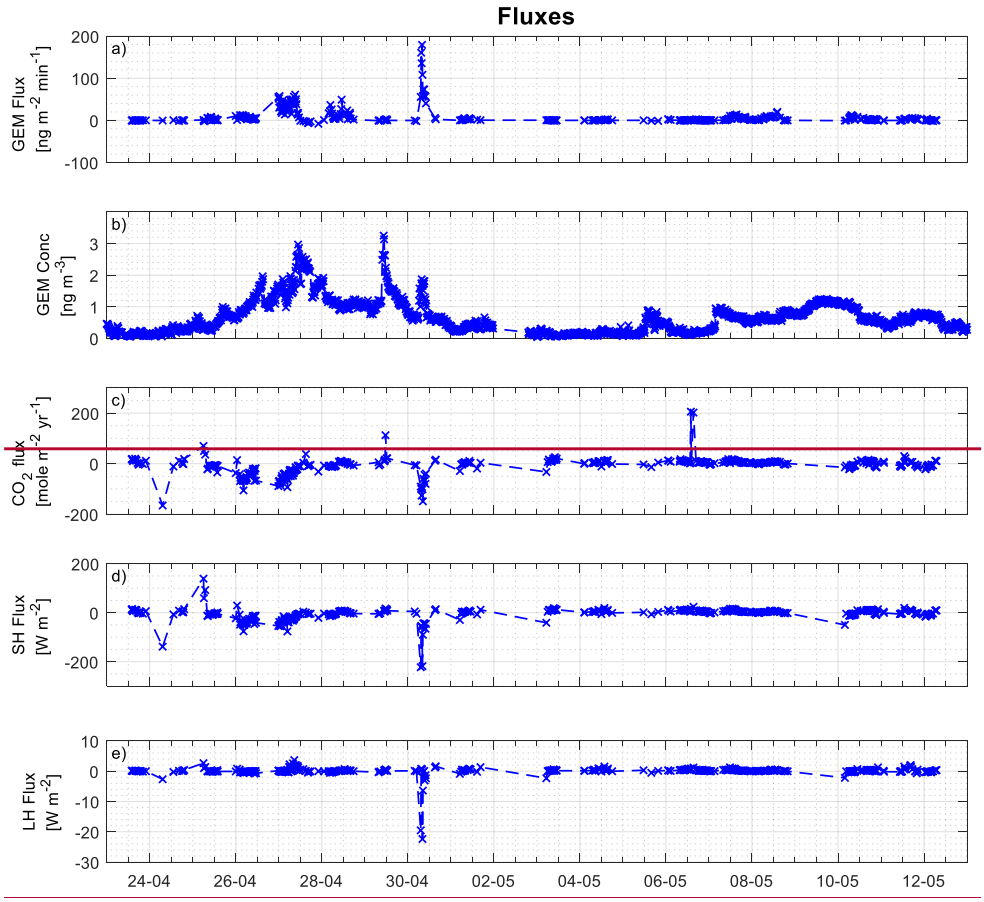
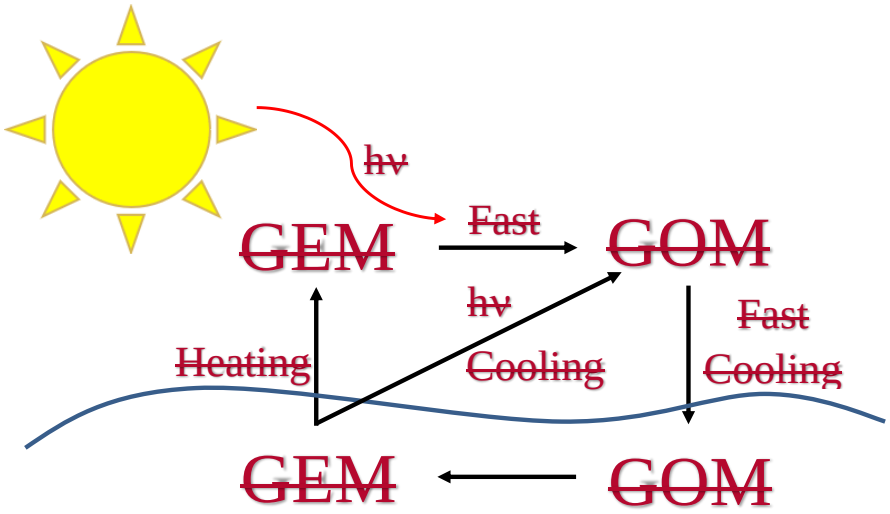


Figure 7: ~~**Fluxes and GEM concentration over time. a) GEM flux in ng m^{-2} min^{-1}, b) GEM concentration in ng m^{-3}, c) CO_2 flux in mole m^{-2} yr^{-1}, d)**~~ **Sensible and latent heat flux in panel a) and b), respectively. Both are measured in W m^{-2} and three events are highlighted**~~**, e) Latent heat flux in W m^{-2}**~~**.**


hv
GEM
Fast
GOM
hv
Fast
Heating
Cooling
Cooling
GEM
GOM

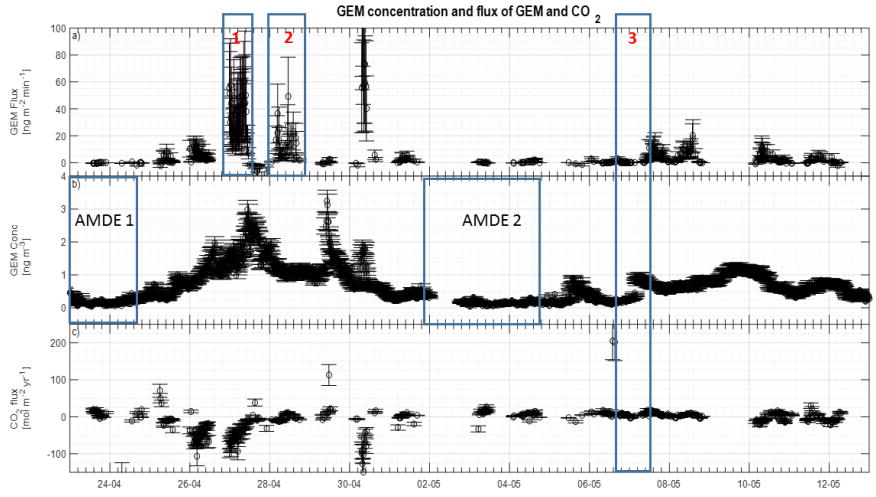

GEM concentration and flux of GEM and CO 2
a)
b)
c)
1
2
3
AMDE 1
AMDE 2
GEM Flux (ng m-2 min-1)
GEM Conc (ng m-3)
CO2 flux (mol m-2 yr-1)
24-04
26-04
28-04
30-04
02-05
04-05
06-05
08-05
10-05
12-05

Figure 8: ~~Schematic of possible pathways for~~ **GEM** concentration **and** fluxes of CO_2 and GEM over time. a) GEM flux in ng m^{-2} min^{-1}, b) GEM concentration in ng m^{-3}, and c) CO_2 flux in mol m^{-2} yr^{-1}. Three events and two~~GOM during~~ **AMDEs** are highlighted.

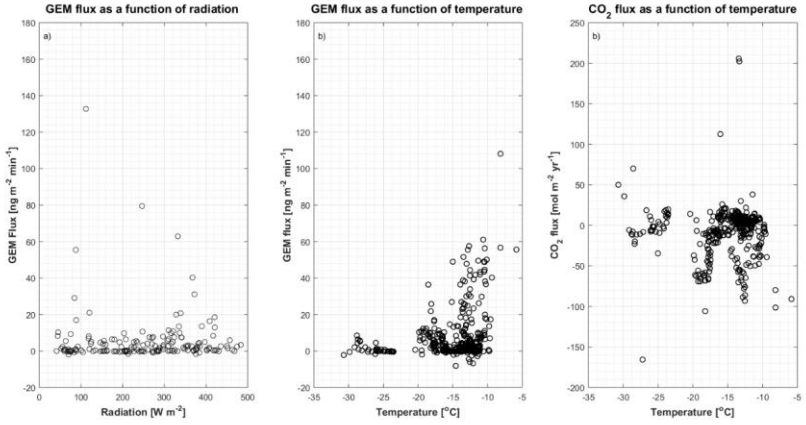


Figure 9: Correlation between GEM and CO_2 flux and temperature. a) GEM flux in ng m^{-2} min^{-1} as a function of solar radiation, b) GEM flux in ng m^{-2} min^{-1} as a function of temperature, and c) CO_2 flux in mol m^{-2} yr^{-1} as a function of temperature.

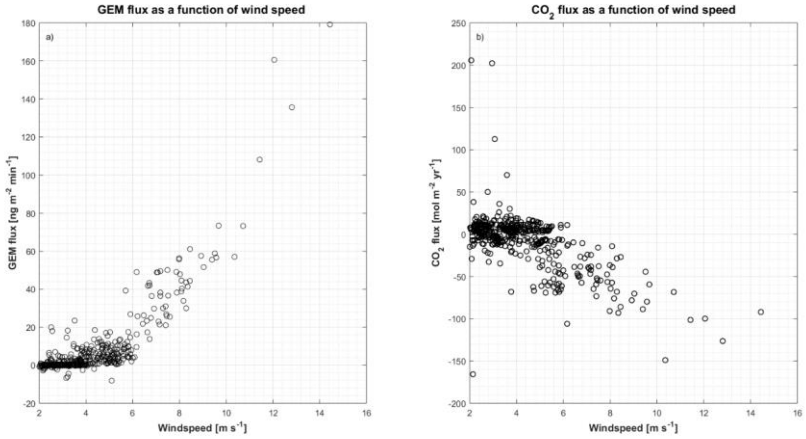


Figure 10: Correlation between GEM and CO_2 flux and wind speed. a) GEM flux in ng m^{-2} min^{-1} as a function of wind speed, and b) CO_2 flux in mol m^{-2} yr^{-1} as a function of wind speed.

Table 1: Summary table over reported GEM fluxes in the Arctic. The units are changed from those within the references for better comparison.

Flux	Site	Method	Reference
Mean: 8.9 ng m^{-2} min^{-1} Range: -8.1-179.2~~0 190~~ ng m^{-2} min^{-1}	Villum Research Station, Station Nord, Greenland	Relaxed eddy accumulation	Present study
Mean: 0.050 ng m^{-2} min^{-1} (in reference: 1.0 µg m^{-2} 14 $days^{-1}$)	Barrow, Alaska	Flux gradient method	Brooks et al. (2006)
Mean: -0.60 ng m^{-2} min^{-1}	Alert, Canada	Flux gradient method	Cobbett et al. (2007)
Mean: -0.004 ng m^{-2} min^{-1}	Ny Ålesund, Svalbard	Flux gradient method	Manca et al. (2013)
Median: 0.12 ng m^{-2} min^{-1}	Ny Ålesund, Svalbard	Flux gradient method	Steen et al. (2009)
Range: 0.001-0.007 ng m^{-2} min^{-1}	Station Nord, Greenland	Flux gradient method	Ferrari et al. (2004)
Range: 0-0.8 ng m^{-2} min^{-1}	Ny Ålesund, Svaldbard	Flux chamber	Ferrari et al. (2005)
Max: 0.58 ng m^{-2} min^{-1}	Ny Ålesund, Svalbard	Flux chamber	Ferrari et al. (2008)
Mean: 0.13 ng m^{-2} min^{-1}	Ny Ålesund, Svalbard	Flux chamber	Sommar et al. (2007)

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