Autor response to Reviewer Comments

We would like to thank again the five reviewers and the editor for their positive feedback and for handling this manuscript in a very constructive and efficient way. Below are the author response to Reviewer comments 1-5, where the reviewers comments are in normal black font **and the author response are in blue bold font.** The second part of this document contains the manuscript text where all the changes made during the revision are marked in red.

Reviewer #1

The manuscript is well writen, exemplarily concise and of high scientific quality. One problem is, however, that the data presented already to some degree been published in Obrist et al. (2017) doi: 10.1038/nature22997.
The present manuscript refers to this Nature paper more than 20 times, which hampering a throughout reading obtaining comprehensive informaton from text, tables and figures.

We thank the reviewer for his positive assessment and the constructive comments.

The Hg0 flux dataset is the same as presented in Obrist et al. 2017. The 2017 Obrist study focused on a mass balance of Hg input vs. output in the tundra ecosystem. In this context Hg0 fluxes were presented as cumulative fluxes and Hg stable isotopes were used as source tracers. In the 2500 word letter format of Obrist et al 2017 we had to be very concise and could not discuss individual features in the dataset. In this study we re-visit the flux dataset and discuss for first time diurnal variations in fluxes and how they impact atmospheric concentrations. We also present for the first time Hg0 isotope data of interstitial snow and soil air, which was not presented in Obrist et al.

Based on this reviewers comment as well as other reviewers comments we will provide a clearer definition of the objectives of this study in the revised manuscript to highlight the added value of this paper compared to the Obrist et al 2017 paper as follows: “In our previous work we showed that atmospheric Hg(0) deposition to vegetation and soil represents 70% of total atmospheric deposition leading to high Hg levels in Arctic soils (Obrist et al., 2017;Olson et al., 2018). In this study we explore the use of novel mercury stable isotope measurements of Hg(0) in in interstitial snow air and soil pore air to identify the processes driving tundra Hg(0) deposition. We further discuss the effect of terrestrial-atmosphere exchange processes and planetary boundary layer stability on atmospheric concentrations and Hg stable isotope signatures of Hg(0).“

A basic issue is that a summary tabulaton of flux and ancillary data sta9s9cs (number of observa9ons, flux data coverage (%), % of data rejected due undeveloped turbulence or fetch limita9ons etc. etc.) is missing in both papers. Please, provide a table in the main part or in a supplement.

Mercury flux was calculated for each 30 min, so we have a total of 17568 data points for one full year (i.e., from Oct. 2015 to Sep. 2016). For the sonic data set, we have 10% of missing data (when the Monin-Obukhov length was not measured due to instrument or acquisition failure), 86% of unstable (when z/L was between −2 and −0.1), neutral (z/L between −0.2 and 0.1), and stable (z/L between 0.1 and 2) conditions that were used for the flux calculation, and 4% of very unstable/very stable conditions (z/L less than −2 and more than 2, respectively) that were removed from the data set. Besides, 92% of the Hg gradient data were correctly measured (only 8% of missing Hg concentration measurements). That means that we really calculated a Hg flux for 79% of the time.

A summary of this information was added to the revised manuscript.

The uncertainty in flux measurements is not mentoned and quantfied. Such a discussion should also include that the flux deriva9on is obtained by asynchronous Hg0 sampling of the two heights.

Quality control of flux measurements has been discussed in Obrist et al. 2017 as follows: "For quality control, sampling lines were confirmed to be free of contamination during each field visit (approximately every six weeks, using Hg-free air; model 1100, Tekran). In addition, line intercomparisons were conducted at the same intervals to test for line biases between the upper and lower inlet lines; for this, both upper and lower inlet lines were set at the same height and measurements were conducted to assess offset. Line intercomparison tests showed no substantial line offsets throughout the study, with the exception of one time when a leak was detected and immediately fixed, and fluxes before that time were corrected"

Gradient based measurement techniques are currently the best available method for measuring net ecosystem exchange fluxes of gaseous elemental mercury. To keep the manuscript concise, we prefer to not discuss general methodological shortcomings in this manuscript, in particular since the main objective of the study was to develop and discuss the Hg stable isotope tracer in terrestrial atmosphere exchange.

The measured Hg0 depositon velocties should be mentoned and discussed with literature data.

We measured net ecosystem exchange fluxes (Hg0 deposition – Hg0 re-emission), since there were no independent measurements of Hg0 re-emission we cannot calculate net Hg0 deposition or deposition velocities from our data.

Correlaion analysis between measured gases, flux and environmental parameters is not presented.

The focus of this study lies on discussing trends in diurnal variation and time series, were correlation analysis is not very powerful. An extensive discussion of correlations between measured gases, fluxes and environmental parameters would in our view lead a much longer manuscript. The manuscript is already quite extensive with 8 Figures and we prefer to keep it in the present length.

To improve the readability, consider assigning the oxida9on state of Hg in delta and capital delta nota9ons (e.g. δ202Hg0, Δ199HgII) when found appropriate. **The nomenclature used in this study is established in the Hg stable isotope community**

Page 2, Line 1: *drawn down*, consider revising **sentence revised**

Page 2, Line 14 – 15: Lindberg *et al.* 1998 is outdated (suggesting foliage as net source of Hg0). Consider e.g. Bash and Miller (AE, 2009) or Castro et al. (Atmosphere, 2016) **We consider the work of Lindberg et al 1998 as pioneering and would like to give them credit for this and keep the reference. We added the two references suggested by the reviewers to the manuscript.**

Page 3, Line 16: "1.5m apparat", mistake? **Typo corrected**

Page 4, Line 25: an aerodynamic... consider the aerodynamic... **revised as suggested**

Page 4, Line 29 – 30: Φh the universal temperature profile, provide a reference for the mathematical form used. **The respective reference was added to the manuscript: Monson and Baldocchi, 2014: ISBN 978-1-107-04065-6 (Terrestrial biosphere-atmosphere fluxes. Cambridge University Press)**

Page 5, Line 21: Provide ±SD of the mean **We added the standard deviation of the flux measurements**

Page 6, Line 10: ... remained relatively low... try to be more concise (numbers) **We defined low as <0.1 ng m^{-3} and adjusted the manuscript accordingly**

Page 6, Line 16: ODE's without explanation. Define Ozone depletion events as ODEs. **The definition of ODE's was added**

Page 6, Line 22: Provide median also, if there is a substantial difference with mean **We added the median of the flux to the revised manuscript**

Reviewer #2

This manuscript is well written and represents the work of a strong field and laboratory team focused on mercury deposition to the Arctic. The study is well conceived and presented. It will be of interest to a variety of leadership, particularly because there is an increasing interest in understanding the source and ultimate fate of Hg in permafrost soils. I have some small to moderate comments/recommendations:

We thank the reviewer for this thorough and constructive comments

Title: "Insights" is not a strong word for this study. I recommend a far better title. "Mercury stable isotopes reveal XYZ on the terrestrial-atmosphere exchange of Hg(0) in arctic tundra"

The problem with the suggestion of the reviewer is that we would have to highlight only one major finding and through this we would give the others less attention. We therefore prefer to keep the rather general title.

This brings me to a question about the conclusions (more later): what does this study say about the seasonal net in versus out of Hg with respect to the snow pack, inferring snow melt, and summer soils? I kept hoping they would provide a seasonal diagram with the Hg % deposited, % re-emitted, and overall fluxes for their site.

The overall fluxes and how they are distributed over the different seasons were discussed in Obrist et al. 2017. In order to avoid too much overlap between two studies (see comment to reviewer 1) we refer to the refer to the Obrist et al. study for overall mass balance.

Page 1: 12: in arctic mercury Make sure "Arctic" versus "arctic" are correct You could say "the Arctic mercury cycle" **changed as suggested**

17-18 net emission fluxes based on the AMDEs or over the entire spring there was an overall net loss? **Net re-emission was observed in the entire spring, see discussion in section 3.2. The sentence starts with in spring, we therefore consider this statement to be clear, no changes made.**

32: Hg emission **changed as suggested**

33: such as the Arctic, through **changed as suggested**

36: (AMDEs), leads **changed as suggested**

Page 2: 32: Toolik Lake is on the Arctic Coastal Plain of Alaska. Not the Interior. **changed as suggested**

Page 3: 15: an assembly with two 47mm diameter single stage filters (?) membrane **Filter assembly is the technical term used by the manufacturer and we prefer to keep this terminology in the manuscript, no changes made (see Figure 1B in the SI)**

16: apart **changed as suggested**

18: Since the site visits were every 6-8 weeks: did the filter void spaces fill up? **Soil air lines were positioned under-ground and covered by soil. We did not inspect the filter packs during site visits, to minimize disturbance of the sampling system. When the soil was saturated with water we saw a decrease in pressure/flow rate of the sampling system and manually switched off the sampling to minimize the risk of water intrusion. No changes made to the manuscript**

20: The 5.7 to 17.7 m3. Is this for the long term or short term deployments? **This information is for both, short and longterm deployments as indicated by the word overall, no changes made**

22: no comma after 22:00 **changed as suggested**

24: what is “sufficient Hg for analysis”? **information added (<2.5 ng)**

26: the soil pore **changed as suggested**

29: no comma after IAC trap **changed as suggested**

30: no comma after oven system **changed as suggested**

Page 4: 11: were determined **changed as suggested**

31: Here Teflon has the registered trademark but not earlier when “Teflon” is written (page 3, line 15) **Trademark sign added to page 3**

Page 5: 5: do you mean sonic sounder? There is little information on the meteorologi- cal measurement instrumentation except perhaps here? **Correct, we used a Metek USA-1 sonic anemometer (Metek GmbH, Elmshorn, Germany). The respective information will be added to the revised manuscript.**

Was wind direction measured and analyzed? Any association between MDEs and prior wind from the coast? Any association at all with wind direction and the Hg values measured? **We added HYSPLIT back trajectory analysis to the revised manuscript to track the origin of the air masses.**

Results and Discussion Were there any measurements during snow melt? How/why were the different time intervals selected? They seem arbitrary. Perhaps non-AMDE winter and AMDE conditions instead of winter and spring? The “spring” is actually colder than “winter.” **The spring window includes snow-melt conditions, where no AMDE’s were observed. We therefore prefer to keep the terminology. The observation of the reviewer is right, in winter 2015/2016 average temperatures were higher than in spring. For atmospheric mercury redox chemistry and atmospheric boundary layer stability the solar radiation is more important than absolute temperature. This situation was very unusual, normally temperatures in winter are colder and**

around -40°C but in this particular winter temperatures were around the freezing point for a couple of days around new year.

Where are the data from 5 April to 3 May?

Was snow melt part of the 3 May to 9 Sep timeframe? Or an inundated tundra surface following melt?

Any relationships between summer seasonal thaw and Hg?

The Snow melt period was included in the spring season discussion (Paragraph 3.2), which was renamed. The systematics of Hg0 isotope signatures in interstitial snow air during the snow melt period are shown in Figure S3. In General it has to be recognized that during snow melt mercury is expected to be emitted to the atmosphere in pulses, which we were able to track through the flux measurements, however our Hg stable isotope sampling scheme had a too course resolution to track such short-term pulses.

30: under the snowpack **changed as suggested**

38: coastal snowpacks **changed as suggested**

Page 6: 4: remove “also” as “possibly” is already in there **changed as suggested**

8 (Figure 3): How were AMDEs defined?

The main text Figure order is 1, 2, 8, 3, 6, 4, 5, 7 Please reorder in numerical order **Figure order was corrected**

16: similar AMDE events **changed as suggested**

8-20: Was there any analysis of the wind back trajectories or the Barrow (now UtqiagÌG˘vik)basedGMDozonetoidentifywhethertheAMDEswereregionaltothecoast? **Good suggestion, we will include backward trajectories to the revised manuscript**

Page 7: 8-9: each night, and the strongest, **changed as suggested**

24-28: Here and elsewhere where these types of data are presented. Are the different pools statistically significantly different? Providing the analytical errors is helpful but a statistical analysis of these data is in order. From a visual perspective the standard deviations likely cross over and there is no significant difference. **We agree that statistics have been missing and will add the results of statistical t-test in the revised manuscript.**

Page 8 24: data in Figure 7. Same comment as above about statistical analyses **The results of the statistical tests are provided in the main text (P7, L32 and P8, L23-24 of the Discussion version).**

39: strongly affect **changed as suggested**

Conclusions: I really like the information in this manuscript and how it is presented. There is a lot of work here.

However, the conclusions read like a summary of the results. This study could go far in identifying the seasonal aspects of Hg deposition and re-emission but the authors mostly just summarize. All the way back to the title word “insights” I recommend they go farther.

What can they say about the Hg seasonality of deposition in the Arctic?

In the introduction the authors start with Hg being a pollutant and then introduce AMDEs and talk about snowpack re-emission. A large question there is- what frac- tion of snowpack Hg makes it into runoff and of that how much ends up stored in soils?

They then mention tundra soils can draw down summertime Hg(0). So can they say at all what the overall fluxes are from the soils and vegetation exchange with the atmo- sphere?

From the abstract: in winter. . .. Small overall Hg(0) deposition. Is this a net over the winter? i.e. the snowpack at the end of winter has more Hg than earlier in winter? What does this say about snow melt which this study seems to ignore? Are there measurements from the snow melt period? If so, they should be incorporated here so that a total “year round” net Hg deposition can be calculated.

And in spring there were AMDEs and post-AMDE re-emission. But the total net for spring was an overall loss of H(0) from the snowpack? Where did this added snowpack Hg(0) come from to be lost?

Finally, in summer, what was the overall net increase/deposition? And taken in total what were the yearly net fluxes? I feel this set of questions are important because of the still uncertain seasonal loss versus loading calculations folks have been trying to make. This study may have the most up to date information to address this need. They cite the Douglas et al., (2012) review for some mention of this (page 1, 37-38) but that paper provides a wide range of re-emission values.

In general, we agree with the reviewer about the “summary” character of the conclusion paragraph and in the revised manuscript we will provide a more concise discussion on the implications of our study also in the context of climate change. Concerning most questions raised by the reviewer here we refer to our Obrist et al. 2017, Nature study, where we discuss the ecosystem mass balance including the seasonal variation. We would also like to mention that no runoff was measured in this study, we have therefore a very limited evidence to discuss overall Hg stability in soils with respect to runoff and prefer to focus the scope of this study on terrestrial – atmosphere exchange.

Reviewer #3

Overall, I enjoyed reading the manuscript by Jiskra et al. on "Insights from mercury stable isotopes on terrestrial – atmosphere exchange of Hg(0) in the Arctic tundra". I agreed with another review that perhaps some information and data have already been presented in previous papers by the team, but I also think this is a very nice "wrap up" paper for all these results, they are complicated and I think the authors did an excellent job to put together the story, despite with some degree of uncertainty. **We would like to thank reviewer 3 for this very positive assessment and his constructive comments.**

I agree with most comments posted by Referee 1 & 2, I only have minor comments here and one suggestion as listed below:

P.2 L3: State percent of Hg to Arctic Ocean derived from Arctic Rivers? I thought Sonke et al. (2018 PNAS) found that values. **It's 44-50 t/year, the number was added to the revised manuscript**

P.2 L4: Suggest ".... bioaccumulates and bio- magnifies....", without the latter, we don't have too much Hg problems. **In our understanding of the terminology, the word bioaccumulation includes bioconcentration and biomagnification (see. Alexander, D. E., Bioaccumulation, bioconcentration, biomagnification. In *Environmental Geology*, Springer Netherlands: Dordrecht, 1999; pp 43-44.). no changes made to manuscript**

P.2 L21: Do you want to emphasize abiotically, photochemically and microbially induced re-emission of Hg(0)? How they may be distinguished by Hg isotopes? **In this introduction we want to keep the discussion simple and do not want to emphasize any particular re-emission process. We refer to the publication of Jiskra et al. 2015 with respect to the use of Hg stable isotopes to distinguish different re-emission processes in soil samples. Since in our study we did observe a depletion of Hg(0) in soil gas the re-emisstion pathways were no subject of discussion. no changes made to manuscript**

P.2 L28: Regarding to "triple isotopic fingerprint", I think we mainly rely on MDF and odd-MIF for that, less so with even-MIF, right? **No, even-MIF (e.g. Δ^{200}Hg) is an important tracer for atmospheric redox processes and in contrast to odd-MIF the even-MIF signature is not subject to fractionation during post deposition processes. This is why we use a combined triple isotopic fingerprint. We refer to Enrico et al. 2016 and Obrist et al. 2017 SI for in-depth discussion. no changes made to manuscript**

P.2 L29: Regarding to "60-90% of Hg in soils is derived from Hg(0) uptake by vegetation", does this already account for wet vs. dry deposition only? how about geogenic source? **Most studies cited in this context included a potential geogenic source and the percentages provided are relative to the total Hg in soils. Note that for organic soil horizons the geogenic contribution can generally be neglected, for the mineral soils the geogenic contribution varies with bedrock and can make up for example 40 % of the total Hg in the mineral B horizons at Toolik field station (see Obrist et al. 2017 for details on source attribution). no changes made to manuscript**

P.3 L24/25: State the lowest amount of Hg needed for isotopic analysis. **>2.5 ng, this information was added, please note that this is the absolute minimum required, normally we aim to recover at least 10 ng which allows for duplicate Hg isotope analysis.**

P.3 L30/31: Not quite clear to me about "40 vol.% 2HNO3:1HCl"? **This refers to a 4.2 N HNO_3, 1.2 N HCl oxidizing acid, manuscript was changes accordingly.**

P.5 L29: Typo-arCtic snow **corrected**

P.5 L39: Wrong unit: ~2000 ng m-2 **corrected**

P.6 L35: Is it correct to refer the text to Fig. 6 here? **Thanks for spotting this error, we refer to Figure 4 here. Manuscript changed accordingly**

P.7 L1/2: For "...as a promising tracer to distinguish between atmo- spheric deposition of Hg(II) in precipitation...", do you mean to distinguish deposition of precipitation Hg(II) from gaseous Hg(0)? **No, this sentence refers to the possibility to distinguish between Hg(II) deposition and direct Hg(0) deposition. Gaseous Hg(0) is oxidixed e.g. during vegetation uptake and when analyzing e.g. a soil sample Hg originating from vegetation uptake is not present as gaseous Hg(0) anymore but as Hg(II) complexed to soils. However, this Hg inherits the Hg**

stable isotope fingerprint of atmospheric Hg(0), which can be distinguished from Hg(II) that was deposited through precipitation. No changes made to the manuscript.

P.7 L31: Such large, estimated enrichment factor is interesting to see, would be interesting to propose how to "test" that experi- mentally. **We are working on this but do not want to go into detail in present manuscript.**

P.8 L1-10: This is cool explanation! **Thanks**

Last suggestion: Besides summarizing better on the seasonal differences on these processes as suggested by another ref- eree, I wonder if vegetation uptake is the dominant pathway for Hg(0) to deposit onto arctic tundra soils, should the authors consider here (or another paper) to show the global warming effects on Hg(0) deposition in longer summer in the future, and any impacts on Hg isotopic signatures in soils? **Our results do not allow direct conclusions on how climate change will impact Hg and Hg stable isotope systematics in the Arctic tundra. For the revided manuscript we will consider to address some potential implications of climate change on Arctic terrestrial-atmosphere exchange and highlight areas for further research.**

Reviewer #4

This study combines Hg fluxes and Hg isotopes in atmospheric Hg(0) and Hg(0) from snow air and soil air to investigate the fate of Hg(0) in Arctic tundra terrestrial environ- ment. This study is part of a larger, systematic study, which I think is well planned and well carried out. The data on Hg isotopes in soil air and snow air is very novel, and they indeed provide new insight in Hg cycle in Arctic and support the conclusions from many previous studies about terrestrial-air Hg cycle that were based on experiments and field observations. The paper is also well written and the data is clearly and prop- erly analyzed and interpreted. Overall, I recommend the publication of this paper with minor revisions: **We thank reviewer 4 for this constructive and positive assessment.**

General comment:

The observation of opposite Hg isotope signals between snow air and soil air is indeed interesting. I think it would add some value to this paper if the authors can give a more thorough thoughts on this, especailly regarding the mechanism of Hg isotope signals in snow air. The current interpretation relying on lichen uptake does not seem to be very convincing. The source and process of Hg in lichen and snow air could be very different. Are there any redox processes within snow that could produce the isotope pattern in snow air and what is the possible mechanism?

In the revised manuscript we will provide a more nuanced discussion on Hg stable isotope systematics in soil and snow air.

Specific comment:

1. P6, L1: it is a little confusing for the word “complementary”. Does lichen and snow air represent two complementary pools of Hg? Lichen represents a long term accumulation of atmospheric Hg(0) throughout the year, whereas snow air is a more temporary pool of Hg. The source and process of Hg in lichen and snow air could be very different.

We agree and have revised the respective paragraph in order to provide a more accurate explanation

2. P6, L26-31: This section is about AMDE season, but why suddenly you switch to the discussion about May, which is after the three AMDE events? What about the isotope signals in snow air during AMDE? Should this be mentioned?

We agree that this was confusing and renamed the chapter to “spring”, which includes the AMDE events and smowmelt. During AMDE’s we saw a shortterm increase in the Hg(0) concentration in snow air. However, we were not able to sample specifically for Hg(0) snow air during AMDE’s for Hg stable isotope analysis. The time periods were to short and with a very low sampling rate in the snow air they would not be isotopically resolvable.

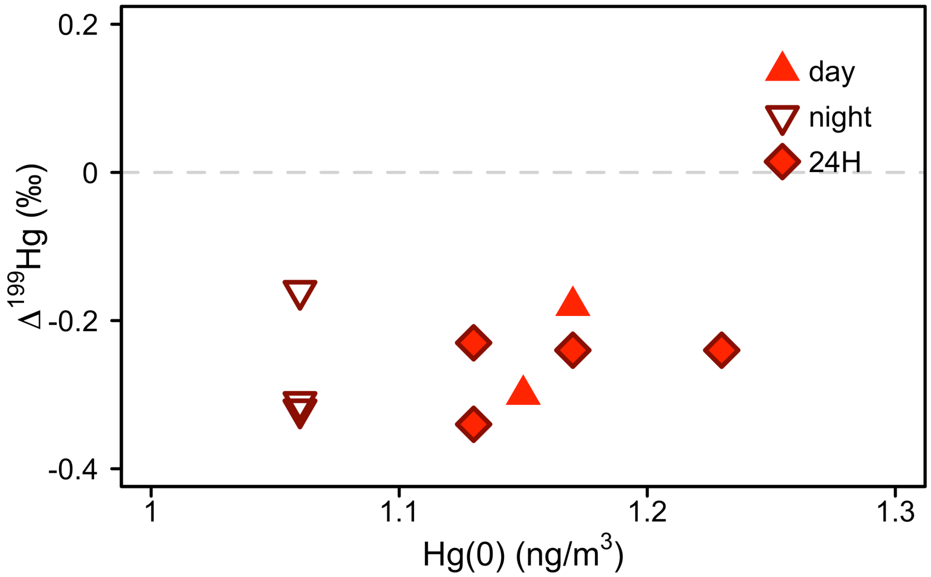
3. P6, L35: Figure 6 seems to be a wrong figure, it is not about even MIF, do you mean figure 4? **Yes, thanks for spotting this, error was corrected**

4. Figure 4: the x axis should be explained. **The x axis is explained as: Mass dependent fractionation (δ^{202}Hg), which is defined in equation 1. In our view no further explanations are needed, no changes were made**

5. P8, L1: “do not only reflect”, delete “do” **changed as suggested**

6. P8, L27: Could you show the change of MIF with Hg(0) concentration?

In the manuscript we write that nighttime and daytime Δ^{199}Hg values are similar, as a consequence of which there is no significant variation of Δ^{199}Hg with Hg(0) concentration. For the courtesy of the reviewer we show a corresponding figure below.



7. P8, L8-9: I agree, but this does not explain your high enrichment factor, which does not distinguish between pure foliar uptake and the net effect of uptake and re-emission. Re-emission would indeed affect the d202Hg and you certainly need to discuss this scenario, but re-emission likely occurs in all situations and would not cause the difference between yours and other studies. Furthermore, re-emission is accompanied by MIF, but your data shows no change of MIF between day and night.

We disagree with the suggestion that Hg re-emission occurs at all time. There is are several papers showing that net foliar Hg re-emission only occurs during daytime and during nighttime a net uptake was observed (e.g. Fu, X.; Zhu, W.; Zhang, H.; Sommar, J.; Yu, B.; Yang, X.; Wang, X.; Lin, C. J.; Feng, X., Depletion of atmospheric gaseous elemental mercury by plant uptake at Mt. Changbai, Northeast China. *Atmos. Chem. Phys.* 2016, *16*, (20), 12861-12873. or Yuan, W.; Sommar, J.; Lin, C.-J.; Wang, X.; Li, K.; Liu, Y.; Zhang, H.; Lu, Z.; Wu, C.; Feng, X., Stable isotope evidence shows re-emission of elemental mercury vapor occurring after reductive loss from foliage. *Environmental Science & Technology* 2018.). Furthermore, the odd-mass Hg isotope signatures provide a strong indication for photochemical processes, suggestion that photoreduction is the dominant process causing foliar Hg re-emission. Therefore, we are confident in our assumption that Hg(0) re-emission predominantly occurs during daytime. As explained in the manuscript daytime deposition/re-emission processes are not expected to be traceable in atmospheric Hg concentration of stable isotope signature due to strong mixing with tropospheric air. No changes were made to the manuscript.

8. P8, L11-15: I agree with this interpretation and I believe this is a more likely inter- pretation than the re-emission scenario. The d202Hg in atmospheric Hg(0) is not only affected by foliar uptake. Mixing with other Hg sources should be considered in the first place. The Rayleigh model shown in Figure 6S is based on the assumption that the change of d202Hg was completely caused by processes, which should be clarified.

We agree that the calculation of a fractionation factor for foliar Hg(0) uptake from the diurnal variation observed is only possible based on the assumption that foliar uptake if the dominant factor for the variation and that there are no other major processes or sources. We will clarify this assumption in the revised manuscript. We would like to re-emphasize that the study was conducted in the arctic tundra, hundreds of km away from the next anthropogenic Hg source. As discussed in the manuscript, the diurnal patterns in Hg concentration in relation to CO_2 concentration and boundary layer stability provide strong evidence that the variation observed is indeed from vegetation uptake of Hg(0) and not from different sources.

9. P8, L32: How did you estimate the <5% of total Hg deposition flux? Can you elabo- rate a little? The concentration of Hg(0) in soil air is almost lowered by half compared to atmospheric Hg(0). This seems to be a significant sink. **We compared the soil uptake flux estimated by Obrist et al. 2014 with the net ecosystem exchange flux measured at Toolik field station. We clarified this in the revised manuscript.**

10. P8, L34-35: I agree that the difference between soil air and atmosphere is caused by uptake of Hg(0) by soil because the isotope signals are very consistent with the experimental work. However, the opposite Hg isotope signals between soil air and snow air do not directly support that argument that soil Hg(0) sink is minor, because the isotope signals of Hg(0) in snow air is likely controlled by other mechanisms, which I believe is not clearly identified. **See discussion to comment 1 above.**

Reviewer #5

Overall, I think this is a very nice paper, certainly worthy of publication in Biogeo- sciences. I think the authors do mostly a good job of integrating their previous and directly related work to the results of this study, but I can possibly agree with other reviewers that it does at times come across as slightly confusing what things are new findings and what are not. That said, the paper overall hinges on very novel measure- ments of Hg isotopes in both snow interstitial air and soil air. It also presents some nice gradient based measurements of Hg flux and atmospheric stability, which I think do add nicely to the other parts of the paper. I do think the previous work, since it complements these new and novel measurements so well, is in the end largely written in a way that I think is entirely acceptable. If anything, the authors could perhaps go out of their way a little more in the conclusions to more explicitly pinpoint and take credit for the particular novelty of this work in comparison to their previous work. **We thank the reviewer for his positive assessment re-assuring us that the overall structure of the manuscript is justified.**

Specific comments:

Final paragraph of introduction: I find the write-up of these objectives miss the mark a little because they are vague. Is the purpose really just to "better understand" some- thing or is it more pointed in trying to examine whether certain hypotheses hold up when doing some novel measurements? The list of measurements and such comes across as somewhat less focused than is actually presented. I think it is totally fine that this paper is a little descriptive, but I do think this last "purpose" paragraph could be a little more specific. **We agree with the revewer's comment and also in response to the comments of reviewer 1 we will provide a more concise and specific description of the objectives in the introduction: "In our previous work we showed that atmospheric Hg(0) deposition to vegetation and soil represents 70% of total atmospheric deposition leading to high Hg levels in Arctic soils (Obrist et al., 2017;Olson et al., 2018). In this study we explore the use of novel mercury stable isotope measurements of Hg(0) in in interstitial snow air and soil pore air to identify the processes driving tundra Hg(0) deposition. We further discuss the effect of terrestrial-atmosphere exchange processes and planetary boundary layer stability on atmospheric concentrations and Hg stable isotope signatures of Hg(0). "**

Line 36 of page 3: Is this large a variation in sample yield problematic for isotope analyses? It seems large to me, especially for mass dependent work, but if it is no issue, this could be stated here. **In general, an incomplete sample yield can lead to mass dependent fractionation during sample pre-concentration. However, based on our data and the extensive QA/QS we have no indication of such a bias. We also would like to stress that at least part of the variation in sample yields is owed to the uncertainty in Hg concentration and cumulative flow measurements.**

First half of first paragraph of section 3.1: This discussion is a little hard to follow because this study measures Hg isotope values in interstitial air, but refers to other studies that measure Hg isotopes in snow itself. Given the discussion, it seems a little unclear whether the snow interstitial air isotope signature is slightly processed (e.g., partially deposited) atmospheric mercury or is re-emitted from the snow itself into the interstitial air. I am sure this is a minor thing and just a point of clarity. **We revised the respective paragraph**

Line 35, page 6: I am unsure about the jump to referring to figure 6 here. I do not believe either of figures 4 or 5 have been introduced yet. **This was an error, we referred to Figure 4 here. The manuscript has been changed accordingly**

Line 18, page 7: Though this says Figure 1I, it looks like "figure eleven". Perhaps this could be formatted differently to avoid confusion unless this is the required convention? **We added a space between 1 and I to avoid misinterpretation as 11.**

Figure 2: I am unclear on whether the upper values are air above the snowpack or are indeed interstitial snow air? They appear to be above the average snow heights. **Correct, the snowpack height was unusually low in the winter 2016 and the highest inlet of the snow tower (30cm) was sampling in the atmosphere over the course of the campaign as indicated by the average snow height.**

Insights from mercury stable isotopes on terrestrial – atmosphere exchange of Hg(0) in the Arctic tundra

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Abstract. The tundra plays a pivotal role in the Arctic mercury (Hg) ~~cycling~~cycle by storing atmospheric Hg deposition and shuttling it to the Arctic Ocean. A recent study revealed that 70% of the atmospheric Hg deposition to the tundra occurs by gaseous elemental mercury (GEM or Hg(0)) uptake by vegetation and soils. Processes controlling land – atmosphere exchange of Hg(0) in the Arctic tundra are therefore central, but remain understudied. Here, we combine Hg stable isotope analysis of Hg(0) in the atmosphere, interstitial snow and soil pore air, with Hg(0) flux measurements in a tundra ecosystem at Toolik field station in northern Alaska (USA). In dark winter months, planetary boundary layer (PBL) conditions and Hg(0) concentrations were generally stable throughout the day and small Hg(0) net deposition occurred. In spring, halogen-induced atmospheric mercury depletion events (AMDE's) occurred, with fast re-emission of Hg(0) after AMDE's resulting in net emission fluxes of Hg(0). During the short snow-free growing season in summer, vegetation uptake of atmospheric Hg(0) enhanced atmospheric Hg(0) net deposition to the Arctic tundra. At night, when PBL conditions were stable, ecosystem uptake of atmospheric Hg(0) led to a depletion of atmospheric Hg(0). The night time decline of atmospheric Hg(0) was concomitant with a depletion of lighter Hg(0) isotopes in the atmospheric Hg pool. The enrichment factor, ε~~^{202}Hg~~$^{202}\mathrm{Hg}_{\mathrm{vegetationuptake}}$ = −4.2 ‰ ~~±~~(± 1.0) ‰ was consistent with the preferential uptake of light Hg(0) isotopes by vegetation. Hg(0) flux measurements indicated a partial re-emission of Hg(0) during daytime, when solar radiation was strongest. Hg(0) concentrations in soil pore air were depleted relative to atmospheric Hg(0) concentrations, concomitant with an enrichment of lighter Hg(0) isotopes in the soil pore air ($\varepsilon^{202}\mathrm{Hg}_{\mathrm{soilair\text{-}atmosphere}} = -1.00$ ‰ (± 0.25 ‰) and $E^{199}\mathrm{Hg}_{\mathrm{soilair\text{-}atmosphere}} = 0.07$ ‰ (± 0.04 ‰)). These first Hg stable isotope measurements of Hg(0) in soil pore air are consistent with the fractionation previously observed during Hg(0) oxidation by natural humic acids suggesting abiotic oxidation as a cause for observed soil Hg(0) uptake. The combination of stable isotope fingerprints with Hg(0) flux measurements and PBL stability assessment confirmed a dominant role of Hg(0) uptake by vegetation in terrestrial-atmosphere exchange of Hg(0) in the Arctic tundra.

1 Introduction

Mercury (Hg) is a high priority pollutant causing neurodevelopmental deficits in children and cardiovascular disease in adults (Budtz-Jørgensen et al., 2000;Roman et al., 2011). Arctic populations are particulary exposed to high Hg levels, despite few local anthropogenic Hg emissions sources, due to their traditional diet consisting of high trophic level seafood (Sheehan et al., 2014). Anthropogenic Hg emissions from mid latitudes reach remote ecosystems, such as the Arctic, through long-range transport of gaseous elemental mercury (GEM or Hg(0)) (Douglas et al., 2012). It has long been thought that springtime oxidation of Hg(0) driven by photochemically produced bromine radicals Br• on surface snow, named “atmospheric mercury depletion events” (~~AMDE~~AMDEs), leads to enhanced deposition of divalent mercury (Hg(II~~)~~)) in Arctic regions (Steffen et al., 2008). Such Hg(II) deposition to the snowpack during AMDE's, however, can be subject to photoreduction and fast re-emission back into the atmosphere, minimizing the net load of Hg by AMDE's to snow (Douglas et al., 2012;Johnson et al., 2008).

Tundra soils play a central role in the Arctic Hg ~~cycling~~cycle by storing atmospheric Hg deposition from where it can be mobilized and transported to the Arctic Ocean ~~(Obrist et al., 2017;Sonke and Heimburger, 2012;Sonke et al., 2018).~~(Obrist et al., 2017;Sonke and Heimburger, 2012;Sonke et al., 2018). Over millennia, tundra vegetation and soils have drawn ~~down~~ Hg(0) ~~from~~out of the atmosphere, resulting in one of the largest pools of Hg (408 – 863 Gg Hg, top 1 m) stored at the Earth's surface (Obrist et al., 2017;Olson et al., 2018;Schuster et al., 2018). Arctic rivers ~~have recently been recognized to~~ deliver ~~large amounts~~44 – 50 Mg a^{-1} of Hg to the Arctic Ocean ~~(Fisher et al., 2012;Sonke et al., 2018)~~(Dastoor and Durnford, 2014;Sonke et al., 2018). In aquatic ecosystems, Hg can be transformed to methyl-Hg that bioaccumulates in the aquatic food chain resulting in elevated Hg concentrations in high trophic level fishes and mammals (Outridge et al., 2009;Douglas et al., 2012).

On a global scale, vegetation uptake of atmospheric Hg(0) represents the dominant pathway of atmospheric Hg deposition to terrestrial surfaces, resulting in strong seasonal variation of atmospheric Hg(0) concentrations with minima in summer when vegetation activity is highest (Jiskra et al., 2018). Direct Hg(0) flux measurements over selected surfaces (e.g., soil, snow, or leaves), however, do not always provide conclusive answers about the direction and magnitude of Hg exchange between terrestrial ecosystems and the atmosphere. For example, a review of 132 terrestrial-atmosphere Hg(0) flux studies conducted over various surfaces in the last 30 years estimated a wide range of net fluxes in the range of −513 to 1650 Mg a^{-1} (37.5th to 62.5th percentile) (Agnan et al., 2016). In recent years, a number of studies using Hg(0) flux measurements based on micro-metrological methods directly quantified net ecosystem exchange fluxes of Hg(0) over terrestrial ecosystems (i.e., at the ecosystem-level), including atmosphere-vegetation exchange and underlying soil/litter contributions (Lindberg et al., 1998;Fritsche et al., 2008;Bash and Miller, 2009;Castro and Moore, 2016;Osterwalder et al., 2017). Measurements of multi-level Hg(0) gradients and interstitial snow and soil pore air provided additional constraints on the terrestrial surface exchange flux (Sigler and Lee, 2006;Moore and Castro, 2012;Fain et al., 2013;Obrist et al., 2014;Fu et al., 2016b;Agnan et al., 2018).

Hg stable isotopes are a powerful tool to study the deposition and re-emission pathways of Hg to terrestrial ecosystems. The Hg stable isotope fingerprint of soil samples reflects the source contribution of atmospheric Hg(0) dry deposition, Hg(II) wet deposition, and Hg from geogenic origin as well as processes fractionating Hg isotopes during post-deposition processes, e.g., re-emission (Demers et al., 2013;Jiskra et al., 2015;Enrico et al., 2016). Mercury has seven stable isotopes, which can undergo mass dependent fractionation (MDF, described by δ^{202}Hg), mass-independent fractionation of odd-mass-number isotopes (odd-MIF, described by Δ^{199}Hg and Δ^{201}Hg), and even-mass-number isotopes (even-MIF, described by Δ^{200}Hg and Δ^{204}Hg), thereby producing a multi-dimensional isotopic fingerprint (Obrist et al., 2018). Atmospheric Hg(0) and Hg(II) in wet deposition exhibit distinct Δ^{199}Hg and Δ^{200}Hg signatures (Gratz et al., 2010;Chen et al., 2012;Sherman et al., 2012b;Demers et al., 2013;Enrico et al., 2016). Foliar uptake of atmospheric Hg^0 discriminates heavier Hg isotopes, leading to consistently lower δ^{202}Hg values reported in foliage compared to atmospheric Hg(0) (Demers et al., 2013;Enrico et al., 2016;Obrist et al., 2017;Yu et al., 2017;Yuan et al., 2018). Using the triple isotopic fingerprint to distinguish between Hg(0) and Hg(II) deposition, an increasing number of studies around the globe revealed that 60-90% of Hg in soils is derived from Hg(0) uptake by vegetation (Demers et al., 2013;Jiskra et al., 2015;Enrico et al., 2016;Zheng et al., 2016;Obrist et al., 2017).

This paper is part of a larger study aiming to better understand the fate of Hg in Arctic tundra ecosystems, ~~centred~~centered around a two-year field campaign ~~in interior~~on the Arctic Coastal Plain of Alaska. In Obrist et al. (2017), we performed a two-year mass balance of terrestrial-atmosphere exchange over the ~~tundra and showed that Hg(0) uptake by vegetation and soil represents 70% of total atmospheric deposition.~~Arctic tundra. We also investigated the spatial distribution of Hg in tundra soils (Olson et al., 2018), and spatial and temporal patterns of Hg in snow (Agnan et al., 2018) and in vegetation (Olson et al., 2019). ~~The goal of the present study is to better understand the processes controlling terrestrial-atmosphere exchange of Hg and the impact of these processes on atmospheric Hg(0) concentrations. For this purpose, we use Hg stable isotopes of Hg(0) in the atmosphere and in interstitial snow and soil pore air to assess the role of Hg(0) uptake by vegetation, Hg(0) oxidation in soils, and re-emission processes. We compare the systematics in Hg stable isotopes during different seasons of the year and study diel variations in combination with Hg(0) flux measurements and other auxiliary measurements.~~In our previous work we showed that the uptake of atmospheric Hg(0) by vegetation and soil represents 70% of total atmospheric deposition and has led to high Hg levels in Arctic soils (Obrist et al., 2017;Olson et al., 2018). In this study we explore the use of novel Hg stable isotope measurements of Hg(0) in interstitial snow air and soil pore air to identify the processes driving tundra Hg(0) deposition. We further discuss the effects of terrestrial-atmosphere exchange processes and planetary boundary layer stability on the Hg(0) concentration and Hg stable isotope signature measured in the atmosphere.

2 Materials and methods

2.1 Study site

The study was conducted at Toolik field station (68° 38′ N, 149° 36′ W) on the Arctic Coastal Plain in northern Alaska, USA, 180 km inland from the Arctic Ocean coast. All measurements were conducted on an acidic tussock tundra, on aquiturbels soils with an active layer of 60 – 100 cm (Obrist et al., 2017). The climate of Toolik field station is characterized by low mean annual temperatures of −8.5 °C and mean annual precipitation of 312 mm yr^{-1} (Cherry et al., 2014). During the one-year Hg isotope campaign from October 2015 to September 2016, the tundra was snow-covered during 248 days (Agnan et al., 2018), leading to a relatively short snow-free growing season.

2.2 Hg stable isotope sampling and measurement

Hg(0) was continuously sampled in the atmosphere (0.3 m and 2 m above ground), in interstitial air of surface snow (0 m and 0.1 m above ground) and in soil pore air (0.4 m below ground) at low flow rates of 0.2 L min^{-1}. Interstitial snow air for Hg(0) stable isotope measurements was sampled from a dedicated snow tower adapted from Seok et al. (2009), consisting of an ~~aluminium~~aluminum construction with three gas inlets on horizontal bars at 0 m, 0.1 m and 0.3 m above ground (Figure S1 A). Two soil wells as described in Obrist et al. (2017) were dedicated to Hg(0) stable isotope sampling of soil air. Each soil well consisted of two 47mm single stage filter assembly (Savillex, Eden Prairie, USA) with Teflon® filter membranes gas inlets, positioned 1.5m ~~apparat~~apart in soil pits at 0.4 m depth (Figure S1 B).

Hg(0) was trapped on iodated activated carbon (IAC) traps (Brooks Rand, 0.1 g in custom made 12 cm long glass tubes with an inner diameter of 4mm, (Fu et al., 2014)) and samples were changed manually during site visits every 6-8 weeks. During site visits in March and June 2016, higher temporal resolution (2-4 days) sampling was conducted with higher flow rates of 1.5-2 L min^{-1}. Overall, total volumes of sampled air per sample ranged from 5.7 to 17.7 m^3 (Table S1). During the growing season (June to September 2016), diel variation of atmospheric Hg(0) was assessed using two parallel sampling lines operated with a time switch. Daytime samples were collected from 06:00 to 22:00~~,~~ and nighttime samples were collected from 22:00 to 06:00. Of the 14 soil pore air samples taken during the one-year Hg isotope campaign, only three samples contained sufficient Hg (>2.5 ng) for isotopic analysis. The reason for this is that, in particular during winter months, the Hg(0) in soil pore air was largely depleted (below detection limit of ≈0.1 ng m^{-3}) (Obrist et al., 2017;Agnan et al., 2018), making isotopic characterization of the soil pore air Hg(0) pool impossible during this time period.

The protocol for Hg stable isotope measurements of Hg(0) was adapted from Fu et al. (2014). We used lower amounts of IAC trap material (0.1 g) to reduce possible matrix effects during cold-vapor generation. Breakthrough was tested in the lab and under field conditions by connecting a Tekran 2537 after the IAC trap~~,~~ and Hg(0) measurements were always below the detection limit (<0.1 ng m^{-3}). IAC traps were combusted in a two-stage oven system~~,~~ and Hg was recovered in a ~~40 vol.% 2HNO$_3$:1HCl~~4.2 N HNO$_3$, 1.2 N HCl oxidizing acid trap. Hg stable isotope ratios of trap solutions were measured by cold vapor separation multi-collector inductively coupled plasma mass spectrometry (CV MC-ICP/MS) at the Observatory Midi-Pyrénées, Toulouse (Jiskra et al., 2019;Sun et al., 2013). 6 process blanks and 1 field blank were measured during the sample processing and were on average 0.25 ng Hg/trap (max 0.85 ng Hg/trap), representing 1-2 % of typical Hg amounts collected during sampling periods. Amounts of Hg collected on IAC-traps sampling atmospheric Hg(0) were compared to Hg(0) concentration measurements with a Tekran 2537 and revealed sample yields of 107 ± 23 % (mean ± 1 SD, n = 22).

Mass dependent fractionation (MDF) of Hg stable isotopes is reported in small delta notation (δ) in per mil (‰) deviation from to the reference NIST 3133 Hg standard:

$$\delta^{xxx}\mathrm{Hg} = ({}^{xxx/198}\mathrm{Hg}_{sample}/\,{}^{xxx/198}\mathrm{Hg}_{NIST3133} - 1) \times 10^{3} \tag{1}$$

where 'xxx' refers to measured isotope masses: 199, 200, 201, 202, and 204. Mass independent fractionation (MIF) is reported in capital delta notation (Δ), which is defined as the difference between the measured δ^{199}Hg, δ^{200}Hg, δ^{201}Hg, and δ^{204}Hg values and those predicted for MDF relative to δ^{202}Hg using the kinetic MDF law:

$$\Delta^{xxx}\mathrm{Hg} = \delta^{xxx}\mathrm{Hg} - \mathrm{SF}^{xxx} \times \delta^{202}\mathrm{Hg} \tag{2}$$

where SF^{xxx} is the mass-dependent scaling factor of 0.252 for ^{199}Hg, 0.502 for ^{200}Hg, 0.752 for ^{201}Hg, and 1.493 for ^{204}Hg (Blum and Bergquist, 2007). Hg isotope enrichment factors associated with two pools ($\varepsilon^{xxx}\mathrm{Hg}_{\mathrm{pool1-pool2}}$ and $\mathrm{E}^{xxx}\mathrm{Hg}_{\mathrm{pool1-pool2}}$) were calculated from the difference in MDF and MIF signature between two pools (pool 1 and pool 2) as follows;

$$\varepsilon^{xxx}\mathrm{Hg}_{\mathrm{pool1-pool2}} = \delta^{xxx}\mathrm{Hg}_{\mathrm{pool1}} - \delta^{xxx}\mathrm{Hg}_{\mathrm{pool2}} \tag{3}$$

$$\mathrm{E}^{xxx}\mathrm{Hg}_{\mathrm{pool1-pool2}} = \Delta^{xxx}\mathrm{Hg}_{\mathrm{pool1}} - \Delta^{xxx}\mathrm{Hg}_{\mathrm{pool2}} \tag{4}$$

The MDF enrichment factors of a reaction ($\varepsilon^{xxx}\mathrm{Hg}_{reaction}$) ~~was~~were determined by fitting a linear regression model (lm function of R) to the observational data following Mariotti et al. (1981):

$$\delta^{xxx}\mathrm{Hg}_{residual} = \delta^{xxx}\mathrm{Hg}_{0} + \varepsilon^{xxx}\mathrm{Hg}_{\mathrm{reaction}} \times \ln f \tag{5}$$

where $\delta^{xxx}\mathrm{Hg}_{residual}$ corresponds to the Hg isotope signature of the residual Hg(0), $\delta^{xxx}\mathrm{Hg}_{0}$ corresponds to the initial Hg(0) isotope signature and f to the fraction of Hg(0) remaining in the gas phase. Note that for high $f > 0.4$ the systematic error of this simplified approach is minimal. The MIF enrichment factor ($\mathrm{E}^{xxx}\mathrm{Hg}_{reaction}$) was calculated as follows:

$$\Delta^{xxx}\mathrm{Hg}_{\mathrm{residual}} = \mathrm{E}^{xxx}\mathrm{Hg}_{\mathrm{process}} \times \delta^{xxx}\mathrm{Hg}_{\mathrm{residual}} \tag{6}$$

The long-term precision was assessed through repeated analysis of the ETH-Fluka Hg standard, which yielded values of −1.44 ± 0.19 ‰, 0.08 ± 0.1 ‰, 0.02 ± 0.1 ‰, 0.02 ± 0.09 ‰, −0.03 ± 0.2 ‰ (2σ, n = 73) for δ^{202}Hg, Δ^{199}Hg, Δ^{200}Hg, Δ^{201}Hg, and Δ^{204}Hg, respectively, in agreement with published values (Jiskra et al., 2015;Smith et al., 2015). The Almaden standard was measured less frequently and results were -0.58±0.15‰, -0.02±0.09‰, 0.00±0.1‰, -0.06±0.12‰, -0.04±0.23‰ (2σ, n=21) for δ^{202}Hg, Δ^{199}Hg, Δ^{200}Hg, Δ^{201}Hg, and Δ^{204}Hg, in agreement with previously reported values (Demers et al., 2013;Jiskra et al., 2015;Enrico et al., 2016).

2.3 Hg(0) flux measurements

Micrometeorological flux measurements to quantify Hg(0) exchange at the ecosystem level were conducted using ~~an~~the aerodynamic gradient flux method. Surface-atmosphere flux was calculated by measurement of concentration gradients in the atmosphere above the tundra in conjunction with atmospheric turbulence parameters as follows:

$$F_{Hg^0} = -\cancel{\frac{k \times u_* \times z}{\phi_h\left(\frac{z}{L}\right)}}\frac{k \times u_* \times z}{\phi_h} \times \frac{\partial c(Hg(0))}{\partial z} \quad (7)$$

where k denotes the von Karman constant (0.4), u_* the friction velocity, z the measurement height, ϕ_h~~(z/L) the universal temperature profile, L the Monin-Obukhov length, and ∂c(Hg(0))/∂z the vertical Hg(0) gas concentration gradient.~~ the Monin-Obukhov scaling coefficient (dimensionless) (Monson and Baldocchi, 2014), and ∂c(Hg(0))/∂z the vertical Hg(0) gas concentration gradient. Hg(0) concentrations at heights of 61 cm and 363 cm above the soil surface were measured through 0.2 µm Teflon® inlet filters connected to ~35 m of perfluoroalkoxy-polymer (PFA) lines. A valve control system with three-way solenoid valves (NResearch, West Caldwell, NJ, USA) allowed switching between the gradient inlets every 10 min. A set of trace gas analysers with a total sampling flow of 1.5 L min^{-1} was connected to the gradient inlets by solenoid valves. The trace analysers included an air mercury analyser (Model 2537A, Tekran Inc. Toronto, Canada) and a Cavity Ring-Down (CRD) greenhouse gas analyser to measure CO_2, H_2O, and CH_4 (Los Gatos Research, San Jose, USA). Fluxes were calculated only during periods of appropriate turbulence following (Edwards et al., 2005) and as described in (Obrist et al., 2017). Gradient data recorded during very stable ($\zeta > 2$) and very instable ($\zeta > 2$) were removed from the dataset (4%). Overall data coverage was 79%. For the analysis, only flux data with wind direction from the tundra (40° - 300° N) were considered (73%). No gap filling was performed. For quality control, sampling line blanks and line inter-comparisons where the two gradient lines were put on the same height were performed approximately every 6-8 weeks (Obrist et al., 2017). The planetary boundary layer (PBL) stability was assessed through the stability index (ζ, dimensionless), where:

$$\zeta = \frac{z}{L} \quad (8)$$

where z represents the height of the Metek USA-1 sonic anemometer (Metek GmbH, Elmshorn, Germany), i.e., 236 cm above ground, and L represents the Monin-Obukhov length. The PBL was considered stable when $\zeta > 0.1$, instable when $\zeta < -0.1$, and neutral for $-0.1 < \zeta < 0.1$ (Peichl et al., 2013). During the sampling period, auxiliary variables showed the following daily average values: air temperature of −7.4 °C (from −40.6 to 20.4 °C), relative humidity of 74% (from 37 to 98%), and the wind speed of 2.36 m s^{-1} (from 0 to 7.82 m s^{-1}).

2.3 Backward trajectory modelling

Backward trajectories of air masses were modelled using the HYSPLIT transport and dispersion model (Stein et al., 2015) of NOAA Air Resources laboratory accesses through the READY website (Rolph et al., 2017).

3 Results and Discussion

We divide the presentation and discussion of results into three seasons of the year. In winter (20 Oct 2015 to 17 Mar 2016), the tundra site was continuously snow-covered and the climatic conditions were characterized by low temperatures (mean = −17.8 °C, hourly max = 1.2 °C) and low solar radiation (mean = 0.02 kW m^{-2}, hourly max = 0.41 kW m^{-2}). In spring (17 Mar 2016 – 05 Apr 2016), temperatures were low (mean = −19.2 °C, hourly max = −2.4 °C) and the tundra was still snow-covered, however solar radiation increased (mean = 0.13 kW m^{-2}, max = 0.54 kW m^{-2}) and occasional atmospheric mercury depletion events (~~AMDE~~AMDEs) were detected at the study site (Obrist et al., 2017;Agnan et al., 2018). During summer (03 May

2016 – 09 Sep 2016), air temperature was above freezing (mean = 6.7 °C, hourly max = 25.1 °C), solar radiation was high (mean = 0.19 kW m^{-2}, hourly max = 0.80 kW m^{-2}), and the study site was predominantly free of snow.

3.1 ~~Wintertime~~ Winter

Over the winter period, atmospheric Hg(0) concentrations and CO_2 mixing ratios were relatively constant and there was little diel variation (Figure 1 A, Figure S2). Low solar radiation led to relatively stable PBL conditions throughout the day (Figure 1 B). Hg(0) flux measurements revealed a small deposition ~~(mean: −~~(-0.~~26~~34 ± 5.8 ng m^{-2} h^{-1}~~)~~ mean ± 1SD, median = -0.2 ng m^{-2} h^{-1} (Obrist et al., 2017). The Hg(0) net deposition flux is supported by observed depletions of atmospheric Hg(0) in interstitial snow air (0.69 ± 0.22 ng m^{-3}, mean ± 1SD, 0 and 0.1 m sampling height) relative to atmospheric levels (1.07 ± 0.04 ng m^{-3}, mean ± 1SD) (p = 0.02, two-sided t-test), implying a net sink of atmospheric Hg(0) ~~sink~~ in the ecosystem (Figure 2 C). ~~The depletion~~A wintertime Hg(0) sink can either occur by (i) Hg(0) deposition to Artic snow, (ii) uptake by soil or litter, or (iii) assimilation by vegetation still active under the snowpack. Depletion of atmospheric Hg(0) in interstitial snow air was associated with an increase in δ^{202}Hg (1.08‰ ± 0.20 ‰ versus 0.77 ‰ ± 0.16 ‰ in ambient Hg(0), mean ± 1SD, p = 0.02, two-sided t-test) (Figure 2 A) and a decrease in Δ^{199}Hg ~~(−~~(-0.31 ‰ ± 0.05 ‰ versus ~~−~~-0.23 ‰ ± 0.06 ‰ in ambient Hg(0), mean ± 1SD, p = 0.04, two-sided t-test) (Figure 2 B). Both Hg(0) dry deposition to surface snow (Douglas and Blum, 2019) and by vegetation uptake (Demers et al., 2013;Enrico et al., 2016;Obrist et al., 2017) ~~has~~have been reported to discriminate heavier Hg(0) isotopes, consistent with these observations in the interstitial snow air. ~~A wintertime Hg(0) sink can either occur by Artic snow, soil, or vegetation still active under snowpack.~~ From a mass balance perspective, however, Hg(0) dry deposition to snow is considered to only play a minor role in the interior ~~arctic~~Arctic tundra. For example, using snow data in Agnan et al. (2018), we calculated a total seasonal snow Hg pool of only 50 ng m^{-2} at Toolik Field station. Assuming that all this Hg in the snow was originating from the dry deposition of Hg(0), this would account for <10% of the Hg(0) deposition during the snow-covered period (total of 2.4 µg m^{-1} ~~yr~~a^{-1} (Obrist et al., 2017)). ~~Recently~~In contrast, Douglas and Blum (2019)~~, however,~~ recently suggested that Hg(0) dry deposition to snow was the major source of Hg in meltwater collected on the coast of the Arctic Ocean close to Utqiagvik (former Barrow~~,~~), ~400 km north-west of Toolik field station. In snow on the coast of the Arctic Ocean, concentrations of halogens, which are considered to mediate reactive Hg(0) uptake, are elevated compared to inland sites (Douglas and Sturm, 2004;Agnan et al., 2018;Douglas et al., 2017) leading to much higher snow Hg pools ~~(~~~(>2000 ng ~~m^2~~m^{-2}) in coastal ~~snowpack~~snowpacks (Douglas et al., 2017)~~.~~ ~~Both MDF and MIF signatures in interstitial snow air Hg(0) are complementary (i.e., in opposite direction) to the Hg isotope signatures observed in lichen at the same site (δ^{202}Hg = −0.80 ‰ ± 0.20 ‰, Δ^{199}Hg = 0.20 ‰ ± 0.21‰, mean ± 1SD, n = 12) (Olson et al., 2019). Lichen can~~. A major wintertime Hg(0) deposition pathway to soils would be inconsistent with the observed enrichment in heavier Hg(0) isotopes in the interstitial snow air (Figure 2 A), as Hg(0) oxidation by humic acids in soils would lead to more negative δ^{202}Hg values (Zheng et al., 2018) (see discussion below in section 3.3.3). Hg(0) re-emission from snow was insignificant in winter due to the absence of sunlight, as indicated by lower Hg(0) concentrations in interstitial snow air than in the atmosphere. By excluding snow and soil uptake as dominant deposition pathway, we infer that uptake of Hg(0) by ground vegetation and/or litter on the soil surface may be driving Hg(0) deposition during the winter months. MDF and MIF signatures observed in interstitial snow air Hg(0) would be consistent with Hg(0)) uptake by lichen. Hg isotope signatures of lichen measured at the same site (δ^{202}Hg = −0.80 ‰ ± 0.20 ‰, Δ^{199}Hg = 0.20 ‰ ± 0.21‰, mean ± 1SD, n = 12) were in the opposite direction of interstitial snow air Hg(0) (Olson et al., 2019). Lichen have been reported to actively exchange CO_2 for photosynthesis under snow cover (Kappen, 1993), and could possibly take up atmospheric Hg(0) also during winter months. ~~In contrast, Hg(0) oxidation by humic acids in soils would lead to more negative δ^{202}Hg values (Zheng et al., 2018) (see discussion below in section 3.3.3), and hence would be inconsistent with the observed enrichment in heavier Hg(0) isotopes in the interstitial snow air (Figure 2 A and Figure 8).~~

3.2. ~~AMDE season~~Spring

During spring 2016, ~~three~~two major AMDE's occurred ~~at~~(event 1 and 3, Figure 3). During both events air masses were transported from the Arctic coast or the Arctic Ocean to Toolik Field station ~~(Figure 3). During the first AMDE (~~as inferred from HYSPLIT backward trajectory modelling. During 19 Mar 2016 ~~-~~– 20 Mar 2016~~, –~~ (event 1 in Figure 3), atmospheric Hg(0) concentrations dropped below detection limit (<0.1 ng m^{-3}), while atmospheric Hg(II) concentrations remained ~~relatively~~ low (<0.1 ng m^{-3}) with the exception of individual spikes up to 0.4 ng m^{-3}. During ~~the second AMDE (26 Mar 2016 – 29 Mar 2016, event 2 in Figure 3) atmospheric Hg(0) concentrations temporally decreased to 0.75 ng m^{-3} and Hg(II) concentrations remained enhanced around 0.2 ng m^{-3} for two days while turbulent PBL conditions prevailed. During the third AMDE (~~1 Apr 2016 – 3 Apr 2016~~, –~~ (event 3 in Figure 3), atmospheric Hg(0) concentrations at times decreased below detection limit ~~(<0.1 ng m^{-3})~~ while Hg(II) concentrations remained high around 0.4 ng m^{-3} for two days. During the similar AMDE events 1 and 3, O_3 mixing ratios dropped below 10 ppb~~, whereas during event 2, O_3 remained high (>30 ppb).~~. Van Dam et al. (2013) previously reported that during AMDEs ~~and ODEs observed~~also ozone depletion events (ODEs) occurred at Toolik field station, ~~similar~~concurrent AMDEs ~~events~~and ODEs were also observed on the coast in ~~Barrow~~Utqiagvik ~400 km to the north-west. They suggested that AMDEs and ODEs ~~are~~were driven by bromine emissions from the Arctic ocean and transported to different extents to the interior tundra (Van Dam et al., 2013). ~~For example, during~~During event 1, no elevated Hg(II) concentrations were observed, thus we assume that air depleted in Hg(0) concentration was transported to Toolik field station while the deposition of Hg(II) likely occurred closer to the coast. Air masses were coming from the south during 26 Mar 2016 – 29 Mar 2016 (event 2 in Figure 3) where atmospheric Hg(0) concentrations temporally decreased to 0.75 ng m^{-3}, O_3 remained high (>30 ppb) and Hg(II) concentrations remained enhanced around 0.2 ng m^{-3} for two days while turbulent PBL conditions prevailed. The source of these enhanced Hg(II) levels transported from the Brooks Range mountains remains unknown.

~~Figure 3D displays measured Hg(0) fluxes during these AMDE periods~~During the period of AMDEs (17 Mar 2016 – 5 Apr 2016) ~~showing strong Hg(0) re-emission after the three AMDEs. On average, a~~an overall net Hg(0) re-emission ~~of~~ (1.~~5~~6 ± 11 ng m^{-2} h^{-1} mean ± 1SD , median = 0.28 ng m^{-2} h^{-1}) was measured which peaked after the Hg(II) deposition, making the ~~time of AMDEs~~AMDE period the only ~~period~~time of the year ~~where~~when net Hg(0) re-emission occurred (Obrist et al., 2017). Strong Hg(0) re-emission from the snowpack has been reported during and after AMDEs due to fast reduction of Hg(II) deposition (Johnson et al., 2008;Douglas et al., 2012).

Snowmelt occurred in May in 2016 ~~and~~where snow height ~~quickly~~ declined rapidly between May 7 (24 cm) and May 13 (0 cm) and possibly a small Hg(0) deposition occurred (−0.24 ± 3.9 ng m^{-2} h^{-1} mean ± 1SD, median: 0.08 ng m^{-2} h^{-1}). In contrast to wintertime patterns, the interstitial snow air Hg(0) during snowmelt showed low Δ^{199}Hg values of −0.62 ‰ and –0.44 ‰ versus −0.23 ‰ ± 0.06 ‰ in ambient Hg(0) (Figure S3B). The negative Δ^{199}Hg values in Hg(0) suggest a substantial contribution of Hg(0) re-emission after photoreduction of Hg(II) in snow, which exhibited negative Δ^{199}Hg values with a minimum of −1.37‰ (Obrist et al., 2017). This observation is consistent with previous chamber experiments, where negative Δ^{199}Hg of −2.08 ‰ were reported for Hg(0) re-emission from snow (Sherman et al., 2010).

Even-MIF (Δ^{200}Hg) is considered not to be affected by post-deposition processes such as re-emission (Sherman et al., 2010;Enrico et al., 2016), providing a conservative tracer for the pathway of atmospheric Hg deposition. Δ^{200}Hg values measured in snow impacted by AMDEs at Toolik field station and other sites in Alaska (Obrist et al., 2017;Sherman et al., 2010;Sherman et al., 2012a) are similar to the Δ^{200}Hg values of atmospheric Hg(0) (Figure ~~6~~4) (−0.06‰ ± 0.06‰ versus

−0.05‰ ± 0.04‰, mean ± 1SD). This similarity can be explained by a quantitative oxidation of atmospheric Hg(0) to Hg(II) (e.g., event 1 in Figure 3) that is deposited to snow. Hg(II) in snow thereby inherits the isotopic composition of the source Hg(0) due to conservation of mass, irrespective of the isotopic fractionation factor associated with Hg(0) oxidation. Several samples exhibited Δ^{200}Hg values between that of atmospheric Hg(0) and Hg(II) in precipitation measured in temperate regions (Figure 4). This intermediate Δ^{200}Hg signature can be explained by either AMDEs with non-quantitative oxidation due to limited Br oxidant availability (e.g., event 2 in Figure 3), or a mixing of AMDE-derived Hg(II) with ~~non-AMDE~~ Hg(II) present in the overlying Arctic free troposphere. Even MIF (Δ^{200}Hg) has been suggested as a promising tracer to distinguish between atmospheric deposition of Hg(II) in precipitation, which exhibits positive Δ^{200}Hg anomalies, and direct Hg(0) deposition (e.g., uptake by vegetation), which exhibits small negative Δ^{200}Hg (Enrico et al., 2016;Sun et al., 2019). We caution that the presence of AMDEs complicates the use of Δ^{200}Hg for mixing model based Hg deposition calculations in the Arctic (Obrist et al., 2017).

3.3 ~~Summertime~~ Summer

3.3.1 Drivers of diel cycling in atmospheric Hg(0)

Figure 5 represents a time series of atmospheric Hg(0) concentration and CO$_2$ mixing ratio, PBL stability and Hg(0) fluxes during mid-summer (15 Jul 2016 – 28 Jul 2016). Atmospheric Hg(0) concentrations generally declined during each night, and the strongest Hg(0) depletions (Hg(0) <1 ng m^{-3}) were observed when the PBL was stable ($\zeta > 0.1$, events 2 and 3 and green bars in Figure 5 B). These Hg(0) nighttime minima coincided with maxima of atmospheric CO$_2$ mixing ratios of 410 to 420 ppm. These patterns are consistent with measured Hg(0) deposition fluxes during nights (daily minima at ~~03~~00:00, −2.56 ± 0.~~35~~22 ng m^{-2} h^{-1} (mean ± 1SD), Figure 1I), ~~and~~under corresponding CO$_2$ accumulation in the PBL driven by nighttime CO$_2$ soil respiration (Wofsy et al., 1993;Schlesinger and Andrews, 2000;Grant and Omonode, 2018). During nights with unstable PBL conditions (e.g., event 1 in Figure 5), diel Hg(0) and CO$_2$ variations were much lower or absent due to increased mixing with free tropospheric air containing background levels of Hg(0) and CO$_2$. During late summer (Figure S4, 20 Aug 2016 – 31 Aug 2016), the longer duration of stable nocturnal PBL conditions led to even more pronounced nighttime depletions in Hg(0). During daytime under strong solar radiation, flux measurements showed net Hg(0) emission around noon (daily maxima at ~~12~~11:00, ~~3.~~2.9 ± 0.~~83~~92 ng m^{-2} h^{-1} (mean ± 1SD), Figure ~~1I~~1 I). Daytime Hg(0) re-emission, however, did not lead to a build-up of atmospheric Hg(0) above the surface due to prevailing turbulent conditions allowing efficient mixing with background free tropospheric air. These patterns demonstrate how atmospheric Hg(0) and CO$_2$ are both controlled by the magnitude and direction of the net ecosystem exchange fluxes in conjunction with PBL stability. Overall, flux measurements showed the tundra ecosystem to be a net sink of atmospheric Hg(0) over the duration of the growing season (−0.76 ± 6.3 ng m^{-2} h^{-1} mean~~: −0.12~~ ± 1SD, median: -1.2 ng m^{-2} h^{-1}).

3.3.2 Hg isotope fractionation during foliar uptake of atmospheric Hg(0)

Figure 6 shows a scatterplot of atmospheric Hg(0) concentrations and the δ^{202}Hg values sampled during different times of the day in summer 2016. Hg(0) sampled during the night was characterized by ~~a~~ lower Hg(0) ~~concentration~~concentrations (1.06 ± 0.13 ng m^{-3}), ~~a~~ higher δ^{202}Hg (1.31 ‰ ± 0.15~~‰),~~‰) and ~~a~~ similar Δ^{199}Hg values (−0.28 ‰ ± 0.08 ‰) (22:00 – 06:00, mean ± 1SD, n = 4), compared to Hg(0) sampled during the day~~, with~~ (Hg(0) = 1.16 ± 0.11 ng m^{-3}, p = 0.001; δ^{202}Hg = ~~1.07 ‰ ± 0.19‰ ,~~0.95 ‰ ± 0.22‰, p = 0.01; Δ^{199}Hg = −0.~~24~~26 ‰ ± 0.~~08‰ (~~05‰, p = 0.70, mean ± 1SD, 06:00 - 22:00, ~~mean ± 1SD,~~ n = 2; 24 h, n= 4; p-values based on 2-sided t-tests). An enrichment of heavy atmospheric Hg(0) isotopes during nights is consistent with the preferential uptake of light Hg(0) isotopes by vegetation (Demers et al., 2013;Enrico et al., 2016;Obrist et al., 2017;Olson et al., 2019;Yuan et al., 2018;Yu et al., 2016), the dominant Hg(0) deposition pathway at the study site (Obrist et al., 2017). ~~The enrichment factor ε~~Attributing the diurnal concentration and δ^{202}Hg ~~for~~variation of Hg(0) to vegetation uptake~~ of Hg(0), determined based on Figure 6, was~~, we calculated an enrichment factor of vegetation uptake, $\varepsilon^{202}\mathrm{Hg}_{\mathrm{vegetationuptake}}$, of −4.22 ‰ ± 1.01 ‰ (mean ± 1 se, $R^2 = 0.68$, $p = 0.003$) (Figure S5~~).~~) using a Rayleigh model. Enrico et al.(2016) estimated ~~a~~an $\varepsilon^{202}\mathrm{Hg}_{\mathrm{plant\text{-}air}}$ of −2.6 ‰ for foliar uptake by sphagnum moss, using a Rayleigh model to fit the atmospheric Hg(0) concentration and δ^{202}Hg measured at two locations, a mountain site unaffected by local terrestrial-atmosphere exchange and a peat bog where Hg(0) in air was depleted by foliar uptake. Similarly, observations of the difference in δ^{202}Hg between plants and atmospheric Hg(0) suggested $\varepsilon^{202}\mathrm{Hg}_{\mathrm{plant\text{-}air}}$ between −1 and −3‰ (Demers et al., 2013;Enrico et al., 2016;Obrist et al., 2017;Olson et al., 2019;Yuan et al., 2018;Yu et al., 2016). At Toolik field station, the difference between δ^{202}Hg in vegetation relative to atmospheric Hg(0) was also considerably lower (range of −1.29 to −2.09 ‰, depending on vegetation species (Olson et al., 2019)), than the fractionation factor derived from the atmospheric pattern.

This discrepancy can be explained by the fact that δ^{202}Hg signatures measured in vegetation ~~do~~ not only reflect the isotopic fractionation during foliar uptake but also contain a re-emission component. Hg(II) reduction is expected to lead to more positive δ^{202}Hg values in the residual, foliar Hg(II) fraction, irrespective of the reduction mechanism (Bergquist and Blum, 2007;Zheng and Hintelmann, 2010;Kritee et al., 2007;Jiskra et al., 2015). Re-emission of foliar Hg is supported by observed negative shifts in odd-mass isotope MIF (Δ^{199}Hg) in vegetation relative to Δ^{199}Hg of atmospheric Hg(0) which have been observed at Toolik field station (Olson et al., 2019) and elsewhere (Enrico et al., 2016;Demers et al., 2013). Positive Δ^{199}Hg in atmospheric Hg(0) re-emitted from foliage has recently been constrained by flux bag experiments (Yuan et al., 2018). It is therefore expected that the fractionation factor of foliar uptake is larger than just the difference between δ^{202}Hg in foliage and Hg(0) in the atmosphere. Instead, the difference reflects a net fractionation consisting of the isotopic fractionation during foliar uptake, as well as during foliar reduction and re-emission.

Our observation that the fractionation factor derived from δ^{202}Hg of atmospheric Hg(0) (Figure 6) is larger than the difference of δ^{202}Hg between vegetation and the atmosphere could also be associated with the diel variation of Hg(0) fluxes and PBL dynamics. During daytime, atmospheric turbulence is higher and therefore local signals of terrestrial re-emission are expected to be diluted by mixing with background Hg(0). At night, when the PBL is stable, foliar uptake of lighter Hg(0) isotopes is imprinted on the residual atmospheric Hg(0).

3.3.3 Sink of Hg(0) in soil inferred from Hg stable isotopes

At our study site, soil pore air Hg(0) concentrations were below ambient levels measured in the atmosphere all year (Obrist et al., 2017), with an average concentration of 0.54 ± 0.14 ng m^{-3}, indicating a consistent sink of Hg(0) in soils. Hg(0) in soil pore air showed a lower δ^{202}Hg (−0.01 ‰ ± 0.39 ‰) and a higher Δ^{199}Hg (−0.18 ‰ ± 0.07 ‰) (mean ± 1SD, n = 3) compared to ambient atmospheric Hg(0) (Hg(0) = 1.1 ± 0.09 ng m^{-3}, $p = 0.001$, δ^{202}Hg = 0.81 ‰ ± 0.18 ‰, $p = 0.057$, Δ^{199}Hg = −0.25 ‰ ± 0.04~~‰;~~‰, $p = 0.27$; 24 h, mean ± 1SD, p-value of 2-sided t-test, n = 6) during the summer and fall ~~period~~periods, when we were able to quantify soil pore air isotope patterns. Fitting the Hg stable isotope fractionation trajectory for MDF and MIF of three data points of soil pore air samples and the atmospheric Hg(0) samples resulted in enrichment factors of $\varepsilon^{202}\mathrm{Hg}_{\mathrm{soilair\text{-}atmosphere}}$ = −1.00 ‰ ± 0.25‰ (mean ± 1 se, $R^2 = 0.69$, p~~=~~ = 0.005) (Figure 7 A) and $E^{199}\mathrm{Hg}_{\mathrm{soilair\text{-}atmosphere}}$ = 0.07 ‰ ± 0.04 (mean ± 1 se, $R^2 = 0.32$, $p = 0.11$) (Fig. 7 B). Recently, (Zheng et al., 2018) investigated Hg stable isotope fractionation during oxidation of dissolved Hg(0) by low molecular weight thiol compounds and natural humic acids (HA). For oxidation by HA~~,~~, they reported an enrichment of light Hg(0) isotopes ($\varepsilon^{202}\mathrm{Hg}_{\mathrm{Hg(0)\text{-}Hg(II)}}$ = −1.54 ‰ ± 0.05 ‰, mean ± 1 se) and a positive odd-mass Hg MIF ($E^{199}\mathrm{Hg}_{\mathrm{Hg(0)\text{-}Hg(II)}}$ = -0.18 ‰± 0.03 ‰, mean ± 1 se) in the residual Hg(0) fraction (Zheng et al., 2018). Our limited number of soil air measurements (n = 3) ~~are in agreement~~agree with the fractionation trajectory for HA oxidation (red straight lines in Figure 7), suggesting abiotic oxidation in soils as a cause for observed soil Hg(0) uptake. In spite of a consistent soil Hg(0) sink in soils, Obrist et al. (2014) estimated that the soil Hg(0) sink results in ~~only minor Hg(0) soil uptake (<-0.03 ng m^{-2} h^{-1}) due to low diffusivity. We estimate that at Toolik field station, such a soil Hg(0) sink would only account for <5 % of the total Hg(0) deposition flux observed.~~small Hg(0) fluxes (<-0.03 ng m^{-2} h^{-1}) due to low diffusivity. Comparing the soil Hg(0) uptake flux reported by Obrist et al. (2014) to the net ecosystem flux measured at Toolik field station, we estimate that such a soil Hg(0) sink would only account for <5 % of the total Hg(0) deposition. This is consistent with Hg stable isotope data showing an opposite direction of soil air δ^{202}Hg compared to interstitial snow air Hg(0) in respect to wintertime atmospheric Hg(0) (Figure 8), suggesting that minor soil uptake of Hg(0) does not ~~significantly modify~~strongly affect interstitial Hg(0) patterns in the snowpack above.

4 Conclusions

We document that ~~atmospheric Hg(0)~~ the concentrations and the isotopic composition of atmospheric Hg(0) are strongly affected by terrestrial-atmosphere exchange, in particular by vegetation uptake, of Hg(0~~) in an Arctic tundra ecosystem.~~). While directions and magnitudes of the terrestrial-atmosphere exchange ~~varies~~vary with season and time of the day, atmospheric stability and the dynamics of the PBL strongly affects atmospheric Hg(0) concentrations. ~~In Arctic winter, in the absence of light and with permanent snow cover, the terrestrial-atmosphere exchange of the tundra ecosystem shows a small but steady net Hg(0) deposition. Atmospheric Hg(0) concentrations were relatively constant throughout the day as a consequence of stable PBL conditions and little variability in surface exchange fluxes. During several weeks in spring when AMDEs were present, terrestrial-atmosphere exchange was dominated by photochemically-driven Hg(0) re-emission from the snow surface, leading to higher atmospheric Hg(0) concentrations during the daytime when solar radiation was higest. During the growing season, the terrestrial-atmosphere exchange was dominated by vegetation uptake of Hg(0). Hg(0) re-emission from vegetation and possibly from soil surfaces counteracted Hg(0) uptake by vegetation, leading to strong diel Hg(0) variations with net Hg(0) deposition during the night and early morning and net Hg(0) emission around noon during high solar radiation.~~ During the vegetation period, atmospheric~~Hg(0) concentrations were continuously depleted in interstitial snow and soil pore air.~~ ~~The first Hg stable isotope measurements of Hg(0) in soil air indicated that the soil Hg(0) sink was driven by Hg(0) oxidation by natural organic matter. However, we observed no isotopic traces of this Hg(0) soil sink in the interstitial snow air and atmosphere above. Atmospheric~~ Hg(0) isotope systematics were dominated by vegetation uptake of Hg(0) discriminating heavy Hg(0) isotopes in the residual atmospheric pool, which manifested itself most strongly during ~~the vegetation growth season in summer and during~~ stable PBL conditions at night. We found a larger discrimination of heavier Hg(0) isotopes during foliar uptake when deriving a ~~-~~fractionation factor from atmospheric Hg(0) observations, compared to deriving this factor based on the difference measured between bulk Hg in vegetation and atmospheric Hg(0). While this discrepancy is not fully understood, it may be attributed to photoreduction and re-emission of lighter Hg(0) isotopes during the day. Hg(0) concentrations were continuously depleted in interstitial snow and soil pore air. ~~Overall the study shows the potential of using Hg stable isotopes to better understand the mechanisms driving terrestrial-atmosphere exchange of mercury.~~Hg stable isotope measurements of Hg(0) in soil air reported for the first time indicated that the soil Hg(0) sink was driven by Hg(0) oxidation by natural organic matter. However, we observed no isotopic traces of this Hg(0) soil sink in interstitial snow air and the atmosphere above and concluded that soil uptake of Hg(0) made only a minor contribution to the net ecosystem exchange of Hg(0). Based on the stable isotope signatures of Hg(0) in soil and snow pore air and mass balance considerations, we infer that the uptake of Hg(0) by ground vegetation and/or litter on the soil surface likely was responsible for Hg(0) deposition during the winter months. The combination of stable isotope fingerprints with Hg(0) flux measurements and PBL stability assessment confirmed a dominant role of Hg(0) uptake by vegetation in Arctic tundra Hg cycling.

Atmospheric temperatures increased twice as fast in the Arctic as in temperate regions over the last two decades (Cohen et al., 2014). The increase in Arctic temperatures was accompanied with an earlier snowmelt in spring and thus a longer vegetation period and higher maximal greenness of Arctic vegetation (Box et al., 2019). Vegetation uptake is estimated to currently drive the deposition of 210 Mg Hg yr^{-1} of atmospheric Hg(0) to the Arctic tundra (Obrist et al., 2017;Sonke et al., 2018). With an ongoing warming and greening trend associated with climate change an amplification of the Arctic tundra Hg(0) vegetation pump can be expected. Contrarily, higher soil temperatures leading to permafrost thaw and degration and development of thermokarsts bear the risk of re-mobilization of large amounts of Hg currently stored in Arctic tundra soils (St. Pierre et al., 2018;Olson et al., 2018;Schuster et al., 2018). The net effect of these complex alterations in Arctic mercury cycling driven by climate change is currently poorly understood and the risk needs to be assessed.

Acknowledgments

This project was funded by H2020 Marie Sklodowska-Curie grant 657195 and Swiss National Science Foundation grant PZ00P2_174101 to MJ, European Research Council grant ERC-2010-StG_20091028 to JES and U.S. National Science Foundation, award numbers 1304305, 1739567, and 1848212 to DO. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (http://www.ready.noaa.gov) used in this publication.

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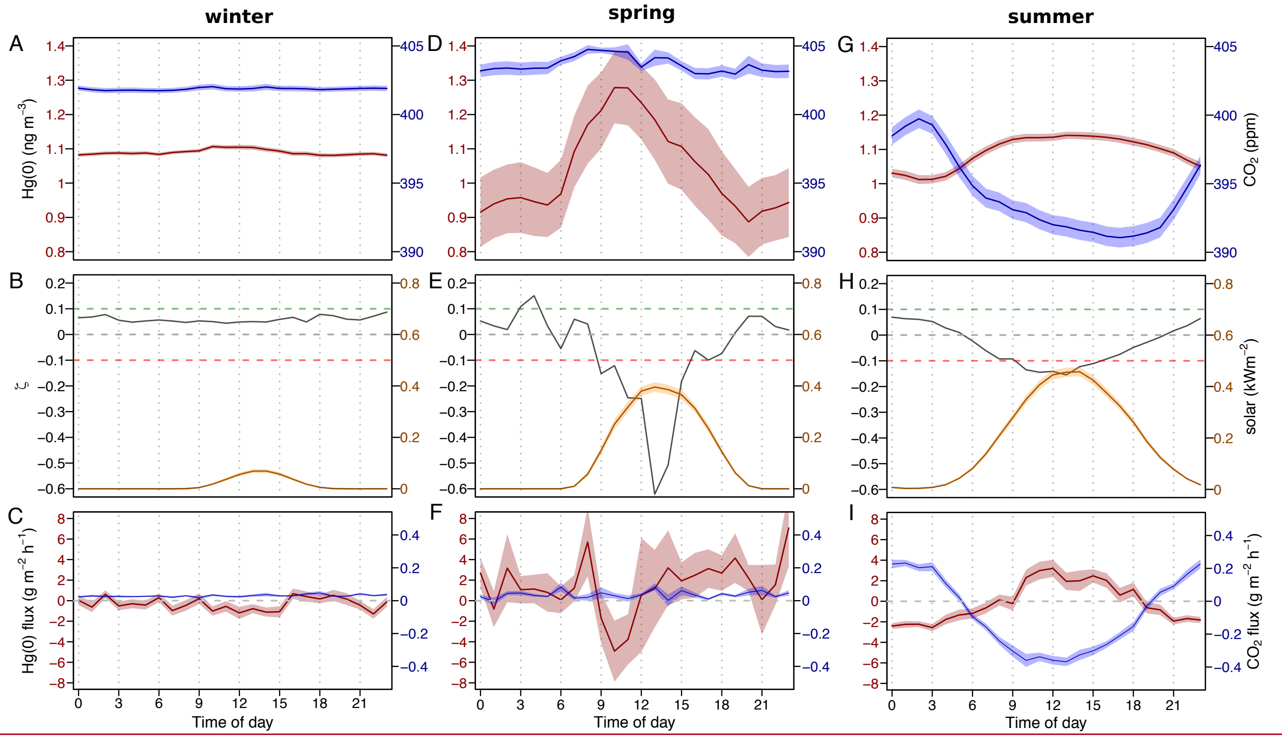


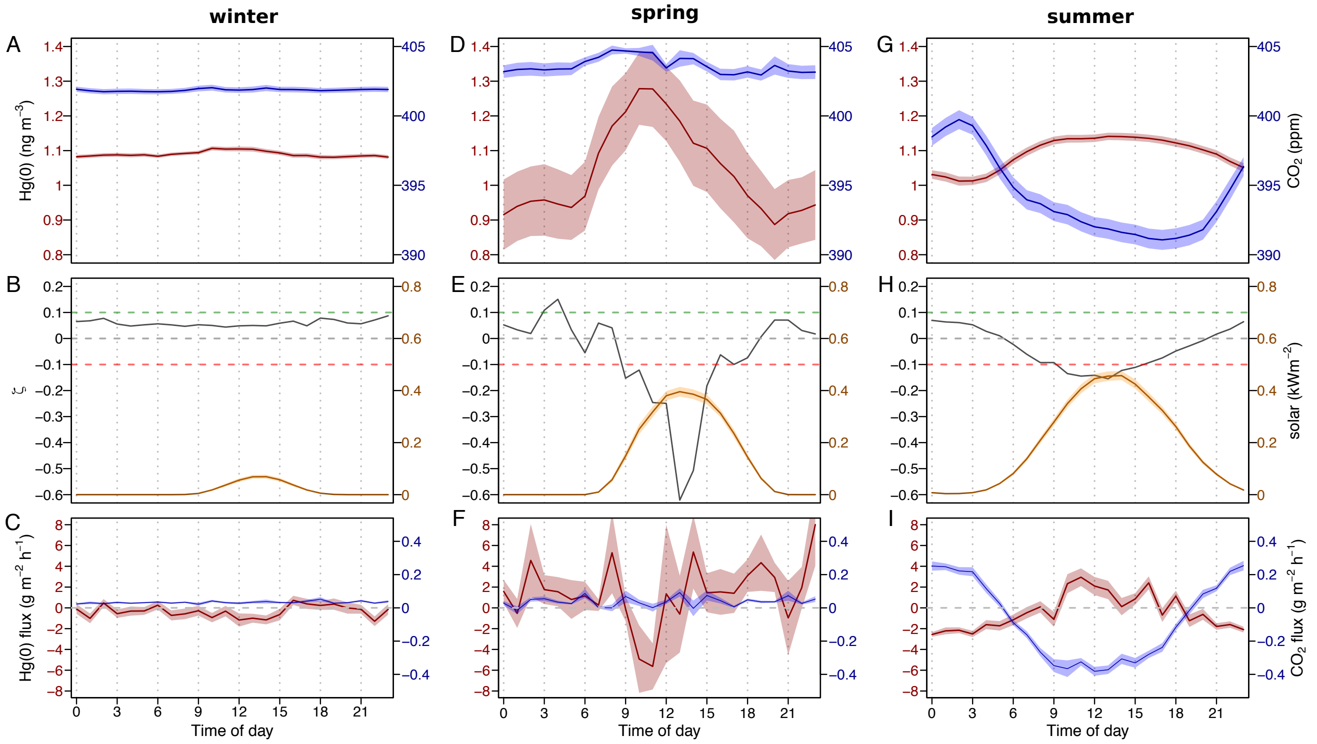


Figure 1: Diel variation during different seasons of the year of A, D and G: average Hg(0) concentration in red and CO_2 mixing ratio in blue in the atmosphere (2 m height). B, E, and H: median planetary boundary layer stability parameter (ζ, grey), where positive values represent stable conditions, and solar radiation (yellow), C, F, I: average Hg(0) flux in red and CO_2 flux in blue. The shaded areas in A and C represent the mean ± 1 SD interval of concentration and flux measurements, respectively.

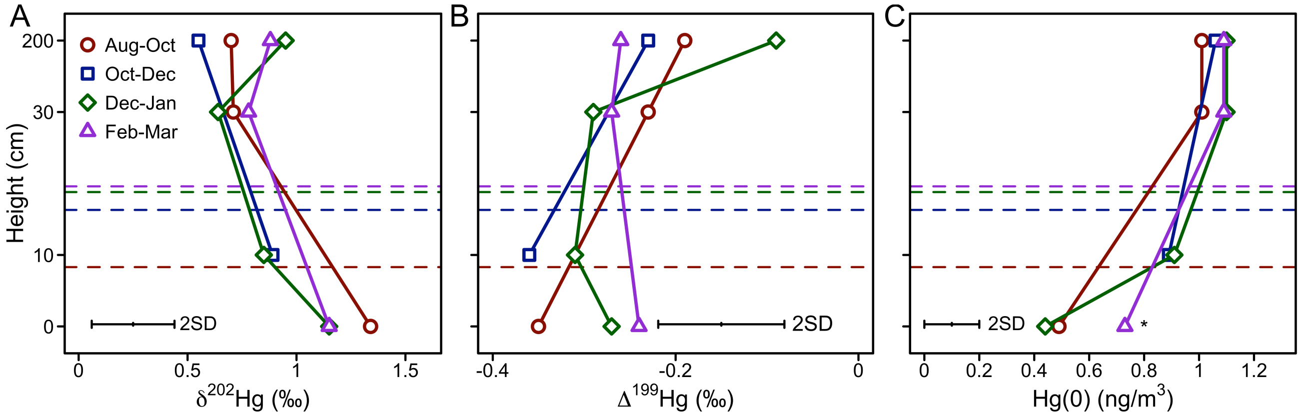
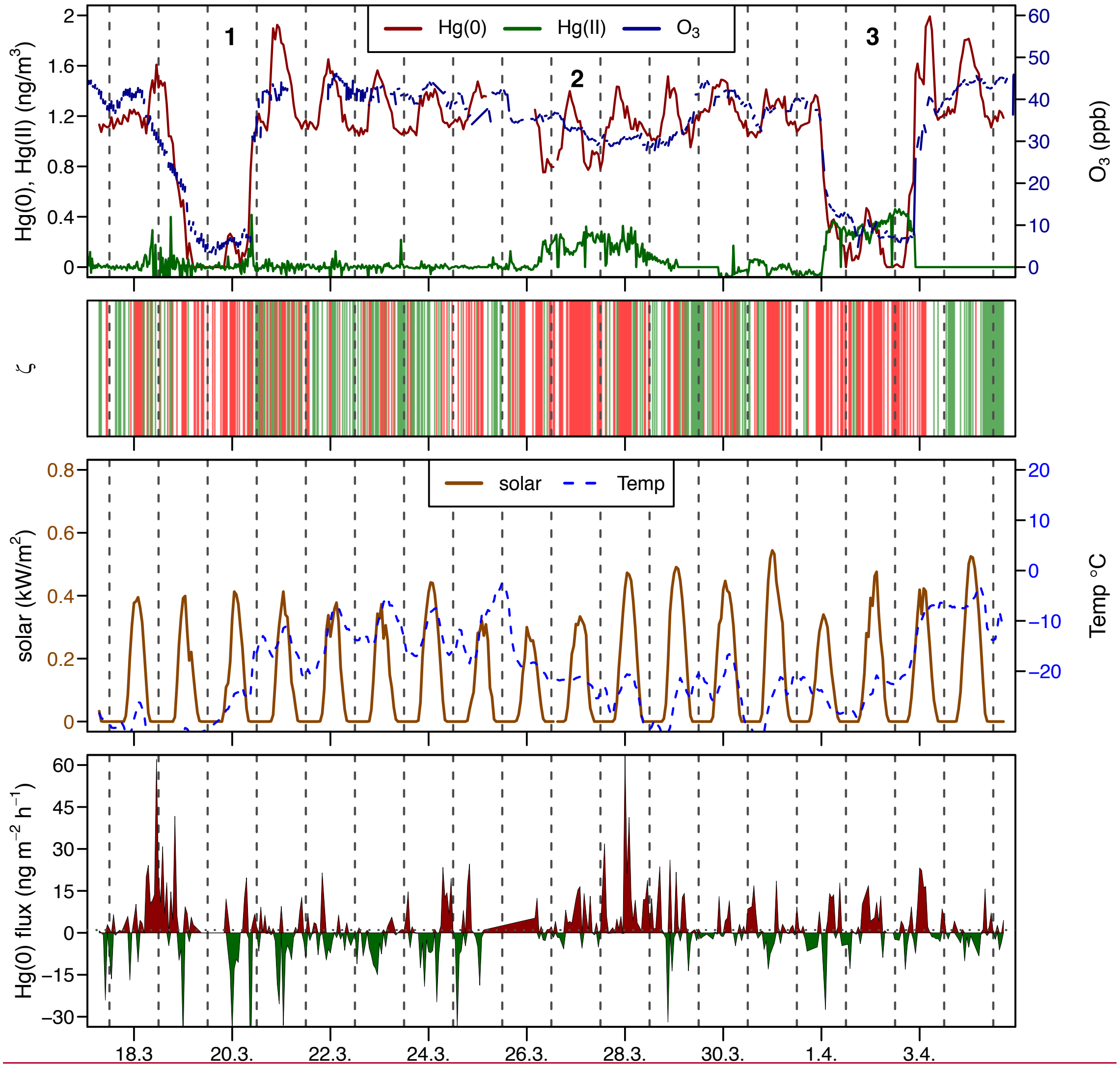


Figure 2: Hg(0) measurements in interstitial snow air profiles A: mass dependent fractionation stable isotope signature of Hg(0) (δ^{202}Hg), B: mass-independent fractionation stable isotope signature of Hg(0) (Δ^{199}Hg), and C: mean Hg(0) concentration. Note that the Hg(0) concentration marked with * was calculated from Hg recovered on the IC-traps, while other Hg(0) concentration profiles were measured by an automated trace gas system deployed in the snowpack (Agnan et al., 2018). The dashed horizontal lines represent the average snow height during the respective period.



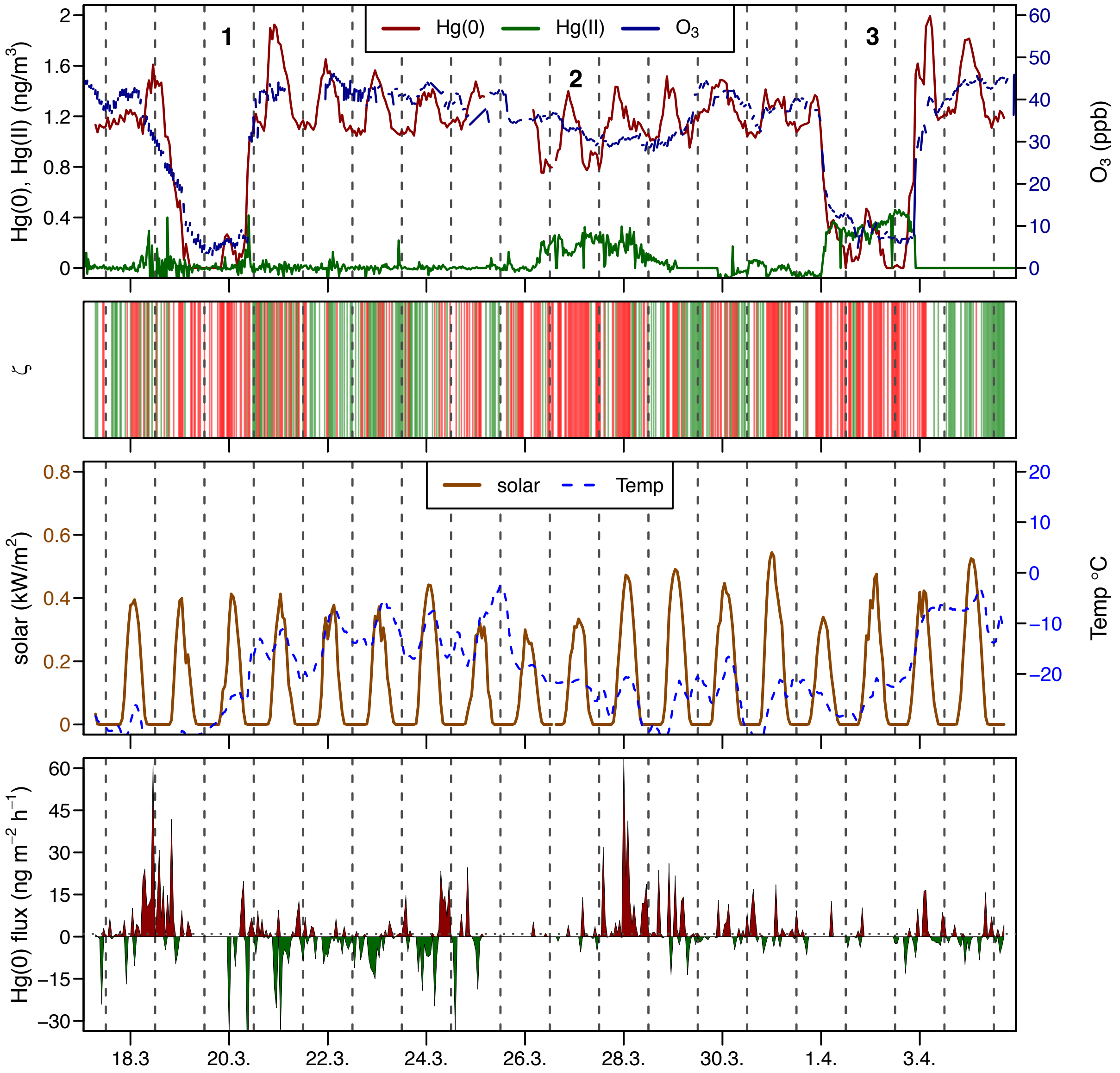
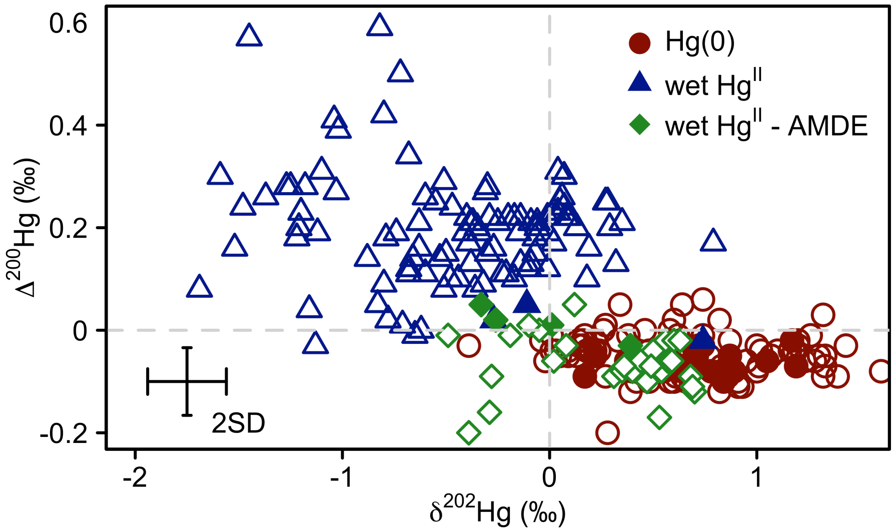


Figure 3: Time series during springtime AMDEs period (18.3.2016-4.4.2016), A: atmospheric Hg(0) (red), atmospheric Hg(II) (green) concentration, and O_3 mixing ratio (blue), B: planetary boundary layer stability (ζ), where the shaded areas in green represents stable conditions (ζ > 0.1) and shaded areas in red represent turbulent conditions (ζ < -0.1), C: solar radiation and air temperature, and D: Hg(0) flux, where Hg(0) deposition is in green and Hg(0) re-emission is in red. Midnight is indicated by dashed lines. Strong AMDEs when Hg(0) concentrations dropped (1,3) or Hg(II) concentrations increased (2) are marked by numbers.



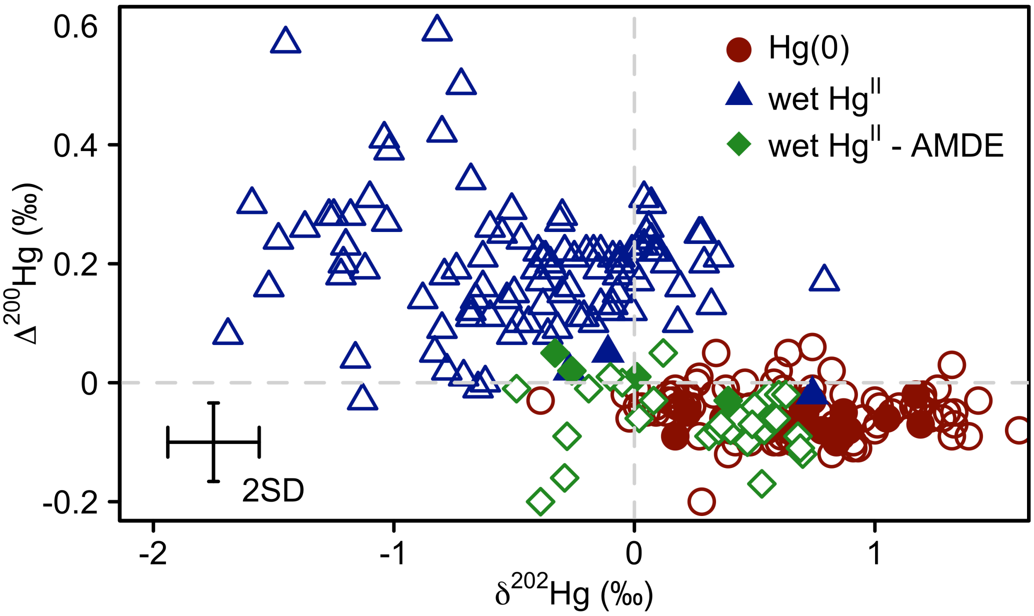
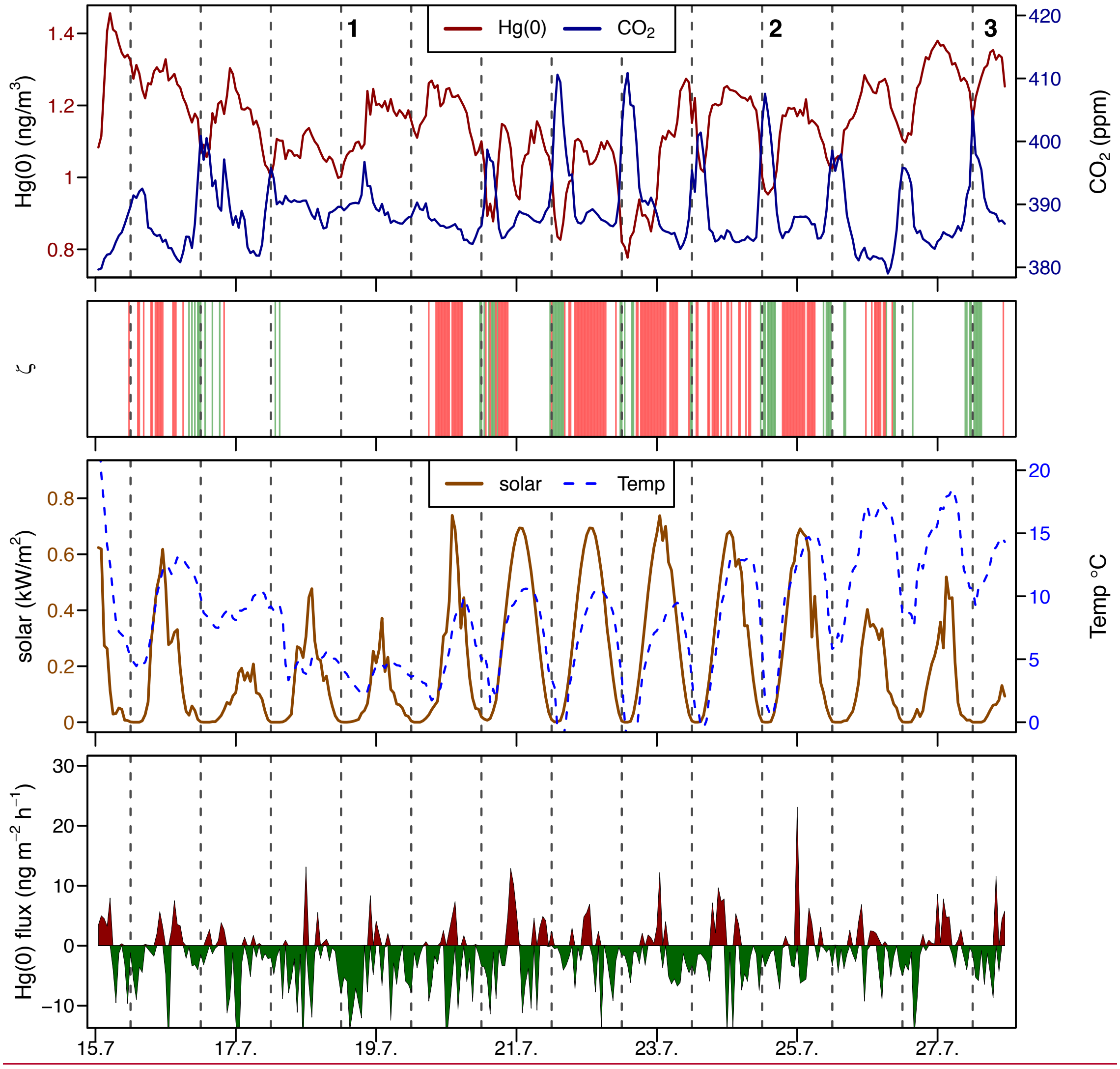


Figure 4: Mass dependent fractionation (δ^{202}Hg) versus even mass-independent fractionation (Δ^{200}Hg) of atmospheric Hg(0) (red circles) Hg(II) in wet deposition sampled at locations or during seasons when no AMDEs occurred (blue triangles), and Hg(II) in Arctic show sampled during springtime AMDE season (green diamonds) for the Arctic tundra at Toolik field station (filled symbols), and reported from elsewhere (empty symbols). Atmospheric Hg(0) data are from (Gratz et al., 2010;Demers et al., 2013;Demers et al., 2015;Fu et al., 2016a;Enrico et al., 2016;Obrist et al., 2017), Hg(II) in wet deposition are from (Demers et al., 2013;Sherman et al., 2015;Chen et al., 2012;Gratz et al., 2010), and Hg(II) in snow from AMDEs are from (Obrist et al., 2017;Sherman et al., 2010;Sherman et al., 2012a). Error bars represent the analytical precision determined by the 2 SD from multiple measurements of an inhouse standard.


Hg(0)
CO2
1
2
3
Hg(0) (ng/m3)
1.4
1.2
1
0.8
CO2 (ppm)
420
410
400
390
380
ζ
solar
Temp
solar (kW/m2)
0.8
0.6
0.4
0.2
0
Temp °C
20
15
10
5
0
Hg(0) flux (ng m−2 h−1)
30
20
10
0
−10
15.7
17.7.
19.7.
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23.7.
25.7.
27.7.

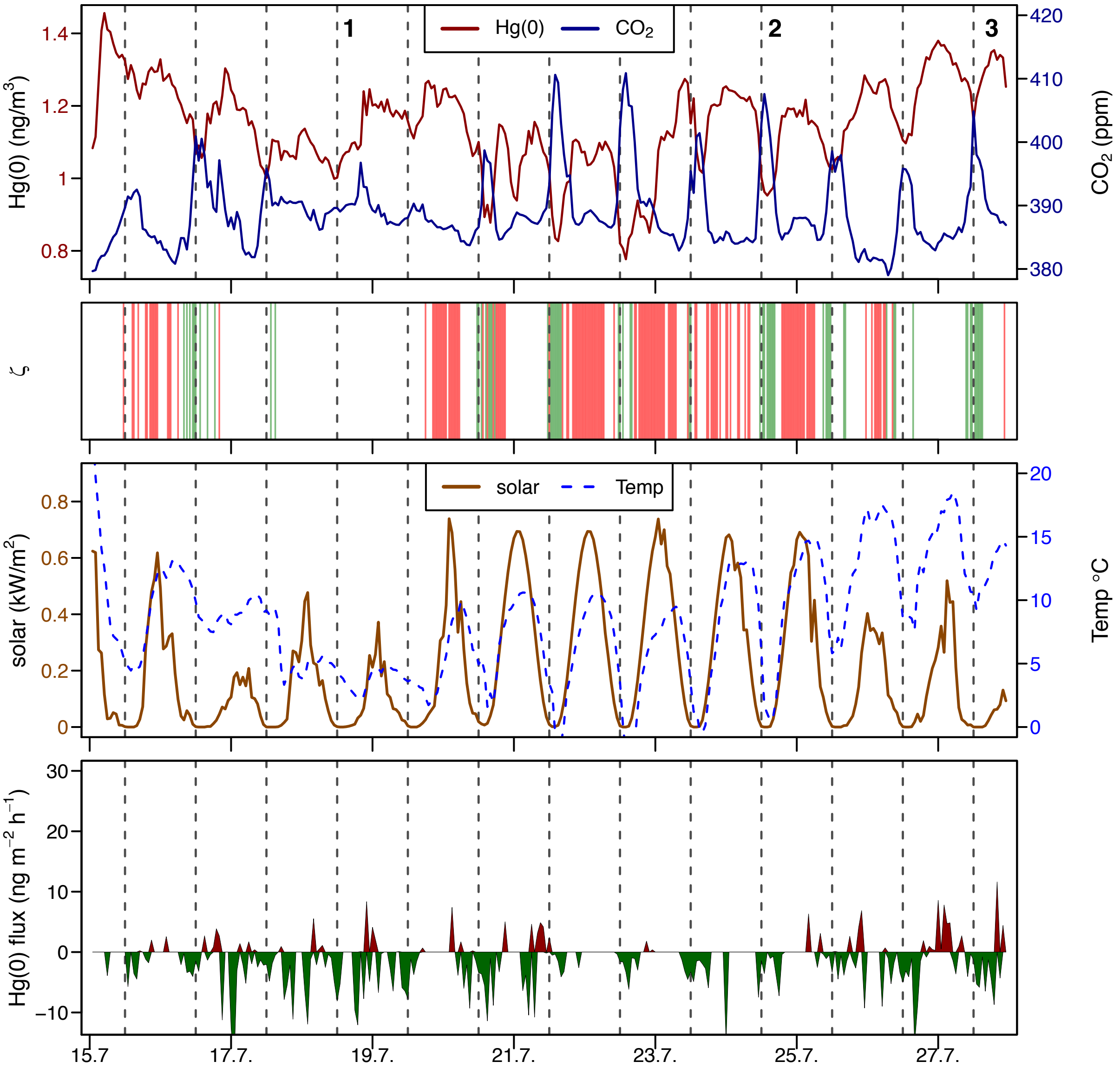

Figure 5: Time series during a midsummer period (15.7.2016 – 28.7.2016), A: atmospheric Hg(0) concentration and CO_2 mixing ratio, B: median planetary boundary layer stability (ζ), where the shaded areas in green represents stable conditions (ζ > 0.1) and shaded areas in red represent turbulent conditions (ζ < -0.1), C: solar radiation and air temperature, and D: Hg(0) flux, with Hg(0) deposition in green and Hg(0) re-emission in red. Midnight is indicated by dashed lines.

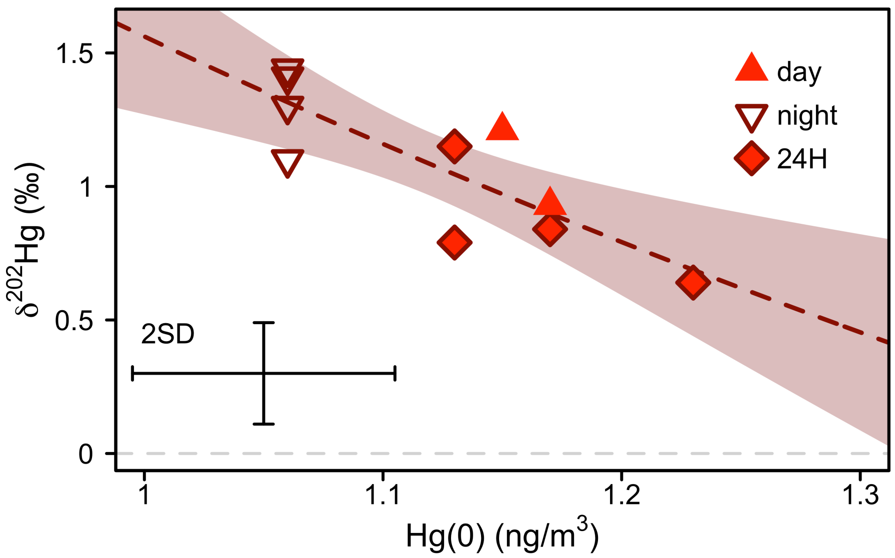

Figure 6: Mass dependent Hg isotope signature (δ^{202}Hg) of atmospheric Hg(0) versus Hg(0) concentration during the snow-free growing period (11 Jun 2016 – 10 Sep 2016). The dashed line represents a non-linear Rayleigh fit and the shaded area the 95% confidence interval (see main text). Error bars represent the analytical precision determined by the 2 SD from multiple measurements of an in-house standard.

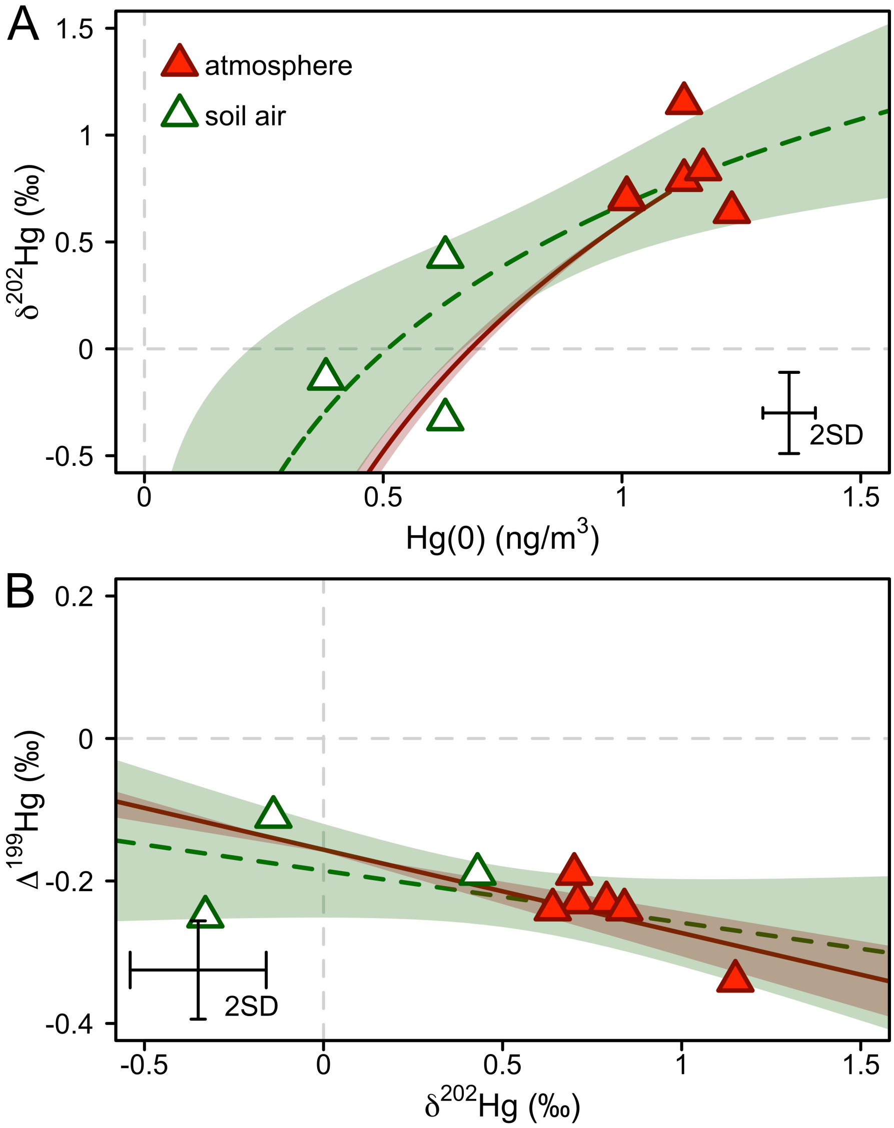

Figure 7: Hg stable isotope systematics of Hg(0) in the atmosphere during summer/fall and in soil pore air measured during the same time period A: Mass dependent Hg isotope signature (δ^{202}Hg) against Hg(0) concentration B: Mass independent Hg isotope signature (Δ^{199}Hg) against mass dependent Hg isotope signature (δ^{202}Hg). The dashed green lines represent the regression of a Rayleigh model (A) and a linear model (B). The straight red lines represent the trajectories for abiotic dark oxidation of Hg(0) by natural humic acids (HA) from Zheng et al. (2018). For comparison with observations, the intercept of the linear regressions was adjusted to fit through the average of atmospheric Hg(0). The shaded areas represent the 95% confidence interval. Error bars represent the analytical precision determined by the 2 SD from multiple measurements of an in-house standard.

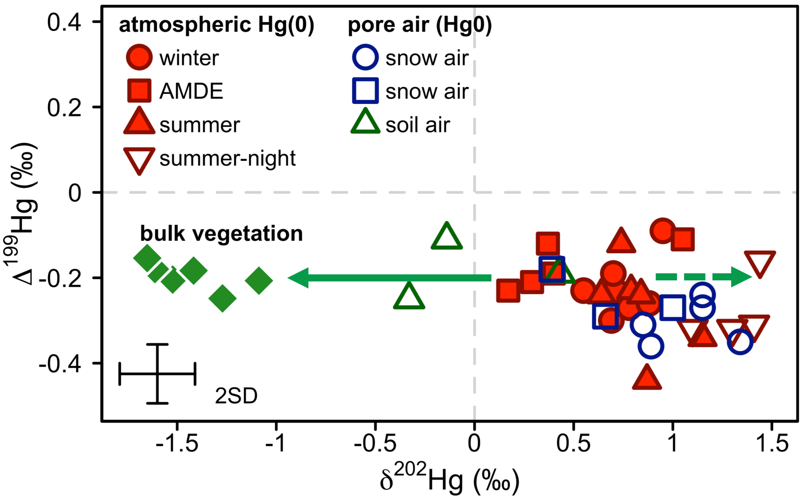

Figure 8: Overview of Mass independent Hg isotope signature (Δ^{199}Hg) against mass dependent Hg isotope signature (δ^{202}Hg) of atmospheric Hg(0) (red) and Hg(0) in pore air of snow (blue) and soil (green) during winter (circles), AMDE season (squares) and summer/fall (triangles). Bulk vegetation measurements (green diamonds) are reproduced from Obrist et al. (2017). The straight arrow represents the fractionation during Hg(0) uptake by vegetation, the dashed arrow represents the expected development of the corresponding residual Hg(0) pool. Error bars represent the analytical precision determined by the 2 SD from multiple measurements of an in-house standard.