We greatly appreciate the constructive recommendations provided by both reviewers. We report below our point-by-point response to the critiques and highlights to the changes made to the manuscript. For ease of discussion, we have numbered the reviewer’s comments.

Response to REVIEWER #1 comments:

Specific comments

(1.1) The authors need to more fully explore the implications of their study with respect to Hg loading in alpine snowpacks and the possibility that Hg in the snowpack represents an important source of Hg to ecosystems after snowmelt. Can the authors estimate the relative flux of GEM from the snowpack versus the amount of Hg wet deposited in snowfall? If this cannot be done quantitatively, the authors should at least qualitatively place the results of their study within this larger framework and discuss the implications of their data more fully in the Conclusions section.

Response: Our setup did not allow for quantitative determination of snow-to-atmosphere GEM fluxes, and calculating fluxes based on GEM concentration gradients between the top layer of the snowpack and the inlet located ~80 cm above the snow surface would be a stretch, in our view. This is the reason we decided not to over-interpolate the results and not quantitatively compare snowpack GEM fluxes to other watershed fluxes such as snowmelt fluxes and wet deposition. We agree with the reviewer that this would be an interesting and important aspect for future study, e.g. by means of flux chambers that could be added to the experimental setup.

However, we discuss the implications of photochemical GEM losses based on watershed mass balance studies mentioned in the introduction. We now mention in the abstract that photochemical GEM production in surface snow dominates through the entire winter, and clarify in the conclusion section that this is the first study to show so (please note that previous studies based on manual point observations were not able to make such statements conclusively). Similarly, we state that highest photochemical re-emission occurs after snowfall, a key information for future studies, so they can focus on most relevant periods for snow GEM losses. In regard to dark oxidation of GEM in the lower snowpack, we conclude qualitatively that “transport processes and redox reactions within lower snowpack, however, are likely too small to drive significant vertical redistribution of total Hg in the snowpack.”

(1.2) Although the authors state that they collected data both in 2009 and 2011/2012, only the data from the 2009 study are presented in the figures and discussed in the text. The authors should discuss and present their results from the 2011/2012 sampling campaign as well. By describing the sample collection but not the results, it leaves the reader wondering whether the results from 2011/2012 are contradictory to those from 2009. If there is not room within the manuscript to do this fully, these data could be included in a supplementary section. Alternatively, if it is more appropriate to do so, the authors could focus this manuscript only on the 2009 data and present the 2011/2012 data in a subsequent publication.

Response: A new Tekran GEM monitor was purchased and received just prior to the 2011/2012 experiment. A number of instrumental problems were encountered during the immediate and first deployment of this monitor at the site. Consequently, while the analyzer was operated throughout
the entire winter period, the record of available data is quite patchy, covering ~54% of the snow-covered period. In addition, during the 2011/2012 season we conducted a second experiment at the same site to investigate spatial variability of snowpack gas concentrations. For that experiment we occasionally sampled from a network of inlets that were all at 30 cm height above the ground and were distributed around the primary snowtower. Consequently, those periods further reduce the snowtower data record. Despite the intermittency, the available data do, however, show the same features that were seen in the 2009 data. Therefore, while we prefer to not graphically show these data, we believe that this demonstrated reproducibility of the results of this experiment is worth mentioning.

(1.3) In addition, the authors chose specific dates as examples (e.g., in Figures 1 and 6) of the phenomena they describe but it is not always clear why these dates were chosen. The authors should describe their methods for choosing to present these data (e.g., they are exemplary of the entire study or represent the most complete data sets, etc.).

Response: Figures 1, 4, and 6 of our manuscript report data selected from specific dates. We have now clarified why these dates have been chosen. Figure 1 shows two days (DOY 58 and 59) of GEM data in the SIA (Snow Interstitial Air) at all snowpack depths sampled. We selected DOY 58 and 59 because wind speed was low and they were exemplary of the entire study, thus allowing to illustrate how the snowtower system operates with no artifacts induced by natural ventilation. Figure 4 shows 20 days of data, a period chosen for its limited changes in total snowpack height. Figure 6 reports data from DOY 92-101, a period characterized by constant soil moisture and thus a relatively constant flux of CO2 from soils.

(1-4) The authors should discuss whether changes in the height of the atmospheric sampling inlet above the snowpack impacted the measured GEM concentrations. It appears that the concentrations measured at this inlet were fairly stable throughout the study period. However, it seems possible that concentrations could have been elevated if the inlet was very close to the surface of the snowpack due to collection of GEM that was photochemically produced and emitted from the snowpack. Did the authors observe such a relationship?

Response: We did not observe any obvious dependence of the atmospheric GEM concentrations on the height of the inlet above snow surface. To demonstrate this further, we calculated atmospheric GEM (mean +/- StdDev) for different height intervals:

- Height of atmospheric inlet above snow surface lower than 90 cm: 498 observations
- Height of atmospheric inlet above snow surface between 90 cm and 105 cm: 419 observations
- Height of atmospheric inlet above snow surface larger than 105 cm: 237 observations

For all three height intervals as defined above, atmospheric GEM was 1.3 +/- 0.1, i.e., a level identical to the one calculated when considering all data available from this study. We added a sentence to the manuscript to specify that GEM in the atmosphere measured during our study was not dependent on the height of inlet above snow surface.

(1-5) I would suggest that the authors reorganize section 3.1 so that it is clearer to the reader. It seems that it would make most sense to first describe the general trends in the data (as starts on pg. 15433, line 21) and the GEM concentrations throughout the year (Figures 2 and 3), and then describe the detailed diurnal cycling using the example in Figure 1.
Response: in section 3.1, we chose to first illustrate how the snowtower system operates by providing data collected over a 7-inlet cycle, i.e. during a 70 min period. The snowtower sampling system is a quite complex setup and we believe that figure 1a and 1b are really helpful for the reader to understand its operation.

(1-6) The authors discuss various oxidants that may cause dark destruction of GEM within the snowpack. This discussion would be aided by the measurements of O3 and NO that were made throughout the snowpack. If these data do not fit in the manuscript, they could be presented in a supplemental section.

Response: We actually did not measure NOx in 2009, i.e. during the GEM sampling period. We do refer in the discussion to NOx measurements conducted at this site during winter 2007 with the same snowtower sampling device – we now clarify this in the revised manuscript.

Ozone was measured simultaneously with GEM during the winter 2009. However, the reviewer is correct that ozone data were not included to the manuscript. The reason is that ozone concentration patterns do not exhibit daily or seasonal cycling; NWT snowpack ozone data have been extensively reported and discussed in two previous publications (Bocquet et al., 2007; Helmig et al., 2009). We now refer to these two publications and state: “Ozone in the Niwot Ridge snowpack declines at a fast rate with depth, resulting in less than 10% of ozone remaining ~50 cm below the surface (see ozone data in Helmig et al., 2009 and in Bocquet et al., 2007); similar ozone gradients were again observed during this campaign (data not shown).” If ozone was the main GEM oxidant, then the upper snowpack layers would exhibit the strongest GEM sink, and GEM loss from ozone would be lower in the deeper snow. Further, the relatively stable day-night snowpack ozone concentrations (i.e. lack of diurnal cycles) would not be able to explain the highly dynamic patterns of GEM in the snowpack.

(1-7) In addition, the authors should clearly discuss the balance between diffusive transport of GEM down through the snowpack (resulting in the lag in max GEM concentrations), advective transport of GEM up through the snowpack due to high surface winds, and oxidation of GEM within the snowpack. What factors (oxidants? Meteorology? Snow physics?) control the relative importance of these processes in the different snow layers?

Response: We have modified the manuscript to be more specific about the factors driving the importance of diffusive transport of GEM, advective transport of GEM (also referred as “GEM natural ventilation” in the manuscript), and GEM oxidation. We agree with the reviewer that these questions are of high interest, however, despite our unprecedented spatial and temporal coverage of measurements, the data do not allow to explicitly quantify the degree to which each of these individual processes contribute to observed GEM patterns. These processes are discussed as follows:

- Diffusive transport is dependent on snow physical characteristics, such as porosity and tortuosity. These variables are discussed in section 3.3 where we report Fick’s first law. We have modified the section 3.2 to state that diffusive transport is a key parameter for the observed GEM patterns.
- In section 3.2, we investigated in detail a 20-day period in late winter (from DOY 82 to 102). This allowed us to clearly identify wind speed as another key-parameter and to show that advective transport contributes to the observed GEM patterns in the NWT snowpack.
- Factors driving GEM oxidation are discussed in section 3.3.
We now also clarify that a compensation point between advective and diffusive transports on one side, and oxidation on the other side, is observed at ~135 cm below the snow surface, where GEM concentrations average about 0.4 ng m$^{-3}$, and diel variability is no longer evident (section 3.3).

1-8 The authors should further explore the correlations that they observe between GEM in the upper snow layers, solar radiation, and recent snowfall. Are these correlations statistically significant (Figure 5)? In addition, there are peaks in GEM on days 95 and 96 that are associated with very low amounts of solar radiation. The authors hypothesize that photochemical reduction produces the GEM in the upper snow layers, but these data may suggest that there are other significant reductants of GEM in the upper snow layers.

Response: We agree with the reviewer that, interestingly, our data reveal elevated GEM concentrations in the top layer of snowpack during both high and low solar radiation periods. However, enhanced GEM during low radiation days were always coinciding with recent deposition of fresh snow. This is an important finding of our paper, that we discuss as follows: “The NWT data suggest that fresh snow provides a new reservoir of photoreducible Hg(II) and that highest surface snow GEM levels are hence linked to the deposition of fresh snow. Notably, these elevated GEM levels occurred during periods with relatively low solar radiation (as snowfall was related to cloudy conditions), further suggesting that photochemical production of GEM is not radiation-limited at this site.” We also modified the last sentence of the abstract to even more emphasize this important observation. We conducted a statistical significance test on these correlations; results (P-values) were added to Figure 5.

1-9 The authors should more fully discuss the results of the snowpit THg sampling. Although the authors state that they sampled THg in the snowpits throughout the season (p. 15426, line 22), they only discuss THg concentrations in two pits sampled on March 9 and April 27 (section 3.4). It also does not seem correct that March 9, 2009 was the start of the snow season. Were other pits sampled during the season? If not, why do the authors believe that these snowpits were representative of the snowpack throughout the season? In addition, because Figure 7 was not included in the PDF version of this manuscript, it is difficult to assess the trends in THg concentration described by the authors.

Response: The reviewer is correct here when pointing out two errors in our manuscript:

- The introduction section statement p. 15426-line 22, was not correct. In this study, we report and discuss only two snow pits collected on March 9 and April 27, 2009. The phrase “through the season” was replaced by “two snow pits were excavated in our study”.
- March 9 cannot be considered the start of the snow season. This statement was removed from the manuscript.
- We apologize for omission of Fig. 7 in our initial submission; this figure was made available online a month before closing of the interactive discussion.

We are not claiming that the two snowpits are representative for the entire season (specifically snowmelt periods are not covered in our study). However, the two snowpits were sampled at the beginning and at the end of the SIA GEM sampling period to specifically investigate if the bottom layers of the snowpack could be a possible Hg sink driven by the GEM oxidation processes. The interpretation of the results from both approaches (i.e., investigating THg in snowpits and GEM dynamics) agree in that transport processes and redox reactions were too small to drive significant
vertical redistribution of total Hg in the snowpack. We clarified section 3.4 of the manuscript to better describe the objectives of snow pit sampling.

Technical Corrections

Pg. 15425, line 17: Suggest that “Hg storage reservoir” should be “Hg storage reservoirs”.
Response: Corrected as suggested.

Pg. 15426, line 10: Suggest that “Hg emission” should be “Hg emissions”.
Response: Corrected as suggested.

Pg. 15427, line 16: Suggest that “interstitial snow air” should be “snow interstitial air”.
Response: Corrected as suggested.

Pg. 15428, lines 10-11: I would suggest that the authors indicate that the sampling proceeded from X height inlet to X height inlet. This will make the sampling sequence clearer.
Response: Corrected as suggested.

Pg. 15430, line 1: Suggest that “for total Hg” should not be stated twice in this sentence.
Response: Corrected as suggested.

Pg. 15430, lines 7-10: The authors should discuss the results of measurement of bottle blanks for the snow THg samples. This is especially important because the authors did not clean the bottles using BrCl and because concentrations of THg in snow can be extremely low.
Response: Corrected as suggested. We included the THg concentrations determined during our study on 4 field blanks.

Pg. 15433, line 15: Suggest that “12:00am” should be “12:00pm”.
Response: Corrected as suggested.

Pg. 15433, line 22: Suggest that “Sects. 2 and 3” should be “Sects 3.2 and 3.3”.
Response: Corrected as suggested.

Pg. 15434: Figure 3 does not clearly show the “strong diurnal concentration fluctuations” in GEM as the authors state (line 13). Because each day is represented by such a small space on the figure, it is very difficult to observe the diurnal cycles on this annual plot.
Response: We now also refer to Figure 2 and highlight DOY 37 to 64 for this statement. In our view, however, this figure does indeed exemplify that diurnal patterns occur throughout the season (note the fine-scale color variations).

Pg. 15436, line 10: Suggest that “Fig. 2b” should be “Fig. 2a”.
Response: Corrected as suggested.

Pg. 15436, lines 14-17: This sentence is confusing. I would suggest that the authors rewrite it so that their meaning is clearer. This sentence has been rephrased. Pg. 15437, line 1: Suggest that “20-days” should be “20-day”.
Response: Corrected as suggested.
Pg. 15438, line 12: Suggest that this sentence should read “. . . in the 0-30 cm depth layer in response to fresh snowfall.”
Response: Corrected as suggested.

Pg. 15438, lines 13-17: This sentence is long and confusing. The authors should restate so that their meaning is clearer.
Response: This section was modified as follows: “A similar analysis was conducted on the winter 2011/2012 data. The 2011/2012 data record overall spans a longer time period, i.e. from earlier to later in the snow cover season. However, due to instrument problems and a different experimental protocol, this record has fewer snow precipitation events for consideration. Nonetheless, results show similar tendencies, i.e. elevated SIA GEM levels during and immediately following snowfall events, and consequently confirm the findings drawn from the year 2009 data.”

Pg. 15439, lines 21-26: I would suggest that the authors switch the order of these last two sentences to improve the logical flow of their arguments.
Response: Corrected as suggested.

Pg. 15440, lines 22-23: This section may be confusing to readers. I would suggest that the authors add a clause to this statement indicating that the ratio should be constant if changes in GEM concentration are driven by snow physics and wind-induced advection.
Response: This section has been modified as follows: “Changes in the ratio defined in equation (2) with snowpack depth should be constant if changes in GEM and CO$_2$ are both driven by snow physics or wind-induced ventilation; if ratios change with depth, this would be indicative of GEM chemical sinks (or sources) within the snowpack.”

Pg. 15440, line 25: Suggest this sentence is changed to read: “. . . thereby allow assessment of GEM chemical sinks . . .”
Response: Corrected as suggested.

Pg. 15441, line 6: It appears on Figure 6 that the GEM/CO2 ratios in the lower snow layers are lower than the normalized value in the upper layer. However, the ratios (as plotted) are not negative.
Response: We clarified this in the text. It is stated that all non-normalized concentration and flux ratio results are negative due to the opposite sign of concentration gradients and fluxes of CO$_2$ and GEM; non-normalized negative ratios also increase toward zero with depth. Thus, normalized ratios are positive, and decrease toward zero with depth. We chose to normalize flux ratio data shown in Fig. 6 to make this data display clearer for the reader.

Pg. 15441, lines 18-20: Does Figure 3 include data from NWT or from another site located further south? This statement is confusing because it suggests that the data presented in Figure 3 are from another site.
Response: No, we stated “further south” as our site is at mid-latitudes as compared to polar and sub-polar studies. We clarified this and add latitude coordinates to this section.

Pg. 15442, line 1: Suggest that “ozone is” should be “ozone are”.
Response: Corrected as suggested.
The authors should add references to this statement.

Response: We now cite the study from Hall et al. (1995) in the manuscript.

Suggest that “4-days” should be “4-day”.

Response: Corrected as suggested.

Suggest that “understandings” should be “understanding”.

Response: Corrected as suggested.

Suggest that “dynamics” should be “dynamic”.

Response: Corrected as suggested.

Suggest that “. . . may indicate a potential GEM production..” should be “. . . may indicate potential GEM production. . .”

Response: Corrected as suggested.

Figures: Figure 4: It is difficult to tell the different colored lines apart on this figure and in the figure legend. I would suggest that the authors make the lines in the legend thicker.

Response: We modified both the legend and the thickness of lines on Figure 4.

Figure 5: I would suggest that the authors use the same temporal reference frame for both the y-axes labels and the figure legend (i.e., 1 day after versus 1 day before).

Response: The caption of Fig. 5 was corrected.

Figure 7: This figure was not included in the online PDF version of this manuscript.

Response: We apologize for this figure missing to our BGD manuscript. As soon as this review was published online, we posted the missing figure on the BGD webpage.

Response to REVIEWER #2 comments:


Response: We added the Fisher et al. reference to our introduction, and clarified the role of terrestrial ecosystem as source of mercury in the Arctic.

(2-2) Page 15247 line 9: Could you give more details on the actual snow cover and snow-fall events during your study periods?

Response: Two sentences were added to section 2.1 and now provide more detail on snow cover and snow-fall events during the 2009 sampling period.

(2-3) Page 15432 line 20: Does the "entire measurement campaign" refer to the 2009 data (as implied by the next sentence) or to 2009 and 2011-2012. If so, why are data from 2011-2012 not included in Figure 2?

Response: Please see response to comment (1.2).
(2-4) Page 15433 line 8 and page 15435 line 15: How deep is the photolytic zone? Could you estimate this based on structural characterisation of the snow-pack. I’d guess this is less than 60 cm which would further support your conclusion in the importance of transport processes.

Response: The thickness of the photolytic zone is discussed in section 2, and we conclude “From the interpretation of these data we conclude that GEM production at the NWT Soddie site mainly occurs in the 0-30 cm depth layer” (page 15435, line 15).

(2-5) Page 15435 lines 26: I’m surprised that Hg(II) complexes with Cl- can be photolyzed by solar light, as the absorption is well below 300 nm; rather around 200 nm. (Kunkely, H., Horvath, O. and Vogler, A.: Photophysics and photochemistry of mercury complexes, Coordination Chemistry Reviews, 159 IS, 85–93, doi: 10.1016/S0010-8545(96)01307-0, 1997.) Are there newer data to support this mechanism?

Response: We agree with the reviewer that in theory mercury complexes such as chlorocomplexes cannot be broken up by sunlight light with wavelengths longer than 290 nm. Mercury complexes such as HgCl2, HgCl3-, HgCl42- exhibit absorption maxima in the UV at wavelengths of ~200, 240, and 234 nm, respectively, according to Kunkely et al. (1997). However, some evidence of Hg(II) photoreduction in seawater (mainly HgCl2) under addition of dissolved organic carbons has been observed by Costa and Liss (2000). These authors demonstrate that although photolysis of chlorocomplexes is unlikely with natural sunlight irradiation in laboratory experiments, it may occur in the natural environment.

(2-6) Page 15436 line 20. This numerical simulation was done for diffusion through porous snow taking porosity and tortuosity into account, wasn’t it?

Response: Yes, we took into account both snow porosity and tortuosity, which we clarify in section 3 and refer to at this point as well. We did not provide further details on this in the manuscript as the modeling was only a minor point of this study. However, here is further information for the reviewer:

Snow porosity was calculated from snow density profiles collected weekly at the Soddie site in the framework of the LTER program a few hundred meters away from our gas sampling site. No direct determination of tortuosity was available for this site. At the polar location, Summit, Greenland, Albert and Shultz (2002) reported that tortuosity of the surface wind packed snow of ~2.0. This is larger than expected for the NWT snowpack because the Summit wind-packed snow is less permeable. To take into account this uncertainty, we tested three hypothetical conditions, with tortuosity values of 1, 1.5, and 1.8, respectively. Modeling results obtained with all three tortuosity conditions tested show the same conclusion: at night, diffusion alone would result in lower GEM levels in the top snow levels than what was observed.


Response: We did not observe crystals growing from vapor phases (e.g., hoar) at the surface of the NWT snowpack such as described in the arctic study. Therefore we did not include this discussion and citation in our manuscript.
(2-8) Page 15439 line 4 I was wondering, if the snow is permeable throughout the whole measurement campaign or if ice layers might have formed that inhibit diffusive transport. Do CO2 or NO data support the permeability?

Response: The reviewer is correct that ice lenses may exist in the snowpack. We examined density profiles collected in an adjacent open meadow area with similar vegetation and slope characteristics ~30 m away from our site. These profiles show that few ice lenses existed in the snowpack during April and May, 2009. Furthermore, Seok et al. (2009) in their investigation of the effect of ice layers on gas diffusion in the NWT snowpack (measuring CO2), concluded that the snow gradient sampling technique is rather robust against the influence of ice lenses and crusts. We have included a statement in section 3 to (i) report that ice lenses could exist in the investigated snowpack, and (ii) discuss their eventual impact on the diffusion calculation.

(2-9) Page 15439 line 10 Please specify “adsorption energy”. If you refer to DHads this would not be sufficient to estimate the partitioning, as it neglects the entropy. You would need to discuss DGads or K. Also, both quantities are standard quantities. Please give the standard state.


Response: The reference to the Ferrari et al. (2004) paper, reporting an adsorption energy of -61 KJ mol⁻¹ for adsorption of GEM onto snow surfaces, has been removed from the paper. We now emphasize the low K value (i.e., adsorption equilibrium constant) estimated from lab measurements and extrapolated to 270K as reported by Bartels-Rausch et al. (2008). These authors used standard quantities for their calculation. They demonstrate the negligible partitioning of GEM with snow or ice for the environmental temperature experienced at our site.

(2-10) Page 15443 As temperatures approach 0 C I would suggest that liquid water might be present. Impurities and geometric contrains in grain boundaries can stabilize water well below 0 C. The role of the quasi-liquid layer is much more speculative (Bartels-Rausch, T., Jacobi, H. W., Kahan, T. F., Thomas, J. L., Thomson, E. S., Abbatt, J. P. D., Ammann, M., Blackford, J. R., Bluhm, H., Boxe, C. S., Domine, F., et al.: Relationship between snow microstructure and physical and chemical processes, Atmos. Chem. Phys. Discuss., 12(11), 30409–30541, doi:10.5194/acpd-12-30409-2012, 2012.)

Response: We appreciate this reference to the interesting review by Bartels-Rausch and others. Specifically, this review points out the confusion provoked by the naming “quasi liquid layer (QLL)”. As discussed in this review, the QLL refers to properties approaching a super-cooled liquid. It is likely that the NWT snowpack, where temperatures of the deep snow layer and the soil underneath the snowpack are relatively stable and close to 0°C, did not experience super-cooled liquid water but rather liquid water. Bartels-Rausch and others (2012) discuss that geometric constraints can stabilize liquids in reservoirs, even below the eutectic temperature (Nye, 1991). So we agree with the reviewer that involving QLL in our discussion was incorrect. We revised the manuscript accordingly and are no longer considering QLL chemistry, but instead disordered interfaces where liquid water can exist even at temperature slightly below 0°C. We also added reference to the publications by Bartels-Rausch et al. (2012), and Nye (1991).

(2-11) Page 15443 line 21. Your data set give the unique opportunity to show the importance of freeze-induced reactions in the field. Just for curiosity, have you looked for episode where your
snow-pack might undergo freezing (at temperatures below 0 °C due to melting point depression).

Do those data indicate a decrease in GEM?

Response: We investigated correlation between snow temperatures and GEM concentrations in the snow interstitial air. No clear relationship between these two parameters could be established with our data:

- In the top layers of the snowpack, where snow temperature experienced above and below 0°C values, GEM production was superseeding GEM oxidation processes.
- In the bottom layers of the snowpack, were we clearly identified GEM oxidation, the snow temperature was stable and close to 0°C during the entire campaign. The NWT snowpack did not undergo large freezing-thawing events at these depths.

References


Seok, B., Helmig, D., Williams, M. W., Liptzin, D., Chowanski, K., and Hueber, J.: An automated system for continuous measurements of trace gas fluxes through snow: an evaluation of the gas diffusion
Corrected Figures:

Revision of Figure 4.
Revision of Figure 5.