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Discussions

Interactive comment on “Mercury in arctic tundra snowpack: temporal and spatial concentration patterns and trace–gas exchanges” *by* Yannick Agnan et al.

Anonymous Referee #1

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General comments

The authors investigated snow Hg dynamics in the interior arctic tundra at Toolik, Alaska. They compared their results to a temperate snowpack in the Rocky Mountain, Colorado and conclude that photochemical Hg(0) losses from the snowpack in models should be adjusted and treated differently in arctic and temperate snowpacks. I think that this research provides some very interesting results and the manuscript is fairly well written. However, to my opinion, it lacks a thorough comparison to other studies performed in polar regions and a discussion on instrumental limitations. I think that the manuscript will be appropriate for publication in The Cryosphere after the authors

address the major comments discussed below.

Major comments

The conclusion of the manuscript (see above) derives from two main observations. Firstly, low concentrations of Hgtot and Hgdiss were measured in surface snow. Secondly, the photochemical formation of Hg(0)gas in the snowpack was largely absent.

1. I am quite surprised by the very low Hgtot concentrations in surface snow samples reported in this study, especially during depletion events. This raises concern about the potential influence of drifting snow. While the authors admit that the Toolik snowpack is subject to significant drifts and changes in snowpack height, there is no discussion on potential consequences and uncertainties.

2. While I agree that the photochemical formation of Hg(0)gas in the snowpack is most likely low compared to a temperate snowpack, I would like to see a comparison to other studies performed in polar regions. To me, the Toolik snowpack is more similar to a polar than a temperate snowpack (e.g., given permanent darkness/sunlight periods).

3. Additionally, there is no discussion on instrumental/analytical uncertainties. I would for instance very much like to know how the results collected with the two Tekran instruments compare. I expect a 10-20 % difference and wonder if the conclusions remain valid taking that analytical uncertainty into account. I also wonder whether the upper inlet in the snowpack was too far from the surface in spring, explaining why the authors did not observe any photochemical production of Hg(0)gas in the upper layers.

The following line by line comments should be useful to fully comprehend and address the major comments.

Line by line comments

Page 2, lines 21-22: “In the Arctic and Antarctic, Hg cycling also is affected by atmospheric Hg depletion events (AMDEs) which are observed primarily in the springtime along coastal locations (Dommergue et al., 2010; Schroeder et al., 1998; Steffen et al., 2008).” The authors should also cite Angot et al. (2016a), latest review paper about mercury in polar regions which includes a discussion on the occurrence and frequency of AMDEs in recent years.

Page 2, line 28: Typo; McMurod should be McMurdo.

Page 4, lines 6-8: “Atmospheric air sampling was performed using the top snow tower air inlet (...), as well as on a nearby micrometeorological tower at a height of 3.6 m above ground.” How do the results compare? Did you collect data with two different Tekran instruments? If so, it would be an easy way to answer the following comment.

Page 4, lines 10-11: “Gaseous Hg(0) concentrations were measured using two Tekran 2537B analyzers, one for interstitial snow air measurements and the other shared for soil gas and atmospheric measurements.” Did you check how the results from the two instruments compare? What is the associated uncertainty? According to several studies, the analytical uncertainty is about 10-20 % (e.g., Slemr et al., 2015) and this should be taken into account when comparing data acquired with different instruments. See major comments.

Page 4, line 12: “Air sampling was alternated between different snowpack heights every 5 min so that a full sequence of air extraction from the snowpack (six inlet heights) was achieved every 30 minutes.” If I understood correctly, you just collected one data point per inlet height. Could there be any significant sampling-induced snowpack ventilation influencing the results?

Page 4, line 27: “The top 3 cm of the snowpack was collected in triplicate.”

1. What was the approximate distance between the replicates? According to lines 3-5 on page 6, the Toolik snowpack is subject to significant drifts and changes in snowpack height. Did you take that into account when interpreting the transect data? See major comments.

2. According to lines 30-31 on page 5, average data are shown as mean ïĆś standard deviation. Were the replicate surface snow samples pooled together for analysis, similarly to snowpit samples? If so, what does the standard deviation reported in Table S2 stand for?

Page 5, lines 7-9: “The detection limits, determined as 3-times the standard deviation of blank samples, averaged 0.08 ng/L. For statistic purpose, values below the detection limit (DL) were included as 0.5xDL. Recoveries, determined by 5 ng/L standards analyzed every 10 samples, averaged between 93 and 107 %.” If I understood correctly, the analytical uncertainty is of 7 % at 5 ng/L. Given that most of the concentrations you analyzed are < 1.0 ng/L, did you check what the analytical uncertainty at that concentration is? I expect it to be much higher (∼50%?). Additionally, is the analytical uncertainty the same for Hgtot and Hgdiss? I am asking because you say later (page 13, lines 1-2) that Hgtot concentrations were much more variable than Hgdiss concentrations.

Page 6, lines 24-25: “The transect between Toolik and the Arctic Ocean performed in March 2016 showed snowpack height ranging between 30 and 66 cm”. How can you explain the difference? Could it be due to drifting snow? If so, how can you compare Hg concentrations at various depths and locations? See major comment.

Page 7, line 3: “compared to the literature from temperate snowpacks”. It seems to me that your reference is the study by Fain et al. (2013) in Colorado. “compared to the literature from a temperate snowpack” would be more appropriate here. Additionally, while I understand why you compare your results to those obtained in the Rocky Mountain (same instrumental setup and so on), I would like to see a more thorough comparison to other studies performed in polar regions (e.g., Angot et al., 2016b; Steffen et al., 2014).

Page 7, lines 10-12: “The Hg(0)gas measurements consistently showed strong concentration gradients in the atmosphere-snowpack-soil continuum with highest concentrations in the atmosphere (on average, 1.18 and 1.09 ng/m3, respectively) and lowest concentrations in soils (mostly below the detection limits for both years, i.e., <0.05 ng/m3)."

1. Could you please add the standard deviations?

2. Is this gradient significant given the large error bars in the snowpack (see Fig. 4)?

3. It's just a detail, but I think that the detection limit for the Tekran 2537 is 0.10 ng/m3.

Page 7, lines 23-25, referring to AMDEs: "During one of these periods shown in Figure S2, Hg(0)gas concentrations in the snowpack showed variable Hg(0)gas levels generally following Hg(0)gas concentration changes in the atmosphere above".

1. What do you mean by "generally following"? Is there a correlation between concentrations in the atmosphere and upper layers of the snowpack?

2. Could you please add the following data on Figure S2?

a) Ozone in the atmosphere b) Snow height (is the inlet at 20 cm above the ground far from the surface?) c) Hgtot in surface snow samples d) Hg(II) concentrations in the atmosphere (the data do exist according to Obrist et al. (2017)).

3. How can you explain the peaks at 10 cm above the ground (e.g., daytime on Mar 28th, 29th and 30th)? Was the temperature in the snowpack or the sample line stable? Could it be Hg(II) released from the sample line and analyzed as Hg(0)?

4. According to table S2 you collected surface snow samples during the AMDE. I am very surprised by the very low concentration (1.46 ng/L). This is rather unusual during a depletion event. How does it compare to other studies (e.g., Steffen et al., 2014)? If we do a back of the envelope calculation based on Hg(0) and Hg(II) concentrations in the atmosphere, what should be the concentration in surface snow to have a coherent Hg budget? With 1.46 ng/L in surface snow and $\sim$0.4 ng/m3 of Hg(II) according to Obrist et al. (2017), I have the feeling that there is Hg missing in the budget. If so,

a) How reliable are the Hg(II) measurements? What is the analytical uncertainty? Is

an underestimation of Hg(II) concentration conceivable?

b) Since Toolik snowpack is subject to significant drifts and changes in snowpack height, are you 100 % sure that you collected surface snow samples? If you collected deeper layers due to drifting snow that could explain the unusually low concentrations during the depletion event.

Page 7, lines 32-34: "This pattern was consistent for two independent soil profiles measured at this site, one mainly representing an organic soil profile and one profile dominated by mineral soil horizons". I do not understand this sentence. Was the experimentation carried out at two different locations with different soil composition? There is no mention of this in the Materials and Methods section.

Page 8, lines 25-27: "Analysis of ïĄĎHg/ïĄĎCO2 ratios showed no statistically significant differences from the top to the bottom of the snowpack". It seems like the authors used the mean concentration at each height to calculate the ïĄĎHg/ïĄĎCO2 ratios. Given the quite large error bars for Hg(0)gas in the snowpack (Fig. 4), it is not really surprising that such a calculation yields insignificant differences. On the contrary, Fain et al. (2013) calculated the ratio for each day. Did you try to do it this way?

Page 9, lines 7-10: "No consistent temporal trends in Hgtot or Hgdiss were observed with increasing duration of winter in both seasons, and no correlations were observed with air temperature (red line). One noticeable period of enhanced surface snow Hg concentrations was April 2016 when both Hgtot and Hgdiss concentrations exceeded 1 ng/L."

1. Is there an anti-correlation between Hgtot and Hg(0) in the atmosphere?

2. See previous comments regarding the magnitude of the concentrations. How do a maximum of 1 ng/L compare with other studies performed in polar regions?

Page 9, line 12: "Due to the low snow height on the frozen lake." Why is the snow height lower on the frozen lake? Drifting snow?

Page 9, lines 15-16: “Measurements of Hgtot and Hgdiss across a large North slope transect (about 200 km) in March, 2016 showed concentrations of 0.70 ïĆś 0.79 and 0.24 ïĆś 0.20 ng/L, respectively.” Are you referring to surface snow or to average snowpack concentrations?

Page 9, lines 16-19: “Concentrations of Hgdiss of the 5 northernmost stations were statistically significantly higher compared to those measured in the 4 stations located in the interior tundra which included the Toolik site where the mean Hgdiss concentrations were 0.33 and 0.11 ng/L for the same period, respectively”.

1. Please add the standard deviations (in the text and on Figure 7)

2. I would like to see a critical discussion of these results, notably in light of drifting snow issues and analytical uncertainty (50 % at such low concentrations?).

Page 9, line 23: “similar to concentration of Hg”. Where is that discussed in the manuscript?

Page 11, lines 11-12: “Hg(0) concentration profiles in the arctic snowpack are inherently different to patterns observed in lower latitude snowpacks”. Now may be a good time to compare your results to other studies in polar regions (see comment page 7, line 3).

Page 11, lines 23-25: “We speculate that a reason for the general lack of Hg(0)gas formation and volatilization in snow includes substrate limitation due to very low total snow Hg concentrations, several times lower compared to concentrations in temperate snowpacks.” While I agree that this is a possible explanation, I would like to see a more thorough discussion of other conceivable hypothesis, including instrumental limitations. A few ideas:

1. The comparison between your results and those by Fain et al. (2013) is based on data acquired in winter and early spring. I would expect Hg(0)gas formation and volatilization to start in spring, when the sun is back. What is the difference in UV

load between Toolik and Colorado at that time of year? That could explain a lower photo-reduction in the upper layers of the snowpack at Toolik.

2. Atmospheric and snowpack Hg(0) concentrations were collected using two different Tekran instruments. Could a 10-20 % difference between the instruments explain why Hg(0)gas in surface snow is not higher than in ambient air (especially Figure 4c)?

3. ∼85 % of photo-reduction occurs in the top two e-folding depths (King and Simpson, 2001). Fain et al. (2013) observed a diurnal cycle 0-60 cm below the surface. But the density/nature of the snowpack is most likely very different at Toolik.

a) You recorded the physical properties (e.g., density) of the snowpack. Could you compare your results to those obtained by Fain et al. (2013)? According to Durnford and Dastoor (2011), the range of chemically active depths may be explained by physical differences in the snowpacks.

b) The e-folding depth is about 5 cm at Alert (King and Simpson, 2001) while Poulain et al. (2004) reported that photo-reduction occurred in the first 3 cm of snow. I am worried that the upper inlet in the snowpack (the one at ∼40 cm above the ground, Fig. 4c) might be too far from the surface. This is more obvious on Fig.3 if you compare the distance between the upper inlet and the surface in your case and in Fain et al. (2013).

4. What about the occurrence of fresh snow at Toolik vs. Colorado? Fresh snow provides a new reservoir of photoreducible Hg(II) and highest surface snow Hg(0) levels are linked to the deposition of new snow (Faïn et al., 2013).

Page 12, lines 1-2: “This illustrates that the Hg(0)gas uptake occurs in soils rather than in the snowpack.” The way the ratios are plotted, I am not sure I understand why you can conclude that uptake occurs in soils rather than in the snowpack.

Page 12, line 10-11: “which we attribute to higher variability in upper snowpack concentrations due to variable atmospheric Hg(0)gas levels”. Isn’t it in contradiction with error bars (Fig. 4 and 5)? I actually don’t understand why (Fig 5) a ratio based on highly variable concentrations (e.g., 0 cm) can be less variable than a ratio based on less variable concentrations (e.g., upper inlet). Am I missing something?

Page 12, line 23: “relatively weak and infrequent AMDEs”. I quibble but the AMDE reported on Fig. S2 does not look weak to me. About the frequency, how many AMDEs did you observe? You can use a 1.00 ng/m3 threshold to calculate the frequency of occurrence (Angot et al., 2016a; Cobbett et al., 2007; Steffen et al., 2005).

Page 12, line 31-32: “Total Hg concentrations in all snow samples collected were always much higher than Hgdiss levels”. Can we really say that concentrations are “much higher” given the range observed (0-1 ng/L)? By the way, I don’t see anywhere Hgtot concentrations from the transect.

Page 13, line 10: “(...) and few studies include inland sites such as Toolik”. What is the range of concentrations at these inland sites? Which studies are you referring to?

Page 14, line 27: “Fresh surface snow”. There is no mention of the fact that you collected fresh surface snow in the Materials and Methods Section.

Figure 2: Why don’t you report the standard deviation for each green bar?

Figure 4: What does “soil: organic/mineral” refer to?

Figure 7: Please add standard deviations.

Figure 8: I really like this Figure but aren’t the various concentrations (<DL, 0.25, 0.50) in the range of the analytical uncertainty?

Figure 9: The colors are really difficult to read. Can you use something else than shades of blue? Maybe a gradient from blue to red.

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