Response to referee comments

We would like to thank the referees and editor for the interest in our work and the helpful comments and suggestions to improve our manuscript. We have carefully considered all comments and the replies are listed below. The changes have been marked in the text using blue color.

Anonymous Referee #2

General comments

Yin et al. present total gaseous mercury measurements from an extraordinary environment in "Long-term monitoring of atmospheric TGM at a remote high altitude site (Nam Co, 4730 m a.s.l.) in the inland Tibetan Plateau". The results are important as mercury data from a remote site are interpreted that is located between two major mercury emission regions the Indo-Gangetic plain in southern Asia and China in the west. With a box model and a relatively small set of parameters, the major seasonal and diurnal changes could be reproduced. The results fill an important gab in understanding atmospheric back ground concentrations of gaseous mercury in an especially important part of Asia. A slight drawback might be that only TGM as chemical parameter is measured during the study, despite others are mentioned (ozone, black carbon, RGM *: : :*). However, the data set is concisely analyzed and the findings are supported by box model simulations. Trajectories and potential source contribution functions were calculated and used for source allocation. I suggest publication in ACP after a few comments have been addressed.

Response: Thanks for your valuable advice and comments.

I agree with Referee #1 that the expression "Long-term" for the study is not appropriate. Moreover, the number of Figures should be restricted to about 10: Figure 2 could be moved to the supplementary material. Figures 11-14 have a large overlap regarding the displayed information. Either one should be selected or a combination of two of them might be displayed in the main text, the others can be moved to the supplementary material.

Response: We modified the title to "Multi-year monitoring of atmospheric TGM at a remote high-altitude site (Nam Co, 4730 m a.s.l.) in the inland Tibetan Plateau" in lines 1-2.

Thank you for the suggestion. We have moved Figs. 2, 12 and 13 to the supplementary material. Fig. 11 (new number 10) and Fig. 14 (new number 11) were kept in the paper as they provide two different

viewpoints on the air mass transport. The first shows transport by cluster and the second by season.

Fig.2 was moved to the supplementary material (Fig. S4) and sentence was changed in line 260: "The frequency distribution of TGM at the Nam Co Station was normally distributed (Fig. S4)."

Fig. 12 was moved to supplementary material (Fig. S5) and sentences were changed in lines 378-380: "Most HYSPLIT trajectories originated from the west of Nam Co including the western and central Tibetan Plateau, the southwestern part of the Xinjiang Uygur Autonomous Region, South Asia, Central Asia and Western Asia. Very few trajectories originated from eastern China (Fig. S5)."

Fig. 13 was moved to supplementary material (Fig. S6) and sentences were changed in lines 388-390: "Areas including IGP, the southern part of the Xinjiang Uygur Autonomous Region, the western part of Qinghai province and areas near the Nam Co Station in the Tibet Autonomous Region were identified as overall high potential sources regions and pathways (Fig. S6)."

Specific comments

Lines 79-81. The importance of background measurements between two major mercury source areas should be explained in more detail. Is the change in the background or the actual deviations from the background the important information, i.e., the episodic events?

Response: The decrease of TGM at the Nam Co Station was similar to many sites. This was stated in this study in Sec. 3.1 as: "The monthly average TGM at the Nam Co Station showed a weak decrease (slope = -0.006) during the entire monitoring period, and the decrease was more pronounced in the summer (slope = -0.013). Despite the short time span of the TGM time series with some missing data mostly in the winter, the slight decrease of TGM especially in the summer was in agreement with a recent study using plant biomonitoring which identified a decreasing atmospheric mercury since 2010 near Dangxiong county (Tong et al., 2016) as well as decreases of TGM at other sites (Slemr et al., 2011; Zhang et al., 2016)". WRF-FLEXPART results revealed that the high concentrations of atmospheric mercury (above 2 ng m^{-3}) at the Nam Co station were associated with the air mass transported from the east and though Lhasa, which was also probably due to the further impact from eastern Indo-Gangetic Plain and the possibility of episodic transport events from China as stated in lines 371-373.

Lines 85-86. Similarly, as the previous comment. Be more explicit: Tibetan plateau is an important part of the global mercury cycle *: : : .* Is it an ideal place to monitor TGM or an important sink?

Response: Thanks for your suggestion. Changed as suggested in lines 89-91: "Notably, mercury records from glaciers and lake sediments suggest that the Tibetan Plateau is an important part of the global mercury cycle, acting as both a sink (mercury deposition to snow) and a source (release of mercury from melting ice) (e.g., Kang et al., 2016; Yang et al., 2010; Sun et al., 2017, Sun et al., 2018)."

Line 180-185. This appears to be an important result and should be mentioned in the conclusions.

Response: Thanks for your suggestion. Changed as suggested in lines 440-441: "An exploratory box model simulation shows that this diurnal profile can be accurately represented using TGM reductions 24 hours per day, TGM increases near sunrise and sunset, and dilution due to vertical mixing."

Line 184. "... constant TGM deposition" – how is this justified considering diurnal soil temperature change and the major fraction of TGM being volatile GEM?

Response: We have changed "deposition" to "reduction," and we have also changed the explanation of the box model as described above. The point of the box model was to illustrate that known processes were not able to match the measured diurnal profile of TGM concentrations. We did indeed expect that temperature would account for some of the variation, but it did not in the model. This suggests that future modeling efforts will be required to explore the impact of soil emissions as well as snow and ice melting on concentrations at Nam Co.

Line 281-282. As before: "... constant TGM deposition" – please support this by a mechanism, and further on, "*: : :* TGM emissions in the early evening *: : :* ". - This statement seems to be in contradiction to what is said before. To clarify the contributions a modified Figure 8 as stacked bar plot would help.

Response: The description was changed from "deposition" to "reduction" and from "emission" to

"increase" to highlight the fact that the box model is a hypothetical experiment to see which processes would be required to accurately represent the measured diurnal profile. We would like to note that the combined 5 inputs are hypothetical factors that were found to match the diurnal profile of TGM. As such, they are not based on known mechanisms but rather are there to emphasize the need for further research to identify the factors influencing the diurnal profile. Figure 8 cannot be made as a stacked bar plot – this would necessitate a more detailed process analysis study which is outside the bounds of the current paper. The description of box model was modified in lines 201-208: "TGM at the Nam Co Station is expected to be well mixed and the site is not influenced by local sources. It is therefore expected that a box model should be able to reproduce the diurnal profile of concentrations. A box model that accurately simulates the diurnal profile of TGM would provide constraints on known processes affecting the concentrations. Comparisons with measured profiles would further identify missing processes in the model. This approach was used for reactive mercury at the same site, where it identified the role of the reduction of reactive mercury to gaseous elementary mercury mediated by sunlight (de Foy et al., 2016b). A box model was made that included free parameters to represent known chemical reactions and dispersion processes. An optimization algorithm was used to identify the parameters required to fit the model to the data, as was done in de Foy et al. (2016b)"; and 210-215 "A simplified exploratory model was therefore sought that would represent the measured diurnal variations as simply as possible, according to Occam's razor. Although this model does not yield direct information on known processes, it does identify the kinds of processes and their magnitude that would be required to accurately represent the measured diurnal profile. The final model combined the following 5 inputs: TGM increases at sunrise and in the early evening, constant TGM reductions 24 hours a day, a constant lifetime for TGM loss during daylight hours and TGM dilution due to vertical mixing".

Lines 294-300. Mixing versus oxidation: as TGM (GEM+ RGM) is measured this explanation is vague.

Response: Thanks for your suggestion. Changed as suggested in lines 325-329: "As the temperature and radiation increased, so did the boundary layer height which developed into a convective mixed boundary layer and generated greater vertical mixing between the surface and loft. At the same time, the surface wind speed also increased. With increased vertical and horizontal dispersion, TGM released from

the surface was diluted during the daytime (Liu et al., 2011; Lee et al., 1998)."

Lines 346-347. This part also reflects an important finding which could be emphasized in the conclusions.

Response: Thanks for your suggestion. Changed as suggested in lines 437-438: "Peak concentrations of TGM at the Nam Co Station were associated with air masses from the eastern Indo-Gangetic Plain with the possibility of episodic transport events from China."

Line 370. What is the new finding compared to the Beiluhe site study {Ci, 2016 #16007},

Response: The box model in this study was found that reproduced the measurements of atmospheric mercury at site in the Tibetan Plateau accurately, and it provided constraints on known processes affecting the concentrations. Furthermore, Box model results in this study illustrated that surface-air fluxes of mercury were connected to atmospheric mercury with dilution effect.

Line 426. The average of 1.33 ng m-3 is almost in agreement with Ci et al. {, 2016 #16007}

Response: The concentrations of atmospheric mercury at both of these sites in the Tibetan Plateau were very low illustrating the pristine environments of atmosphere at both sites. Study of diurnal variation of atmospheric mercury in this study probably can supplement existing studies at Beiluhe.

Lines 430-431. What is stated? Currently it sounds self-evident.

Response: Compared with other high-altitude background sites, the low concentration of TGM at the Nam Co Station in the winter may be due to the reduction of mercury due to halogen, as discussed in Sec. 3.2. We explained these in lines 286-292: "Compared to other high-altitude background sites in the mid-latitudes in Europe (Fig. 4) (Denzler et al., 2017; Fu et al., 2016a; Ebinghaus et al., 2002) and sites in mid-latitudes in the US (Holmes et al., 2010; Weiss-Penzias et al., 2003; Sigler et al., 2009; Yatavelli et al., 2006), the lower concentration of TGM at the Nam Co Station in the winter might be indicative of

atmospheric mercury removal in the winter caused by reactive halogens (Br and Br_2). The reaction rates for these reactions are a strong inverse function of temperature (de Foy et al., 2016b; Goodsite et al., 2004), and they are accompanied by lower surface ozone concentration (Yin et al., 2017), which is catalytically destroyed by halogens (Bottenheim et al., 1986; Obrist et al., 2011)."

Lines 436-437. It appears to be in contradiction to a previous interpretation (comment on statement in Lines 281-282).

Response: Thanks for pointing this out. Note that the contradiction is only apparent; we have adjusted the sentence in lines 439-441 to clarify the continuity in our results: "At the Nam Co Station, the diurnal TGM profile had a peak 2-3 hours after sunrise and reached its lowest concentration before sunset. An exploratory box model simulation shows that this diurnal profile can be accurately represented using TGM reductions 24 hours per day, TGM increases near sunrise and sunset, and dilution due to vertical mixing."

In lines 439-440, we stated that "At the Nam Co Station, the diurnal TGM profile had a peak 2-3 hours after sunrise and reached its lowest concentration before sunset.". In lines 312-315, we stated that "The best match in the box model was obtained by using variables including constant TGM reduction throughout the day, TGM increases at sunrise, TGM increases in the early evening, TGM dilution due to vertical mixing and a lifetime of TGM loss during daylight hours (Table 2)." The diurnal peak of TGM at the Nam Co Station was happened 2-3 hours after sunrise, and it was because the accumulation of TGM emissions. While the lowest concentration before sunset was due to the strong dilution in the afternoon and they were supported by the results of box model.

Line 442. The transformation GEM -> RGM was analyzed in detail by de Foy et al. {, 2016 #16006}, but it does not reflect an important fraction.

Response: Thank you for pointing this out. According to the previous study, RGM concentrations were much lower than GEM at the Nam Co Station (de Foy et al., 2016). But we want to make sure the potential impact was stated in this study.

Line 443. Due to insolubility of TGM *: : :* – less soluble GEM? At least the RGM part should be better soluble. Please, be more specific.

Response: Thanks for your suggestion. The RGM was < 2% of TGM at the Nam Co Station, so the TGM measured at the Nam Co Station was mainly GEM. Comparing to black carbon and hexachlorocyclohexanes discussed in this study, TGM was less soluble. Sentences were added in lines 145-147: "At the Nam Co Station, the TGM fraction consists mostly of GEM (more than 98%). The operationally defined RGM accounted for less than 2% of TGM (Figure S1 in supplementary material in de Foy et al., 2016b). We consider the Tekran data to represent TGM in line with previous studies (e.g. Kock et al., 2005; Slemr et al., 2008; Müller et al., 2012)".

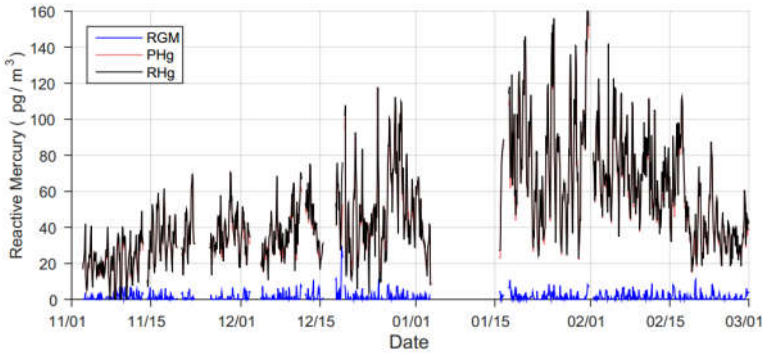

Figure S1: Time series of Reactive Mercury (RHg) and its components Reactive Gaseous Mercury (RGM) and Particle-bound Mercury (PHg) in supplementary material in de Foy et al., 2016b

Figure 9. Pink line, what does q (k kg-1), Please give more information in the figure caption.

Response: Thanks for pointing this out. q is the symbol used for specific humidity and we modified Fig.8 as you suggested (new number 8).

References referred to in the comments:

Ci, Z., Peng, F., Xue, X. and Zhang, X., 2016. Air–surface exchange of gaseous mercury over permafrost soil: an investigation at a high-altitude (4700?m?a.s.l.) and remote site in the central Qinghai–

Tibet Plateau. Atmos. Chem. Phys., 16(22): 14741-14754.

de Foy, B. et al., 2016. First field-based atmospheric observation of the reduction of reactive mercury driven by sunlight. Atmospheric Environment, 134: 27-39

Slemr, F., Brunke, E.-G., Labuschagne, C., and Ebinghaus, R.: Total gaseous mercury concentrations at the Cape Point GAW station and their seasonality, Geophys. Res. Lett., 35, L11807, doi:10.1029/2008GL033741, 2008

Kock, H. H., Bieber, E., Ebinghaus, R., Spain, T. G., and Thees, B.: Comparison of long-term trends and seasonal variations of atmospheric mercury concentrations at the two European coastal monitoring stations Mace Head, Ireland, and Zingst, Germany, Atmos. Environ., 39, 7549–7556, doi:10.1016/j.atmosenv.2005.02.059, 2005

Müller, D., Wip, D., Warneke, T., Holmes, C. D., Dastoor, A., & Notholt, J. (2012). Sources of atmospheric mercury in the tropics: continuous observations at a coastal site in Suriname. Atmospheric Chemistry and Physics, 12(16), 7391-7397.