

Response to comments from referee #2

Anonymous Referee #2

The manuscript entitled “Observation and analysis of speciated atmospheric mercury in Shangri-la, Tibetan Plateau, China” details the atmospheric mercury concentrations at a site in south-central China. This site is part of the Global Mercury Observation System (GMOS) and reporting of the data is potentially important. Unfortunately the paper does little to advance our understanding of atmospheric mercury cycling or atmospheric chemistry and physics in general. The results are not surprising, could have been arrived at by some quick HYSPLIT back-trajectories, and are not at a level that should be reported in a journal with a high impact factor like AC&P. Also several statements are not backed up by data or even a clear explanation. For example, the authors suggest that a diurnal pattern of GOM could possibly be caused by oxidation of Hg⁰ with stronger solar radiation. However, the authors suggest no mechanism or offer any measurements to substantiate this statement. This oxidation typically occurs in the Arctic, at coastal sites, or areas with high atmospheric halogen concentrations. As far as I can tell this site is none of these. Also in the conclusions the authors state “The TGM concentration was higher during the daytime mainly due to the diurnal surface temperature shift” but there is no data to support this.

Response: We thank the reviewer for recognizing the significance of our observation effort and for providing the recommendations that help us improve the manuscript. The Shangri-La site is a unique area to study regional transport from South Asia because it is a high altitude site near the border between China and the important source regions in India and Southeast Asia that The Indian summer monsoon can also influence the climate in Shangri-La. Therefore we thought it is also influenced by the Indian Summer Monsoon. This is the primary motivation of this monitoring effort not to mention that there have been few Hg data in the study region. New findings regarding the anthropogenic impacts of Hg emission from South Asia are reported in the manuscript. This is a site that is fundamentally different from the Arctic sites and therefore we did not include the halogen chemistry typical of the Arctic environment. We have presented additional data analysis in the revised manuscript to address the reviewer’s specific comments and technical concerns.

Pg 11045 Line 10: “< 10 g km⁻² of Hg annually” needs a citation

Response: we already made the citation in the description of Fig. 1 and gave the source of data (AMAP/UNEP, 2013) (P4, L3).

Pg 11046 Line 3 – 19: Were the measurements conducted with a Tekran speciation unit? If not then there needs to be significantly more information provided. What denuders from what company were used? What filters (part number) from what company were used for PBM? Were there separate sampling streams for GOM and PBM? Were samples collected manually then desorbed later? If so were multiple denuders used? This can introduce bias and data on the variability between the denuders needs to be provided. Was the same 2537A used to analyze the PBM and GOM and GEM? If so there should be gaps in the data, and if not there is some error that needs to be discussed. Has this system been used for other studies? If not then a diagram of the instrument set up is required. Also the dates when GOM and PBM were

measured needs explicitly stated.

Response: The sampling of GOM and PBM in this study was performed manually followed by detection using Tekran 2537A, not with the Tekran speciation unit. The sampling method was similar to the automated process via Tekran speciation system. Both PBM and GOM samples were collected continuously and analyzed immediately after the sampling cycle. For continuous measuring PBM and GOM, we prepared additional denuders, filter holders, impactors and filters for collecting PBM so that the sampling cycle can be continued. Each new filter for PBM collection was placed in a filter holder with an impactor placed before the filter in inlet line. An unused KCl-coated denuder was also installed in a separate sampling line with an impactor. Once a two-hour sampling period was completed, the prepared PBM and GOM sampling lines were installed swiftly for the next sampling cycle. The replaced filter and denuder were then immediately heated to 900 °C and 500 °C using a pyrolyzer for three heating cycles (15 min) to convert PBM and GOM into Hg⁰, which is analyzed by the Tekran 2537A. The typical replacement time of each denuder and filter was very short (almost 10 minutes). Using this sampling protocol, twelve GOM and twelve PBM samples can be collected a day. We have made this clear in the revised manuscript (P4, L25-P5, L6).

Pg 11049 Line 12: “level” should be “levels”

Response: The text has been changed as suggested (P7, L12).

Pg 11049 Line 19: “TGM mean concentration at the SAWRS was slightly higher” this is HUGE understatement. Nearly twice as high is not “slightly higher” and should not be called a “background” site in any way. If it must be called a “background” site then it should be referred to as a “Chinese background” site because the concentrations are much too high to be considered a global background site.

Response: Yes, SAWRS is a regional background site, the TGM level at SAWRS was much higher than the global background value, because it is closed to the southwest China which is huge mercury sources area. We have checked and revised as suggestion (P7, L19).

Pg 11050 Line 1: “possibly the weak local” should be “possibly weak local”

Response: The text has been changed as suggested (P7, L21).

Pg 11050 Line 3: “prevailing westerly,” should be “prevailing westerly wind,”

Response: The text has been changed as suggested (P7, L24).

Pg 11050 Line 4: “measured at in Korea” should be “measured in Korea”

Response: The text has been changed as suggested (P7, L23).

Pg 11050 Line 6: How is 2.04 ng m⁻³ at Cape Hedo a higher concentration than the 2.55 ng m⁻³ mean measured at SAWRS?

Response: We meant that the 2.04 ng m⁻³ at Cape Hedo is also higher than the background concentration in the Northern Hemisphere. We have made the statement clear in the revised manuscript. (P7, L22-26)

Pg 11050 Lines 11 – 14: Higher TGM levels with northerly winds and elevated TGM associated with southerly winds? Is there something missing here? Are winds from the north and south both high in TGM? If so what is the range in concentrations for the southerly winds?

Response: The higher TGM concentration was associated with winds coming from the north and south as shown in Fig. 3 ($2.5\sim 2.7\text{ ng m}^{-3}$ for northerly winds and $2.5\sim 2.6\text{ ng m}^{-3}$ for southerly winds, compared to $2.3\sim 2.5\text{ ng m}^{-3}$ for winds from the east and west). This has been made clear in the revised manuscript (P8, L3- 9).

Pg 11050 Lines 11 – 12: “: : northerly winds that carried domestic emissions from West China: : ” Were there any tracers measured to provide proof that these were domestic emissions from this area? I need more convincing here, the evidence is not definitive and needs support.

Response: The explanation of the doubt is in the first paragraph of section 3.4. In this paragraph, we discussed the figure 11, we note that Cluster 4, although relatively infrequent (4%), was associated with the highest TGM concentrations (mean = 3.9 ng m^{-3}) due to the passing of air masses over known source regions in Sichuan province. The area has a high background TGM level (3.98 ng m^{-3}) caused by industrial and domestic coal combustion, smelting industries, cement production, and biomass burning (P11, L17-21).

Pg 11050 Lines 16 – 17: “low TGM concentrations.” What is meant by this? What is the range or mean?

Response: Here we meant that the concentration associated with the winds from the east and west was lower ($<2.5\text{ ng m}^{-3}$). This has been made clear in the revised manuscript (P8, L5).

11050 Line 18 – 19: “The air mass in the east-west direction: : ” What mountains did the air mass need to cross in each direction? What are the elevations compared to the measurement site? Distance from site? Is the site in a valley? This should be described better in the methods section: : :

Response: We agree with the reviewer that the site description can be more specific. The SAWRS is located at a mountaintop in Hengduan Mountain area, the mountain ranges of Hengduan Mountain are run in the north-south direction. Kawa Karpo and Gongga Mountain both are more than 6000 m a.s.l. and almost 150 Km away from site. Kawa Karpo is located in the northwest of SAWRS and Gongga Mountain is northeast of SAWRS. Therefore the air masses in the east-west direction needed to cross high mountains to reach the SAWRS. We already added the description in the section of Materials and methods as suggested (P3, L25-31).

Pg 11051 Line 3 – 4: “Another possibility is the oxidation of Hg⁰ caused by stronger solar radiation.” What mechanism is being suggested here? This typically occurs in the Arctic, at coastal sites, or sites with high atmospheric halogen concentrations, but I do not think this site falls into these categories, so is there evidence to back up this statement?

Response: Because we did not measure the oxidants of Hg in this study, but SAWRS is located in a very high elevation area (3580m a.s.l) which has much stronger solar radiation

compared to the low elevation area, therefore we deduce that the oxidation of GEM could be a possible reason of high GOM according to previous reports in polar area. Additionally, the low relative humidity could be benefit to elevate GOM from GEM. And previous study at a high elevation research laboratory in the Rocky Mountains reported that the build-up of GOM is limited to the presence of dry air (P8, L18-26).

Pg 11051 Line 11: What does the term “generally” mean? Were they statistically significantly lower? If so what are the statistics?

Response: We agree with the reviewer that the statement can be more specific. At SAWRS, AT, RH and RF were lower during non-monsoon period compared to the values in monsoon period. We have also revised the text to reflect the specific description (P8, L32-33).

Pg 11051 Line 12 – 13: “associated with high WS, from Tibetan Plateau caused the lower observed TGM.” How did these air masses “cause” lower TGM? Fewer sources? More forests? What proof is there?

Response: We agree with the reviewer that the statement can be more specific. The statement was based on the results of cluster analysis (section 3.4). The reasons for the lower TGM concentration were fewer anthropogenic emissions and possibly the greater degree of air dilution caused by the stronger wind. We have made this clear in the revised manuscript (P10, L19-27).

Pg 11051 Line 13 – 14: “The TGM level was highest in spring: :” Is this statistically significant? If so what is the p value? N?

Response: The higher TGM level in spring is statistically significant via independent sample test, the p value=0, N=69532

Pg 11051 Line 17 – 18: “Elevated TGM” What does this mean? Are the concentrations above the mean? Above 2.5 ng m⁻³?

Response: We thank the reviewer for pointing this out to help improve the clarity. The criterion for the “elevated” level is above 2.5 ng m⁻³. We have made the criterion more explicit in the revised manuscript (P9, L3-6).

Pg 11051 Line 22: What is a “general negative correlation”? Is it a statistically significant correlation? If so what are the r and p values?

Response: The negative correlation is statistically significant ($r=-0.83$, p value=0) via independent sample test and we have deleted the “general” in the revised manuscript (P9, L9-10).

Pg 11051 Line 25 – 26: “enhanced Hg uptake by vegetation: :” What vegetation surrounds the site? What is the process by which this occurs?

Response: Thank you very much for pointing out this. In our new manuscript, we did not think “enhanced Hg uptake by vegetation”. Because, SAWRS is surrounded by alpine forest and the major vegetation kinds in south area of SAWRS are alpine and evergreen broad-leaved trees and what the enhanced Hg uptake by vegetation just happened during ISM

period is impossible. In our new manuscript, we think during ISM period, clean Indian Ocean air mass and water vapor can flow into inland and lead to high RH and low TGM. In addition, during rainfall formation, cumulus process also could cause dilution of Hg in atmosphere. We already deleted this part and supplemented the other rational explanation in revised manuscript (P9, L8-15).

Pg 11051 Line 26 – 27: “: : which has been observed several earlier study in Chang- Bai Mountain and in the Northeast US: :” should be “: : which has been observed by two earlier studies in the Chang-Bai Mountains in China and the Rocky Mountains in the US: :” If the authors are making this statement, significant discussion is needed. The site in the US was a very high elevation site, far above tree line and quite there was quite a bit of discussion. Please put this study into perspective with those studies and tell us in detail why this may be a vegetation effect.

Response: Thank you very much for your attention! We already deleted this part and supplemented the other rational explanation in revised manuscript (P9, L8-15).

Pg 11051 Line 28: “winter months were” should be “winter months was”

Response: The text has been changed as suggested (P9, L15).

Pg 11052 Line 2: What does “not substantial” mean? What was the mean, range, and standard deviation?

Response: We meant that the variability of WS was not significant and have made it clear in the revised manuscript (P9, L17).

Pg 11052 Line 4 – 6: What does “substantial seasonal variability” mean? Are there significant differences? If so what are the p values?

Response: It is mean the variation was distinct. P value=0 via two- tail test.

Pg 11052 Line6: “5 times of the” should be “five times the”

Response: The text has been changed as suggested (P9, L23).

Pg 11052 Line 6: “. Similar pattern: :” should be “A similar pattern: :”

Response: The text has been changed as suggested (P9, L23).

Pg 11052 Line 10: “were high in autumn and winter: :” what does “high” mean? How high? Compared to what?

Response: Compare to the PBM level (29.14 pg m^{-3}) in spring and summer, the PBM level (37.78 pg m^{-3}) was higher in autumn and winter.

Pg 11052 Line 14: “Trajectories analysis” should be “Back-trajectory analysis”

Response: The wording has been revised as suggested (P10, L3).

Pg 11052 Line 15 – 16: “air mass from Burma, Vietnam, Laos, Kampuchea and Thailand, likely of biomass burning origins.” Is there any data to back up this statement? Other

atmospheric tracers? Information on forest fires or biomass burning of any kind?

Response: We appreciate the reviewer's insightful comment. The satellite images of MODIS for biomass fires provide a good representation of the biomass burning activities (<https://earthdata.nasa.gov/data/near-real-time-data/firms/active-fire-data#tab-content-7>) and we agree with the reviewer that the primary burning season is in spring season. Therefore, high PBM level in autumn could be caused by the local anthropogenic sources, but previous measurement of atmospheric Hg in Southeast Asia reported quite high TGM concentrations (Sheu et al., 2013). This suggested that the rapid development of industry in the Indochina Peninsula might also have contributed to the elevated atmospheric Hg concentrations to some extent. We already revised it as suggested (P10, L3-12).

Pg 11053 Line 1: "three high Hg events". Why are two highlighted in red and one in blue?

Response: We thank the reviewer for pointing this out and would like to clarify it. The event marked in red represent the causes of these events are not only impacted by local airflow but also long-term transport; while blue just represent the local airflow impact.

Pg 11053 line 11: "Figure 1" There are no back-trajectories on Figure 1.

Response: We thank the reviewer for catching this. It should be Figure 10 and it has been corrected in the revised manuscript (P11, L2).

Pg 11053 Line 13 – 14: "The elevated concentration in this event was likely to be contributed by the domestic emissions." How do you know this?

Response: The peak cannot be explained by the transport of air masses as indicated by trajectory analysis and therefore it was suspected to be caused by domestic emissions that are closer to the monitoring site.

Pg 11055 Line 5: Northern Hemispheric background is $1.5 - 1.7 \text{ ng m}^{-3}$ not $1.5 - 2.0 \text{ ng m}^{-3}$.

Response: The values have been revised as suggested (P12, L22).

Pg 11055 Line 10: "level" should be "levels"

Response: The word has been changed as suggested (P12, L26).

Pg 11055 Line 11 – 12: "The TGM concentration was higher during the daytime mainly due to the diurnal surface temperature shift." This was not proven in the manuscript. Thorough discussion needed. Is this referring to the cold air drainage off of the mountains? If so are there any measurements of boundary layer height? Balloon launches? Modeling?

Response: Thank you very much for your attention! Yes, the relationship between surface temperature and TGM had not been discussed in the revised manuscript. We already deleted the wording and revised as suggested (P12, L27-28).

Pg 11055 Line 13 – 14: "and the in situ photochemical productions of might have contributed to the occasional high GOM concentrations." First, this should be "and in situ photochemical production might contributed to occasionally high GOM concentration." And second, this is not supported by any data and therefore cannot be a main finding of the paper.

Response: We have made the editorial revision as suggested (P12, L29-30). Regarding the photochemical production, it is a logical reasoning from the strong solar irradiance at the site and was not included as the primary finding in this work.

Table 1. Some indication of the number of samples should be given.

Response: We have added the indication of the number of samples (P17).

Fig. 1. The countries should be delineated and labeled.

Response: We agree and have labeled the countries (P18).

Fig. 2. Five-min mean implies that many samples were taken and a mean was taken. Is this correct? If not then “Five-min mean” should be “Five-min samples”.

Response: Yes, because we set Tekan 2537A to get a data every five minutes.

Fig 3. “roses” should be “rose”

Response: We thank the review for catching the typo and have corrected it in the revised manuscript(P20).

Fig 4. Second and third sentences are results and should not be in the figure legend.

Response: We agree with the reviewer’s suggestion and have shortened the caption(P21).

Fig 5. Not sure what the second sentence in the legend is saying and third sentence is a result and should not be there.

Response: We agree with the reviewer’s suggestion and have shortened the caption(P22).

Fig 6. Sentence two and three are results.

Response: We agree with the reviewer’s suggestion and have shortened the caption(P23).

Fig 7. What do the boxes indicate and why are they different colors?

Response: We appreciate the reviewer for pointing out this. Highlighted in red represent the causes of these events are not only impacted by local airflow but also long-term transportation; while blue just represent the local airflow impact.

Fig 8 and 9 legends have results that should not be there.

Response: We agree with the reviewer’s suggestion and have made new figures(P25,P26).

Fig 10 is not referenced in the text.

Response: This has been addressed in an earlier comment and we thank the reviewer for pointing this out (P10, L33).

Fig. 11 should be more clearly described in the text and only the information needed to interpret the figure given in the legend. As it is it makes no sense.

Response: We agree with the reviewer’s suggestion and have shortened the caption (P28).

Fig. 10 to 14 could be deleted.

Response: These Figures are very important to analyze the long range transport of Hg and potential resources for SAWRS.

References

AMAP/UNEP: Technical Background Report for the Global Mercury Assessment 2013, in, Arctic Monitoring and Assessment Programme, Oslo, Norway/UNEP Chemicals Branch Geneva, Switzerland, 2013.