Response to reviewers' comments on "Observation and analysis of speciated atmospheric mercury in Shangri-la, Tibetan Plateau, China" by Zhang et al.

Dear Editor,

We appreciate the helpful comments provided by the reviewers to our paper and have incorporated their recommendations in the revised manuscript. The detailed and constructive remarks indeed improve the quality of our manuscript. Our point-by-point response to the reviewers' comments is given below. The corresponding changes have also been indicated in the response. I hope that the revised manuscript meets the publication standards of *Atmospheric Chemistry & Physics*.

I look forward to hearing from you soon.

Sincerely,

Dr. Xinbin Feng
State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, PR China

Anonymous Referee #1

P4-5: Description of sampling and analysis of speciated atmospheric Hg is still unclear and missing details. Please state how long was the sampling cycle and how long was the desorption/analysis cycle. It doesn't seem feasible for the site operator to replace the GOM and PBM sampling lines every two hours at nighttime even if it takes only 10 minutes. The samples appear to be analyzed offline, but it was not stated in the paper. If it's done offline, it doesn't seem feasible to analyze GOM and PBM samples at nighttime (revised paper states the samples were analyzed immediately on P5, L14-15). This is why the reviewer comment suggested including the procedures for storing the denuder and quartz filter samples to minimize sampling errors and contamination.

Response: There are two parallel sets of the denuder-based systems for GOM and PBM sampling. While one is sampling, the other is being analyzed and getting ready for next sampling cycle. Each sampling cycle lasted two hours and each desorption/analysis cycle took approximately one hour. We had about one hour for GOM and PBM detection, and another hour for re-installing the denuder, filter and impactor (P4, L27-28; P5, L14-16 in the revised manuscript). During the analysis and installation, the other denuder-based system continuously collected GOM and PBM and therefore the analysis can be achieved nearly at real time. At the end of the sampling cycle, we only needed to replace the pre-installed denuder, filter and impactor section connected to the sampling pump. The replacement typically took less than 10 minutes. Because the measurement of GOM and PBM were continuously performed 24 hours, two field technicians took shifts for completing the measurement (one during daytime and the other during nighttime). Therefore, the denuder and quartz filter samples were NOT stored offline.

P5, L11: The year for the Landis et al. citation is missing.
Response: We thank the reviewer for pointing this out and have revised the wording as suggested (P5, L20).

P6, L6: Should be "Negative IMI indicates northerly wind that pushes the air back to the Indian Ocean." Please mention here that the IMI is correlated with rainfall intensity in the revised paper. This was only explained in the response to comments.
Response: We thank the reviewer for pointing this out and have revised the wording as suggested (P6, L14-19).

P6, L28: The order of the reference citations need to be corrected. Specify which Landis et al. 2002 reference is being referred to here. Please double check other citations with the reference list.
Response: We thank the reviewer for pointing this out and have revised the wording as suggested (P5, L20; P7, L6).

P8, L17: It should be mentioned in the revised paper that data were not available to support the explanations and that "It is speculated that diurnal mountain valley breezes..."
Response: No, we did not quantitatively estimate the movement of mountain valley breezes because of the limited field condition. The presence of the diurnal mountain valley breeze was based on our sensory observation of the winds at the site. We have followed the reviewer's recommendation to note that the mountain breezes were not quantitatively measured. We have revised the wording as suggested (P8, L30-32).

P8, L22-24: The relative humidity data provided here do not correspond with the average diurnal pattern of relative humidity in Fig. 4, which shows lower RH in the afternoon period than overnight and morning. Please revise this. I believe you wanted to show lower RH was associated with higher GOM.
Response: We thank the reviewer for pointing out this overlook. We meant to state that the relative humidity in the afternoon (14:00~20:00) was 58.24%, much lower than the night and morning (21:00-13:00) value of 81.47%. We have revised the discussion to reflect this (P9, L2-4).

P8, L22-30: Not enough data analysis has been done to rule out other factors influencing the diurnal patterns (e.g., mountain/valley breezes suggested in the reviewer comment or other factors). It should be mentioned in the revised paper that data were not available to support the explanations and that the explanations are possible theories.
Response: We agree and have made it clear that the inference is a hypothesized cause (P9, L5-9).

P9, L14: It's not conventional to use $p = 0$; it should be $p<0.001$ or $p<0.0001$. Also in P10, L3, it should be $p<0.05$ or some other significance level.
Response: We thank the reviewer for pointing this out and have revised the wording as suggested (P9, L27; P10, L13).

P9, L30 to end of paragraph: This sentence is a run-on sentence with several grammatical errors.

Response: We thank the reviewer for pointing this out and have revised the wording as:

In the cold season, the air mass arriving in Shangri-La was primarily carried by the Westerlies with relatively higher wind speed (mean = 2.34 m s^{-1} in winter). These air masses passed through several strong source regions in South and Southeast Asia, potentially transporting mercury to the SAWRS. The slightly higher GOM could be caused by local photochemical transformation under low RH (54.7%) (P10, L6-10).

P10, L14-17: Despite finding weak correlation coefficients and explaining in the response to comments that weak scavenging is a possible reason, the revised paper continues to state that "This may indicate the role of increasing wet scavenge process that played in the lower GOM and PBM concentrations during the ISM period". There are also grammatical errors in the previous sentence. The conclusion also stated, "moist air during the ISM significantly decreased GOM and PBM levels." These statements need to be revised to reflect the statistical analysis results.

Response: We agree with the reviewer on this point. The lower PBM and GOM could be caused by the higher RF and RH during the ISM season. We have revised the wording as:

The GOM and PBM levels were relatively lower from late spring to summer during the ISM period, likely a result caused by the higher RF and RH (Table 1) (P10, L24-25).

P10, L25-29: This sentence is a run-on sentence with several grammatical errors.

Response: We thank the reviewer for pointing this out and have revised the wording as:

During the ISM period, WD was mainly from the southeast with relatively low wind speed (mean = 1.63 m s^{-1} in summer) and high precipitation. High TGM peaks were not observed consistently (P10, L32-34).

P10, L32: Should be "These two reasons..."

Response: We thank the reviewer for pointing this out and have deleted these words and revised the statement as suggested (P10, L32-34).

Table S1 (Supplement): This table was not mentioned anywhere in the revised paper. The statistical analysis results for the trajectory clusters should be incorporated into the discussion in section 3.4. Please clarify if these are the statistical analysis results to assess whether TGM concentrations between the trajectory clusters were statistically different. The table caption is different from the response to comment #33 for Reviewer #3. According to Table S1, the mean TGM concentrations were not statistically different between clusters 1 and 2 and between clusters 2 and 3. The discussion in section 3.4 needs to be revised to reflect these statistical analysis results.

Response: We thank the reviewer for pointing this out. The original Tables S1 has been edited and shown as Table S4 in the revised manuscript due to other reviewers' comments. We have also added the discussion in the end of the first paragraph of section 3.4 as:

The mean TGM concentration in Cluster 4 was significantly higher than the mean concentrations associated with the other three clusters (Table S4). 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 caused by industrial and domestic coal combustion, smelting industries, cement production, and biomass burning (Fu et al., 2008). Air masses of Cluster 3, the most frequent transport sector, also had high TGM concentrations (mean = 2.6 ng m^{-3}). Cluster 3 had the shortest trajectories that move across Southeast Asian region where extensive biomass burning occurred during early spring. The trajectory endpoints of Cluster 3 had relatively lower altitude (Fig. 12) and coincided with the fire hotspots observed by MODIS satellite (Fig. S6), suggesting that the emissions from the biomass burning can be transported to the SAWRS. (P11, L23-33).

Anonymous Referee #2

This manuscript is much easier to read, however, I still have major procedural concerns with this manuscript. My first major concern is with the statistics performed in the manuscript. In section 3.2 the authors discuss seasonal differences based on a "two-tail test", which to me implies a two tail t-test. This test is not acceptable for evaluating differences across seasons (4 groups). Instead an analysis of variance in conjunction with a post hoc test (e.g., Tukey's HSD) should be used to evaluate differences among seasons. Alternatively, if the data is not normally distributed then a Kruskal-Wallis test (non-parametric statistical test) in conjunction with a Dunn's test could also be used. The confusion over these basic statistics calls in to question the results obtained from the cluster analysis, a much more advanced statistical technique. This concerns me that the authors may also be trying to do too much with their data.

Response: We appreciate the reviewer's insightful comment and have performed the statistical tests (Tukey's HSD test) as suggested. TGM concentrations in spring are statistically different from those in autumn ($p<0.001$, Table S1) and winter ($p=0.004$, Table S1). GOM concentrations in winter were significantly higher than those in the other three seasons ($p<0.001$, Table S2). The concentrations of PBM in autumn were statistically higher form summer ($P=0.001$, Table S3) and winter ($p<0.001$, Table S3). We have revised the discussion in the revised manuscript (P9, L18; P10, L3; P10, L13).

Further, in my first review I (and all other reviewers) had significant concerns about the measurement techniques. The authors have not addressed these concerns beyond adding a couple of sentences in the response to reviewers. Not acceptable. First off the major intent is to compare their data to other data in networks such as AMNet and GMOS. However, the data in those networks (particularly AMNet) are strictly standardized with identical equipment and identical operating parameters. This study does not adhere to those standards. For instance, they use a 47 mm diameter quartz filter in a Teflon filter holder to measure PBM. This is not a standard (or standardized) technique. Therefore, in order for the data obtained in this study to be compared to data in other areas a standardized technique should be used. An alternative would be to show data (or offer references) comparing the performance of this system with the standardized Tekran 1130 and 1135 units. However, reluctance to do anything of the sort has made me very suspicious of the data.

Response: The measurement of GOM and PBM was achieved by a manual method. The procedure of sampling and analysis of the manual method is analogous to the Tekran speciation system using identical denuders (Fig. 1) as the Tekran system with KCl coating. The only difference was the manual operation. We have multiple Tekran speciation units (deployed to other sites) and understand the operation of the sampling.

The 47-mm quartz filter was the Whatman Grade QM-H Quartz Filter from GE healthcare (http://www.gelifesciences.com/webapp/wcs/stores/servlet/catalog/zh/GELifeSciences/products/AlternativeProductStructure_21531/28418567). It is constructed with fine quartz fibers with low heavy metal content. This filter can withstand a heating temperature up to 900 ℃. The other difference of the filter is that the filter of manual method is of 47-mm diameter compared to the 21-mm filter used in the Tekran system. Fine particulate (<2.5 μm) mercury samples were collected onto the filters. The glass inlet and impactor are identical to the apparatus of Tekran speciation system. Our apparatus followed the setup of J. Munthe et al. (2001), Mary M. Lynam et al. (2002), Landis et al. (2002). We have added the detailed description and available references in revised paper (P4, L34~ P5, L3; P5, L19; P14, L21& P15, L3).

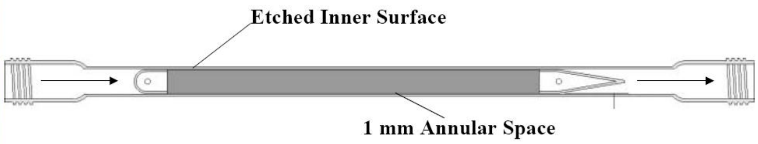


Fig. 1: Quartz denuder.

The Tekran speciation units have been used and tested extensively and much information exists on their design and performance. I need to see a diagram or a picture of the system used in this study, the description makes no sense to me. “An unused KCl-coated denuder was also installed in a separate sampling line with an impactor.” So do this mean there were three sample trains? One for “TGM”, one for GOM, and one for PBM?

Response: The manual denuder-based sampling system is analogous to the one used in the Tekran speciation unit. As shown in Fig. 2, the denuder, the inlet and impactor was the identical to Tekran speciation unit, and the temperature conditioner can keep a 40-50 ^{0}C for denuder during the sampling period via the heating tape. And the flow meter and vacuum pump was connected to the outlet of denuder, therefore we could get the total volume of sample gas in the two-hours sampling period. Fig. 3 shows the installation of denuder-based sampling unit at the site. Fine particulate (<2.5 μm) mercury samples were collected onto the filters. And the GOM and PBM were collected simultaneously during sampling cycle via denuder-based sampling unit. TGM is continuously measured Tekran 2537 except when collected GOM/PGM are being measured. This procedure is identical to the sampling and measurement cycle as the Tekran speciation unit.

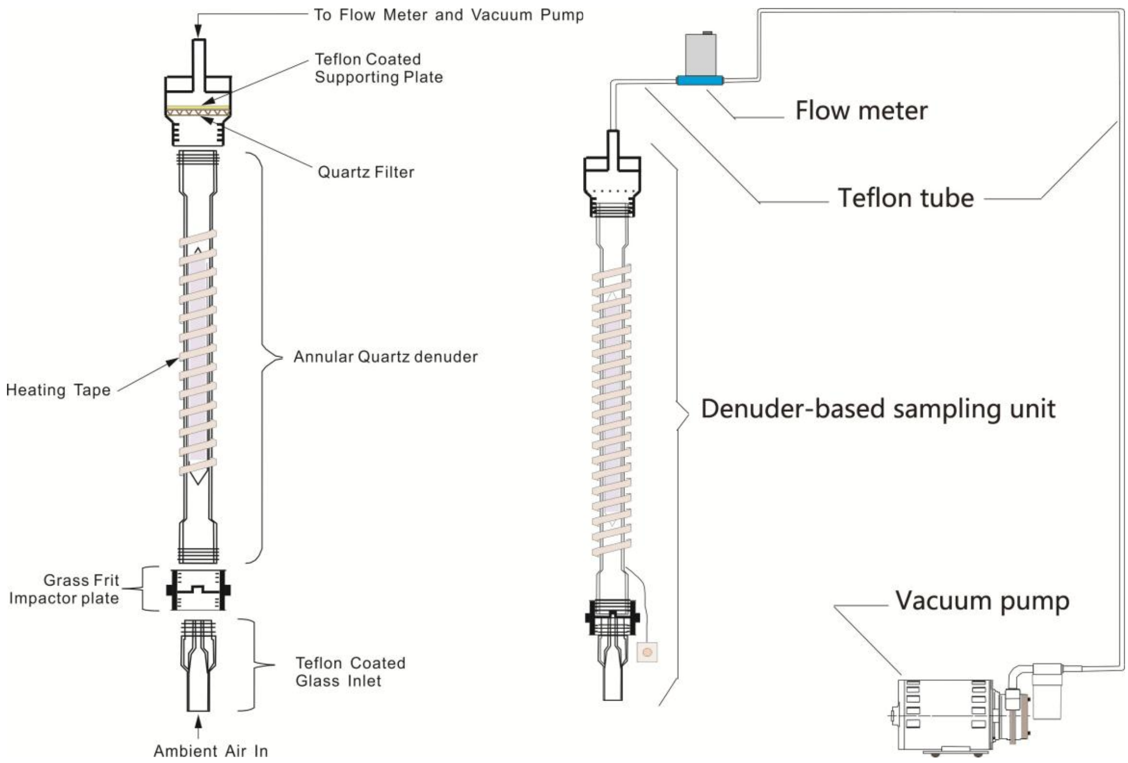


Fig.2: The denuder-based sampling unit.

Fig.3: The picture of denuder-based sampling unit.

I have serious concerns about the measurement concepts. These concerns originate from the indication on Page 5 Line 11 that "Analytical procedures for PBM and GOM described by Landis et al. were followed." The issue is that there are two Landis et al papers cited (2002a and 2002b) and neither of those papers has the procedure described here for analyzing filters for PBM. Landis et al.

2002b discusses using 47mm quartz filters, but these filters are microwave digested in HNO3 and analyzed as a liquid sample. Is that what was done here (no it looks like heat only was used)? If not how were the filters handled? Were they heated in the Teflon holders (I hope not)? The statement "the trap and denuders were rapidly heated to 900 and 500 °C using a pyrolyzer for three heating cycles to convert PBM and GOM into Hg0…" (And several other in this paragraph on Page 5) is directly out of a paper that has used a Tekran speciation unit and does not apply here. A pyrolyzer in a Tekran speciation system is a specific piece of quartz chip filled glass heated to 800 °C to ensure there is no deposition as the sample moves through the sample train. I suspect that is not what was used here.

Response: We appreciate the reviewer's insight and would like to clarify the measurement approach that we used for GOM and PBM. We cited J. Munthe et al. 2001, Mary M. Lynam et al.2002, Landis et al. (2002a) to describe the apparatus for the sampling of GOM and PBM. Indeed, Landis's paper has not described the procedure of PBM analysis, but in J. Munthe and Mary M. Lynam's papers, the procedure of PBM analysis was described, the difference is that Mary M. Lynam used the nitrogen to carry mercury to 2537A, here we used zero gas to carry mercury to 2537A. Our procedure is identical to Tekran speciation system. Microwave digestion was NOT carried out. Instead, as shown in Fig.4 and Fig 5, a denuder from URG Corporation was used for the GOM sampling (Fig. 6). A separate PBM quartz trap of identical connector was used for PBM sampling. The detection of PBM signals was achieved using the paralyzer at 900 ^{0}C. During the heating, the Teflon holder was NOT heated. We recognize that Tekran uses quartz chip to prevent mercury deposition in the Regenerable Particulate Filter (RPF) Assembly in the 1135 unit. In our manual method, the Teflon line from the trap to the inlet of Tekran 2537A (Fig. 4) was short (~1 m) and therefore the mercury deposition in the Teflon line is negligible. We have added the description in revised paper (P5, L19-28).

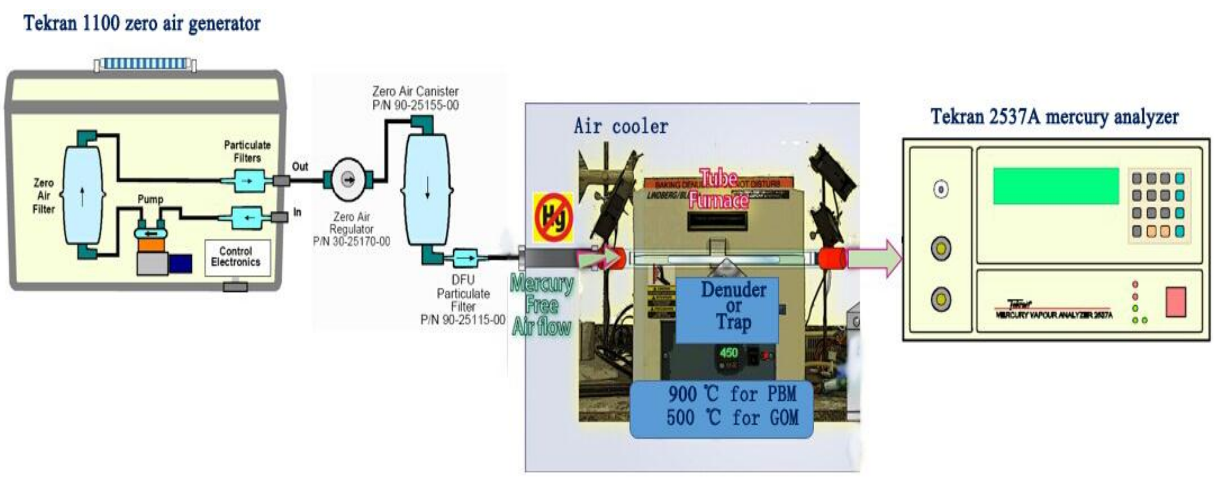


Fig 4: The diagram of GOM and PBM analysis

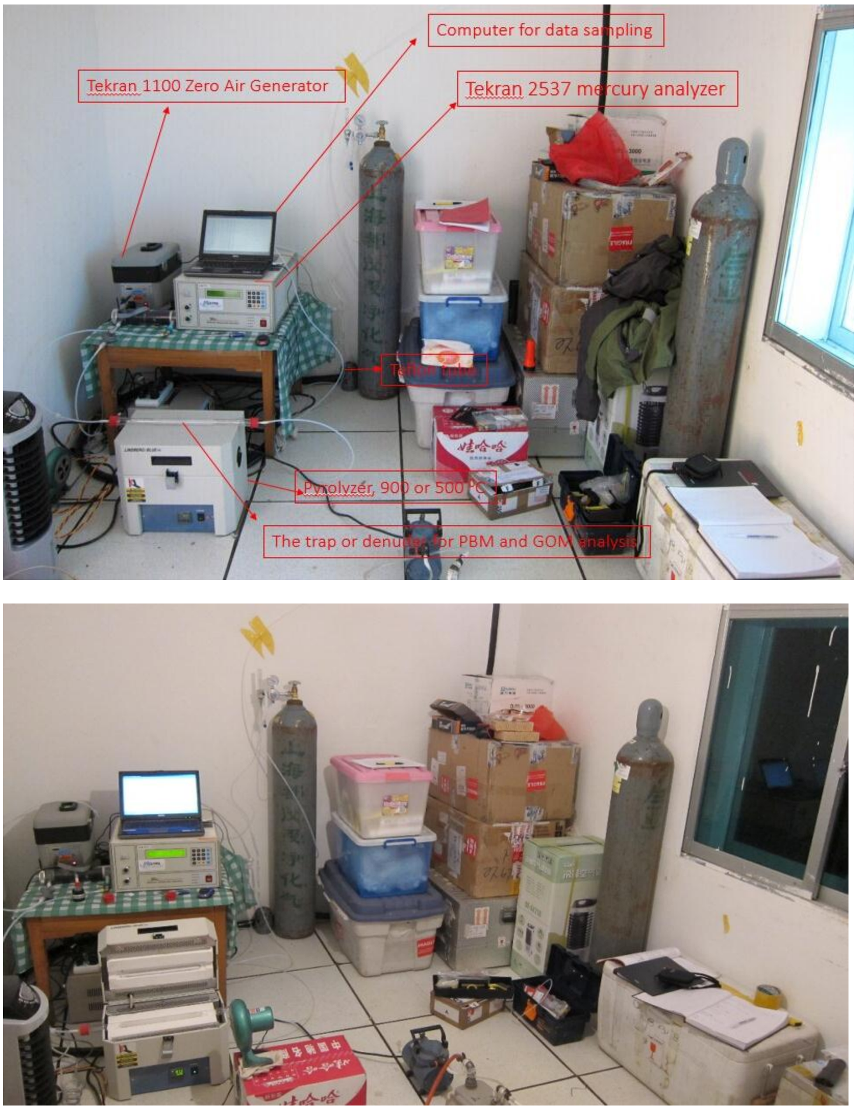


Fig 5: The diagram of analysis unit for measuring GOM and PBM.

Fig. 6: The hollow quartz denuder from URG Corporation (middle).

Further, since this is not a standard procedure (where the filters and denuders can be monitored over a period of time) the reported blanks are of significant concern. For example, the median PBM concentration in winter is 15.23 pg m-3, which would mean for a 10 L min-1 flow rate over 60 minutes, 9.14 pg of Hg was collected on the filter. The reported blank is 6.62 pg, not good for an untested technique. It is even worse when looking at the denuder. The median concentration in spring is 1.05 pg m-3 which translates to 0.63 pg of Hg collected – well below the reported blank of 1.67 pg. Again not acceptable for comparison to networks and standardized, QA/QC'ed data. Unless a significant amount of comparison, or examples of this system being used in other studies where speciation units were used are given then I am very suspicious of the reported GOM and PBM concentrations. In fact in Line 20 on page 5 the authors state that a signal of less than 2 pg "is indistinguishable from the blank." If this is the case then most of the reported GOM data is invalid.

Response: We appreciate the reviewer's careful review and would like to clarify it. The system blank has been deducted from the reported PBM values. In other words, the sampled PBM signal was in fact 15.76 pg. Deducting the 6.62 pg of the blank from the detected signal, 9.14 pg was used for calculating the PBM concentration. The variability of the system blank was 2.29 pg. Since the signal in this case was 15.76 pg and the measurement uncertainty of the system blank was 2.29 pg, the reported PBM is of statistical significance. Similarly, the signal for the 0.63 pg used for calculating GOM was 2.30 pg. Compared to the variability of the blank (0.66 pg), the signal is also of statistical significance. We have also deleted the values below the variability of the system blank (0.66 pg m^{-3} of GOM and 2.69 pg m^{-3} of PBM) and made the new statistics for GOM and PBM (Table 1). These changes have been described in revised paper (P1, L21; P10, L4-5).

I have personally, manually sampled ambient air with denuders to be analyzed for GOM concentrations. This task is not trivial. What style of denuders were used? What filters were used? These are questions that I asked in my original review that were completely ignored by the authors. Were the denuders heated in a tube or clamshell furnace? If so what end caps were used? My own experience has shown me that the end caps can heat up during the heating in a furnace and can liberate Hg from the end caps. How was this prevented?

Response: As discussed in our earlier response, we used the identical denuder in Tekran speciation system. We used the Whatman Grade QM-H Quartz Filter for sampling PBM (http://www.gelifesciences.com/webapp/wcs/stores/servlet/catalog/zh/GELifeSciences/products/AlternativeProductStructure_21531/28418567). As shown in Fig. 4, the denuders and traps are heated in the furnace that fits the size of denuder. The end caps were the URG plastic caps (Fig. 5) and not heated during the analysis. In addition, air-cooler was used for decreasing the temperature of caps. We have added the description in revised paper (P5, L25).

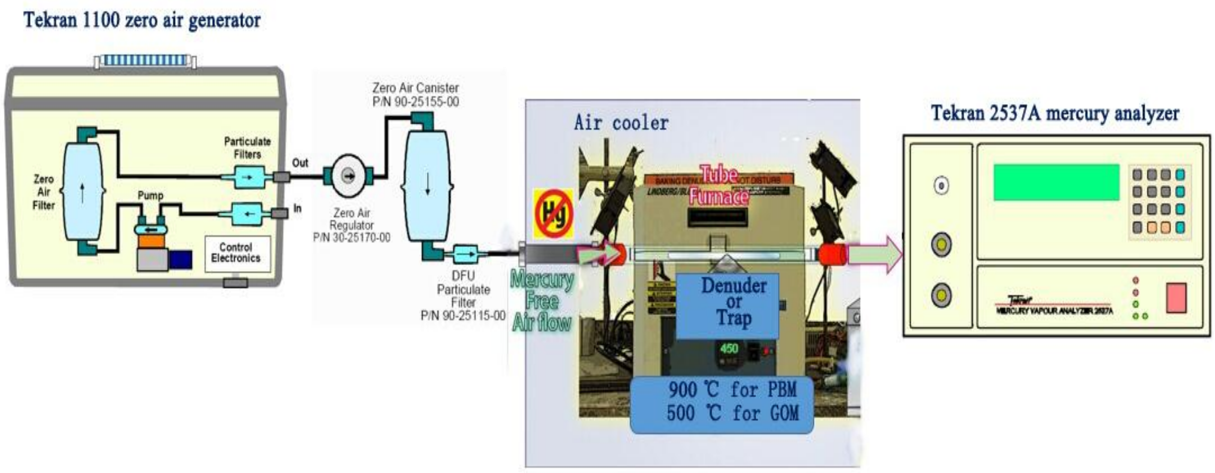


Fig 4: The diagram of GOM and PBM analysis

I am not completely committed to the use of the Tekran speciation system and greatly support other types of measurements for GOM and PBM, but the authors have to perform their "due diligence" and convince the community of the effectiveness of their system for measuring PBM and GOM. So if the authors can show proof of this performance, provide exact procedures that actually pertain to their system then I would be satisfied only after an additional review.

Response: In our preceding response, we described the procedure of the manual method in details. We hope that these ease the reviewer's concern of the measurement.

We want to thank the reviewer for the detailed comments below. For those editorial suggestions, we have made corresponding revisions in the revised manuscript. The technical comments are addressed below and implemented in the revised manuscript as indicated.

Specific Comments

1. Pg 1 Line 14: "speicated" should be "speciated"
   Response: The wording has been revised as suggested (P1, L14).

2. Pg 1 Line 19: "westerlies": either needs capitalized throughout if referring to the "anti-trade" winds or referred as westerly winds.
   Response: The wording has been revised as suggested (P1, L19).

3. Pg 1 Line 22: This sentence should be "From HYSPLIT back-trajectory analysis, we determine that high TGM concentrations (> 2.5 ng m-3) were associated with transport of dry air that carried regional anthropogenic emissions from both Chinese domestic (e.g., western China) and foreign sources (e.g., Burma, Bengal Bay, north India).
   Response: The wording has been revised as suggested (P1, L22-26).

4. Pg 1 Line 25: Sentence beginning with "Backward trajectories…." should be deleted. It was already redundant with the earlier sentence even before I changed it.
   Response: The wording has been revised as suggested (P1, L22-26).

5. Pg 1 Line 32: remove "sources" from after anthropogenic.
   Response: The wording has been revised as suggested (P2, L2).

6. Pg 2 Line 2: Hg0 should be GEM. Be consistent.
   Response: The wording has been revised as suggested (P2, L4).

7. P2 L3: should be "remote areas"
   Response: The wording has been revised as suggested (P2, L5).

8. P2 L4: should be "that bioaccumulates and biomagnifies"
   Response: The wording has been revised as suggested (P2, L6).

9. P2 L6: "specie" should be "species"
   Response: The wording has been revised as suggested (P2, L8).

10. P2 L15-16: "The long-term" should be "Long-term"
    Response: The wording has been revised as suggested (P2, L18).

11. P2 L17: should be "trends" and "patterns"
    Response: The wording has been revised as suggested (P2, L19).

12. P2 L19: should be "there have been" should also be "efforts to establish"
    Response: The wording has been revised as suggested (P2, L21).

13. P2 L2: should be "location between"
    Response: The wording has been revised as suggested (P2, L31).

14. P2 L32: should be "there are an increasing"
    Response: The wording has been revised as suggested (P2, L33).

15. P3 L4: should be "air pollutant emissions"
    Response: The wording has been revised as suggested (P3, L4).

16. P3 L5: should be "accelerates glacier"
    Response: The wording has been revised as suggested (P3, L6).

17. P3 L6: should be "to the Tibetan"
    Response: The wording has been revised as suggested (P3, L7).

18. P3 L6-7: should be "through the Indian"
    Response: The wording has been revised as suggested (P3, L8).

19. P3 L7: should be "in snow packs"
    Response: The wording has been revised as suggested (P3, L8).

20. P3 L15: “mercury” should be “Hg”

    Response: The wording has been revised as suggested (P3, L16).

21. P3 L17: “Hg” twice

    Response: The wording has been revised as suggested (P3, L18).

22. P3 L19: should be “for model assessment, for understanding”

    Response: The wording has been revised as suggested (P3, L20).

23. P3 L20: should be “establishing a global”

    Response: The wording has been revised as suggested (P3, L21).

24. P3 L21: should be “partners around the world”

    Response The wording has been revised as suggested (P3, L22).

25. P3 L26: “in the Hengduan”

    Response: The wording has been revised as suggested (P3, L27).

26. P3 L28: “form” should be “from” and “located to the northwest”

    Response: The wording has been revised as suggested (P3, L29).

27. P3 L29: should be “30 km north”

    Response: The wording has been revised as suggested (P3, L30).

28. P3 L30: what exactly are the “closest large point sources”?

    Response: It means that the biggest point sources near SAWRS are in Kunming city, we have revised the wording as suggested (P3, L31).

29. P3 L32: should be “it is defined”

    Response: The wording has been revised as suggested (P3, L34).

30. P4 L9: should be “Teflon”

    Response: The wording has been revised as suggested (P4, L10).

31. P4 L11-12: Instead of Schroeder et al., 1995 it should be “(Tekran Instruments Corp., Toronto, Ontario, Canada)”

    Response: We thank the reviewer for pointing this out and have revised the wording as suggested and deleted the cited reference (P4, L13).

32. P4 L15: Hg0 should be GEM

    Response: The wording has been revised as suggested (P4, L17).

33. P4 L16: Hg0 should be GEM

    Response: The wording has been revised as suggested (P4, L17).

34. P4 L17: should be "using a Tekran 2505"
    Response: The wording has been revised as suggested (P4, L18).

35. Hg0 should be GEM
    Response: The wording has been revised as suggested (P4, L19).

36. P4 L18: Does accuracy mean recover of the GEM spike from manual GEM injections?
    Response: Yes, it means recover of the GEM spike from manual GEM injections.

37. P4 L18: should "calibrations was"
    Response: The wording has been revised as suggested (P4, L20).

38. P4 L24 – P5L28: did not read for typos do to my major concerns mentioned earlier. At a minimum this section needs a complete re-write.
    Response: We have added some special description for the sampling unit and the procedure of GOM and PBM analysis in this section, and revised the wording as suggested (P4, L27; P4,L1~ P5, L3; P5, L14; P5, L19; P5, L25; P14, L21& P15, L3).

39. P5 L31 – 32: What equipment was used for these measurements?
    Response: Meteorological parameters were continuously monitored via automatic weather station (PH-SLFH, made in China) at the SAWRS, we have revised the wording (P6, L9).

40. P6 L13: "trajectories" should be "trajectory"
    Response: The wording has been revised as suggested (P6, L24).

41. P6 L15: Why is it HYSPLIT4 here and not anywhere else?
    Response: We performed the back trajectory analysis via HYSPLIT4, so we already revised all the HYSPLIT into HYSPLIT4 (P1, L25; P6, L19).

42. P6 L13: How high is "high" TGM concentrations?
    Response: We have added the mean TGM value of the three peaks as suggested (P7, L23-25).

43. P6 L14: How high is "high" TGM concentrations?
    Response: We have added the mean TGM value of the three peaks as suggested (P7, L23-25).

44. P6 L15-16: What is the proposed mechanism for a monsoon increasing TGM concentrations? Wind direction?
    Response: The increasing TGM concentrations in monsoon period is most likely caused by long-term transport of Hg from South and Southeast Asia's anthropogenic emissions and biomass burning. Based on the trajectory data associated with the high Hg concentrations, the air mass was predominantly from South and Southeast Asia (Fig 11). During the transport process, the elevation of trajectory endpoints was 500 m agl. Since the elevation of Shangri-La area is higher than the source regions from the south, the air mass from these regions can move up to the

SAWRS. This is also evidenced by the low trajectory height of Cluster 3. We have made the discussion in section 3.4 (P11, L28-33).

45. P7 L27: Remove “Like some previous studies” and “in Korea” should be “at Korean”
Response: The wording has been revised as suggested (P8, L7).

46. P8 L12: What is “cumulus process”? This term appears many times in the manuscript. Since it is so important a thorough discussion is needed.

Response: In this manuscript, cumulus process refers to the vertical mixing that causes the dilution of air mass and the condensation of water vapor at higher altitude. Since the process will enhance the air mixing, the concentration of Hg can therefore be diluted. Coupled with the scavenging of divalent mercury to atmospheric water, the measured TGM is therefore lower. We have added the discussion in the revised manuscript (P8, L24-26).

47. P8 L24: “concentrations” should be “concentration”
Response: The wording has been revised as suggested (P9, L4).

48. P8 L25: “and the mean GOM of the other time period was 7.34 pg m-3” should be “and 7.34 pg m-3 for the other period”.
Response: The wording has been revised as suggested (P9, L4).

49. P8 L25-26: “A possible reason…into water vapor.” This statement is incorrect and not consistent with the previous statements. Do the authors mean “higher relative humidity” and not “lower relative humidity”?
Response: We thank the reviewer for pointing this out, the statement is correct. We have revised the previous statements as suggested by other reviewer (P9, L5).

50. P8 L29-30: “influence from local” should be “influence of local” and “and from the photochemical productions” should be “and the photochemical production”
Response: The wording has been revised as suggested (P9, L8-9).

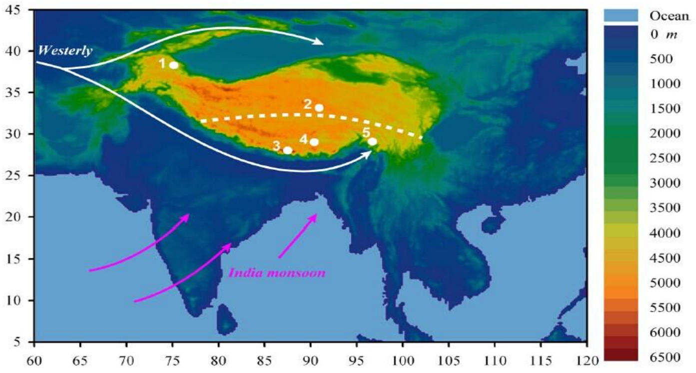
51. P9 L1-27: What is “Sig”? should this be a p value? It appears multiple times.
Response: Yes, we meant the p value and have made the changes throughout the manuscript

52. P9 L17: Should this be TGM and not GEM?
Response: The statement has been revised as suggested (P9, L27-31).

53. P9 L31: “m/s” should be “m s-1”
Response: The wording has been revised as suggested (P10, L8).

54. P9 L32: What is a “south tributary of westerlies”? I am not familiar with tributaries of wind.

Response: Earlier studies established that the Westerlies from central Asia form two tributaries (north and south) due to the barrier of Tibetan plateau. Here we referred to the tributary moving through the south side of the Himalaya–Hindu Kush range.



Baiqing Xu et. al., 2009, www.pnas.org_cgi_doi_10.1073_pnas.pnas.0910444106

55. P9 L33: "effected" should be "affected"
Response: The statement has been revised as suggested (P10, L8-10).

56. P10 L8: "Back" should be "back"
Response: The wording has been revised as suggested (P10, L20).

57. P10 L11: "Southeast" should be "southeast"
Response: The statement has been revised as suggested (P10, L20-22).

58. P10 L12: "Southeast" should be "southeast" and "china" should be "China"
Response: The wording has been revised as suggested (P10, L23).

59. P10 L13: "likely resulted from" should be "caused by"
Response: The statement has been revised as suggested (P10, L22-25).

60. P10 L16: "scavenge" should be "scavenging"
Response: The statement has been revised as suggested (P10, L22-25).

61. P10 L23: "from the south" should be "from south"
Response: The wording has been revised as suggested (P10, L31).

62. P10 L25: "high Hg peaks" – what form of Hg? TGM, GOM, PBM? And "appeared frequently" should be "frequent".
Response: Hg is mean TGM. We thank the reviewer for pointing this out and the statement has been revised as suggested as suggested (P10, L32-34).

63. P10 L26: remove "which is in the Tibetan Plateau"
Response: The wording has been revised as suggested (P10, L32-34).

64. P10 L27-28: "the air flow will move speed slackened and formed cloud" should be "the wind speed will lower and clouds will form."

Response: We thank the reviewer for pointing this out and have deleted the sentences because of new statement (P10, L32-34).

65. Did not edit section 3.4 due to my concerns mentioned earlier.

Response: We have provided the statistical analysis in the SI and provided additional discussion as addressed in the earlier comment. The discussion has been made in the revised manuscript (P9, L18; P10, L3; P10, L13； P11, L23~33).

66. Conclusion section is redundant with other sections.

Response: We have made the conclusion section more succinct as suggested (P12, L31~P13, L7).

Anonymous Referee #3

The authors have made some changes following reviewers' comments and suggestion. Overall, however, the revised manuscript still lacks the integrity and quality to meet the standards for publication in Atmospheric Chemistry and Physics. One major problem is the lack of direct or indirect data to support the proposed mechanisms regarding the temporal variation in Hg concentration and speciation. The proposed emissions sources, such as biomass burning, are also highly speculative because of lack of supporting evidence, too. Considering the value of these data that could contribute to the understanding of regional and global Hg transport and cycling, I think the authors need to analyzed their data and revised the manuscript again very carefully before it can be considered for publication in Atmospheric Chemistry and Physics.

Response: We thank the reviewer for providing the suggestions. During the measurement period, CO was not measured to provide direct evidence for the biomass burning sources because of this exploratory observational campaign. After this campaign, we have set up another site at Mt. Ailao with concurrent measurement of Hg and CO. Based on the data (Wang et al., 2014, in preparation), we have confidence in the biomass burning sources identified in this work. We have also followed the reviewer's recommendations to further revise our manuscript and feel that the paper has been significantly improved. We hope that this will meet the publication standards of ACP.

1, The manuscript needs to be proofread carefully. Errors can be found throughout the manuscript. For example, "bioaccumulates" in line 4 of page 2 should be "bioaccumulate" and "low" in line 18 of page 8 should be "high". Some sentences are not easy to understand, for example, line 27-30 of page 7.

Response: We thank the reviewer for pointing this out and have gone through another round of careful editorial revisions and the readability of the revised manuscript has been improved.

2, Data QA procedure is not provided. How did the authors decide if the data is OK to use or not? Or the authors just used all the data reported from the instrument without any screen criteria?

Response: This study is part of the Global Mercury Observation System (GMOS) and we carefully followed the GMOS Data Quality Management which was developed following Standard Operating Procedures and enables the quality control of raw data retrieved from near real-time monitoring stations (http://sdi.iia.cnr.it/geoint/publicpage/GMOS/sdi/). In our data set, the A/B cartridge bias needs to be < 10%, and the divergence between the two concentrations need to be < 20%. Using data quality assurance criteria of GMOS, the data completeness in this study was 92.6% of the total sample size. We thank the reviewer for pointing this out and have added the statement in revised paper (P6, L2-4).

3. The description of sampling instrument is not very clear. I think the authors should prepare a figure or diagram showing how the manual GOM and PBM sampler was connected to the Tekran 2537A. Was the TGM measurement continued when analyzing the GOM and PBM samples?

Response: We agree with the reviewer that a figure helps illustrates the sampling scheme. As displayed in Fig.2 and Fig.3, the denuder, inlet and impactor was identical to Tekran speciation unit, and the temperature conditioner keep the denuder at 40-50 ^{0}C during the sampling period. The quartz filter was also of the same specification as the filter used in Tekran speciation unit, except with a larger diameter (47mm). The GOM and PBM were collected simultaneously during sampling cycle using two parallel denuder-based sampling units (Fig. 2 and Fig. 3). Since this is an off-line analysis system, the Tekran 2537 did not connected to the sampling unit (Fig. 4 and Fig. 5) and the TGM was continuously measured except during the analytical cycles of GOM and PBM.

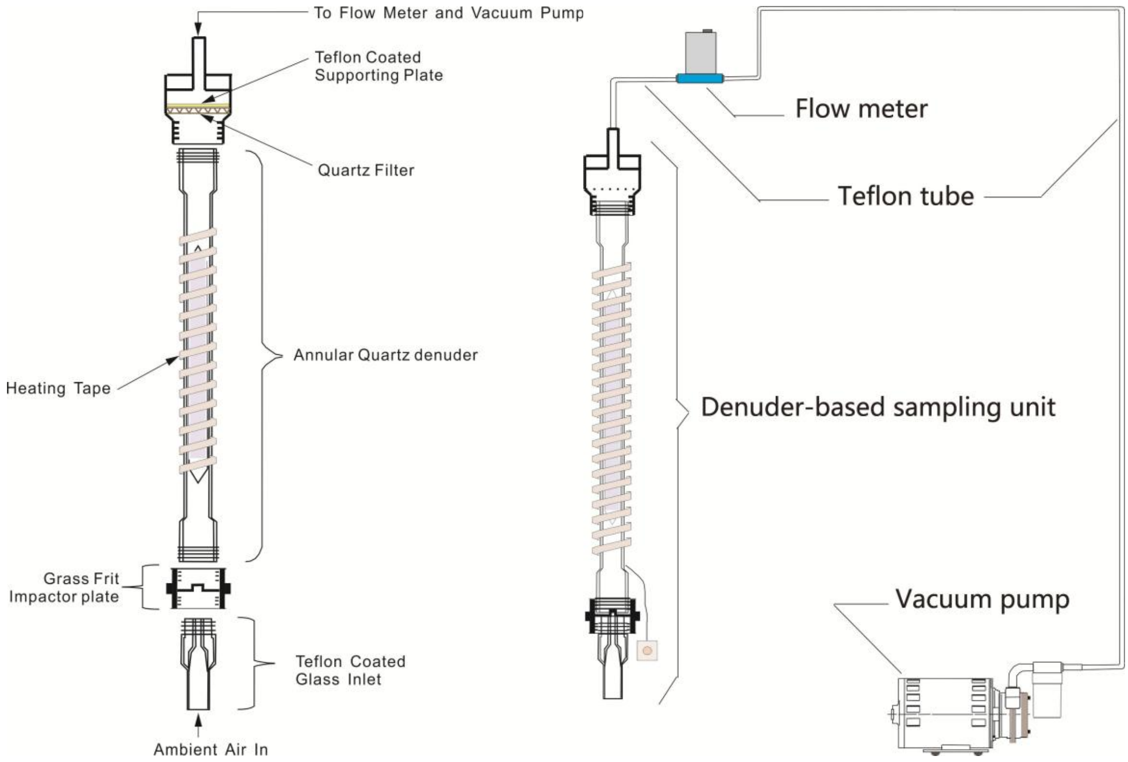


Fig.2: The denuder-based sampling unit.

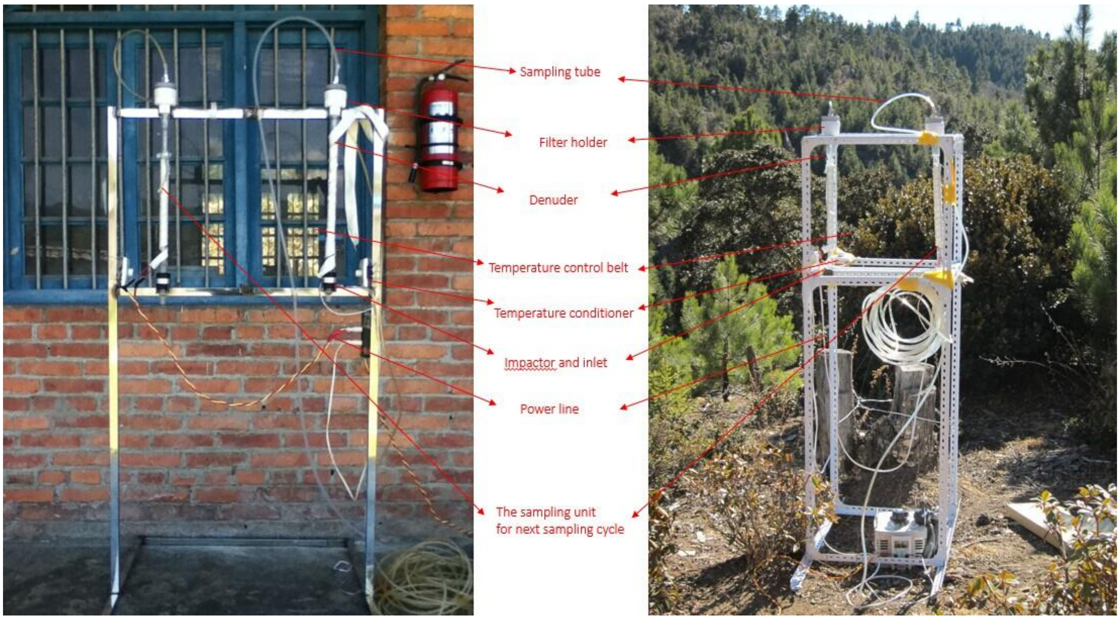


Fig.3: The picture of denuder-based sampling unit.

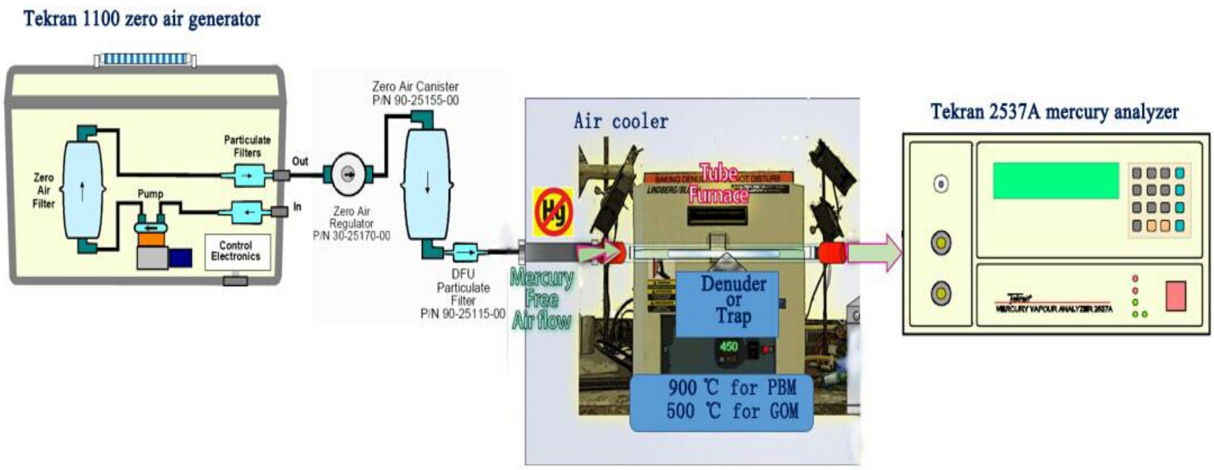


Fig 4: The diagram of GOM and PBM analysis

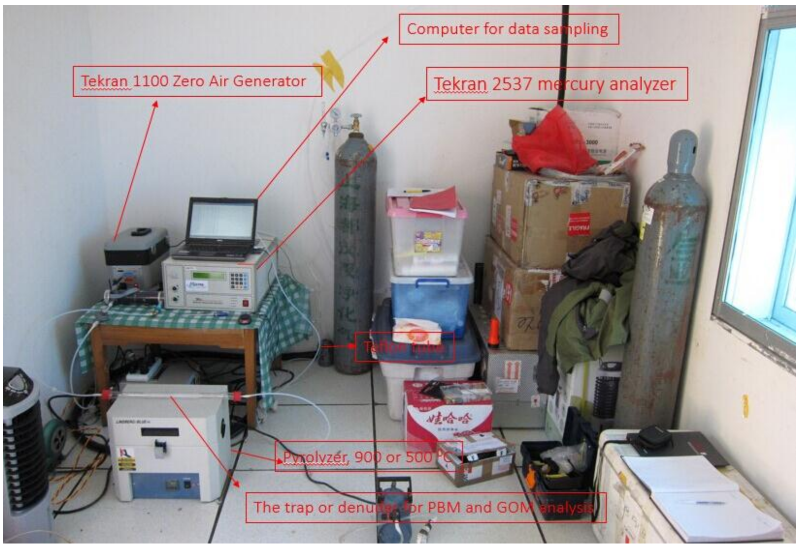


Fig 5: The diagram of analysis unit for measuring GOM and PBM.

4. Page 5, Line 11: Landis et al., which year?

Response: We thank the reviewer for pointing this out and have revised the wording as suggested (P5, L20). The year of this paper from Landis et al. is 2002.

5. Page 7, Line 7: please change “nij” to “Nij”.

Response: We thank the reviewer for pointing this out and have revised as suggested (P7, L17).

6. Page 7, Line 24-26: “As a remote background site, ...” References are required to support this statement.

Response: We have added the references (Obrist et al. 2008; Fu et al., 2012a) as suggested (P8, L5).

7. Page 8, Line 11-13: I don’t understand why the cumulus process could cause dilution of the air masses and gave lower TGM concentrations. Although the authors indicated this would be further discussed in section 3.3, I don’t see a real discussion there. Any reference to back up this statement?

Response: In this manuscript, cumulus process refers to the vertical mixing that causes the dilution of air mass and the condensation of water vapor at higher altitude. Since the process will enhance the air mixing, the concentration of Hg can therefore be diluted. Coupled with the scavenging of divalent mercury to atmospheric water, the measured TGM is therefore lower. We have added the discussion in the revised manuscript (P8, L24-26).

8. Page 8, Line 22-24. Here the authors said that relative humidity was higher in the afternoon than at night and in the morning. However, in Figure 4, it shows clearly that RH was lower in the afternoon. Please double check which one is correct. Because of this inconsistency, the follow-up discussion is problematic.

Response: We thank the reviewer for pointing this out. This is our overlook and we have corrected it in the revised manuscript (P9, L2-4). The relative humidity in the afternoon (14:00~20:00) should be 58.24%, lower than the night and morning (21:00-13:00) of 81.47% (P9, L15-17).

9. Page 9, Line 19-22: The authors first suggested that the lower TGM in late fall and winter months was due to more stagnant wind that limited the regional transport. In the next sentence, however, the

authors then suggested that the variation in wind speed was not likely to cause the observed TGM seasonal variation. These two sentences seemed to contradict each other.

Response: The latter sentence was intended to point out that the variation of wind speed in fall and winter was not significant to force the observed TGM variation in the two seasons. We have made this clear in the revised manuscript (P9, L31-34).

10. Page 9, Line 33 to Page 10, Line 1: "....., therefore the GOM level at SAWRS could be effected primarily by local photochemical transformation or meteorological conditions, as compared to the subsidence of free troposphere". If local photochemical transformation is so important why GOM level peaked in winter not summer?

Response: The low relative humidity could cause the elevated GOM in winter due to the weaker scavenging of produced GOM. In summer, the Indian summer monsoon transports wet air mass to Shangri-La and there was frequent rainfall, causing a lower GOM level.

11. Page 10, Line 5-6: "Therefore the local anthropogenic sources could contribute to the high PBM level at SAWRS". What kind of local anthropogenic sources? In section 2.1, the authors indicated that SAWRS is a remote site and the closest large point sources are in Kunming, about 500 km away. This statement implies that there is no local anthropogenic source near SAWRS. Besides, if there is influence from local anthropogenic sources, I would expect to see high values of TGM and PBM, and maybe GOM, occur concurrently? Is this the case?

Response: Shangri-La is a remote area far away from large point sources, but there are small villages in Shangri-La area where household heating using biofuel burning (wood, yak dung and coal) can be occasionally detected in autumn. We have added the discussion in revised paper (P10, L15-18).

12. Page 10, Line 9-10: "Due to increasing consumption of resource, these areas are expected to release remarkable Hg to the atmosphere". This is purely a guess. Please provide real data or references to support it.

Response: We made this inference based on the observation of high atmospheric Hg in Thailand reported by Sheu et al., 2013. The reference has been cited in the revised manuscript (P10, L22).

13. Page 11, Line 28-29: "The most likely source region was South Asia's biomass burning activities". No data to support this statement.

Response: We thank the reviewer for pointing this out. We have carefully cross verified the time and locations of the back trajectory endpoints with the maps of MODIS fire hotspots, and found that the high TGM concentrations associated with Cluster 3 coincided with the fire hotspots. This evidence is also reflected in the PSCF plot (Fig. 15). We have supplemented the modeling evidence in the SI (Fig. S6) and also provided the discussion in the revised manuscript (P11, L29-33).

References:

J. Munthe, I. W.angberg, N. Pirrone, A.Iverfeldta, R. Ferrara, R. Ebinghaus, X. Feng, K. Gardfeldt, G. Keeler, E. Lanzillotta, S.E. Lindberg, J . Luh, Y. Mamane, E. Prestbo, S. Schmolke, W.H. Schroeder, J. Sommar, F. Sprovieri, R.K. Stevens, W. Stratton, G. Tuncel, A. Urba, Intercomparison of methods for sampling and analysis of atmospheric mercury species, Atmospheric Environment, 35, 3007–3017, 2001.

Mary M. Lynam, Gerald J. Keeler, Comparison of methods for particulate phase mercury analysis: sampling and analysis, Anal Bioanal Chem, 374, 1009–1014, DOI: 10.1007/s00216-002-1584-4, 2002.