

## ***Interactive comment on “Observation and analysis of speciated atmospheric mercury in Shangri-la, Tibetan Plateau, China” by H. Zhang et al.***

**Anonymous Referee #1**

Received and published: 24 May 2014

General comments:

Overall, the discussion paper provided some insights into the potential sources and atmospheric circulation patterns affecting speciated atmospheric mercury at a remote high-elevation site in western China. I can understand from the discussion paper that this site location is an important background site because the air emissions transport to the site covers a large area (including Asia, Europe, and north Africa), and it will be able to monitor the regional air quality as countries, such as China and India, continue to rapidly develop. The paper provided some discussion of the regional-scale (Indian Summer Monsoon) and localized (mountain valley breeze effects) atmospheric patterns that may influence mercury concentrations at the sampling site, which should always be discussed when conducting air quality analysis studies. However, the discus-

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sion paper currently lacks the data to support some of the explanations of the mercury results and more detailed discussions are needed throughout the paper, as described in the specific comments below. In addition to these issues, there were many errors in the discussion paper that need to be corrected before it can be accepted for publication in ACP.

Specific comments:

Pg 11042, line 15: “...Backward trajectory analysis of air masses associated with TGM levels”. This statement is vague. What TGM levels are you referring to? Did you mean high TGM levels?

Pg 11042, line 21-23: You should mention that Hg needs to be in an oxidized form before it enters ecosystems through wet deposition.

Pg 11043, line 2-5: The range of mean or median concentrations in remote sites should be reported, instead of the range because the range of GEM, GOM, and PBM that you are reporting for remote sites are considered very high. Are you including sites in the polar region as remote? In this case, GOM and PBM may be elevated during atmospheric mercury depletion events. But you have not referenced any monitoring studies conducted in polar regions.

Pg 11044, line 1-5: Can you describe more clearly the importance of the three studies mentioned? Is the first sentence related to the second sentence since it was mentioned that the Tibetan glaciers are melting more rapidly due to black carbon and Hg concentrations in snow packs are elevated? Are you implying that the melting of snow due to black carbon would release Hg more rapidly into the environment?

Figure 1: What is the source of data for the anthropogenic emissions? Please state whether they are annual emissions.

Pg 11045, line 9-10: Please include the source of the Hg emissions data.

Pg 11045, line 23: Include the percent accuracy of the Hg vapor analyzer based on

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manual injection calibrations.

Pg 11046, line 3: Please clarify whether this denuder-based system is separate from the TGM measurements using the Hg vapor analyzer.

Pg 11046, line 6-7 and 9-10: Were the PBM and GOM samples analyzed immediately after the sampling cycle? It doesn't seem feasible to replace the impactor and quartz particulate filter after every sampling and analysis cycle when the PBM and GOM samples are being collected every 2 hours. Were the PBM and GOM samples were collected continuously? How many PBM and GOM samples were collected each day? These procedures are also different from the automated Hg speciation system (Tekran models 1130 and 1135 used in Hg monitoring networks, e.g. AMNet), which does not require replacement of the impactor or the quartz particulate filter after every sampling cycle. Please clarify the procedures.

Pg 11046, line 20-30: Please clarify that the manual analysis of the denuders and quartz filter were conducted because it is different from the automated Hg speciation system used in other Hg monitoring networks. How long was the analysis cycle and were the denuders and trap analyzed immediately after sampling? Describe how the quartz filter which collects PBM < 2.5 $\mu$ m was introduced into the traps and analyzed. If the denuders and quartz filters were not analyzed immediately after sampling, how were the samples stored and how long after sampling were the samples analyzed?

Pg 11047, line 15-17: What is the range of values for the IMI and what do the values indicate? What value is considered a high IMI or low IMI? Is this value correlated with the rainfall intensity?

Pg 11047, line 26: What tool or software did you use to conduct the cluster analysis? There are different types of cluster analysis. Please indicate which type was used.

Pg 11048, lines 1-12: More details on the cluster analysis method should be included or if you believe this method has been used many times in previous studies, please

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provide several references, e.g. were the latitude and longitude endpoints clustered separately? How many clusters were chosen? What do you mean by the endpoints of trajectories in the same cluster were averaged (I assume the latitude and longitude were averaged separately)?

Pg 11049: Please include Wij (weighting factor) in Equation 1, since it is part of the equation.

Pg 11050, line 8-9: The Koch et al. reference is for two European locations (Mace Head, Ireland, and Zingst, Germany). Please check references carefully and include background TGM measurements from North America.

Pg 11050, lines 24-30: Do you have data to support the effect of mountain valley breezes on diurnal TGM concentrations? Previous studies have also reported higher TGM concentrations and wind speeds during the daytime and lower TGM at night for non-elevated sites as well. But these results were not indicative of mountain valley breezes. The explanation is a good theory for a high elevation site, but it needs to be better supported with data.

Pg 11051, lines 1-7: These explanations need to be supported with data. How low was the relative humidity in the afternoon and how high were the GOM concentrations? You mentioned the oxidation of Hg<sup>0</sup> but do you have the data to support this, e.g. measurements for oxidants of Hg? Could the higher GOM concentrations be due to the mountain valley breezes discussed in the previous paragraph? Without the data and more detailed discussion, I find the last sentence of this paragraph not convincing and too vague.

Pg 11051, line 22: If you are going to mention correlation, please provide the correlation coefficient.

Pg 11051, lines 23-24: What is RH/AT? Is it the ratio of two parameters or is it either parameter (RH or AT)? Please explain why higher RH causes lower TGM concentrations

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or provide some references to support this finding. RH likely has no effect on GEM because it is not water soluble. GOM is more water soluble, but GOM concentrations are typically 100 times lower than GEM. Why do you think RH will have a significant effect on TGM?

Pg 11051, line 24-27: Do you have data to support that the decrease in TGM is due to enhanced Hg uptake by vegetation? E.g., dry deposition rates, CO<sub>2</sub> data was used in Obrist et al. (2008), etc. Can you find some studies that have estimated how much Hg is removed from the atmosphere by vegetation uptake and include these results?

Pg 11052, lines 8-10: Your data shows that GOM and RH are strongly negatively correlated. What does the strong negative correlation suggest in terms of potential atmospheric processes and sources? Fain et al. (2009) discussed about the potential transport of free tropospheric (dry) air masses that are elevated in GOM to the Rocky Mountains site. Does this apply to the SAWRS, why or why not? If it does, please discuss this mechanism and why the GOM concentrations at SAWRS are much lower than those observed at other sites affected by the subsidence of free troposphere (125-145 pg m<sup>-3</sup>).

Pg 11052, lines 18-20: The weak correlation with rainfall doesn't support the scavenging of PBM and GOM by precipitation; therefore, you should not state that the correlations indicate scavenging by precipitation. At  $r = -0.18$ , the  $R^2$  is only 0.036, indicating only 3.6% of the variance in GOM is explained by precipitation. It is even lower for PBM.

Pg 11052, line 23: What do you mean by "possible ISM months"?

Pg 11052, lines 23-26 and Fig. 7: You should also explain what a negative and zero IMI value indicate.

Section 3.3: Can you conclude there was a strong effect of the ISM on TGM concentrations? It appears only one of the 3 elevated TGM events were related to the ISM

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because of the southerly airflows. You mentioned that the ISM is associated with higher rainfall. Can you add more discussion on how the rainfall events affected TGM, GOM, and PBM?

Pg 11053, lines 16-17: "...were grouped into four clusters (Fig. 11) to understand the regional transport pathways." This statement is very vague. What is the purpose of analyzing the back trajectories using cluster analysis?

Pg 11053, lines 17-19: The average trajectory for cluster 1 in Fig. 11 does not appear to pass over Siberia. Please state the results carefully.

Pg 11054, lines 13-15 and Fig. 13: The back trajectories associated with the lower quartile of TGM don't appear very different from those associated with the upper quartile of TGM (Fig. 12). They also do not appear to be from random directions (same airflow directions in Fig. 13 as Fig. 12). Please explain in more detail how they are different. If Fig. 12 and Fig. 13 are similar, it suggests the air masses don't really contribute to elevated Hg.

Pg 11054, lines 19-21 and Fig. 14: Did you conduct a seasonal PSCF analysis? The study that you mentioned is related to the seasonal changes of air movement caused by monsoons. If you want to say the PSCF analysis supports the previous study, you should present the seasonal PSCF results.

Pg 11055, line 7: Be more specific in the conclusion about which meteorological factors affected the seasonal variation of TGM.

Pg 11055, lines 9-10: You have not described in the discussion how the moist air from ISM affected GOM and PBM concentrations. Please include more discussion about this before making this conclusion.

Pg 11055, lines 11-12: Your discussion of the diurnal TGM trend in pg 11050 did not include temperature. Why are you mentioning in the conclusion that it is mainly due to a diurnal temperature shift?

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Technical corrections:

Pg 11042, line 2: "This study reports the speciated concentrations..."

Pg 11042, line 6: "Gaseous Oxidized Mercury, GOM)", to be consistent with Gaseous Elemental Mercury in previous line

Pg 11042, line 8: "...potential influence of the Indian summer monsoon (ISM) and westerlies on the atmospheric transport of mercury."

Pg 11042, line 9: "The mean  $\pm$  standard deviation concentrations of ...", to clarify which statistic follows the  $\pm$ .

Pg 11042, line 14: "low PBM and GOM levels were attributed to...". Wet scavenging is a form of deposition. Did you mean dry and wet deposition? If it is only wet scavenging, you can delete deposition because it is redundant.

Figure 1 caption: "The location of SAWRS, anthropogenic Hg emissions (gkm<sup>-2</sup>) and major cities in Asia with a large population and industrial production." Please check for grammar.

Pg 11044, line 24: "The SAWRS is a remote highland site located in Hengduan Mountains area southeast of the Tibetan Plateau."

Pg 11045, line 4: "Other large cities (Chengdu, Guiyang and Chongqing) are east of Shangri-La.", a close parentheses is needed.

Pg 11045, line 6: "Southeast Asia is due southeast." Southeast Asia seems too broad of an area. Why do you need to mention this? Is Shangri-La not part of southeast Asia?

Pg 11045, line 8: "There are no large-scale industrial activities and fossil fuel consumption in the area."

Pg 11045, line 13: "The inlet of the heated Teflon..."

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Pg 11045, line 24-25: The sentence was already stated at the beginning of this paragraph.

Pg 11046, line 3: "The annular denuder tubes..."

Pg 11046, line 21: You repeated the reference to Landis et al.

Pg 11047, line 17-18: Please check the HYSPLIT website for the correct reference citation.

Pg 11048, lines 13-15: The description of PSCF needs to be moved down, before the PSCF equation.

Pg 11048, lines 16-18: This sentence needs to be moved up to the cluster analysis section.

Pg 11048, line 25: "Overall, more than ..."

Pg 11049, line 13-14: "(9.7 $\pm$ 10.2 ngm<sup>-3</sup> in Guiyang, Fu et al., 2011; 6.74 $\pm$ 0.37 ngm<sup>-3</sup> in Chongqing, Yang et al., 2009)", there is an extra )

Pg 11050, line 1: "...possibly weak local sources." "Shangri-La is located between East Asia and South Asia, which are regions with large Hg emissions (Fig. 1)."

Pg 11050, lines 9-10: "The elevated background level of TGM at the SAWRS is likely caused by strong regional sources in Asia."

Pg 11050, lines 15-16: "...the weak emissions in the Shangri-La County south of the monitoring site."

Pg 11050, line 19: "Fig. 4 displays the average diurnal trend...", are you showing an average diurnal trend?

Pg 11053, line 11: Figure 1 should be Fig. 10

Fig. 11: Please label the average trajectory with the cluster number so that readers can easily identify the trajectory cluster in the figure while reading the discussion.

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Pg 11053, line 29: "...Cluster 2, also infrequent, could be..."

Fig. 12: "The air masses with high Hg from South and Southeast Asia occurred in autumn and summer", not the winter. Please make sure the caption and the discussions in the text are consistent. "The rest of the air masses were from west Asia,..."

Fig. 14: SAWRS is repeated in the first sentence of the caption.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 11041, 2014.