Reply to interactive comment on “Atmospheric mercury concentration and chemical speciation at a rural site in Beijing, China: implication of mercury emission sources” by L. Zhang et al.

To comments from Anonymous Referee #2:

This study measured the speciated mercury concentrations in the atmosphere for an entire year at a rural site in Beijing, China. The authors found that this site was highly affected by anthropogenic emissions. The authors also evaluated the seasonal cycle and diurnal cycles of different mercury species at this site. They compared the mercury concentrations with CO, O3, and PM2.5, which further releases source information of mercury. Meanwhile, the authors also employed back-trajectory analysis to explore the source region of mercury over this site.

The paper was clearly written and the results were well discussed with proper details and depth. Clearly, this paper deserves to be published on this journal. However, the authors still need to address the following points before it’s accepted for formal publication.

Reply: We thank the reviewer for supporting the publication of our manuscript. We address all of the reviewer’s comments below. The original comments are in black and our responses are in blue.

One general comment regarding this paper is that the authors need a better discussion and explanation for the seasonal variation of Hg concentrations. At this site, the highest seasonal average GEM concentration occurs in summer, while the lowest value occurs in winter. This is actually the opposite of those of the observations over other sites in the North Hemisphere. A summer minimum is often reported at these sites because of the stronger oxidation and subsequently deposition loss during summertime (e.g. Holmes et al., 2010; Lan et al., 2012; Song and Selin, 2013). Why did Miyun site show a totally different seasonal cycle? Meanwhile, the discussion for the diurnal cycle of speciated mercury concentrations in section 3.3 is also a little bit too superficial and lack of quantitative information.

Reply: The discussion on seasonal variation has been modified in the revised manuscript. Please see Line 217-220 and Line 229-231 on Page 9.

Because of the mercury oxidation process in summer, GEM should be minimal in summer. However, the impact of interregional mercury transport is also very important at Miyun site. In winter, Miyun’s GEM is more influenced by the remote west and north area (whose air mass is cleaner). On the contrast, Miyun’s GEM in summer is more influenced by the south and east area as far as the YRD region, whose air pollution is severe. The anthropogenic mercury emissions in different areas play a key role in the seasonal variation of mercury at Miyun site.

The overall daytime and nighttime average concentrations of GEM, RGM and PBM have been added in the revised manuscript. Please see Line 233-235 on Page 9:

“The overall daytime average concentrations of GEM, RGM and PBM were 3.13 ng/m^3, 11.5 pg/m^3 and 83.6 pg/m^3, respectively, while the overall nighttime averages of the three species were 3.30 ng/m^3, 8.7 pg/m^3 and 112.0 pg/m^3, respectively.”

Line 104-108: I suggest show the boundaries for your definition of “regional” and “interregional” source regions in Fig. 1. This is helpful for people not familiar with the names of the mentioned provinces.

Reply: The boundaries of “local” and “regional” have been added to Fig. 1. The region outside “regional” is all “interregional”.

Line 161-164: The weighting function defined in equation (2) actually punishes grid points with small nij values. Can you provide more explanation and/or reason to do this? Probably a couple of references would be helpful. It was not clearly stated in the current manuscript.

Reply: PSCF is a ratio of m_{ij} and n_{ij}. A small n_{ij} may result in a high PSCF value with large uncertainty. For large n_{ij}, the PSCF value is more statistically stable. That is why the weighting function is necessary. More details can be found in the study of Polissar et al. (1999). The reference has been added. Please see Line 172 on Page 7.

Reference: Polissar, A. V., Hopke, P. K., Paatero, P., Kaufmann, Y. J., Hall, D. K., Bodhaine, B. A., Dutton, E. G., and Harris, J. M.: The aerosol at Barrow, Alaska: long-term trends and source locations, Atmos. Environ., 33, 2441–2458, 1999.

Line 167: Does it really make sense to divide your domain into 0.5 degree x 0.5 degree grids even if you are using 1 x 1 degree meteorological data?

Reply: The endpoints of each back-trajectory are generated by hour. At a typical 5 m/s speed wind, the distance between two endpoints is about 18 km which is much less than 0.5 x 0.5 degree grids (about 50 km in mid-latitude regions). Although the wind fields are interpolated from 1 x 1 degree meteorological data, the reliability can be assured because of the continuity of air.

Line 182-183: Only existing literatures for observations conducted in China are tabulated in Table 2. This point was clear in the table but not here.

Reply: This point has been clarified. Please see Line 198 on Page 8.

Line 197: To my knowledge, the API is decided by the concentration of pollutant which has the severe pollution compared with their own thresholds. I guess PM could be the dominant pollutants in these events. Can you clarify it about this point?

Reply: PM_{10} is the dominant pollutant for Beijing’s API in the heavy pollution episodes. This point has been clarified. Please see Line 210-211 on Page 8:

“It should be noted that PM_{10} is the dominant pollutant for Beijing’s API in the heavy pollution episodes.”

Line 212: Can you explain why the RGM concentration in summer is lower than in fall? Isn’t the summer season has the strongest photochemical productions?

Reply: The heavy pollution episodes in autumn were longer and heavier than those in other seasons due to the disadvantageous diffusion condition, which led to the highest seasonal average RGM concentration in autumn. The average wind speeds for winter, spring, summer and autumn were 1.11, 1.71, 1.24 and 1.05 m/s, respectively. Please see Line 229-231 on Page 9.

Line 226: Can you observe inverse correlation relationship between GEM and RGM in these hours, as suggested by Timonen et al., 2012? The peak of RGM occurs in the afternoon; however, the GEM is the lowest in the morning, e.g. 8:00-10:00 AM in fall. Is this against your conclusion that GEM is oxidized to RGM?

Reply: The inverse correlation between GEM and RGM is usually found in remote sites. The Miyun site is largely influenced by both local and regional emission sources. Therefore, this is not against the conclusion that GEM is oxidized to RGM. Since anthropogenic source plays an important role in autumn, the daily variation of wind direction has a large impact on the GEM concentration. In autumn, the dominant wind directions are North and Northwest from 20:00 to 7:00, Southeast and East from 8:00 to 10:00, South from 11:00 to 13:00, Southwest from 14:00 to 17:00, and West from 18:00 to 19:00. The lowest GEM at 8:00-10:00 AM in autumn is probably due to the relatively clean air mass from southeast and east to the Miyun site.

Line 227-228: I don't get this point. How is pollution episode associated with higher RGM concentrations? Is there any casual effect between them?

Reply: The description of this point has been modified as follows:

"The RGM concentration peak for autumn is higher than that for summer, which is due to the disadvantageous diffusion condition in autumn."

The average wind speeds for winter, spring, summer and autumn were 1.11, 1.71, 1.24 and 1.05 m/s, respectively. The disadvantageous diffusion condition in autumn aggravated the influence of local primary RGM emission sources in Beijing. As we mentioned in Section 4.2, the ratio of RGM to O_3 could be an indicator of local primary sources. Higher RGM/O_3 ratio in autumn suggests higher influence from local primary sources.

Line 293-299: The discussion regarding the intercept of the trend line is very interesting, because previous studies were more focused on the slopes.

Reply: We intend to extract more information from multi-pollutant relationships.

Section 4.3: Have you investigated the relationship between PBM/PM2.5 ratio and temperature and RGM concentrations? Do they comply with the relationship observed by Rutter and Schauer 2007?

Reply: We checked the relationship between gas-particle partitioning coefficients for reactive mercury and the temperature ($Log(K_p^{-1})$ and T^{-1}, K_p=PBM/$RM_{2.5}$/RGM), based on the study of Rutter and Schauer (2007). Significant correlation was found for summer (r=0.63), while no significant correlation was found for other seasons. This result indicates that the correlation is more significant under higher temperature, which can also be recognized in Fig.2 in the study of Rutter and Schauer (2007). The relationship observed by Rutter and Schauer (2007) is not fully applicable at the Miyun site.

Fig. 3: I suggest draw monthly values, instead of "seasonal" ones. So you don’t bother to define the different seasons. The reader can also get more information from your plots.

Reply: Monthly GEM statistics have been given in Fig. 3 instead of seasonal ones. Please see Fig. 3 and Line 213-214 on Page 8. However, the RGM and PBM data in some certain months are not sufficient. Only seasonal variations of RGM and PBM can be given.