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Interactive comment on "Diel variation of mercury stable isotope ratios record photoreduction of PM$_{2.5}$-boundb mercury" *by* Qiang Huang et al.

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We thank the reviewers for their constructive comments and suggestions. We have completed the revision of the manuscript according to the comments and suggestions provided by the reviewers. We appreciate very much all comments made by the reviewers; they are very valuable for improving the readability of the manuscript and interpretation of the protocol. Detailed Response, Marked Manuscript and Revised Supporting Information were also combined into a PDF file in supplement. In the marked version, the revised areas are in red color. Please check the file in supplement. Blow we have compiled our point-by-point responses to the comments.

Detailed Responses to Referees

1 Anonymous Referee 1

1.1 Huang et al. present a study on diurnal particulate (aerosol) Hg isotope variation in Beijing. I have reviewed this MS previously for EST and I was curious to see how the MS evolved following my previous suggestions. I regret to say that these have been largely ignored, so I paste here my previous review because it is still of interest: “Huang et al.’s study is unique and the variations observed, with lower Hg concentrations and higher Hg MIF during daytime, are rather interesting and novel. The authors interpret this as evidence for in-aerosol photoreduction of Hg, which would be an important result if it were true. The MS is fairly well written, organized and cited.

– Thank you for your comments. We have addressed the comments below.

1.2 Although at first sight I agree with the interpretation, I find that the authors privilege the photoreduction interpretation without much in-depth discussion of alternative interpretations. For example, the current gas-aerosol partitioning model (Amos et al., 2012, ACP) suggests divalent gaseous Hg (GOM) to partition to aerosol at low temperatures. The authors should estimate and discuss if this process can lead to their concentration observations.

– Thanks for the above comments. In this study, we observed that PBM (mass-based concentration) is greater during night-time than daytime for consecutive day-night pairs. We agree with the reviewer that the PBM is likely affected by gas-aerosol partitioning of GOM, in addition to the impact of sources. It is intuitive that the partitioning equilibrium depends on both temperature and GOM level. Adsorption or partitioning of GOM from air to PM is an exothermic process; lower temperature at night-time favors stronger adsorption of GOM on PM than at day-time. For example, Rutter and Schauer (2007) and Amos et al. (2012) proposed gas-aerosol partitioning models, which suggest that more divalent gaseous Hg (GOM) may partition onto aerosols at lower temperature. If we assume that GOM could remain a constant level during daytime and night-time, relatively lower temperature at night-time should result in higher PBM in the night-time than in the daytime. However, the assumption of constant GOM over day-night time is likely untrue. According to several recent studies, the GOM measured in the field also exhibits significant diel variation, with higher GOM concentrations found during the daytime than at night (Lan et al., 2012; Liu et al., 2007; Poissant et al., 2005), likely due to the photo-oxidation of GEM. For example, the GOM measured during the spring season in Salt Lake city was equal to or lower than 4 pg m^{-3} at night-time and was as high as 20 pg m^{-3} during daytime (Lan et al., 2012). Another study reported that the GOM measured in the urban area of Detroit, Michigan was lower than 9 pg m^{-3} at night and as high as 13 pg m^{-3} during day-time (Liu et al., 2007). Apparently, the temperature effect on PBM concentration due to favored adsorption of GOM during night-time (lower temperature) may be partially (if not totally) off-set by lower GOM levels during night-time. In other words, the net PBM may show less diel variation as predicted from the temperature-dependent partitioning model when GOM is also substantially lowered during the night-time.

To support the above argument, we used an inverse approach and a GOM partitioning model to compute hypothetic GOM levels corresponding to each of our PBM observations at ambient temperature. We used the GOM gas-aerosol partitioning model proposed by Amos et al., 2012, which has the following equation: log10(K^{-1}) = (10±1) – (2500±300)/T, where K = (PBM/$PM_{2.5}$)/GOM with PBM and GOM in common volumetric units (pg m^{-3}), $PM_{2.5}$ in μg m^{-3}, and T in K. We used the measured $PM_{2.5}$-Hg as PBM and assumed that the $PM_{2.5}$-Hg measured for each sample is 100

Similarly, gas-aerosol partitioning of GOM does not likely account for the diel variation of $PM_{2.5}$-Hg concentrations measured in this study. Meanwhile, our data showed that the average Δ^{199}Hg value during the daytime (0.26‰ $\pm$ 0.40‰ 1SD, n = 26) is (statistically) significantly ($p < 0.05$, t-test) higher than during the nighttime (0.04‰ $\pm$ 0.22‰ 1SD, n = 30). This slight diel variation of odd-MIF of Hg isotopes was explained in terms of photoreduction of PBM during daytime. In addition we argue that the diel variations of odd-MIF of Hg isotopes does not result from GOM gas-aerosol partitioning. In general, divalent Hg gas-aerosol partitioning is considered as chemisorption and desorption (Rutter and Schauer, 2007). Prior studies showed that the adsorption/desorption and precipitation of aqueous Hg^{2+} had insignificant odd-MIF of Hg isotopes (Jiskra et al., 2012; Smith et al., 2015), suggesting that the GOM partitioning process may not result in the characteristics of odd-MIF of Hg isotopes we observed for the $PM_{2.5}$ samples.

In conclusion, gas-particle partitioning may increase PBM during the night-time due to relatively lower temperature compared to the daytime. The actual increase of PBM during the nighttime may be off-set by lower GOM levels during nighttime when little or no production of GOM by the photo-oxidation of GEM may occur. It is shown that GOM is high during daytime likely due to stronger photo-oxidation. GOM can be adsorbed on to PM where the active Hg species are also photo-reduced to elemental mercury. Such a dynamic and complex adsorption-photoreduction cycle yields lowered PBM levels, along with characteristic Hg isotope properties. In other words, our thesis is that the photochemical reactions cause the concentration reduction of $PM_{2.5}$-Hg as well as fractionation of the $PM_{2.5}$-bound Hg isotope compositions.

To address these issues, we have included a discussion about the possible effects of gas-aerosol partitioning on the diel variation of PBM. See the revised manuscript on line 358 to 370, it reads: “A possible explanation of the observed effects of diel variation of $PM_{2.5}$-Hg would be the temperature-dependent gas-aerosol partitioning of GOM (Amos et al., 2012; Rutter and Schauer, 2007), which favors more adsorption of GOM on PM during nighttime when atmospheric temperature us relatively lower than daytime. However, the magnitude of such adsorption is also proportional to the GOM concentration in the atmosphere. An inverse calculation exercise (in SI) shows that the higher $PM_{2.5}$-Hg measured for our samples would require higher GOM concentrations during the nighttime, which contradicts with prior findings that GOM concentrations are significantly lower during the nighttime than the daytime as GOM is a product of photo-oxidation processes (Amos et al., 2012; Liu et al., 2007; Poissant et al., 2005). In addition, GOM gas-aerosol partitioning is considered a chemisorption and desorption process (Rutter and Schauer, 2007), which unlikely result in appreciable odd-MIF of Hg isotopes (Jiskra et al., 2012; Smith et al., 2015). Therefore, GOM partitioning would have little or no effect on the observed diel variations of Δ^{199}Hg values for $PM_{2.5}$-Hg."

1.3 I suggest the authors consider the influence of boundary layer dynamics and stratification: daytime turbulence could lead to mixing of above lying, cleaner free tropospheric air with high MIF, whereas nighttime stratification traps Hg emissions with low MIF."

– Thank you for your suggestion. We agree that the boundary layer was higher during the daytime than at night, and daytime turbulence could help to mix the air between bottom and top of the layer. As your suggest, with constant Hg emission and $PM_{2.5}$ deposition rates, Hg^{2+} photoreduction on $PM_{2.5}$ during the daytime may be enhanced at the top of the boundary layer (up to 1500 m) on a sunny day and produce much more positive odd-MIF of Hg isotopes on $PM_{2.5}$, while at night, the lower boundary layer traps a portion of daytime PBM at much low altitudes (mean of about 300 m). The mixing of residual daytime PBM with newly emitted PBM in the thinner boundary layer at night may help to explain why nighttime PBM had odd-MIF values closer to source emissions.

Per your suggestions and comments, we have added a discussion about the possible effects of the difference of boundary layer thickness during daytime and nighttime on the diel variations of Hg isotope ratios in the $PM_{2.5}$ samples we collected. See the revised manuscript on line 371 to 381, it reads: "Variation in atmosphere boundary layer height (ABLH) from 1000 to 1300 m during daytime to less than 200 to 300 m during nighttime may have contributed to the diel variation in Hg isotopic composition of $PM_{2.5}$-Hg (Quan et al., 2013). With a high ABLH during daytime, relatively strong turbulence may help mixing the $PM_{2.5}$-Hg from the surface to the upper free troposphere, where photoreactions may be favored due to higher intensities of ultraviolet radiation on clear days. In contrast, a lower ABLH at night may weaken the vertical transport of $PM_{2.5}$-

Hg, but enhance the contribution from newly produced $PM_{2.5}$-Hg, possibly resulting in higher concentrations of $PM_{2.5}$-Hg with negative or close to zero Δ^{199}Hg values from emission sources and/or GOM. However, vertically-resolved, day-night measurements of Hg stable isotope ratios in PBM and GOM are needed to fully evaluate the effects of various physical processes on diel variation of the Hg isotopic compositions for the $PM_{2.5}$".

1.4 In the current MS submitted to ACP I did not find discussion of gaseous Hg(0) – aerosol partitioning, nor discussion of boundary layer dynamics. The authors should discuss with atmospheric physicists, and see if proxies of boundary layer mixing can be used. For ex. $PM_{2.5}$ itself seems higher during nighttime than daytime, which is likely due to nighttime boundary layer stratification which traps pollutant emissions. Daytime heating of land and ensuing turbulence will mix boundary layer air with overlying free tropospheric air. Such mixing may, or may not, generate all the trends observed. It should be discussed and counter-argumented.

– We agree that, although $PM_{2.5}$ concentrations had insignificant diel variation ($p = 0.887$, paired samples t-test), the change of boundary layer thickness between daytime and nighttime could affect PBM transformations, and we now address the possibility of this effect as described in our comments above.

1.5 In summary, I am convinced that the dataset is novel and of strong interest to the atmospheric Hg community and ACP readers, but I suggest the authors to better think through alternative interpretations, and to respect the reviewing process. The editor and reviewers spend time to try and make your study better.

– Thank you for your suggestions and comments. Although the editor of EST did not give us a chance to response your comments, we truly appreciate the editor and reviewers for their comments on this manuscript. We are very glad to have this chance to respond to your comments at here, and we revised the manuscript accordingly.

1.6 Minor comments:

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Discussion paper

L99. “It is intuitive that, while both D and N $PM_{2.5}$ samples may have similar local or regional sources if the wind trajectory remains unchanged, D samples could have been exposed to more solar radiation than N samples, likely resulting in diel variations in the Hg isotope compositions that are indicative of differences in photochemical transformation of $PM_{2.5}$-Hg.” Not sure this makes sense: if PM-Hg was emitted 1 week ago and travelled across China, the particles went through 7 day/night periods, all receiving more or less the same amount of radiation.

– We have deleted this sentence.

L211. The statistics of diel variations are discussed here, with reference to Table S3. It appears to me that paired T-tests should be reported in the text, and not means and p values for the whole dataset. A key question is whether $PM_{2.5}$ shows diel variation in the paired T-test? The p values in the text do not correspond to metrics in Table S3, so the discussion is hard to follow.

– We have revised this paragraph per your suggestions, which now reads (on line 207 to 215 in the revised manuscript): “T-test results (Table S3) showed that diel variation was statistically significant ($p < 0.05$) for Hg contents, Δ^{199}Hg, and Δ^{200}Hg values, as their p values are 0.005, 0.000 and 0.004 resulting from paired samples t-test, and are 0.003, 0.017 and 0.019 resulting from independent samples t-test. For all samples, Hg contents for D-samples (0.32 $\pm$ 0.14 μg g-1) were lower than N-samples (0.48 $\pm$ 0.24 μg g-1), and Δ^{199}Hg and Δ^{200}Hg values for D-samples (mean of 0.26‰ $\pm$0.40‰ and 0.09‰ $\pm$ 0.06‰ respectively) were higher than N-samples ($-$0.04‰ $\pm$ 0.22‰ and 0.06‰ $\pm$ 0.05‰ respectively). However, $PM_{2.5}$ concentrations and δ202Hg had statistically insignificant ($p > 0.05$) diel variation, as their p values are 0.887 and 0.052 resulting from paired samples t-test, and are 0.909 and 0.053 resulting from independent samples t-test”.

L171. Why 24h back trajectories and not more? What is known about PBM lifetime in the Chinese boundary layer? I think there is a discussion in Horowitz et al., ACP, 2017 on this.

– Per your suggestion, we changed to 72-h back trajectories in the revised manuscript. The results of such 72-h back trajectory frequencies are shown that the dominant air masses (over 90

L342. “Interestingly, negative Δ^{199}Hg values in daytime $PM_{2.5}$-Hg were only observed during a rainy day and an extreme smog event. Scavenging of locally produced GOM during rain or smog events may therefore have contributed to the reversal of the odd-MIF signature of Hg collected as $PM_{2.5}$ at these times.” Why would local GOM have a negative Δ^{199}Hg? Not clear to reader.

– We have revised these sentences for clarity (see the revised manuscript on line 341 to 346): “Interestingly, negative Δ^{199}Hg values in daytime $PM_{2.5}$-Hg were only observed during a rainy day and an extreme smog event. Since the Hg emitted from local sources had close to zero and negative values of odd-MIF, higher humidity (such as during rainy days) and heavy pollution (the extreme smog) may enhance the effect of scavenging of locally produced gaseous or particulate Hg during rain or smog events, which may therefore have contributed to the reversal of the odd-MIF signature of Hg collected as $PM_{2.5}$ at these times”. âĂČ

2 Anonymous Referee 2

2.1 This manuscript quantified the diel variation of Hg isotope composition of particulate bound mercury (PBM) and revealed that daily photochemical reduction of divalent Hg is of critical importance to the fate of $PM_{2.5}$-Hg in urban atmospheres. The topic is quite interesting and is important for understanding global mercury cycling. Publication is suggested after minor revision.

– Thank you for your comments.

2.2 Line 114 Is one air sampler enough? PBM concentration in the air is quite small. To obtain enough mercury for isotope analysis, especially when the sampling time was reduced, it seems that we need more samplers.

– We used one sampler for collecting the PM samples. Among the 61 $PM_{2.5}$ samples we collected, 56 had sufficient Hg mass for Hg isotope analysis. It would be better if two or more samplers were used simultaneously for sampling so that (1) sufficient mass of PBM can be obtained for isotope analysis and (2) replicates could be used for isotope analysis.

2.3 Line 163 Why do you choose the height of 500 m?

– In our back trajectory modeling, we used 500 m as the average boundary layer height in Beijing according to a prior study by (Xiang et al., 2019). The estimated backward HYSPLIT trajectories of air masses should be acceptable. Alternatively, we also used different arrival heights (200, 500, 1000 m above ground level) for estimating the backward trajectories. The results indicate that the transport pathways are not very sensitive to the selected heights within the studied area. Per your comments, we have added detail information in the revised version of the Supporting Information.

2.4 Figure 2 This figure is too busy. Instead listing all data according to time series, is it possible to classify the figure into several subgroup according to the topic you wants to discussed? This figure can be moved to supporting information.

– Per your suggestion, we have revised Figure 2 as following, which shows the chronological sequence of MIF (Δ^{199}Hg and Δ^{200}Hg) and MDF (δ202Hg) of the 56 samples collected during the daytime (D, red) and nighttime (N, blue), along with selected weather data including cumulative hours of sunshine (Solar) and air mass backward-trajectory directions.

2.5 Figure 2(a) How to explain the negative value of Δ^{199}Hg on Sep 28?

– The explanation had been described in Line 363 to 373. “Interestingly, negative Δ^{199}Hg values in daytime $PM_{2.5}$-Hg were only observed during a rainy day and an extreme smog event. Since the Hg emitted from local sources had close to zero and negative values of odd-MIF, higher humidity (such as during rainy days) and heavy pollution (the extreme smog) may enhance the effect of scavenging of locally produced gaseous or particulate Hg during rain or smog events, which may therefore have contributed to the reversal of the odd-MIF signature of Hg collected as $PM_{2.5}$ at these times. In addition, the negative Δ^{199}Hg values in $PM_{2.5}$ may have resulted from the contribution of biomass burning with limited photoreduction effect during periods of less sunshine (Fig. 2 and Table S1) since plant foliage has negative Δ^{199}Hg values (Yu et al., 2016) and more negative Δ^{199}Hg values (down to -0.53‰ of $PM_{2.5}$-Hg in Beijing were related to biomass burning, a source of $PM_{2.5}$-Hg south of Beijing in autumn (Huang et al., 2016)."

2.6 Figure 2(f) all legends are suggested to be listed on the top of this figure. It is difficult to find "clear" "cloudy" "rain" in this figure.

– We have revised the legends in the revised Figure 2(d).

2.7 Line 356 "While our results cannot exclude the effects of other possible processes, such as oxidation, adsorption (and desorption), and precipitation, based on the limited previous studies (Jiskra et al., 2012; Smith et al., 2015; Sun et al., 2016), these processes are not likely to be important to the diel variation of odd-MIF of Hg isotopes in $PM_{2.5}$-Hg we observed." The observed isotope fractionation is a phenomenon while the photochemical reduction is one process leading to this phenomenon. How can you exclude the impact from other processes? Evidences are required to prove this conclusion.

– We agree that these observations may be the result of multiple processes. We now address the possible contributions of two additional physical process, adsorption of GOM to PM and reduced boundary layer mixing of PBM at night (see responses to Referee 1).

2.8 Figure 5(a) What is the main reason that caused the variation of Δ^{199}Hg during the night time? Is it possible caused by measurement error? If this is true, it is better to point out this in method part.

– Our data showed that the Δ^{199}Hg values ranged from 0.01‰ to 0.30‰ for the nighttime samples in Figure 5(a) and ranged from -0.51‰ to 0.55‰ for all nighttime samples in this study. The method we used for quantifying Hg isotopes bears an uncertainty (2SD) of 0.06‰ for Δ^{199}Hg for the samples. Statistically, differences between Δ199Hg values for daytime and nighttime samples were clearly significant and should not have been caused by uncertainty of the method. To help readers understand this issue, we have added the measurement uncertainty in the caption of Figure 5.

Reference:

Amos, H.M., Jacob, D.J., Holmes, C.D., Fisher, J.A., Wang, Q., Yantosca, R.M., Corbitt, E.S., Galarneau, E., Rutter, A.P., Gustin, M.S., Steffen, A., Schauer, J.J., Graydon, J.A., St Louis, V.L., Talbot, R.W., Edgerton, E.S., Zhang, Y., Sunderland, E.M., 2012. Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition. Atmospheric Chemistry and Physics 12, 591-603.

Huang, Q., Chen, J., Huang, W., Fu, P., Guinot, B., Feng, X., Shang, L., Wang, Z., Wang, Z., Yuan, S., Cai, H., Wei, L., Yu, B., 2016. Isotopic composition for source identification of mercury in atmospheric fine particles. Atmospheric Chemistry and Physics 16, 11773-11786.

Jiskra, M., Wiederhold, J.G., Bourdon, B., Kretzschmar, R., 2012. Solution speciation controls mercury isotope fractionation of Hg(II) sorption to goethite. Environmental Science Technology 46, 6654-6662.

Lan, X., Talbot, R., Castro, M., Perry, K., Luke, W., 2012. Seasonal and diurnal variations of atmospheric mercury across the US determined from AMNet monitoring data. Atmospheric Chemistry and Physics 12, 10569-10582.

Liu, B., Keeler, G.J., Dvonch, J.T., Barres, J.A., Lynam, M.M., Marsik, F.J., Morgan, J.T., 2007. Temporal variability of mercury speciation in urban air. Atmospheric Environment

41, 1911-1923.

Poissant, L., Pilote, M., Beauvais, C., Constant, P., Zhang, H.H., 2005. A year of continuous measurements of three atmospheric mercury species (GEM, RGM and Hg-p) in southern Quebec, Canada. Atmospheric Environment 39, 1275-1287.

Quan, J.N., Gao, Y., Zhang, Q., Tie, X.X., Cao, J.J., Han, S.Q., Meng, J.W., Chen, P.F., Zhao, D.L., 2013. Evolution of planetary boundary layer under different weather conditions, and its impact on aerosol concentrations. Particuology 11, 34-40.

Rutter, A.P., Schauer, J.J., 2007. The effect of temperature on the gas–particle partitioning of reactive mercury in atmospheric aerosols. Atmospheric Environment 41, 8647-8657.

Smith, R.S., Wiederhold, J.G., Kretzschmar, R., 2015. Mercury isotope fractionation during precipitation of metacinnabar (β-HgS) and montroydite (HgO). Environmental Science Technology 49, 4325-4334.

Xiang, Y., Zhang, T., Liu, J., Lv, L., Dong, Y., Chen, Z., 2019. Atmosphere boundary layer height and its effect on air pollutants in Beijing during winter heavy pollution. Atmospheric Research 215, 305-316.

Yu, B., Fu, X., Yin, R., Zhang, H., Wang, X., Lin, C.-J., Wu, C., Zhang, Y., He, N., Fu, P., Wang, Z., Shang, L., Sommar, J., Sonke, J.E., Maurice, L., Guinot, B., Feng, X., 2016. Isotopic composition of atmospheric mercury in China: New evidence for sources and transformation processes in air and in vegetation. Environmental Science Technology 50, 9262-9269.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-570/acp-2018-570-AC1-supplement.pdf

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