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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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Huang et al. present a study on diurnal particulate (aerosol) Hg isotope variation in Beijing. I have reviewed this MS previously for ES&T 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. 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) sug-

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Discussion paper

gests 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. 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."

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. PM2.5 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.

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.

Minor comments: L99. "It is intuitive that, while both D and N PM2.5 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 PM2.5-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.

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 PM2.5 shows diel variation in the paried T-test? The p values in the text do not correspond to metrics in Table S3, so the discussion is hard to follow.

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

L342. “Interestingly, negative D199Hg values in daytime PM2.5-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 PM2.5 at these times.”

Why would local GOM have a negative D199? Not clear to reader.

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