Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-1164-RC3, 2019

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characteristics of atmospheric mercury in East China: implication on sources and formation of mercury species over a regional transport intersection zone" *by* Xiaofei Qin et al.

Anonymous Referee #3

Received and published: 11 January 2019

This manuscript presents an analysis of speciated atmospheric mercury (Hg), i.e. gaseous elemental mercury (GEM), particulate-bound mercury (PBM), and gaseous oxidized mercury (GOM), during June 2015 to May 2016 at the Dianshan Lake Station (DSL), Shanghai, east China. The topic is relevant to the Atmospheric Chemistry and Physics. However, the scientific contribution is hindered by a lack of methodology description in certain sections, some debatable analysis, some overreaching conclusions, and the quality of presentation. My specific comments and suggestions are listed below.

Printer-friendly version

Discussion paper

Major concerns

1. There is a lack of in-depth or appropriate analysis

The manuscript proposed quite a few mechanisms regarding to the sources and processes related with speciated atmospheric Hg, including 1) reemissions from surfaces, 2) formation of GOM, 3) formation of PBM, 4) impact of local sources and regional transport, and 5) contribution of the shipping sector. Each item could benefit from a more in-depth or appropriate analysis.

1) reemissions from surfaces

It is concluded that "GEM at DSL exhibited high concentrations in both warm and cold seasons, which was due to the strong re-emission fluxes from natural surfaces in summer. . ." (L506) However, there is no quantitative analysis to support this claim. The authors pointed out that "It has to be noted that since no tracers for the natural emissions (e.g. soils, vegetations, and ocean) were available in this study, the identification of natural mercury sources was not possible." (L390). The reviewer believes that temperature could be used to identify reemission with factor analysis approaches, such as Principal Component Analysis (PCA).

2) formation of GOM and PBM, local vs. regional events

The use of GOM/PBM ratios seems lead to some speculative discussions

a. L359-369, CO and SNA concentrations were used to show that "GOM/PBM ratio was a reliable tracer for assessing the relative importance of regional/long-range transport vs. local atmospheric processing." (L368). Because CO and SNA concentrations are available, perhaps there is little need to use the GOM/PBM ratio, or GEM/CO ratio could be used as in previous studies of atmospheric Hg.

b. Local vs. regional events. The authors stated that "Fig. 12 also demonstrated the increases of GOM along with the ratios of GOM/PBM. The lower ratios of GOM/PBM were associated with lower temperature and O3 concentrations, indicating the more

probable long range/regional events during the cold seasons with relatively weak photochemistry. On the contrary, the higher ratios of GOM/PBM were associated with higher temperature and O3 concentrations, indicating the more probable local events during the warm seasons with relatively strong photochemistry." (L460) This reasoning seems to suggest that "long range/regional events" and "local events" dominate during the cold and warm seasons respectively. The authors may want to present evidence that the study site was shielded from long range transport in some seasons, because most receptors are under the influence of long range transport all the time. In my view, air mass from all directions would have higher temperature and O3 concentrations in summer thus "relatively strong photochemistry" than those in winter, regardless "local" or "long range/regional events". Therefore, higher temperature and O3 concentrations in warm season would indicate "relatively strong photochemistry" but not "local events". Similarly, lower temperature and O3 concentrations in cold season would indicate "relatively weak photochemistry" but not "long range/regional events". The authors may want to amend this section and the related conclusions.

c. GEM levels. It was concluded that "GEM as a function of the GOM/PBM ratios indicated that when the quasi-local sources dominated, GEM concentrations were relatively higher than those events under the regional/long-range transport conditions" (L522-524). L370-382, "In the GOM/PBM ratio bins of less than 2.5, GEM fluctuated with the mean values less than 2.6 ng/m3. The mean GEM concentration increased from 2.61 ng/m3 in the GOM/PBM ratio bin of 2.5-3.0 to 2.8 ng/m3 in the bin of 3.0-3.5, and then remain relatively stable when the GOM/PBM ratio bins higher than 3.0." Indeed, this is the only noticeable increase in GEM (a 7% increase from the bin of 2.5-3.0 to that of 3.0-3.5) among 10 bins, while the change in GEM concentrations between the first and last bin is less than 5%. Nonetheless, the authors stated that "Generally, GEM showed an increasing trend as the GOM/PBM ratios increased while both SNA and CO decreased. The elevation of GEM concentrations tended to be associated with the impact of quasi-local sources. In contrast, under the high SNA and CO conditions when GOM/PBM ratios were lower, GEM was relatively low, suggesting its formation

was not favored via the regional/long-range transport." The authors may need to report the statistical trend (e.g. regression) if any, and clarity what type of GEM "formation was not favored via the regional/long-range transport", and explain why GEM would change with the strength of photochemistry. In case GEM is high in summer due to re-emission when GOM is also high due to higher oxidant levels, then the common course is meteorological conditions, namely ambient temperature, an analysis taking into account seasonal trend of all variables involved could be more appropriate, instead of the seemingly speculative approach employed.

PBM formation

L476, "Fig. 13 shows the statistical pattern of the variation of PBM and GOM in the ascending bins of PM2.5. It was obvious that the concentrations of PBM increased with the concentrations of PM2.5, which was due to both primary emissions and the subsequent process of Hg species adsorbed on particulate matters." The authors may want to provide more evidence or citation to support that increasing PBM with increasing PM2.5 concentrations "was due to both primary emissions and the subsequent process of Hg species adsorbed on particulate matters".

L480, "When PM2.5 concentrations were at relatively low levels under 75 μg/m3, GOM concentrations increased with PM2.5. However, when PM2.5 concentrations exceeded 75 μg/m3, GOM exhibited a slightly decreasing trend as PM2.5 increased. It seemed that when the concentration of PM2.5 reached a certain value, the formation of GOM was inhibited to some extent, which was likely due to the adsorption of GOM onto the particles. " "Statistical analysis showed that when PM2.5 reached a certain value, GOM was inhibited to some extent due to the gas-particle partitioning process." (L34-35) Those statements/conclusion seem to be debatable. As seen in Fig 13, when PM2.5 concentrations exceeded 75 μg/m3, GOM decreased till PM2.5 reached 105 μg/m3 then increased, instead of a slightly decreasing trend. The authors may need to report the statistical trend (e.g. regression) if any and rephrase the statements about inhibitive effects in discussion and conclusion, or omit this passage.

Based on an analysis of a three-day episode (December 30, 2015 to January 1, 2016), the authors concluded that “Under high PM2.5 concentrations, high humidity and low temperature conditions, the gas-particle partitioning process was obvious at DSL, which might be an important pathway for the formation of PBM.” (L532) The authors may want to provide more in-depth analysis of the reliance of PBM on PM2.5 concentrations when temperature and relative humidity levels favor formation of PBM, and justify the use of a three-day episode in winter to represent the year-long study period. My scan of Fig 6 suggests that only in autumn the PBM levels increase with decreasing ambient temperature, not in other three seasons including winter (the three-day episode).

3) contribution of the shipping sector

It is concluded that “shipping emissions” contributed to 20% of GEM based on PMF (L30, L526). However, there is a lack of data support. The authors may want to a) identify the port on Fig 1, b) find out the Hg emission value at and near this port (I believe that researchers from Tsinghua University have some related publications), and compare the shipping sector emission with emissions from other sources, c) for each sample, plot the time series of contribution to GEM by this factor and the wind or air mass direction to verify that this factor indeed represents the shipping sector.

2. The title reads, “Characteristics of atmospheric mercury in East China: implication on sources and formation of mercury species over a regional transport intersection zone”. The authors may want to justify the use of data from a single site to represent 1) atmospheric Hg in East China, and 2) regional transport intersection zone, or rephrase the title. Similarly, some conclusions are a bit over-reaching, e.g. “shipping emission was found to be an important source (19.6%) of atmospheric mercury in East China” (L30)

3. Seasonal trend of Hg species

The differences in seasonal mean TGM concentrations could be too small (max=2.88

ng/m3, min=2.63 ng/m3, the difference is 9%; summer 2.87 ng/m3, spring 2.73 ng/m3, difference 5%) and statistically not significant to support the conclusion of "GEM concentrations were elevated in both cold and warm seasons" (L21) and "GEM at DSL exhibited high concentrations in both warm and cold seasons, which was due to the strong re-emission fluxes from natural surfaces in summer and enhanced coal combustion for residential heating over northern China in winter." (L506). The authors may want to conduct comparison of multiple means (e.g. under ANOVA) for each of the three Hg species, and rephrase the discussion and conclusion in case the seasonal means are not statistically significant. Furthermore, please comment on the reasons of small difference among the four seasonal means if coal combustion for residential heating is enhanced in winter and re-emission fluxes from natural surfaces is strong in summer.

4. Methodology is missing at numerous places. e.g. 1) please explain how to plot "Mean concentrations of (b) GEM, (c) PBM, and (d) GOM as a function of wind speed and wind directions" (L700) in the Method section and why Figures 5(b), (c) and (d) do not represent the frequency of wind directions shown in Figure 5 (a), in the Results section. 2) details of the backward trajectory simulation should be provided, including the model being use, run time, and start height, each with a justification, 3) where and how to use the "weighting function (wij)" (L162), 4) PMF, the treatment of missing data if any, and the total number of samples, 5) what is "the uncertainty of the jth pollutant on the ith measurement" (L187) in your study, 6) how to evaluate whether PMF is able to reproduce the observed Hg concentrations (e.g. time series and/or seasonal means), 7) how was hourly or bi-hourly PBL (assume it means Planetary Boundary Layer) height measured or estimated, 8) how was "secondary inorganic aerosols (SNA)" (L359) or "SNA (sulfate, nitrate, and ammonium) in PM2.5" (L715) monitored, 9) how to conduct analysis with bi-hourly Hg data and hourly data of meteorological parameters and other air pollutants.

5. GOM and PBM could be included in PMF source apportionment. The results (e.g.

sample by sample GEM, GOM, PBM, CO, SNA etc contributions in each factor) might help the identification of age of the air mass, as well as sources and processes related with Hg.

6. Interpretation of PMF results. This section could be improved by a more in-depth analysis and/or citation of existing literature.

Overall, the analysis seems to be subjective at times, leading to invalid or overreaching statements/conclusions based on measurements at one site, a small difference in seasonal or binned concentrations, speculative approaches, or a short episode of a few days. It is recommended to clarify the meaning of local and regional events, whether "local" means local man-made emissions, local re-emission, local photochemical reactions, all of the above; or different item in different sections. Time series (Fig 2) or box plots (Fig 3) of temperature, relative humidity, CO, PM2.5 mass, SNA (sulfate, nitrate, and ammonium, or secondary inorganic aerosols), O3, and GOM/PBM ratios could be employed to depict seasonal trend of those variables, which may help to differentiate the association from causation.

Clarification issues

1. The following items could be included in Fig 1, 1) location of the sampling site, 2) location of the shipping port, 3) the name of all provinces within e.g. 2000 or 3000 km of the sampling site, 4) a scale in the lower-right box, 5) the meaning of the upper-right box, 6) the meaning of the short black line.

2. The provincial level Hg emissions in Wu et al. (2016) could be provided as supplemental information.

3. Please provide the distance between the sampling site and the nearest coastal line, and comment on whether the sampling site is capable of capturing the land-sea circulation.

4. L147, "meteorological data", please provide the height of the instrument about

ground level, and comment on whether the instrument is capable of capturing the meteorological condition in the study area.

5. L149, other pollutants, please provide the reporting or averaging intervals of CO, ozone and PM2.5 mass measurements.

6. L205 and L362, please explain what is “secondary formation”.

7. L302-304, “The potential source regions of all year round PBM were mainly from northeastern China, including Jiangsu, Anhui, Shandong, and Hebei provinces.” Please justify the classification that Jiangsu and Anhui belong to northeastern China.

8. section 3.2.2 (L333), all eight wind directions should be included in the discussion. The authors many want to point out that there is little difference in the wind direction distribution between the GOM/PBM bins of 1-2 and 2-3.

9. Figure 2, please explain the meaning of the red-dish line.

10. Figures 5 (b), (c), (d), what is the meaning of “15 ws”?

11. Figures 9 and 12, please explain the meaning of the bars.

12. Figure 12 caption, “Temperature as a function of the GOM/PBM ratios. . .” Please explain why temperature would change with changing GOM/PBM ratios in the main body.

13. Figure 13, please explain the meaning of the shaded areas.

Editorial suggestions

The use of English language is largely satisfactory. However, the presentation has much room of improvement. Some examples are listed below.

1. The significant number seems to be excessive at times, e.g. one decimal will suffice when presenting Hg concentrations.

2. Avoid the use of first person, i.e. “we”.

3. Please define all abbreviations, e.g. PSCF, PBL, RH, in the main body instead of the headings.

4. Inconsistent expressions, e.g. “Equation 1” (L160), “as below” (L163), “shown as Eq. (3)” (L173); “secondary inorganic aerosols (SNA)” (L359), “SNA (sulfate, nitrate, and ammonium) in PM2.5” (L715); RGM (Figure 6).

5. There are quite a few awkward sentences, e.g. 34-35, L171-172, L268-270, L393 (“Se, As, and Pb, which were typical tracers of coal combustion”), L403-404, L443.

6. There are quite a few awkward phrases, e.g. “obvious” (L35 and other places), “comprehensive” (L86, suggest to remove), “Xij is” (L175) should be “where Xij is”, “about” (L305 and other places, suggest to replace with “approximately”), “As similar as Fig. 9” (L452), “CN” in Table 1 should be replaced with “China”.

7. The manuscript could be shortened by 1) removing some unnecessary material (e.g. L170-186, those model descriptions could be removed by citing the Users Guide by USEPA or other publications), 2) condense the discussion and conduction sections.

8. Figure 2, the seasons seem to be incorrect.

9. Figure 4 caption, suggest to remove “The red line and black line represented the corresponding diurnal variation of RH and wind speed, respectively.” because there are legends to represent each and all variables.

10. Figure 6, the ranges should be, <13, 13-15, 15-17, etc.

11. Figure 8, the ranges should be 0-1, 1-2, 2-3, >3.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1164, 2018.