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Atmospheric Chemistry and Physics Discussions

Interactive comment on "A synthesis of research needs for improving the understanding of atmospheric mercury cycling" *by* Leiming Zhang et al.

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Response to Referee #2 We greatly appreciate the helpful comments from the reviewer, which have helped us improve the paper. We have addressed all of the comments carefully, as detailed below. Our responses start with "R:".

General comments

Dr. Leiming Zhang and colleagues have written a thoughtful review of current challenges in the field of atmospheric mercury cycling. The authors discuss research needs, including: improved emission estimates, dry deposition and air-surface ex-

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change, chemical mechanisms, field measurements of speciated mercury, analysis and application of speciated mercury data, and network harmonization. Prior to publication, I recommend the authors condense the discussion of emissions, chemical mechanisms, and speciated measurements. These topics have been written about at length in the literature. It would serve this review better to briefly acknowledge emissions, chemistry, and measurements, but limit the discussion and refer readers to previous work. That would help focus this paper and highlight the authors' newer insights about data applications and network harmonization.

R: We agree with the reviewer that existing literature has extensively discussed some of the topics. This synthesis paper aims to provide a brief summary of the existing knowledge and to also extend to new insights, thus some repetitions are inevitable and we have tried to credit these to the most appropriate references. We feel the majority of materials need to be kept there for the completeness of the paper, as this reviewer also asked to extend some of the discussions that were missed within these topics.

Line-by-line comments

Page 2-3, lines 20-40: Paragraph beginning with, "Current methods for measurement and model interpretation of the three forms of Hg. . ." This paragraph's purpose is unclear.

R: This synthesis paper is a follow up of a series of review papers published in the ACP special issue mentioned in the previous paragraph. We thus feel it is necessary to give a brief summary of the major contents published in those review papers, which is the purpose of the paragraph.

Page 5, lines 70-76: Discussion about needed improvements to emissions omits anthropogenic releases to freshwater. Since air-surface exchanges can be significant, getting a better handle on releases to water is important for refining our understanding of atmospheric Hg. The first inventory of releases to water was in UNEP [2013], later published in Kocman et al. [2017].

R: The following text has been added in the revised paper: “Anthropogenic releases of Hg to freshwater also need to be better estimated (Liu et al. 2016; Kocman et al., 2017) since Hg in waterbodies can be released into atmosphere through the air-surface exchange processes.”

Page 5, lines 78-79: Please clarify how “a global database of GEM flux from different land covers” would improve estimates of natural Hg emissions. Natural emissions are primarily geogenic, so wouldn’t we need better estimates from volcanoes, fumaroles, and other geological features? Land cover alone wouldn’t help discriminate between primary natural emissions and secondary (aka legacy) anthropogenic emissions.

R: Natural emissions include those from geogenic sources as well as from reemission of previously deposited mercy. The sentence in the original version of the paper applies more to the latter than the former category. We have clarified the wording as follows: “To improve estimation of mercury emission from natural sources, a global database of GEM flux from different land covers and geogenic sources could be developed.”

Page 5, lines 88-89: “Mercury emissions from wildfires is another source that is not well quantified.” Please expand the discussion of wildfire emissions to include relevant work from Friedli et al. [2003], Friedli et al. [2009], and explain more specifically what is “not well quantified”.

R: We have added this information in the revised paper, which reads: “The emission quantity and speciation of mercury from wildfires are not well characterized due to a general lack of observational data. The data presented in Friedli et al. (2003, 2009) provided preliminary estimates based on aircraft measurement and a satellite constrained bottom-up methodology.”

Page 6, line 98: Please quantify, “can constitute significant sources (cf. Eckley et al., 2011)”.

R: We have added this information in the revised paper: “For example, Hg emissions

from areas surrounding two active gold mines in Nevada were estimated to account for 56% and 14%, respectively, of the overall emissions from each mine (area plus point sources)."

Page 6, lines 112-114: "An important future task will be development of numerical modeling techniques that can estimate long term average emissions fluxes from such concentration variability maps obtained in passive sampling campaigns." The sentence is confusing as worded.

R: The sentence has been revised as: "Development of numerical models that can utilize long-term data obtained from passive samplers over a large spatial coverage for emission source strength estimate will also be an important future task."

Page 7, lines 121-124: "Passive air samplers... for extended periods of time." These two sentences are redundant and could be combined.

R: The first one has been deleted in the revised paper.

Page 7, lines 130-133: This short two-sentence paragraph is confusing. Please consider weaving into the paragraph above.

R: The first sentence has been moved to Section 2.5. The second one has been deleted since this point is elaborated in Section 2.5.

Page 9, line 176-177: What about Australia and the polar regions?

R: Yes, these regions also lack of mercury flux data and have been added in the revised paper.

Page 10, lines 193-196: "Many oxidation reactions currently employed in CTMs...are considered implausible based on kinetic and ab initio thermodynamic equations." Recent work from Horowitz et al. [2017] is relevant here. Horowitz and colleagues, including Ted Dibble, updated the chemistry in the GEOS-Chem chemical transport model specifically to rectify the assertion that what was in CTMs was implausible based on

more recent kinetic and thermodynamic studies.

R: This reference was originally cited further down the same paragraph (lines 219-222). A new study (Ye et al., 2017), which was recently submitted, evaluated a regional chemical transport model (CMAQ) modified by implementing a Hg and Br chemical mechanism that included the most up-to-date kinetic data and reactions (Ye et al., 2016) and constrained by an observed vertical profile of BrO. They found that the modified CMAQ-Hg could capture significantly greater seasonal and diurnal variations that the default version failed to do and simulate Hg wet and dry deposition in better agreement with observations or observation-based estimates. Nevertheless, modeling studies like these currently remain few and far between, and this review is intended to promote applications of cutting-edge kinetic research findings in atmospheric Hg chemical transport modeling as Horowitz et al. (2017) and Ye et al. (2017) did.

Pages 11-12, lines 229-236: These research needs have been stated in previous reviews. Please revise to highlight the new aspects of the discussion, or consider deleting from the paper, or significantly condensing and citing previous work (e.g., Gustin et al. [2015]).

R: For a completeness of the paper, we tend to choose the last approach recommended by this reviewer, which is condensing and citing previous work. However, these points are already in the very condensed form with only five short bullets and could not be condensed further. We thus have added more references on these points.

Page 13, lines 260-262: "Existing GOM measurement methods are biases, and new methods under development may also exhibit bias, at least under some conditions." This statement feels obvious. I recommend deleting.

R: Deleted in the revised paper.

Page 16, lines 339-342: "Results generated from these analyses... highly empirically parameterized natural sources." The sentence is confusing as worded.

R: As explained in detail in Cheng et al. (2015a), there are two types of models studying the source-receptor relationships of speciated atmospheric Hg. One type of study is chemical transport modelling, which predicts speciated atmospheric Hg concentrations on regional and global scales based on the knowledge of source emissions, atmospheric dispersion and transport, and chemical and physical atmospheric processes. Another type is receptor-based methods. In this type of study, receptor measurements (e.g., air concentrations, precipitation concentrations, or wet deposition) and back trajectory modelling are used separately and together to predict pollution sources and estimate the contributions of the sources to receptor measurements. Receptor-based methods do not require comprehensive knowledge on source emissions and mercury behavior in the atmosphere; therefore, they are less complicated than chemical transport models. Comparing the results from these two types of models have not been done in literature, and such a practice is recommended here. We have revised the sentences to make this point clearer.

Page 17, lines 346-347: "These model simulations should be reassessed using available speciated Hg data. . ." This is impractical and unproductive. Consider removing the sentence. If the sentence is kept in the paper, please elaborate on what one would hope the reassessment would achieve.

R: Our experiences suggested that such a practice is practical and can be productive. In earlier days when mercury CTMs were first developed, there were very limited speciated mercury data. Thus, most mercury CTMs were only compared and evaluated using monitored mercury wet deposition data. The first comprehensive comparison of CTMs model outputs with speciated data was done for the Canada-US Greta Lakes mercury project (Zhang et al., 2012), in which modeled surface layer oxidized mercury (GOM and PBM) were found to be a factor of 2-20 higher than the monitored data collected in eastern North America. This directly led to another study identifying the potential causes of such large discrepancies (Kos et al., 2013), and more studies on the same topic (Cheng and Zhang, 2017). We thus recommend such comparison to

be done in different model framework (e.g., Bieser et al., 2014),) and in different region of the world (e.g., Asia) where GOM and PBM levels are different from those in North America.

Page 18, lines 369-377: Several papers have been published that have explored the hypotheses listed. Y. Zhang et al. [2016] determined changes in atmospheric Hg could in large part be explained by changes in anthropogenic emissions. Parrella et al. [2013] examined changes in marine boundary layer halogen chemistry and based on their work we can exclude this hypothesis as an explanation. Amos et al. [2014] excluded changes in riverine and wastewater discharges as an explanation.

R: Such information and references have been incorporated in the revised paper, which reads: "For example, changes in anthropogenic emissions likely played a major role in the changes of atmospheric Hg (Zhang et al., 2016), while changes in marine boundary layer halogen chemistry (Parrella et al., 2013) and in riverine and wastewater discharges (Amos et al., 2014) were found to have little impact on mercury trends."

References

R: References provided have all been included in the revised paper.

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