

May 31, 2017

Review of:

Leiming Zhang et al., 2017, A synthesis of research needs for improving the understanding of atmospheric mercury cycling

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 exchange, 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.

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.

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].

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.

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".

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

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.

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

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

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

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.

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]).

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.

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

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.

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.

References

Amos et al., [Global biogeochemical implications of mercury discharges from rivers and sediment burial](#), *ES&T*, 2014

Friedli et al., [Mercury emissions from burning of biomass from temperate North American forests: laboratory and airborne measurements](#), *Atmospheric Environ.*, 2003.

Friedli et al., [Initial estimates of mercury emissions to the atmosphere from global biomass burning](#), *ES&T*, 2009

Gustin et al., [Measuring and modeling mercury in the atmosphere: a critical review](#), *ACP*, 15, 5697-5713, 2015.

Horowitz et al., [A new mechanisms for atmospheric mercury redox chemistry: implications for the global mercury budget](#), *ACP*, 2017

Kocman, D. et al., [Toward an assessment of the global inventory of present-day mercury releases to freshwater environments](#), *Int. J. Environ. Res. Public Health*, 14(2), 138, 2017.

Parrella et al. [2013]

UNEP, [Global mercury assessment 2013: Sources, emissions, releases, and environmental transport](#), 2013.

Y. Zhang et al., [Observed decrease in atmospheric mercury explained by global decline in anthropogenic emissions](#), *PNAS*, doi: 10.1073/pnas.1516312113, 2016