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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Evaluation of discrepancy between measured and modeled oxidized mercury species” *by* G. Kos et al.

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General comments

The authors try to investigate large over-estimations (a factor of 2 to 10) of mercury concentrations from mercury models that was recently reported by Zhang et al. (2012a). They described and compiled various uncertainties from sampling, measurement, and interferences. Then, they try to demonstrate that observation data of oxidized mercury concentrations do not agree with wet deposition of mercury by using model sensitivity cases. In general, the manuscript presents some useful measurement data and has a potential to address uncertainties in mercury models. However, the reviewer is concerned about the evaluation method of uncertainties and unsound model configurations. In addition, the authors need to pay attention on citing references.

Specific comments

Major Issues:

1. Abstract; pages 17246-17247; lines 25-27: “This improvement by a factor of 2 and measurement uncertainties within a factor of 3 to 8 provides a reasonable rationale for the discrepancy of a factor of 2–10 determined by Zhang et al. (2012a).”

The reported range of the measurement uncertainties (a factor of 3 to 8) is too large. Adding all of the uncertainties listed in Table 5 together is counter-intuitive. Measurement uncertainty should not be considered as one direction (negative or positive) as the authors suggested in the manuscript that all of the measurement-related uncertainties are underestimated. Moreover, it is inappropriate to combine measurement uncertainty with model (emission) uncertainty. Model uncertainty need to be evaluated separately.

To calculate a combined standard uncertainty, the authors must calculate standard uncertainties for all the sources of uncertainty in a measurement or set of measurements (typically, 3 times of the standard deviation of the blank). Then, the combined standard uncertainty can be calculated using root sum of the squares (not just summation of everything).

2. Model description; page 17252; lines 11-12: “Mercury is reduced in the aqueous phase photochemically and by the sulfite anion and the hydroperoxyl radical using rate constants from Xiao et al. (1995), Pehkonen and Lin (1998) and Van Loon et al. (2000, 2001).”

Why is the hydroperoxyl radical reduction mechanism (Pehkonen and Lin, 1998) still used in the model? The reduction mechanism has been proved to be invalid under ambient conditions (Ababneh et al., 2006;Gårdfeldt and Jonsson, 2003).

An alternative mechanism (Carboxylic acids) has been proposed by Si and Ariya (2008). Why is the new reduction mechanism not implemented into the model?

3. Section 3.1; pages 17254-17255: The title "Uncertainty of measurements" does not correspond very well with discrepancy of Hg2+ concentration at higher elevation addressed in this section. The authors should address uncertainty of the elemental mercury measurements (e.g. CVAFS) or change the title. There is no direct measurement of oxidized mercury species. Those species need to be collected and then reduced before they can be measured as elemental mercury.

For concentration difference at higher elevation, the authors claimed that it could be as high as a factor of 4 from the data reported by Lindberg and Stratton (1998). The reviewer does not think that this assessment is appropriate. The data should not be used in estimation of measurement or model uncertainty because of sampling at a relatively high elevation (43 m above ground) and two large nearby coal-fired power plants (∼1 GW, ∼20 km). The sampling elevations at the AMNet sites are not likely to be installed at such high elevation above ground. What are the sampling elevations (above ground-level) of the AMNet sites?

To prevent this elevation discrepancy, the authors need to carefully specify model vertical structure in order to separate the ground-level and the upper levels. What is the height of the model's lowest layer?

4. It is unclear why the authors chose to conduct 7 (seven) model sensitivity cases. The authors just reported the results but did not provide sufficient supporting arguments or backgrounds of these sensitivity cases. The authors seem to randomly modify O3 oxidation rates (increase 50% and 100%), remove Hg0 and OH reaction from all the cases except their "best case", assign fraction of oxidized mercury species from chemical reactions in the air, and change mercury species emission ratio (Hg0:Hg2+:HgP) from 50:40:10 to 90:8:2 and 90:5:5. Does the inevitability of decreasing Hg2+ emission by a factor of 5 to 8 reflect poor performance of the model?

GEOS-Chem, a global mercury model, has removed both O3 and OH oxidation mechanisms and replaced them with Br oxidation in recent studies (Amos et al., 2012;Holmes

et al., 2010;Parrella et al., 2012;Zhang et al., 2012b) due to slow reactions of Hg0 with O3 and OH. Why do the authors still rely heavily on these uncertain reactions?

From the model description in section 2.1, the authors have implemented Br chemistry in the GRAHM model but only for marine boundary layer (MBL). Is it possible to fully implement those mechanisms in the entire model domain? In addition, Goodsite et al. (2012) has recently re-calculated their theoretical Hg0 and Br reaction rates published in 2004 (Goodsite et al., 2004). They reported that the atmospheric lifetime of Hg was significantly increased (a factor of two) with their new rates. This related work should be included and discussed in the manuscript.

From Figure 6a, 6b, 6c, and 6d, there are very high concentrations of Hg2+ (∼50 pg m-3) and Hgp (∼10 pg m-3) at Hudson Bay, Canada. What is (are) the cause(s) of these high concentrations? Is it only caused by Br chemistry?

Minor Issues:

1. Abstract; page 17246; lines 14-21: "The discrepancy between simulated and observed concentrations of Hg2+ and Hgp was found to be reduced when a ratio for Hg0:Hg2+:Hgp in the emissions was changed from 50:40:10 (as specified in the original inventories) to 90:8:2 to account for in-plume reduction of Hg0 processes. A significant reduction of the root mean square error (e.g., 19.22 to 11.3 pg m−3 for New Jersey site NJ54) and bias (67.8 to 19.3 pg m−3 for NJ54) for sampling sites in the Eastern United States and Canada, especially for sites near emission sources was found."

From the sentences above, it is unclear whether the improvements of the error and bias refer to Hg2+, HgP, or both. The reviewer suggests declaring it more explicit. Moreover, reporting the results (bias and error) in terms of percentage would aid general audience in better quantifying the improvements.

2. Abstract; page 17246; lines 21-25: "Significant improvements in the spatial distri-

bution of wet deposition of mercury in North America was noticed. Particularly, over-prediction of wet deposition near anthropogenic sources of mercury was reduced by 43 %. On a regional scale, estimated wet deposition improved by a factor of 2 for areas with more than 12 μg m$-$2 yearly average wet deposition."

The authors reported some values (43% and 12 μg m$-$2) in the abstract that the reviewer could not find from the rest of the manuscript. To prevent misunderstandings, the authors need to clarify and need to provide the results in the related sections. Do the authors refer to the results from Fig. 6 and Fig. 7 (sections 3.11 & 3.12)? By the way, please check the grammar in the first sentence.

3. Abstract; page 17246; lines 25-27: "Model sensitivity simulations show that the measured concentration of oxidized mercury is too low to be consistent with measured wet deposition fluxes in North America."

Is it more straight-forward to draw the same conclusion from observed data only (without using the model sensitivity cases)?

4. Introduction; page 17247; lines 4-6: "Knowledge of the relationship between emission and deposition of atmospheric mercury is critical for the development of policies to reduce the levels of mercury in the environment (Wang et al.,2010b)."

The statement is incomplete and does not seem to fit with this manuscript. The stated knowledge is important but we still do not fully understand atmospheric chemistry of mercury and its fate which is much more important to effectively develop mercury-related environmental policies. Moreover, the reviewer could not track the quoted statement from either Wang et al. (2010a) or Wang et al. (2010b).

5. Introduction; page 17249; lines 27-29: "Observation data show considerable variation with little correlation regarding geographic location stressing the importance of local sources (e.g. 8 pg m$-$3 of Hg2+ at remote Ny A°lesund on Sva°lbard vs. 4 pgm$-$3 in urban Rochester, NY)."

How can local sources explain higher Hg2+ concentration at the remote site? The two average concentrations might not be directly comparable since measurement date and time are not reported.

6. Introduction; page 17250; lines 1-3: "The average Hg2+/Hgp ratio from these data is 0.85, illustrating the importance of particulate mercury species in atmospheric processes and the need for models to conform."

Why do models need to conform to the ratio if measurement uncertainty is still very large as the authors concluded in the manuscript?

7. Introduction; page 17250; lines 15-19: "Model results of Hg2+ and Hgp at the 15 AMNet sites were overestimated by a factor of 2–10 for the sum of Hg2+ and Hgp. Zhang et al. (2012b) provide several hypotheses for this discrepancy: (1) too high emission inputs; (2) too fast oxidative conversion of Hg0 to Hg2+ and Hgp; and (3) too low dry deposition velocities."

Zhang et al. (2012b) did not provide those hypotheses.

8. There are too many citations of personal communication in the manuscript. Some of those can be avoided. For example, both Ariya and Steffen are the co-authors of this manuscript; therefore, citing them as personal communication seems awkward.

9. Introduction; page 17251; lines 8-18: It is unclear why Figure 1 appears in this section. Should the figure be reported in the result section? In addition, there is no supporting argument provided in this section why all Hg0 oxidation reactions need to be removed which may cause confusions.

10. Section 2.2; page 17253; line 1: The messages of the section are about sampling, measurement, and data treatment of oxidized mercury in the air but the title of this section "Atomic fluorescence spectrometer setup and sampling" is not quite connected to those messages.

11. Section 2.2; page 17254; line 22: "Statistical calculations and analyses were car-

ried out employing R 2.13."

General audience may not know that R (version 2.13) is a programming language for statistical computing and graphics. The authors may consider rephrase the sentence.

12. Section 3.5; page 17258: This section is very short. It can be combined with section 3.3 to address sampling uncertainties of Hg2+.

13. Section 3.8; pages 17260-17261: The authors described only emission uncertainties from coal-fired power plants but did not mention about natural recycle emissions which may be highly uncertain as well.

14. Section 3.12; page 17267; lines 14-17: "Figure 7 shows a high-resolution (0.15°) wet deposition map plot. Circles contain observational data. For Ex-oxOH estimations results are markedly improved compared to Fig. 6f for high concentration areas such as the Southern United States."

Fig. 6f can not be directly compared with Fig. 7 because both simulations based on model inputs from different years. Fig. 6f was created from the simulation and observation data in 2005 while Fig. 7 based on 2006 data. There is no need to include Fig. 7 in this manuscript.

15. Table 1; page 17280: It would be more informative if the authors also include Hg0 or total Hg in the table. Hg0 is usually reported along with other mercury species.

16. Figures 1-7, 9; pages 17285-17291, 17293: Increase the sizes of text and number. They are too small.

17. Figure 9; page 17293: It would be helpful if the authors can overlay map of the US regions and add latitude and longitude scales in Fig. 2. This will assist audience in reading section 3.12 and Fig. 9.

Technical corrections

1. Pages 17246-17249, 17256, 17261: Both "oxidized" and "oxidised" are used interchangeably in many places of the manuscript. The reviewer suggests using only "oxidized" because it is more widely used word.

2. Page 17251; line 2: Change "Zhang et al. (2012a)….." to "Zhang et al. (2012b)….."

3. Page 17254; line 6: Add parenthesis to "seven" to separate from the number "7".

4. Page 17258; line 10: Change "oxidising" to "oxidizing".

5. Page 17258; line 11: Change "Instrumention-related" to "Instrument-related" or "Operational".

6. Page 17258; line 21: Change "12 - 20% (2s)" to "12 - 20% (2σ)".

7. Page 17259; lines 5-6: Remove all "et al."

8. Page 17260; line 21: Missing references "(EPA year/UNEP year)".

9. Page 17263; line 20: Change "interferents" to "interferences".

10. Page 17268; lines 18-19: Missing bias unit.

11. Page 17272; lines 5-7: "Holmes, C. D., Jacob, D. J., Corbitt, E. S., Mao, J., Yang, X., Talbot, R., and Slemr, F.: Accurate global potential energy surface and reaction dynamics for the ground state of HgBr2, J. Phys. Chem. A, 109, 8765–8773, doi:10.1021/jp053415l, 2009."

The article belongs to Balabanov et al. (2005) not Holmes et al.

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C5520/2012/acpd-12-C5520-2012-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 17245, 2012.