Anonymous Referee #1

We would like to thank the referee for their thoughtful and useful comments. We have provided our responses to the referee's comments below (in blue).

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General comments

The authors present an interesting study of the gas/particle partitioning of divalent inorganic mercury in the atmosphere and its influence on atmospheric mercury deposition rates. The review of the literature on this topic is comprehensive and well done. Previous work had been conducted on the gas/particle partitioning of Hg(II), but this work provides a significant advance on this topic by conducting a synthesis of atmospheric data obtained at five sites across North America to derive a new parameterization of this partitioning as a function of temperature. The new parameterization is consistent with the earlier laboratory work of Rutter & Schauer, and it offers the advantage of being representative of atmospheric ambient conditions.

The incorporation of this parameterization into a chemical-transport model demonstrates the significant influence of Hg(II) gas/particle partitioning for mercury deposition (since Hg(II) is the dominant mercury deposited species). It also improves model performance compared to an earlier simulation where Hg(0) oxidation occurred solely via reaction with bromine species.

In summary, this work provides new experimental information of Hg atmospheric processes and shows improvement over previous modeling results. Therefore, this work deserves publication. There are, however, two points that need to be discussed further, before publication.

1. Mercury speciation in power plant emissions:

This point is discussed in Section 3. The speciation of mercury emitted from coal-fired power plants is an important factor because the model simulation results are very sensitive to the speciation of the emissions of this important source category. The authors recognize that using the standard mercury speciation from emission inventories leads to erroneous results with GEOS-Chem. Since there is experimental evidence of a lower Hg(II) fraction in coal-fired power plant plumes than assumed in standard emission inventories, the authors used a lower Hg(II) fraction for that source category in their work. However, this assumption is the weak part of this work, because it resembles "model tuning" rather than an improvement based on scientific evidence. The authors are very honest when they point out that their assumption of 90% Hg(0) in coal-fired power plant mercury emissions is not consistent with the experimental results of Edgerton et al., who only measured about 84% Hg(0) on average in coal-fired power plant plumes. However, they then justify their choice by referring to the work of Wang et al. (2010), who sampled Chinese power plants and reported a range of 67 to 94% Hg(0) in mercury emissions from those plants. It is unfortunate that the authors did not provide greater detail on the work of Wang et al. Wang et al. found a large fraction of Hg(0) (75 to 94%, with a mean of 86%) after flue gas desulfurization (FGD), which is expected because Hg(II) is very soluble in water and is, therefore, efficiently removed by an FGD system. There are, therefore, two problems with the assumption made by Amos et al. in their work: - 90% Hg(0) is not consistent with the mean values reported by Edgerton et al. (84%) and Wang et al. (83% for the six power plants tested, five with FGD, one without FGD). - The argument for using 90% is tied to power plants with FGD systems and, therefore, should only apply to power plants with such systems and not to all power plants in the inventory (unless all U.S. power plants have FGD). The authors need to be clear about the fact that their assumption is likely to overestimate the Hg(0) fraction in power plant emissions compared to available experimental information and that the value of 90% that was selected has no scientific basis but was used to improve model performance. Such an approach does not account for the possibility that there could be a compensation of errors: for example, a change in the mercury speciation in the emission inventory could compensate for incorrect mercury chemistry in the model or an incorrect inventory for other sources. Without such a clear statement, the results of this work could be considered incorrect and possibly deceiving (since a greater Hg(0) fraction tends to decrease local mercury deposition impacts of power plant emissions). It would be interesting to know the sensitivity of the results to this assumption; for example, how would the model simulation results differ when an average Hg(0) fraction of say 84% is used for power plant emissions? Such results may have a significant impact on environmental policies because the Hg(0) fraction in coal-fired power plant emissions has a significant effect on their local and regional impacts for mercury deposition.

> We now use a Hg(0):Hg(II):Hg(p) speciation of 86.5:9.9:3.6 for fossil fuel sources of Hg from Y. Zhang et al. (2011). This is more consistent with Edgerton et al. (2006) and more extensively justified by Y. Zhang et al. (2011) within the GEOS-Chem modeling framework. We now also quantify the model improvement resulting from changing the speciation of emissions to account for in-plume reduction.

2. Refractory particulate mercury

This is another very important hypothesis (and perhaps an important result) of this work. The authors assumed that emitted particulate mercury is not measured as particulate mercury in ambient instruments because it would be refractory and, therefore, would not volatilize and be detected in the instrument. Model performance would significantly deteriorate if one assumed that this form of particulate mercury was measured. The authors present convincing arguments to justify their assumption but this point remains in question and it would be useful to identify it as an issue that needs to be resolved via additional experiments. It would be appropriate to mention this point in the abstract (it is already mentioned in the conclusion).

We have revised our hypothesis about Hg(p) and now treat it as Hg(II), but explore the effects of simulated Hg(p) as chemically inert in Section 4. We also now mention the issue in the Abstract. Please see responses below to Referee #2's comments about Hg(p) for more detail.

Specific comments

P. 29443, line 14: it would be useful to specify that scavenging by snow occurs during precipitation and not via dry deposition to snow on the ground (e.g., wet scavenging… by snow).

We now specify that scavenging by snow occurs during precipitation,

"Hg deposition to high latitudes increases because of more efficient scavenging of particulate Hg(II) by precipitating snow."

P. 29445, lines 24-25: It may be useful to specify the states or province where these sites are located (it is not obvious to the non New Hampshire resident where Thompson Farm is located).

We now specify the state or province associated with each site,

"RGM and PBM data were obtained from five sites: Reno, Nevada; Thompson Farm, New Hampshire; Outlying Landing Field (Pensacola), Florida; Experimental Lakes Area, Ontario; and Milwaukee, Wisconsin (Table 1)."

P. 29447, line 13: Since the previous sentence mentions organic compounds, it may be useful to add "for mercury" after "We tested this…".

We have added "for Hg",

"We tested this for Hg by performing a multivariate regression, $\log_{10}(K^{-1}) = a + b/T + cRH$, and found no significant dependence on RH at any of the sites."

P. 29447, lines 20-21: Rutter and Schauer had derived different gas/particle relationships depending on the chemical composition of the adsorbing particles. Such variability did not appear in this study. It is mentioned that the effect of aerosol chemical composition on the gas/particle relationship was tested, but that "no obvious relationship was found". This is an important result and it would be useful to the reader to know what kinds of tests were conducted. For example, how much variability do we have among sites in terms of chemical composition?

We have removed the statement "no obvious relationship was found" and modified the text as follows,

"Differences in aerosol composition between sites would be expected to affect the fits (Rutter and Schauer, 2007a,b) but we do not have composition information to pair with the mercury observations."

Did the authors test variability at a given site as a function of season as well?

We have added the following text,

"We investigated seasonal variations in the fits for individual sites but found that the resulting correlations were not robust because of insufficient number of data points and insufficient dynamic range in temperature."

P. 29453, lines 15-17: Do the authors have any idea why the model overpredicts during winter?

We now explain the high wintertime bias in PBM at Milwaukee in the text,

"The high model PBM at Milwaukee in winter is due to a local overestimate of ammonium nitrate aerosol in GEOS-Chem, thought to be caused by excessive N_2O_5 hydrolysis (L. Zhang et al., 2011b)."

P. 29459, lines 14-15: "…increases… from 108 days to 46 days" should be changed to "…decreases…".

Changed.