Itemized Response to Reviewer Comments

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The authors would like to thank the reviewer for the insightful and constructive comments. The changes to the manuscript that were subsequently made, markedly improved the quality of the manuscript. In addition to these changes, we have responded to the comments of the reviewer in an itemized fashion. Reviewer's comments (*in italics*) are unshortened for context and clarity. Responses by the authors are given in **bold type face**.

Interactive comment on "Evaluation of discrepancy between measured and modeled oxidized mercury species" by G. Kos et al.
Anonymous Referee #2; Received and published: 23 August 2012

Recent atmospheric monitoring of elemental mercury, Hg0, divalent gaseous mercury, Hg2+, and particulate mercury, Hgp, have elucidated a gap between the modeled and measured values of these Hg species at the surface. Closing this gap will likely require a re-evaluation of model atmospheric chemical mechanisms, emissions inventories, or both. This paper attempts to address this gap in modeled and measured values by evaluating the uncertainties in the observations and model estimates. However, the evaluation of the measurement uncertainties is brief and does not address potential spatial differences in the uncertainties due to sampling location or the presence of oxidants. The modeling uncertainty analysis is focused on finding emissions and reaction rates that can best replicate the wet deposition and ambient Hg observations rather than evaluating which mechanisms are likely under ambient conditions and what may be missing from current model chemical mechanisms that could potentially close this gap.

"Closing this gap will likely require a re-evaluation of model atmospheric chemical mechanisms, emissions inventories, or both."

The above statement assumes that the current observations of oxidized mercury are reliable and that the problem lies with the model chemistry and the emissions only. Our study illustrates that there are inconsistencies between measurements of mercury in air and water and that these are also inconsistent with the emissions of oxidized mercury. These inconsistencies point to significant uncertainties in the measured oxidized mercury concentrations. Given the inconsistencies between the two measured quantities (air concentrations of oxidized Hg and wet deposition) and the measurement uncertainties, closing the gap between measurement and model estimates requires more robust measurements of Hg species. In addition, sound laboratory data on redox Hg chemistry and accurate speciation of Hg emissions are required to improve the models. All three improvements need to advance for closing the gap. This study illustrates that it is not currently prudent to adjust the chemical mechanism in the models to match the model estimates to the measured data. The purpose of the study is not proposing new chemical mechanisms, but understanding the causes for the gap between measured and modeled Hg species using sensitivity studies.

"the evaluation of the measurement uncertainties is brief and does not address potential spatial differences in the uncertainties due to sampling location or the presence of oxidants"

Measurement uncertainties have been discussed in detail from section 3.1 to 3.7 and form a significant part of our study.

"The modeling uncertainty analysis is focused on finding emissions and reaction rates that can best replicate the wet deposition and ambient Hg observations rather than evaluating which mechanisms are likely under ambient conditions and what may be missing from current model chemical mechanisms that could potentially close this gap."

As mentioned above, this study evaluates the major causes for the gap and is not intended to suggest new chemical mechanisms. There is currently significant controversy in the

literature with respect to the Hg chemical mechanism, kinetics and reaction products. Following is a brief survey (in regular typeface**) of the current controversies surrounding mercury chemistry. A summary of the following discussion has been added to the section on model description in the revised manuscript:**

Gas phase oxidation with ozone (O_3), hydroxyl radical (OH) and halogens have been suggested in the literature as potential oxidants of Hg^0 in the atmosphere. Hg^0 reactions with O_3 and OH have been questioned (Tossel, 2003; Goodsite et al. 2004; Shepler and Peterson, 2003). Using theoretical studies, Tossel (2003) and Goodsite et al. (2004), concluded that Hg^0+OH should not be a significant reaction in the atmosphere since $HgOH^+$, a possible intermediate of the reaction, is likely to dissociate based on the binding energy calculations and the production of $HgO_{(g)}$, as a product of reactions Hg^0+O_3 or Hg^0+OH, is highly endothermic. In contrast, in a more recent theoretical work using a high level theory (NESC/CCSD(T)), Cremer et al. (2008) found the reaction energy of Hg^0+OH to be 12 kcal mol^{-1}(which is comparable to the reaction energy for Hg^0+Br, i.e. 14.4 kcal mol^{-1}) and concluded that the reaction Hg^0+OH is possible in the atmosphere.

$HgO_{(s)}$, predominantly adsorbed on the reactor walls, was observed in Hg^0+O_3 reaction which led Pal and Ariya (2004) to suggest a surface influence in the reaction. However, subsequent studies using much larger reaction chamber and low reactant concentrations of Hg^0+O_3 reaction, suggest that the rate constants obtained previously are free of surface effects and viable in the atmosphere (Snider et al. 2008; Sumner et al. 2005). In a more recent theoretical study, Tossel (2006) suggest that stable oligomers of mercury oxide, HgO_n, can subsist, and therefore it is possible that reaction Hg^0+O_3 may proceed in the atmosphere through complex reaction intermediates, leading to oligomeric HgO_n reaction products in gas phase and/or upon interaction with surfaces (Calvert and Lindberg, 2005; Subir et al. 2011). A direct proportionality of the Hg^0+O_3 reaction rate constant with an increase in CO concentration was reported by Snider et al. (2008) which demonstrates a third-body effect on the Hg^0+O_3 reaction. Most recently, Rutter et al. (2012) experimentally investigated the oxidation of Hg^0 by O_3 in the presence of secondary organic aerosols. They found very good agreement between their reaction rate and the previously published rates confirming that the Hg^0+O_3 reaction is viable in a complex and heterogeneous atmosphere and that the oxidation of Hg^0 by O_3 is not significantly enhanced by reactor walls. They conclude that the Hg^0+O_3 reaction is viable in the atmosphere and recommend inclusion of this reaction in the models. They also propose that the evidence of agglomerates of $HgO_{(s)}$ particles on the reactor wall by Snider et al. (2008) is more consistent with the reaction taking place in free suspension where aerosol particles form from the accumulation of oligomeric reaction products rather than the formation of HgO on the walls.

There is experimental evidence for the oxidation of Hg^0 with O_3 and OH; therefore it is very likely that these reactions are occurring in the atmosphere (perhaps with lower overall reaction rate than determined experimentally) through complex reaction mechanisms in the atmosphere leading to stable products (Calvert and Lindberg, 2005; Subir et al. 2012). In an extensive review of uncertainties in Hg chemistry in atmospheric models, Subir et al. (2012) concluded, “given the relatively high abundance of ozone in the atmosphere, it is plausible that it plays an important role in $Hg^0_{(g)}$ oxidation. However, it is clear that oxidation of $Hg^0_{(g)}$ by ozone exclusively in the gas phase does not occur. Laboratory experiments along with theoretical investigations, however, strongly suggest that third-body effects and surfaces, i.e. solid HgO formation (Snider et al., 2008), not only make this reaction possible in the atmosphere but can also enhance it. A similar conclusion applies to the reaction of $Hg^0_{(g)}$ with OH radicals. Both ozone and OH radicals are present in the urban, remote, and MBL regions of the atmosphere. Their reaction should not be eliminated from mercury models.”

Hg^0+Br reaction is generally accepted as a major oxidation pathway in the atmosphere in the Polar Regions and marine boundary layer, however very little data exists with respect to its importance and mechanism in the global atmosphere. Dibble et al. (2012) state ‘currently used mechanisms in the models are significantly incomplete in describing the fate of the BrHg radical, because they do not include the most likely reactions of that radical in the atmosphere.’ Currently, there is large uncertainty in tropospheric Bromine concentrations; therefore it is difficult to implement and evaluate Bromine oxidation mechanism in the models on global scale. Shepler et al. (2007) reported Hg^0+Br oxidation rate coefficient ~3 times faster than previously published rates; these results can unrealistically change the lifetime of Hg in troposphere against Br oxidation reaction. There is also uncertainty in the dissociation reaction rate constant of HgBr and reaction rate constants for the reaction of HgBr with atmospheric oxidants other than Br are unknown.

Currently, the exact reaction mechanisms and products of Hg^0 oxidation with O_3, OH and Br are unknown and none of the three oxidation pathways (O_3, OH and halogens) can be ruled out based on the literature; the subject is an active area of research and controversial. In the current configuration of the GRAHM, we have chosen to include oxidation of Hg^0 by O_3 and/or OH in global atmosphere and halogen oxidation in marine environments including the Polar Regions where the Hg^0 depletion via Br oxidation has been well demonstrated. We are currently testing various Hg chemistry mechanisms in the model to find suitable mechanism that is applicable in all environments such as continental, marine and Polar Regions in all regimes of the atmosphere (boundary layer to stratosphere); this will be a subject of a separate study.

In our view, it is possible that all of the reactants discussed in the literature are occurring in the atmosphere with varying importance in different environments. Since life time of Hg^0 is long in the atmosphere (1-2 years), presence of several oxidants of Hg^0 in the atmosphere implies that there are significant mercury reduction pathways in the atmosphere that remain to be discovered. The challenge for the Hg chemistry research community (experimental, theoretical and modeling) is to find the exact Hg redox mechanisms. Given the state of the current knowledge of mercury chemistry, the chemical mechanisms employed in the all of the mercury models are currently experimental and it is not possible to call any of them more sound than the other.

Out of 5 global/hemispheric models and several regional models (GEOS-Chem, GLEMOS, DEHM, ECMERIT & GRAHM; variants of CMAQ) only one model (GEOS-Chem) is currently using atomic bromine as the only oxidant of Hg^0 in the atmosphere (Holmes et al. 2010). Holmes et al. (2012) investigated (and not concluded) the possibility of Br as the main oxidant of Hg^0 and compared it with the GEOS-Chem version using O_3 and OH as the main oxidants. Their main findings along with our comments (in brackets) are listed below:

1) The Hg^0 + Br and Hg^0 + OH/O_3 models are equally capable of reproducing the spatial distribution of TGM and its seasonal cycle at northern mid-latitudes.
2) The Hg^0 + Br model shows a very steep decline in Hg^0 concentrations from the tropics to southern mid-latitudes (this result is currently unconfirmed by measurements).
3) Only the Hg^0 + Br model can reproduce the springtime depletion and summer rebound of TGM observed at polar sites.
4) The Hg^0 + Br and Hg^0 + OH/O_3 mechanisms are both consistent with wet deposition in Europe and North America.
5) The Hg^0 + Br model does not capture the summer maximum in wet deposition over the southeast US (underpredicts by 50%) because of low subtropical Br concentrations while the Hg^0 + OH/O_3 model simulates the wet deposition maximum quite well in this region. During these months OH concentrations are high in sub-tropical region leading to high rate of oxidation and convective scavenging in the Hg^0 + OH/O_3 model which is consistent with observations.
6) An observed decline of Hg^0 above the tropopause in global atmosphere is simulated by both the Hg^0 + Br and Hg^0 + OH/O_3 models.
7) Strongest stratospheric depletion of Hg^0 is observed in the Arctic during springtime. Neither of the two models, Hg^0 + Br or Hg^0 + OH/O_3, can explain this depletion.
8) The Hg^0 + Br and Hg^0 + OH/O_3 models yield similar global mercury budgets.
9) The Hg^0 + Br model yields much larger fraction of mercury deposited to the Southern Hemisphere oceans. (This result is currently unconfirmed by measurements).
10) Both the models (Hg^0 + Br and Hg^0 + OH/O_3) significantly overestimate the wet deposition in the US Mid-Atlantic and Midwest Hg emission regions.
11) Currently, both versions of GEOS-Chem constrain atmospheric life time of Hg^0 by invoking an assumed photochemical reduction of Hg^{II} in clouds using a reaction rate that

is adjusted to match the model simulated global mean surface Hg^0 concentrations to the measurements. Holmes et al.(2010) noted that lower end of the Hg^0 + Br reaction rate could be used without a need for atmospheric reduction of mercury. (This choice may result in unrealistically longer life time of Hg^0 in the Polar Regions).

Since Br concentrations are highly uncertain, a combination of model estimates and prescribed values for Br concentrations are used in GEOS-Chem. Holmes et al. (2010) conclude, "both oxidation mechanisms (Hg^0+Br and Hg^0+O_3/OH), and possibly others, may be operating together in the atmosphere, the idealized simulations, as presented in their study, explore the constraints that observations place on the atmospheric chemistry of mercury."

The purpose of current study is to examine the discrepancy between measured and modeled oxidized mercury concentrations in the light of other measurement constraints such as wet deposition which is known to be more reliable measurement compared to the oxidized mercury measurements. To illustrate the problems with the oxidized mercury measurements, several model sensitivity runs were conducted while keeping the configuration of GRAHM same as used in the study by Zhang et al. (2012a). This study serves the purpose of exposing the knowledge gap in Hg chemistry along with uncertainties in measurements of Hg speciation in air and in emissions. The study is not intended to propose new chemical mechanisms. Our study shows that the ratio of Hg^0, Hg^{II} (gas) and Hg^{II} (particle) in the emission inventories, measurements of surface air Hg^{II} (gas and particle) and measurements of wet deposition are currently inconsistent with each other. Emissions suggest significantly high concentrations of Hg^{II} in air and in precipitation in the vicinity of emission sources; however, measured air concentrations of Hg^{II} and measured Hg concentrations in precipitation are not found to be significantly elevated in the vicinity of emission sources compared to the remote regions. Our study highlights that given the current uncertainties and inconsistencies between the measurements, large differences between modeled and observed estimates of oxidized mercury concentrations cannot be viewed as inaccuracies in models alone. Better emission inventories (with respect to speciation), better techniques for measurements of oxidized species, understanding of mercury chemical kinetics in different environments (including in-plume) in all phases are needed.

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General comments

1.The authors suggest that the inclusion of in-plume reduction of Hg^{2+} *improves the model results. However, they acknowledge that there is little current laboratory nor field data to support this process. The "in-plume" reduction sensitivities are performed by simply reducing the ratio of Hg2+ and Hgp emitted. This presents a problem, because (1) no in-plume mechanism is proposed nor evaluated, (2) no justification is presented as to why* Hg_p *would be included in this mechanism, and (3) this part of the manuscript appears to be an emissions sensitivity re-branded as a sensitivity to in-plume processes.*

There is consistent evidence from several modeling studies that an assumption of majority of anthropogenic emissions as Hg^0 **improves the modeling estimates of wet deposition in the vicinity of emission sources (Amos et al. 2012; Zhang et al 2012; Lohman et al. 2006 and this study). There are very few and contradictory in-plume studies that neither confirm nor deny the possibility of in-plume reduction with certainty (Edgerton et al. 2006; Landis et al. 2009; Kolker et al. 2010; Deeds et al. 2013; in press). The main problem is the lack of measurements. Additional field studies are required to improve our understanding of the**

the Hg in-plume processes and emission speciation. In addition, Hg reduction processes in the troposphere are currently not well understood; therefore laboratory kinetics studies are required.

We agree with the reviewer that we have performed emission speciation sensitivity experiments and that the assumed modification of species could originate from inaccurate emission inventories or in-plume reduction. Several flue gas studies suggest the presence of significant oxidized mercury in coal fired power plant emissions (Edgerton et al., 2006; Lee et al., 2006; Deeds et al, in press), therefore it is more likely that modification of mercury speciation takes place in-plume. However, since this hypothesis is unconfirmed, we have revised our manuscript to replace references to 'in-plume reduction' with 'Hg speciation near emission sources' when referring to the related sensitivity experiments. We have performed sensitivity experiments where only Hg^{2+} (gas) emissions were modified (not reported in the manuscript), this simulation results in over-prediction of wet deposition and Hg_p concentrations in the vicinity of emission sources. The air concentrations of Hg^{2+} in gas and particles are very likely in equilibrium with each other, therefore we decided to reduce the emissions of both Hg^{2+} and Hg_p by the same factor. We have added this explanation in the revised manuscript.

References (also added to the manuscript):

Amos, H.M., D.J. Jacob, C.D. Holmes, J.A. Fisher, Q. Wang, R.M. Yantosca, E.S. Corbitt, E. Galarneau, A.P. Rutter, M.S. Gustin, A. Steffen, J.J. Schauer, J.A. Graydon, V.L. St Louis, R.W. Talbot, E.S. Edgerton, Y. Zhang, and E.M. Sunderland (2012), Gas-particle partitioning of atmospheric Hg(II) and its effect on global mercury deposition, Atmos. Chem. Phys., 12, 591-603.

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2.The gas phase model sensitivities do not seem to be driven by the uncertainties in the chemical mechanism or reaction rates. This part of the study appears to be more of a model tuning exercise. The authors clearly state which model configuration compares best to the observations but they do not convince me that this was achieved by using the most feasible chemical mechanisms.

A discussion of the current state of mercury chemistry science is provided in response to reviewer's earlier comments. Given the controversy in mercury chemistry science, it is currently not possible to conclude what is most feasible chemical mechanism. The first two model sensitivity experiments in this study explore the impacts of oxidized mercury emissions and gas phase oxidation of mercury on oxidized mercury concentrations and wet

deposition independently. Using these experiments, we demonstrated that the large discrepancy between model and measurements as reported in Zhang et al. (2012) exists even without any oxidation processes and that the discrepancy is largest closest to the emission sources. Hg oxidation appears to be the main pathway for the oxidized Hg species in the atmosphere. Several experiments were performed to find optimal reaction rate coefficients for the gas phase mercury oxidation with O_3/OH as oxidants that provide global background Hg^0 concentrations comparable to observed concentrations and improve wet depositional fluxes compared to measurements. It is difficult to perform similar sensitivity experiments with Br as a major oxidant because the atmospheric concentrations of Br are currently highly uncertain. We are currently working on several mercury chemistry mechanisms that will be the subject of future study.

Specific comments

1.Abstract lines 7-8: "..., in addition to ... speciation of mercury near emissions sources..." This sentence is confusing. Are you quantitatively exploring the models speciation near sources as well as the uncertainties in the measurements?

The reviewer is correct in his assumption, thank you for the comment. We have removed the "..., in addition to ..." and rephrased the statement clarifying the objective, which now reads: "This study quantitatively explores measurement uncertainties in detail, and discusses the impact of speciation of mercury near emission sources on the oxidized mercury concentrations to better understand the discrepancies in the context of oxidized mercury, i. e. gaseous (Hg^{2+}) and particulate (Hg_p) mercury."

2.Page 17248 Lines 3-6: In the abstract, the authors suggest that including in plume chemistry improved model results, but the language here indicates that there is no recent laboratory nor field experiments to justify this mechanism. Perhaps the authors should recast this model sensitivity as an emissions sensitivity given the uncertainties in the emissions and our ability to make accurate speciated Hg measurements.

We agree with the reviewer and we have replaced the words 'in-plume reduction' with 'Hg speciation near emission sources' while referring to the sensitivity experiments in the revised manuscript.

3.Page 17248: Are the authors suggesting that modeled wet deposition results agree well with measurements because the driving meteorological models capture the observed precipitation well and that the measurements do not consider speciation? If so, this seems like a speculative claim.

This statement in the introduction reports the conclusion findings of an article by Ryaboshapko et al., 2007b; therefore this is not a speculative claim by us.

4.Page 17248 Line 24: Please explicitly specify the MDL for Hg^{2+} *and* Hg_p *here so the reader does not have to flip between the table and this text.*

We assume that the reviewer refers to page 17249, line 24, where a reference to the MDL is made. We added the MDL range (since they vary between instruments and operators) for Hg^{2+} **and** Hg_p **to the text in the brackets and kept the reference to Table 3 for detailed data.**

5.Page 17248 Line 25: Assuming an ambient Hg^0 *concentration of 1.5 ng* m^{-3} *and examining the values on Table 4, a more reasonable fraction of Hg as* Hg^{2+} *and* Hg_p *should be less than 1%.*

Yes, it has been corrected in the revised manuscript.

6.Page 17249 Line 1: "These data ..." Which data? Ny Alesund and Rochester or AM- Net? Given the large variability in the species concentration that the authors specified in the previous sentence, a measure of the variability, e.g. standard deviation or 5th and 95th quantile, in these measurements should be given.

We assume that the reviewer refers to page 17250, line 1. The term “these data” is indeed ambiguous and in fact refers to the data presented in the table. We replaced it with “data from Table 1” and added the ratio “mean ± standard deviation of calculated ratio for all ratio data < 3” for clarity.

7.Page 17251 Paragraph beginning with "Figure 1": The present and past tenses of verbs are used. The authors should pick a consistent tense.

The text was edited for consistency.

8.Page 17252 Line 6: The Bullock and Brehme 2002 citation is not the primary source for the OH reaction rate used in CMAQ.

The citation has been corrected to Pal and Ariya, 2004 and Sommar et al. 2001.

9.Page 17252 Line 9: Why were the halogen reactions only considered in the marine boundary layer?

A discussion of the current state of mercury chemistry science and the approach used in GRAHM is explained above in response to earlier comments by the reviewer.

10.Page 17252 Line 9: "Rate constants are from..." For which reactions? If this has been changed from previous GRAHM studies this needs to be specified.

The statement refers to the rate constants for the halogen mercury chemistry. These have not been changed from the previous study. The text has been improved for clarity.

11.Page 17252 Line 11: The Hg2+ reduction by the hydroperoxyl radical has been shown to be unlikely under normal atmospheric conditions (see Gardfeldt and Jonsson, J. Phys. Chem. A, 107, 2003) and the uncertainty of the aqueous phase reduction was not considered in this paper. Both the wet deposition and ambient Hg^{2+} *concentrations are sensitive to the aqueous phase reduction mechanism (see Pongprueksa et al., Atmospheric Environment, 42, 2008) and the lack of an evaluation appears to be a gap in the analysis performed in this study.*

Concerning the mercury reduction processes, in a review article on Hg chemistry, Hynes et al. (2009) concluded that the atmospheric importance has not been established for any of the suggested reductants for Hg^{II} **so far; so the role of** Hg^{II} **reduction in the global atmosphere remains conjectural. The reduction processes are perhaps occurring in the atmosphere; however only a limited number of reduction pathways in the aqueous phase have been identified. Possible reduction of oxidized mercury on surfaces of atmospheric aerosols, ice and snow etc. could be important but have not been studied so far. Recently, Si and Ariya (2008) studied reduction of** Hg^{II} **by dicarboxylic acids (**C_2**-**C_4**) in aqueous phase. Although they proposed a tentative reaction mechanism, sufficient details are unavailable for its implementation in the model. Moreover, they found that presence of chloride ion and dissolved oxygen significantly inhibited the reduction reaction; therefore this reduction pathway may not be significant in atmosphere. Holmes et al. (2010) noted, "until better constraints on** Hg^0 **oxidation rates are available, it appears that atmospheric reduction is not required to explain any of the major features of the global mercury cycle." Currently, in GRAHM, mercury is reduced in the aqueous phase photo-chemically and by the sulfite anion. We do not use** HO_2 **reduction pathway (This is an error in the manuscript that has been corrected). GRAHM uses lower end of the global Hg emission estimates as well as lower the end of** Hg^0 **oxidation rates; the reduction processes in GRAHM are insignificant and have a negligible impact on the distribution of mercury species in the air.**

12. Page 17252 lines 18-19: "subsequent reactions in the plume, seems to be among the most important parameters." What makes this seem so? On Page 17248 Lines 3-6 the authors *suggested that observational and experimental evidence does not confirm this reaction mechanism.*

These statements have been removed from the model description section in the revised manuscript. We have also expanded the discussion of in-plume field studies to include all field studies conducted so far in section 3.4. The introduction was amended as follows: "While atmospheric mercury reactions have been studied extensively, the impact of in-plume reactions on speciation is less known. While a modelling study suggests reduction of Hg2+ in the plume by SO2 (Lohmann et al., 2006), recent field data did not confirm the suggested reaction mechanism (Deeds et al., in press)."

13. Page 17252 line 26: What was the vertical resolution of the model?

There are 28 levels in the vertical up to 10 hPa. This has been added in the model description section in the revised manuscript.

14. Page 17262 line 11: "established OH/O_3 processes" The OH/O_3 mechanism may be established and widely used in atmospheric models but recent experimental and thermodynamic studies (See Hynes et al. MERCURY FATE AND TRANSPORT IN THE GLOBAL ATMOSPHERE 2009, 427-457, DOI: 10.1007/978-0-387-93958-2_14) indicate that these reactions are not likely to produce gas phase products.

Although, the review by Hynes et al. (2009) indicates that OH/O_3 reactions are not likely in the gas phase; more recent studies are pointing to the likelihood of these reactions in the atmosphere as discussed on our response to earlier comment on Hg chemistry. We have revised the section on 'uncertainties associated with chemistry knowledge gap'; the 'established OH/O3 processes' wording does not appear in the revised text.

15.Section 3.10 should be expanded and the cumulative uncertainties should be better explained.

We have rewritten and expanded the section to better explain the summation of uncertainties.

16.Page 17264 lines 12-14: Does "no emissions" means no Hg^{2+} *emissions in the U.S., North America, or globally? What is the uncertainty in the global emissions?*

'No emissions' means 'no emissions of oxidized mercury globally'. All emissions are considered as Hg^0 **in this simulation. We have added more explanation of the sensitivity model runs in the revised manuscript.**

The uncertainty in global anthropogenic emission is considered to be 20-40% for the main industrial sectors, depending on the region (AMAP Mercury Assessment 2011). Available estimates of natural and re-emissions are within the range of 2,000 to 5,000 t/y (Pirrone et al.2010).

Reference:

Pirrone N., Cinnirella S., Streets D.G., Feng X., Mukherjee A.B., Leaner J., Telmer K., Mason R., Friedli H.R., Finkelman R.B., Stracher G. (2010). Global mercury emissions to the atmosphere from anthropogenic and natural sources. ACPD, 10: 1-33.

17.Page 17264 line 21: Are you sure this is the fault of chemical mechanism? What is the vertical resolution of the layers? Too course of a vertical structure could artificially increases surface concentrations by mixing too much of the stack emissions in the lowest model layer. Are similar biases seen in CO or black carbon emissions? Has the boundary layer height been evaluated against observations?

There are 28 vertical levels up to 10 hPa in the model; the resolution in the boundary layer is not too course. GRAHM is based on Canadian operational weather prediction model;

therefore all the meteorological fields including boundary layer height are routinely verified against observations.

18.Page 17265 line 22: "produced the best results" This is true if the objective is replicating the observations. I am not convinced that this particular model configuration is using the best combination of gas phase chemical reaction rates, mechanism and emissions.

We have provided the discussion on the state of mercury chemistry. Currently, it is impossible to conclude which gas phase mechanism and reaction rates are most realistic. The emissions used in this study are the best available in the literature and these have been referenced adequately in the manuscript.

19.Page 17265 line 23: "spread in the bias" Perhaps the mean error or RMS error would be a more quantitative way of describing this change in the model results.

We have added the error data (RMSE decreasing from 42 to 18 pg m^{-3}) to the paragraph, but would also like to retain the phrase "spread in the bias"; reduced spread in bias means that the spatial variation in the concentration is reduced which can also be seen in figure 4a.

20.Page 17265 line 24: "no significant change" By what metric?

We have added the error data (RMSE decreasing from 10 to 7 pg m^{-3}).

21.Page 17266 lines 22-23: What qualifies the results as noticeably high or markedly improved?

Visual comparison of the observed values provided in the circles with model estimates on the maps for the two model runs provides the basis for the use of above terms in the text.

22.Page 17267 lines 10: "Hg^{2+} *should be higher ..." I do not think that higher surface concentrations are needed to capture the wet deposition fluxes. It may be possible to capture the wet deposition fluxes with a slower or different aqueous phase* Hg^{2+} *reduction mechanism without having to increase surface level* Hg^{2+} *concentrations as shown in the model sensitivities in Pongprueksa et al., (Atmospheric Environment, 42, 2008).*

In our model configuration, the reduction processes are insignificant and complete removal of reduction processes has a minor impact on the wet deposition and the mercury concentrations.

23.Page 17267 lines 14: "Bullock, 2009" is not the correct reference for uncertainties in wet deposition observations. Prestbo and Gay Atmospheric Environment, 43, 2009 is a better source for uncertainties in MDN wet deposition.

The reference has been corrected in the revised manuscript.

24.Page 17268 line 5: It is not clear to me how the factor of 8 uncertainty was derived.

The factor of 8 is a result of the discussion in (the old) section 3.10, now section 3.5. We have clarified section 3.5 following the recommendations of the reviewers, including the derivation of the uncertainty factors.

25.Page 17268 lines 18-19: What are the units of the biases being discussed?

Bias Units are pg m^{-3}**; we have added the units to all bias values in the manuscript.**

26.Figures: The labels on scale bars and axes are generally too small to be legible.

We have replotted the labels in larger font for all figures in the revised manuscript.

27.Figure 5: It is not clear to me that the bias decreases with distance from the emissions source. This plot appears to show that the bias increases with increased concentrations. No information regarding the locations or type of the Hg emission sources were given.

We have used model estimated annual mean concentrations of Hg^{2+} (subplot (a)) and Hg_p (subplot (b)) from the NoChem run (no mercury chemistry, see Table 2) on the x-axis as a measure for the distance from sources. Higher concentration values of oxidized mercury in the NoChem run signify proximity to the emission sources (and vice versa), since no mercury chemistry is executed by the model. We have clarified this point in the caption of Figure 5 as explained in the text.

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