Itemized Response to Reviewer Comments

Manuscript Atmos. Chem. Phys. Discuss., 12, C5520–C5529, 2012

The authors would like to thank the reviewer for the insightful and constructive comments from a very detailed review. 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 below 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.

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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.

The evaluation method of uncertainties has been revised according to the reviewer's suggestions in the revised manuscript. Following is our response (in regular typeface for readability**) with respect to the reviewer's concern on the unsound model configurations. A summary of the following discussion and explanation for the model configuration used in the study has been added to the revised manuscript in the model description section.**

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. As pointed out by the reviewer, Hg^0 reactions with O_3 and OH have been questioned (Tossell, 2003; Goodsite et al. 2004; Shepler and Peterson, 2003). Using theoretical studies, Tossell (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 this reaction and Hg^0+O_3 reaction, 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, Tossell et al., 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 ozone and OH; therefore it is very likely that these reactions are occurring in the atmosphere through complex reaction mechanism (perhaps at a slower overall reaction rate than determined experimentally) 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.

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 as noted above; 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 models. 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. Currently, one of the global models, GEOS-Chem, uses an assumed fast photochemical reduction rate of Hg^{II} in clouds as a necessity for constraining the life time of Hg^0 in the atmosphere to ~1 year (Holmes et al. 2010). 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 (unlike GEOS-Chem) 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.

Although there is consistent evidence from several modeling studies that an assumption of in-plume reduction improves the modeling estimates of ambient oxidized Hg concentrations and wet deposition in the vicinity of emission sources, the reduction mechanism itself is currently unknown (Amos et al. 2012; Zhang et al. 2012; Lohman et al. 2006). 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). Laboratory kinetics studies and additional field studies are required to improve the Hg speciation and reduction processes in models.

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 southeastern 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 subtropical 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. (2012). 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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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).*

Following the advice of the reviewer we have separated the uncertainty calculations for measurements, emissions and model. For "bidirectional" we calculated the root sum of the squares and summarized uncertainties in the same fashion. We also calculated Hg^{2+}, Hg^0 and Hg_p uncertainties separately for clarity. We have also removed the sampling height dependent observations from Lindbergh and Stratton (see below) from calculations, but left them in the list for future investigation leading to a speculative increase in oxidized mercury concentrations.

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?

This has been addressed above in response to the general concern of the reviewer.

3. Section 3.1; pages 17254-17255: The title "Uncertainty of measurements" does not correspond very well with discrepancy of Hg^{2+} *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.*

We have changed the title of the section to "Uncertainty of CVAFS measurements", since indeed only CVAFS (exclusively used by AMNet) measurements are considered. Section 2.2 ("Sampling, measurement and data analysis of oxidised mercury species") explicitly states the measurement principle for Hg^{2+} as reduction and detection as Hg^0.

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?

AMNet sampling elevations are indeed lower than the mentioned 43 m above ground and in the 4-6 m range as per the NADP Site Selection and Installation Manual, Version 1.5 (2011). We have tried to compare the model and observed data at a similar height. However, model estimates do not represent sub-grid scale impacts, therefore if measurements are sensitive to the local conditions, the discrepancy between model and measurement estimates is expected to be large at such sites. Our model has 28 vertical layers and the lowest model layer is within 10 meters to the ground. The model uses normalized hybrid sigma coordinates in the vertical, therefore the height of the levels is not fixed.

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 O_3 *oxidation rates (increase 50%*

and 100%), remove Hg^0 and OH reaction from all the cases except their "best case", assign fraction of oxidized mercury species from chemical re- actions in the air, and change mercury species emission ratio (Hg^0:Hg^{2+}:Hg_P) from 50:40:10 to 90:8:2 and 90:5:5. Does the inevitability of decreasing Hg^{2+} emission by a factor of 5 to 8 reflect poor performance of the model?

In the revised manuscript we have added the rationale and explanation for the model sensitivity experiments in the section on model sensitivity analysis.

The need to decrease the proportion of Hg^{2+} emissions is not a reflection of poor performance of the model. As shown in the study through a sensitivity model simulation without Hg chemistry, we find that even without the production of oxidized mercury by chemistry, the Hg^{2+} concentrations as well as wet deposition are significantly overestimated in the vicinity of emission sources. Since wet deposition scavenges Hg^{2+} (gas and particles) from the free troposphere (clouds) to the surface(in rain below cloud) , the experiment strongly suggests that the Hg^{2+} concentrations should be indeed significantly lower in these regions which is only possible through either reduction of Hg^{2+} in the emission plumes or lower proportion of oxidized mercury in the emissions. The only other possibility is a very strong aqueous phase reduction mechanism in such environments; however such a reduction mechanism is not yet identified and the presence of very high concentrations of Hg^{2+} in gas phase near emission sources remains unresolved. In the experiment without Hg chemistry, there are no model errors occurring from chemistry uncertainties. The transport properties of the model are robust since this is an operational weather forecast model for Canada; its meteorological forecast is routinely evaluated with observations and also inter-compared with other operational weather forecast models of the world.

Amos et al. (2012) and Zhang et al. (2012b), using Br oxidation in their model, have modified the emission ratios of Hg^0: Hg^{2+}:Hg_p based on our study results which were presented at the ICMGP 2011, Halifax.

GEOS-Chem, a global mercury model, has removed both O_3 *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* Hg^0 *with* O_3 *and OH. Why do the authors still rely heavily on these uncertain reactions?*

We have provided a detailed discussion of the current state of the mercury chemical mechanism and the fact that currently all three proposed mechanisms suffer with uncertainties and it is not possible to confirm or rule out any of the proposed oxidants (O_3**, OH and Br).**

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 Hg^{2+} *(~50 pg m-3) and* Hg_p *(~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?*

Yes, it is possible to use the Br chemistry in the entire global atmosphere in the model. We have added a brief discussion of the current uncertainties in Hg chemistry in the section on model description.
AMDEs during springtime contribute to high Hg^{2+} **concentrations in Hudson Bay, Canada through Br initiated chemistry.**

Minor Issues:

1. Abstract; page 17246; lines 14-21: "The discrepancy between simulated and observed concentrations of Hg^{2+} *and* Hg_p *was found to be reduced when a ratio for* Hg^0:Hg^{2+}:Hg_p *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* Hg^0 *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 Hg^{2+}, Hg_P, *or both. The reviewer suggests declaring it more explicit.*

Thank you. We have added the discussed species to the data (Hg^{2+} in the first, Hg_p in the second case).

Moreover, reporting the results (bias and error) in terms of percentage would aid general audience in better quantifying the improvements.

We have added results reported as percentage throughout the manuscript and the abstract. The part of the abstract for the 2 above issues now reads: "The unbiased root mean square error (RMSE) between simulated and observed concentrations of Hg^{2+} are found to be reduced by 42%, when a ratio for Hg^0: Hg^{2+}: Hg_p in the emissions is changed from 50:40:10 (as specified in the original inventories) to 90:8:2. Significant bias and unbiased RMSE reductions (29% and 58%, respectively) for Hg^{2+} and Hg_p is found for sites in the Eastern United States and Canada, especially near emission sources.

2. Abstract; page 17246; lines 21-25: "Significant improvements in the spatial distribution of wet deposition of mercury in North America was noticed. Particularly, overprediction 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.

We have removed the values from the abstract, since they stem from a draft manuscript and were not removed for the submitted version. The grammatical error was corrected.

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)?

No, because the measurements of Hg^{2+} concentrations are reported for the surface air, whereas Hg^{2+} is scavenged in the free troposphere in clouds and in the boundary layer through rain. The model simulates the vertical profiles of Hg species consistent with transport, vertical mixing and oxidation.

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).

We have removed the reference since the statement represents commonly accepted knowledge and amended it as suggested by the reviewer. It now reads: "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, but mercury chemistry, including its sources and sinks are still not fully understood. While most mercury is present in the atmosphere in elemental form (Hg^0), other oxidized mercury species (mostly as Hg^{2+}) contribute significantly to overall processes due to their reactivity with other atmospheric species and constituents (Schroeder and Munthe, 1998)".

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 Hg^{2+} at remote Ny Alesund on Svalbard vs. 4 pgm^{-3} in urban Rochester, NY)."
How can local sources explain higher Hg^{2+} concentration at the remote site? The two average concentrations might not be directly comparable since measurement date and time are not reported.

The reviewer is correct and, therefore, we have simplified the statement to read: "Observation data show considerable variation and concentration of up to 89±150 pg m^{-3} for Hg^{2+} in Baltimore, MD and 80.8 ± 283 pg m^{-3} near a Cement Plant in the San Francisco Bay Area, CA; see Table 1)"

6. Introduction; page 17250; lines 1-3: "The average Hg^{2+}/Hg_p 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?

We agree with the reviewer and have removed the statement from the text.

7. Introduction; page 17250; lines 15-19: "Model results of Hg^{2+} *and* Hg_p *at the 15 AMNet sites were overestimated by a factor of 2–10 for the sum of* Hg^{2+} *and* Hg_p*. Zhang et al. (2012b) provide several hypotheses for this discrepancy: (1) too high emission inputs; (2) too fast oxidative conversion of* Hg^0 *to* Hg^{2+} *and* Hg_p*; and (3) too low dry deposition velocities." Zhang et al. (2012b) did not provide those hypotheses.*

The hypotheses were stated in Zhang et al. (2012a). We apologize for the confusion and made the appropriate corrections.

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.

We have removed personal communication references for Ariya and Steffen throughout the manuscript.

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 Hg^0 *oxidation reactions need to be removed which may cause confusions.*

The figure 1 has been moved to the section on model sensitivity analysis and detailed explanation for the experiment has been added.

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.

The section title was changed to “Sampling, measurement and data analysis of oxidized mercury species”

11. Section 2.2; page 17254; line 22: “Statistical calculations and analyses were carried 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.

The sentence was rephrased and the current version used for calculation updated. The statement now reads: Statistical calculations and analyses were carried out employing R (version 2.14), a programming language for statistical computing and graphics.

12. Section 3.5; page 17258: This section is very short. It can be combined with section 3.3 to address sampling uncertainties of Hg^{2+}.

Section 3.5 (Ozone interference during sampling) was merged into old section 3.3 (now section 3.1.2 Hg^{2+} Sampling uncertainties). All sections were renumbered accordingly.

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.

The study is focused on the uncertainties of oxidized mercury species. There is a general consensus that the emissions of mercury from terrestrial and aquatic surfaces are in the form of elemental mercury; therefore these are not discussed.

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.

We have removed the figure 7 as suggested by the reviewer.

15. Table 1; page 17280: It would be more informative if the authors also include Hg^0 *or total Hg in the table.* Hg^0 *is usually reported along with other mercury species.*

We have included the Hg^0 **data in a separate column (column 1) in the table as suggested.**

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

The labels have been enlarged for all mentioned figures.

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.

We have added a map grid to Figure 2 as requested. Additionally we added validation stations (in blue to differentiate them from the AMNet stations in red) for interpretation of Figure 9 that were previously not included. Station IDs with geographic locations are available in a separate table in the Appendix (Appendix Table 1) in order not to overload the map plot.

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.

We replaced the term as suggested and use American English spelling throughout the manuscript.

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

We made the change to reference the correct article

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

Done.

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

Done here and throughout the manuscript.

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

The heading was changed to "3.1.4 Operational uncertainties"

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

Done

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

The "et al." statements were removed for personal communication and now read: "(Tate, 2011; Eckley, 2011; all personal communication)". A co-author was removed from this list as well.

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

We added the following reference:
Pacyna, E. G., Pacyna, J. M., Sundseth, K., Munthe, J., Kindbom, K., Wilson, S., Steenhuisen, F., and Maxson, P.: Global emission of mercury to the atmosphere from anthropogenic sources in 2005 and projections to 2020. Atmos. Environ., 44, 2487-2499, doi:10.1016/j.atmosenv.2009.06.009, 2010.

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

Done.

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

We have added the units.

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 re- action 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.

Thank you we corrected the incorrect reference, including the year and DOI number

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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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