We thank both referees for their thorough review and insightful suggestions.

Reply to comments by Anonymous Referee # 1

Referee comment:
This manuscript describes a very large collection of work that includes airborne measurement and numerical modeling of atmospheric mercury. Having worked on the development of atmospheric mercury modeling myself until a few years ago, I was interested to see if necessary advances had been made in understanding the sources, transport, transformation and deposition of atmospheric mercury.
I was disheartened (but not surprised) to find that the chemical forms of atmospheric Hg(II) have still not been identified, as the authors state in the Introduction. Having not been directly involved in atmospheric mercury research for a while, I do not feel qualified to judge the merits of the newer measurement technologies used here. But I will say that no modeling assessment should be taken with confidence until we know what materials we are dealing with. The authors note that the emission and deposition of mercury were not investigated as a part of this study. I think it is fair to say that both processes remain uncertain and must be better understood before any confident assessment can be made of the origins of mercury found at any particular location or within any particular region.
Nonetheless, coordinated measurement and modeling campaigns like this one are exactly what is required to direct future research towards the most critical unanswered questions. My only criticism regarding the model sensitivity studies performed here is that bromine was the only reactant considered for adjustment. Oxidation by OH/O3 and BrO was also considered, but only at one set of highly uncertain rates. Even if one was to find a perfect balance of bromine concentration and/or reaction rate that made the simulated mercury concentrations match observations, mercury is in a constant cycle through water, air, soil and vegetation. Any adjustment to the way mercury is added to the cycle or the way it partitions between air and the other media can ruin that balance. I understand why the authors decided not to consider adjustments to sources and de- position. The complexity of the problem becomes overwhelming with all of the possible combinations. But do we really know that bromine is the only important reactant we are uncertain about? I suspect not.
The conclusions of this study rightly point to the need for improved measurement methods. Until we truly know the chemical forms of atmospheric Hg(II), simulation of the en- tire mercury cycle will remain highly speculative. But at this point we still must speculate and the type of modeling performed here is a necessary part of the overall atmospheric mercury research endeavor. Regardless of its limitations, this study provides results that are insightful and the conclusions drawn are all within the bounds of reason. I see no reason to withhold publication and would only recommend a few clarifications and that additional possibilities be mentioned where certain conclusions are drawn.

Author response:
The reviewer has rightly highlighted the significant gaps that exist in our understanding of the sources and sinks of mercury in the atmosphere, and, in particular, oxidants of elemental mercury. The NOMADSS campaign was conducted to address some of these gaps and we collected a unique dataset of simultaneous airborne measurements of total and oxidized mercury over a large region of the free troposphere. We analyze this dataset in our study to address the uncertainty in the oxidation rate of elemental mercury.

We focus our sensitivity studies mostly on the uncertainty in the concentrations of and the oxidation rates with the bromine radical, because studies by Goodsite et al. (2004) and Hynes et al. (2009) have shown oxidation by OH and O_3 to be too slow in the atmosphere. Gratz et al.

(2015) have shown, using a different model, that the OH/O$_3$ pathway alone can explain only 20% of the Hg(II) observed on NOMADSS flight RF-06. Besides, the reported oxidation rates (with OH/O$_3$ and BrO) vary by an order of magnitude or more. An analysis of all possibilities spanning the range of uncertainties in the oxidation rates with Br, OH/O$_3$ and BrO is beyond the scope of our present study, but would be most effective once the major chemical forms of oxidized mercury can been identified. Following this reviewer's suggestion, we have highlighted that definite conclusions as to the main oxidant of atmospheric mercury can only be reached once the chemical form(s) of atmospheric oxidized mercury are directly measured.

Referee comment:
Section 2.2 – Apparently the UW-DOHGS instrument can use either quartz wool or a cation exchange membrane to intercept Hg(II). Does the choice here affect the detection limit (DL) for Hg(II)? Given the problem with quartz wool releasing Hg(II) in humid conditions, it would seem that the DL would be affected. It is certainly unfortunate that 87% of the 532 observations within the boundary layer were below to DL. This is the part of atmosphere that loses Hg(II) to the surface immediately below and quantification of Hg(II) at various heights within the boundary layer would aid in our understanding of its deposition processes. Also, for the entire NOMADSS campaign, only 35% of the Hg(II) measurements were above the instruments DL. I don't recall such a problem with the DL for the older Tekran instruments. Did the discovery of the Tekran's problem with O3 interference raise the DL for that instrument? I think a lot could have been learned if the Tekran instruments had also been used.

Author response:
The detection limit of Hg(II) for UW-DOHGS is 3 times the standard deviation of the difference between the measurements in the two channels in the "same air" configuration (Ambrose et al., 2013). As such, the detection limit does not depend on the filter material. However, the cation-exchange membrane performed better than quartz wool at capturing Hg(II) in humid conditions, and we were able to make more Hg(II) measurements in the boundary layer with the cation-exchange membrane during the last five flights.

The UW-DOHGS and the Tekran 2537-1130-1135 speciation system measure oxidized mercury by two different methods. UW-DOHGS reports Hg(II) as the difference between the THg and GEM channels at a 2.5 minute measurement cycle, whereas in the Tekran system the reactive mercury collected on the KCl coated denuder is thermally desorbed and analyzed at the end of a longer measurement cycle (30 min to 6 hours). The difference in the measurement methods and the averaging time is why the detection limits of the two instruments are different. Besides, recent experimental works has shown that the Hg(II) collection efficiency of the KCl denuder method can be significantly affected by ozone and water vapor (e.g., Lyman et al., 2010; Ambrose et al., 2013; McClure et al., 2014). This issue, and slow sample resolution, limited the practicality of deploying a Tekran speciation system. We refer the referee to Section 2 of Gustin et al., (2015) for a review of the different instruments for measuring oxidized mercury.

For clarification, we will add the following to the revised manuscript:

Pg. 26845 line 5: "In comparison, the Tekran® 2537-1130-1135 speciation system uses KCl denuders to capture gas-phase oxidized mercury, which is subsequently thermally desorbed as elemental mercury for analysis (Landis et al., 2002). The measurement cycle of the Tekran® speciation system is 30 minutes or longer, compared to the 2.5 minute cycle for the UW-DOHGS."

Pg. 26846 line 6: "The Hg(II) DL is calculated using the "same air" configuration, in which the Hg(II) filter is bypassed and both analyzers sample the same air downstream of the pyrolyzer in the THg channel (Ambrose et al., 2013, 2015)"

Referee comment:
Section 2.3.4 – Regarding application of the GEOS-Chem model in a nested global- to-regional configuration, it is good that the same model was applied for both domains. There was strong evidence from the North American Mercury Model Intercomparison Study (Bullock et al., 2008, 2009) that different treatments of physics and chemistry between the global and regional models led to artifacts at the regional boundaries. Also, in this section you state that two additional sensitivity simulations were performed related to Br concentration and reaction rate. But later in section 5, two more simulations are described where Hg oxidation by OH/O3 and BrO are included. To avoid confusion, it would be good to summarize in one location all of the simulations performed.

Author response:
We agree and have added a new table in Section 2.3.4 of the revised manuscript summarizing all the sensitivity simulations.

Simulation	Oxidants	Reaction rate constants (cm^3 molecule^{-1} s^{-1})
	Main simulations	
BASE	Br (Concentrations from the GEOS-Chem full-chemistry simulation)	Hg(0) + Br: $k = 1.46\times10^{-32}\times\left(\frac{T}{298}\right)^{-1.86}\times[M]$ (Donohoue et al., 2006)
3×Br	Br (Concentrations scaled by a factor of 3 in the region bounded by 45°S and 45°N, and 750 hPa and the tropopause.)	Same as BASE
FastK	Same as BASE	Hg(0) + Br: $k = 3.6\times10^{-12}\times\left(\frac{[M]_{T,p}}{[M]_{273.15K,1atm}}\right)$ (Ariya et al., 2002)
	Supplemental simulations	
FastK+0.9BrO	Same as FastK, except BrO concentrations in the free troposphere over the northwest Atlantic Ocean were increased to 0.9 pptv only for the RF-16 simulation.	Same as FastK
BASE+OH/O$_3$	Br, OH and O$_3$ (Concentrations from the GEOS-Chem full chemistry simulation)	Hg(0)+Br: same as BASE Hg(0)+O$_3$: $k = 3.0\times10^{-20}$ (Hall, 1995) Hg(0)+OH: $k = 8.7\times10^{-14}$ (Sommar et al., 2001)
BASE+BrO	Br and BrO (Concentrations from the GEOS-Chem full chemistry simulation)	Hg(0)+Br: same as BASE Hg(0)+BrO: $k = 3.0\times10^{-14}$ (Spicer et al., 2002)

Referee comment:
Section 9 – In the conclusions, the sensitivity simulations dealing with Br radical concentration and reaction rate are discussed. However, there is no mention of the tests with OH/O3 and BrO

oxidation added. I guess I'm just uncomfortable with the focus on bromine as if it were known to be the only reactant. To put the conclusions in proper context, I think it is necessary to mention that we still don't know what the true forms of atmospheric Hg(II) are, and that additional reactions could prove to be important. As a model developer, I have probably not done my career any favors by highlighting the inadequacies of the measurements on which we base our modeling. But it sure would be nice to know what we are really trying to simulate.

Author response:
We agree and have added the following sentence in Section 9 (Pg. 26867, line 29):
"In addition to oxidation of Hg(0) by Br (BASE case), we considered the effect of including O_3 and OH as oxidants but found that the high Hg(II) concentrations observed at 5-7 km could not be reproduced. We also examined the effect of adding the Hg(0)+BrO reaction to the BASE simulation, and found that the model underestimate of Hg(II) at 5-6 km persisted. Our modeling study suggests that the NOMADSS observations are most consistent with the 3xBr simulation and the FastK simulation, however we note that the relative importance of the different oxidation pathways cannot be ascertained before the chemical forms of Hg(II) in the atmosphere have been identified."

Reply to comments by Anonymous Referee # 2

Referee comment:
This is an interesting complex paper that is suitable for ACP. It would be useful for the Hg community for the authors to provide discussion regarding the data obtained with cation exchange membrane, and the detection limit when using this method instead of the pyrolyzer. The authors should discuss whether the data was from the cation exchange membranes or pyrolyzer when discussing the flights, since use of membranes are considered by the authors to be better than the pyrolyzer due to relative humidity. It would be nice to know if the 1σ improved, and how this influenced the method detection limit. Since 2 different methods were used it is important to discuss specific data.

Author response:
For clarity, we used either quartz wool backed by a quartz-fiber filter or cation exchange membrane filters as our Hg(II) trapping medium in the GEM channel of the UW-DOHGS instrument. A pyrolyzer was used in the THg channel. (See Ambrose et al., 2015 for a detailed description of the UW-DOHGS configuration). We think the reviewer's mention of "pyrolyzer" above refers to the quartz wool-based Hg(II) traps.
The detection limit of Hg(II) for UW-DOHGS is 3 times the standard deviation of the difference between the measurements in the two channels in the "same air" configuration (Ambrose et al., 2013). As such, the detection limit does not depend on the filter material. However, the cation-exchange membrane performed better than quartz wool at capturing Hg(II) in humid conditions, and we were able to make more Hg(II) measurements in the boundary layer with the cation exchange membrane during the last five flights.

To clarify this, we have added a new table to the supplement with the type of filter used, detection limit, observed oxidized Hg concentrations, and the ratio of oxidized to total Hg observed for each flight.

Flight number	Hg(II) filter type	Hg(II) DL (pg m^{-3})	Number of Hg(II) observations[a]	Hg(II)[b] (pg m^{-3})	Hg(II) / THg[c] (%)
RF-01	Quartz wool	228	41 (0)	-	-
RF-02	Quartz wool	147	0 (0)	-	-
RF-03	Quartz wool	148	32 (11)	194 ± 31	12 ± 2
RF-04	Quartz wool	160	24 (10)	221 ± 39	15 ± 2
RF-05	Quartz wool	134	72 (2)	163 ± 13	10 ± 1
RF-06	Quartz wool	114	87 (41)	262 ± 41	20 ± 4
RF-07	Quartz wool	58	48 (29)	145 ± 43	10 ± 3
RF-08	Quartz wool	116	91 (26)	178 ± 69	11 ± 4
RF-09	Quartz wool	94	118 (108)	269 ± 85	18 ± 6
RF-10	Quartz wool	134	92 (15)	219 ± 54	15 ± 4
RF-11	Quartz wool	70	81 (25)	147 ± 63	10 ± 5
RF-12	Quartz wool	140	102 (19)	208 ± 72	15 ± 6
RF-13	Quartz wool	83	60 (13)	132 ± 24	9 ± 2
RF-14	Quartz wool	138	80 (15)	232 ± 44	17 ± 4
RF-15	Cation exchange membrane	107	77 (0)	-	-
RF-16	Cation exchange membrane	91	119 (71)	330 ± 191	23 ± 14
RF-17	Cation exchange membrane	68	127 (38)	143 ± 38	10 ± 3
RF-18	Cation exchange membrane	72	126 (69)	125 ± 36	9 ± 2
RF-19	Cation exchange membrane	116	126 (35)	154 ± 33	11 ± 2

[a] In parenthesis: number of ADL Hg(II) observations.

Referee comment:
The authors seem to focus on Hg-Br related reactions. Why do they think these are the most important focus on? It seems air traveling in the free troposphere/stratosphere could have other things to react with (i.e. Ozone) and the authors are stabbing at the chemistry to make the model fit the observations.

Author response:
As noted in our answer to referee #1, we focus our study mostly on Hg oxidation by the bromine radical, because studies by Goodsite et al. (2004) and Hynes et al. (2009) have shown oxidation by OH and O_3 to be too slow in the atmosphere. Besides, Gratz et al. (2015) have shown, using a different model, that the OH/O_3 pathway alone can explain only 20% of the Hg(II) observed on NOMADSS flight RF-06. Nonetheless, we have performed two sensitivity studies with OH/O_3 and BrO as additional oxidants, and have discussed the results in Section 5. In the revised version of the manuscript, we have strived to highlight these additional simulations.

Referee comment:
It might be useful to present the range in % GOM in air relative to TGM for both the pyrolyzer and the cation exchange membranes in some cases.

Author response:
We agree and have added a new table (see above) to the supplement with the type of filter used, detection limit, observed oxidized Hg concentrations, and the ratio of oxidized to total Hg observed for each flight.

Referee comment:
The authors might want to add the caveat that without understanding the chemical forms of GOM in the air modeling is speculative. They have no way of knowing if the form is a HgBr compound, and are essentially changing reaction mechanisms to get the rates they think are sufficient.

Author response:
We agree and have added the following sentence in Section 9 (Pg. 26867, line 29):
"In addition to oxidation of Hg(0) by Br (BASE case), we considered the effect of including O_3 and OH as oxidants but found that the high Hg(II) concentrations observed at 5-7 km could not be reproduced. We also examined the effect of adding the Hg(0)+BrO reaction to the BASE simulation, and found that the model underestimate of Hg(II) at 5-6 km persisted. Our modeling study suggests that the NOMADSS observations are most consistent with the 3xBr simulation and the FastK simulation, however we note that the relative importance of the different oxidation pathways cannot be ascertained before the chemical forms of Hg(II) in the atmosphere have been identified."

Referee comment: Pg 41 line 10 change are to were

Author response: We have made the change in the revised manuscript.

Referee comment: Pg 54 line 14 no significant figures on pg m-3 Line 15 remove The

Author response: We have made the change in the revised manuscript.

Referee comment: Pg 55 remove The.

Author response: We have made the change in the revised manuscript.

Referee comment: It there anyway to compare data collected with cation exchange membranes with that collected using pyrolozyer for a specific comparable air mass?

Author response: The quartz wool and cation exchange membrane were not used together on any of the NOMADSS flights. In laboratory tests, both filters performed identically with respect to dry air retention of $HgBr_2$ (Ambrose et al., 2015).

Referee comment: For RF 16 pg 61 were these measurements made using the cation exchange mem- branes or the pyrolyzer?

Author response: We have reported the type of filter used on RF-16 (Pg. 61 Line 11) and also for RF-06 (Pg. 59, line 12) and RF-09 (Pg. 60, line 9).

Referee comment: For Table 3. For these data what happens if you use the cation exchange membrane data only for the different categories.

Author response:
Table 3 for data from RF-15 to RF-19 (flights with cation exchange membrane) is presented below. The highest concentrations were sill associated with the "low RH/low CO" air masses. The overall comparison between the observations and the three model simulations is similar to that in Table 3 (Table 4 in the revised manuscript).

	All observations	"low RH/low CO"	"low RH/high CO"	"high RH/low CO"	"high RH/high CO"
			Observed Hg(II) pg m^{-3}		
All	99 ± 119	320 ± 206	125 ± 41	152 ± 154	42 ± 31
(ADL)	200 ± 145	336 ± 202	142 ± 34	260 ± 159	109 ± 30
			BASE model Hg(II) pg m^{-3}		
All	32 ± 26	52 ± 34	58 ± 23	10 ± 12	23 ± 15
(ADL)	44 ± 24	49 ± 32	53 ± 13	11 ± 10	43 ± 17
(BDL)	26 ± 24	97 ± 32	73 ± 35	8 ± 14	21 ± 13
			3xBr model Hg(II) pg m^{-3}		
All	31 ± 32	70 ± 42	55 ± 38	10 ± 13	18 ± 15
(ADL)	43 ± 30	67 ± 40	45 ± 21	12 ± 10	36 ± 15
(BDL)	23 ± 30	121 ± 38	83 ± 58	8 ± 14	16 ± 14
			FastK model Hg(II) pg m^{-3}		
All	52 ± 60	100 ± 66	99 ± 73	8 ± 12	33 ± 36
(ADL)	79 ± 55	94 ± 60	90 ± 47	12 ± 16	92 ± 48
(BDL)	36 ± 55	205 ± 90	122 ± 116	5 ± 3	27 ± 28

Referee comment: In the figure captions the authors should describe the symbols for color and greyscale.

Author response: The figures are best viewed in color. We have added to the figure captions a legend of the line and symbol colors.

Referee comment: Figure 7 Some of the air appears to have moved in the boundary layer across S Cali- fornia could this influence your measurements at higher elevation? Same question for Figure 6

Author response: One of the backtrajectories for RF-09 (Figure 7) indeed moved through the boundary layer over southern California. Considering that all other backtrajectories from nearby locations were above an altitude of 5km, we attribute this to uncertainties in backtrajectory modeling. For RF-06 (Figure 6) all backtrajectories remained above an altitude of 5km.

Referee comment: For Figure 2 the authors should make the measurements made with the cation ex- change membranes a different symbol.

Author response: We have added different symbol and color for the Hg(II) measurements made using the cation exchange membrane.

References

Ambrose, J. L., Lyman, S. N., Huang, J., Gustin, M. S., and Jaffe, D. A.: Fast time resolution ox- idized mercury measurements during the Reno Atmospheric Mercury Intercomparison Experiment (RAMIX), Environ. Sci. Technol., 47, 7285–7294, doi:10.1021/es303916v, 2013.

Ambrose, J. L., Gratz, L. E., Jaffe, D. A., Campos, T., Flocke, F. M., Knapp, D. J., Stechman, D. M., Stell, M., Weinheimer, A., Cantrell, C., and Mauldin, R. L.: Mercury emission ratios from coal- fired power plants in the southeastern U.S. during NOMADSS, Environ. Sci. Technol., 49, 10389- – 10397,doi:10.1021/acs.est.5b01755, 2015.

Ariya, P. A., Khalizov, A., and Gidas, A.: Reactions of gaseous mercury with atomic and molecular halogens: kinetics, product studies, and atmospheric implications, J. Phys. Chem. A, 106, 7310– 7320, doi:10.1021/jp020719o, 2002.

Donohoue, D. L., Bauer, D., Cossairt, B., and Hynes, A. J.: Temperature and pressure depen- dent rate coefficients for the reaction of Hg with Br and the reaction of Br with Br: a pulsed laser photolysis-pulsed laser induced fluorescence study, J. Phys. Chem. A, 110, 6623–6632, doi:10.1021/jp054688j, 2006.

Goodsite, M. E., Plane, J., and Skov, H.: A theoretical study of the oxidation of Hg0 to HgBr2 in the troposphere, Environ. Sci. Technol., 38, 1772–1776, doi:10.1021/es034680s, 2004.

Gratz, L. E., Ambrose, J. L., Jaffe, D. A., Shah, V., Jaeglé, L., Stutz, J., Festa, J., Spolaor, M., Tsai, C., Selin, N. E., Song, S., Zhou, X., Weinheimer, A. J., Knapp, D. J., Montzka, D. D., Flocke, F. M., Campos, T. L., Apel, E., Hornbrook, R., Blake, N. J., Hall, S., Tyndall, G. S., Reeves, M., Stechman, D., and Stell, M.: Oxidation of mercury by bromine in the subtropical Pacific free troposphere, Geophys. Res. Lett., doi:10.1002/2015GL066645, 2015a

Gustin, M. S., Amos, H. M., Huang, J., Miller, M. B., and Heidecorn, K.: Measuring and modeling mercury in the atmosphere: a critical review, Atmos. Chem. Phys., doi:10.5194/acp-15-5697-2015, 2015.

Hall, B.: The gas phase oxidation of elemental mercury by ozone, Water Air Soil Poll., 80, 301–315, doi:10.1007/bf01189680, 1995.

Hynes, A. J., Donohoue, D. L., Goodsite, M. E., and Hedgecock, I. M.: Our current understanding of major chemical and physical processes affecting mercury dynamics in the atmosphere and at the air-water/terrestrial interfaces, in: Mercury Fate and Transport in the Global Atmosphere, edited by: Mason, R.

and Pirrone, N., Springer Science + Business Media, New York, NY, USA, 427–457, doi:10.1007/978-0-387-93958-2_14, 2009.

Landis, M. S., Stevens, R. K., Schaedlich, F., and Prestbo, E. M.: Development and characterization of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air, Environ. Sci. Technol., 36, 3000–3009, doi:10.1021/es015887t, 2002.

Lyman, S. N., Jaffe, D. A., and Gustin, M. S.: Release of mercury halides from KCl denuders in the presence of ozone, Atmos. Chem. Phys., 10, 8197–8204, doi:10.5194/acp-10-8197-2010, 2010.

McClure, C. D., Jaffe, D. A., and Edgerton, E. S.: Evaluation of the KCl Denuder method for gaseous oxidized mercury using HgBr2 at an in-service AMNet site, Environ. Sci. Technol., 48, 11437– 11444, doi:10.1021/es502545k, 2014.

Sommar, J., Gårdfeldt, K., Strömberg, D., and Feng, X.: A kinetic study of the gas-phase re- action between the hydroxyl radical and atomic mercury, Atmos. Environ., 35, 3049–3054, doi:10.1016/s1352-2310(01)00108-x, 2001

Spicer, C., Satola, J., Abbgy, A., Plastridge, R., and Cowen, K.: Kinetics of Gas-Phase Elemental Mercury Reactions with Halogen Species, Ozone, and Nitrate Radical under Atmospheric Conditions, Final report to Florida Department of Environmental Protection, 2002.