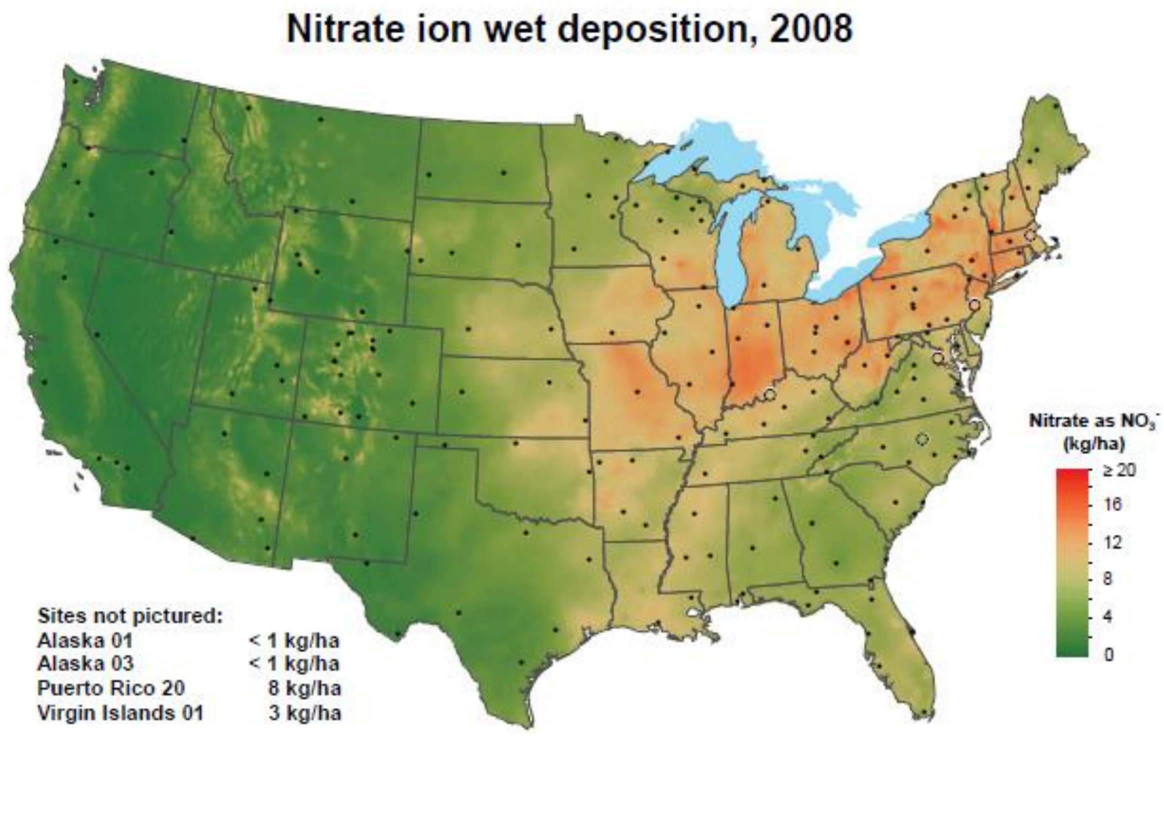
General comment of Referee #3

This paper uses thunderstorm simulations, varying properties of thunderstorms consistent with the Southeast and Northeast U.S., in an attempt to explain the differences in Hg deposition between the regions. The model analyses are useful, explained thoroughly, and well-planned. However, the paper is essentially a model parameter space exploration for soluble tracer scavenging, and the conclusions are phrased such that they apply to the real world. Thus the authors seem to be overreaching in the conclusions and general applicability of this study. In general, without comparison to data (and with no published paper on data to compare to numerically) it is unclear why this study should be about mercury at all. It is essentially asking how a soluble tracer is scavenged due to thunderstorm properties in simulations. This sort of model parameter exploration is useful, but it is a bit dangerous to apply this to a specific tracer and deposition scenario without thorough data analysis. I would suggest that the authors reframe the paper to make clear exactly what they can do, paying attention to previous work on tracer scavenging (e.g. nitric acid) which might help to validate revised conclusions that are circumscribed to apply only to model behavior and not specifically to mercury in the environment.

Our response:

Our primary goal is to understand processes that could explain high mercury wet deposition that is observed in the Southeast US, especially along the Gulf Coast and Puerto Rico, and is disproportionately higher than emissions or concentrations in the boundary layer in this region. US mercury emissions peak in the Ohio River Valley and northeast, but wet deposition in this region is generally lower than along the Southeast. By contrast, nitrate and sulfate deposition occurs over emission regions or slightly downwind. Thus, while we agree that additional observational and modeling analysis of HNO_3 *and nitrate concentrations and deposition would be valuable, these species are not direct analogues for mercury. Because of the human and environmental health consequences of mercury exposure, we believe our study of mercury deposition does not need additional analysis of nitrate. We apologize that these differences between mercury and nitrate deposition and reasons for excluding nitrate (and sulfate) from our analysis were not clear in our initial manuscript. We have clarified these points in the introduction and conclusion.*



The scope of the present study is framed to examine the viability of the following hypotheses: 1) Deep convection is more efficient at removing atmospheric mercury since they access and process mercury from a deeper layer of the atmospheric column; 2) Efficiency of mercury removal by convective storms is dependent on thunderstorm morphology and thus environmental characteristics.

High-altitude observations of atmospheric mercury are indeed limited, as the reviewer says. However, aircraft observations in many locations [Sillman et al., 2007; Talbot et al., 2008; Slemr et al. 2009; Lyman and Jaffe, 2012], including Florida [Sillman et al. 2007], have established that Hg(II) mixing ratios generally increase in the middle and upper troposphere. The GEOS-Chem model reproduces these observed vertical gradients in the troposphere, including their changes with latitude and season [Holmes et al. 2010], which justifies using the seasonal mean concentrations from GEOS-Chem as an initial condition for the RAMS model. While the limited observations prevent us from comparing the RAMS model results against specific individual rain events, we instead we seek to explain broad regional differences and statistical differences between storm types. Our modeling results will further be tested by the upcoming Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks (NOMADSS) field aircraft experiment, which will provide extensive vertical profiles and horizontal surveys of Hg(II) and associated trace gases over the over the East and Southeast US. This field experiment was designed to evaluate the sources and processes impacting mercury wet deposition, among other goals. Thus, our results and predictions are testable with current technology and we expect that our mechanistic understanding of scavenging in rain storms, developed through idealized simulations, will be helpful in interpreting the upcoming field measurements. In the longer term, we hope that cloud microphysical measurements and hydrometeor sampling, using the NSF thunderstorm penetrating aircraft (facility under development) could be used to characterize vertical profiles of mercury in hydrometeors which can be related to thunderstorm morphology. We have modified the manuscript to include the above discussion.

Possibilities for testing the hypotheses are discussed in the discussion section of the manuscript. Specifically:
"*It is difficult to confirm this hypothesis using existing databases, however, it will be tested during the upcoming Nitrogen, Oxidants, Mercury and Aerosol Distributions, Sources and Sinks (NOMADSS) field aircraft experiment, which plans to evaluate mercury wet deposition, among other goals, through extensive vertical profiles and horizontal surveys of Hg(II) and associated trace gases over the over the East and Southeast US." (Section 4)*

We have rephrased the manuscript to address the reviewer's concern regarding extending the results from idealized numerical modeling experiments to real world.

<u>Specific comments and our responses:</u>

Holmes et al. 2010b: this citation is to a conference presentation. It suggests that there is data to support this contention, which has not yet been published as a peer-reviewed paper. Given the authors this paper overlap, why have some of this data not been included?

A manuscript based on this publication will be submitted to a peer-reviewed journal during summer 2013. In the meantime, a digital copy of the conference presentation is available online: http://acmg.seas.harvard.edu/presentations/pdf/cdh/Holmes_Goldschmidt2010.pdf.

p 3578: the actions of thunderstorms on other trace species scavenging could be better summarized. How does solubility play a role? Which species might be similar to mercury, and why? How well do these models reproduce data? Given this, why is the application to mercury novel (i.e. in a model, mercury is going to act just like any other species of similar solubility :::right?)

Nitric acid is probably the best available analogue of Hg(II), as both are water soluble, semivolatile and found in both gas and aerosol form, but there are important differences. We have significantly expanded our discussion of what we learn from past studies of nitric acid and other gases in the introduction, and also clarified how mercury behaves differently:

"Past studies of other trace gases and aerosols in convective clouds have found that their transport and scavenging depends strongly on their solubility. Highly soluble gases, like HNO_3 and GOM, are efficiently scavenged into cloud droplets and rain (Mari et al. 2000; Barth et al. 2001; Yin et al. 2001), while low-solubility gases, such as CO and O_3, can be transported from the boundary layer to the upper troposphere in convective updrafts (Dickerson et al. 1987; Cotton et al. 1995; Halland et al. 2009). In the frozen upper portions of deep convective clouds, the scavenging and removal of soluble gas also depends on whether dissolved gas stays in solution when liquid drops freeze onto hail or graupel, as HNO_3 does (Barth et al, 2001; 2007; Yin et al. 2001). GOM observations in high-altitude clouds are not available, but surface observations of GOM during riming and snowfall conditions suggest that dissolved GOM is also retained during freezing, but not scavenged from gas by ice (Douglas et al. 2008; Johnson et al. 2008; Sigler et al. 2009). Particle-bound mercury is found on polluted urban, sulfate and sea salt aerosols (Murphy et al. 2006; Feddersen et al. 2012) and thus behaves similarly to other hydrophilic aerosols inside clouds. These hydrophilic aerosols partition into cloud water via nucleation or impaction scavenging and are thus scavenged with similarly high efficiency to HNO_3 (Murakami et al. 1983; Jensen and Charlson 1985; Gillani et al. 1995). Washout by rain and snow below clouds further enhances wet deposition of both soluble gases and aerosols (Levine and Schwartz 1982; Feng et al. 2007; 2009). Prior studies also show the viability of utilizing cloud-resolving models in understanding processes related to removal and transport of trace species by convective storms (Barth et al., 2007; Halland et al., 2009)."

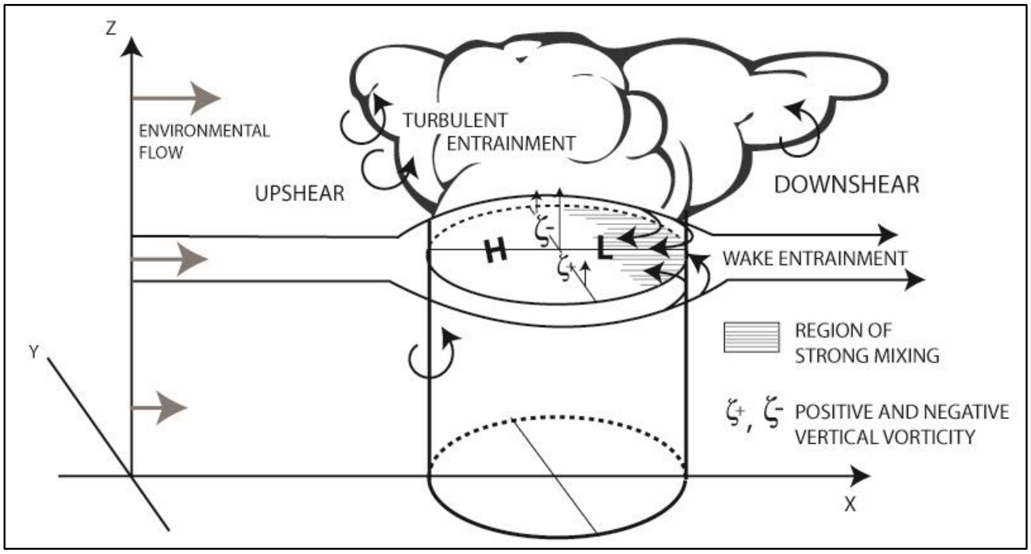
"Despite the similar solubility and microphysical interactions with convective clouds described above, oxidized mercury and HNO_3 exhibit important environmental differences that justify our specific focus on mercury: mercury emissions and wet deposition are not collocated, unlike nitrogen and sulfur; and oxidized mercury concentrations are commonly higher in the upper troposphere than in the boundary layer, unlike most other pollutants. "

p 3579: "meteorological controls on cloud dynamics and microphysics likely explain part of the regional enhancement of mercury deposition in the Southeast". This is an ambitious conclusion and I don't think it is supported in this paper.

Reworded as: "meteorological controls on cloud dynamics and microphysics is a factor that need to be considered in explaining the regional enhancement of mercury deposition in the Southeast."

Section 2.1: A figure might be helpful to explain the different processes of mixing in thunderstorms. I suspect many of the readers of this paper would be mercury and not thunderstorm experts, and this discussion is a bit dense and hard to follow.

A schematic summarizing the processes have been added to the manuscript.



p 3580: Have any previous studies looked at scavenging using these parameter spaces? Again, mercury in model-world is not particularly unique. Does or should this apply to other deposited species?

Yin et al. (2001), examined scavenging and redistribution of soluble gases from the boundary layer by convective clouds. They examined cloud formation in sheared and unsheared environment and used a generic trace species and varied the solubility by adjusting the Henry's law constant. However, the focus of the study was transport and removal of gases from the PBL. We agree with the reviewer that the study could be conducted from a more generalized framework. However, note that the relative proportions on the trace gas within the PBL and upper atmosphere is a factor. We wanted to add the additional constraint of estimates of oxidized mercury from numerical model simulations.

p 3581: If nitric acid was previously simulated, and mercury is exactly the same, what else do we know about nitric acid? One could argue then that if nitric acid were previously evaluated, we know exactly what the Hg behaviour will be.

As discussed above, deposition patterns of nitrate and mercury would suggest that they are not analogous to each other.

p 3582: If RAMS only reproduces half the observed variability, and only where RAMS simulates precipitation amounts, then what impact does this have on results? Does this mean that RAMS is getting the GOM concentrations wrong, or the fraction of GOM scavenged? The latter seems to be a bigger potential problem in interpreting these results.

Our intent here is to show that the performance of parameterization used in this study is comparable to those in other models used for mercury research. The errors are potentially related to three-dimensional distribution of oxidized mercury. Note that prior studies discussed are regional modeling studies, whose results are dependent on the initial and lateral boundary conditions. Also, note some of oxidation pathways for mercury used in the models are still being debated. These are some of the considerations to choosing the idealized model experiment design to focus on physical process.

p 3582 line 20-25: It would be useful here to cite the uncertainties in GOM measurements (Gustin et al., ES&T 2012) and discuss what influence an underestimate of GOM surface concentrations might have on results

Note that we are not utilizing observations, but profiles from GEOSChem simulations. In the text it is noted that GEOSChem values are similar to observations.

p 3583: GOM/HgP – some more discussion about how the processes of GOM and HgP scavenging would be expected to differ would be helpful, here or in the methods section above. Also, what are the timescales are for GOM/HgP conversion and how would they compare to the timescales in the thunderstorm simulations?

Time scales for oxidation of Hg(0) and reduction of GOM and HgP are much longer than the 2-h simulations conducted here, so chemistry is neglected. We now state this assumption in Sect. 2.2:

"Chemical oxidation and reduction are also neglected because reactions in both gas and aqueous phases have time scales much longer than the duration of our simulations (Lin and Pehkonen 1999; Subir et al. 2011)."

We added a paragraph to the introduction describing how GOM and HgP scavenging relate to other species that have been studied previously. Please see the extensive quotation in our response to Reviewer 1.

p 3584: the nomenclature tutorial is potentially useful, but I would suggest that the authors find a way to simplify the discussion so that the reader doesn't necessarily have to remember this throughout.

We agree with the reviewer, but the authors experimented with multiple nomenclatures and the one used in the manuscript is the best terminology that we could devise that balances between the discussion being too awkward and cryptic.

p 3586 line 6: is "PW" meant here?

"PM" has been modified to "PW" as indicated.

p 3587 line 12-15: the idea that thunderstorms can mix the high-altitude reservoir of mercury downwards and make it more susceptible to scavenging later is an interesting hypothesis that is easily testable by measurements. What evidence might exist to support it? There are studies of event-based precipitation for mercury, and it might be useful to look into the record of published studies to see if there is any suggestion of this effect in data that has previously been overlooked.

We are not aware of any such studies to date. One problem is that a good, event based deposition data is not available for mercury.

Figure 9: this doesn't really look statistically significant. What tests were done to ensure this? What is the quantitative comparison?

Differences are statistically significant (95% confidence, 2 sided t-test) for majority of the precipitation range bins (17 out of 25). Of the rest, 6 have differences that are statistically significant at 90% confidence level. Details are show below.

Precipitation range (mm)	Confidence levels: 95%, 90%, <90%
0-1	
1-2	
2-3	
3-4	
4-5	

5-6	
6-7	
7-8	
8-9	
9-10	
10-11	
11-12	
12-13	
13-14	
14-15	
15-16	
16-17	
17-18	
18-19	
19-20	
20-21	
21-22	
22-23	
23-24	
24-25	

p 3590 line 14-15: "This study shows that meteorological conditions in the Southeast US favor more frequent thunderstorms than in the Northeast" – this surely has been discussed before in the literature, and can't be new

The sentence has been modified as follows:

"Thunderstorms occur more frequently in the Southeast US compared to the Northeast. In addition to higher frequency of occurrence of thunderstorms, this study suggests that meteorological conditions in the Southeast favor the formation of thunderstorms with microphysical and dynamic structures that enhance wet deposition removal of GOM and HgP."

Line 18-24: again, this is not a published paper. Here, we have no quantitative information to support this finding. The key to this is "large part" – I don't see evidence for this in Fig 9

For Figure 11(old Fig 9), the mean ratio of concentration between southern and northern sites for all the rainfall bins is ~1.53. We added in Sec 3.5 *the quantitative information of the data used to make the figure: "*For majority of the bins, the mean difference is statistically significant at 95% confidence level. The mean ratio of concentrations between the southern and northern sites for all the rainfall bins in

Figure 11 is ~1.53. " *We also omitted "large," so the text says "part of the Southeast US wet deposition enhancement can be explained…"*

Conclusions: the language in the three main conclusions make it seem like the conclusions apply to the real world rather than model-world, which they don't. I'd suggest rephrasing.

Conclusions have been modified to make clear that the statements pertain to idealized model simulations.