**Response to referee # 1 comments**
We thank the referee for their thorough review and helpful suggestions. The reviewer's comments (in black) and our responses follow.

**General comments**
This paper investigates – using the GEOS-Chem global chemical transport model - how surface deposition of divalent mercury species (Hg(II)) is influenced by Hg(II) production at different atmospheric heights. The authors show that surface deposition is dominated by production in the upper and middle troposphere and highlight the large role of subtropical anticyclones as a global reservoir of Hg(II). This study also shows that regional decreases in anthropogenic mercury emissions will not lead to a proportional regional decrease in wet deposition. The paper is organized clearly, easy to follow, well written, and will make a valuable contribution to the literature. However, I find the evaluation of the model with observations insufficient and not up to date. This paper will be suitable for publication after the authors address the following issues.

Following the reviewer's recommendation, we have significantly expanded our model-observation comparison to include sites outside the MDN, EMEP and AMNet networks.
*Hg(II) concentrations:* We have added comparisons with 14 sites measuring surface Hg(II) concentrations. These include stations from the worldwide GMOS network and stations in China, Taiwan, Germany, and Canada.
*Hg wet deposition:* We have added comparisons with 14 sites measuring Hg wet deposition. These include stations from the worldwide GMOS network and stations in China, Taiwan and Puerto Rico, US.
*High-elevation sites:* The 14 additional Hg(II) surface sites include 5 high-elevation sites (elevation > 1500m).
*Aircraft-based observations:* We have also added model-measurement comparison for 2 aircraft campaigns: the campaign over Tullahoma, TN and NOMADSS.

These comparisons are shown in Figs. S1, S2 and S3 that will be included in the supplement to the manuscript and are also displayed at the end of this document. A description of these measurements that will be included in the manuscript is below.
"Ground-based measurements of Hg wet deposition and Hg(II) surface concentration have been made as part of the Global Mercury Observations System (GMOS) network (Angot et al., 2014; Wängberg et al., 2016; Sprovieri et al., 2016, 2017; Travnikov et al., 2017), and at sites in Europe (Weigelt et al., 2013), Canada, and East Asia (Sheu et al., 2010; Sheu and Lin, 2013; Fu et al., 2015, 2016). We use the 2013-2014 measurements wherever available, but use all sites with one year or more of observations. We exclude sites in China classified as urban, because of proximity to large Hg(II) sources. We include 14 sites with annual-mean measurements of Hg wet deposition (Table S1), and 14 sites with annual-mean measurements of surface Hg(II) (Table S2)."
"We also include aircraft-based measurements of Hg(II) carried out near Tullahoma, Tennessee, USA from August 2012 to June 2013 (Brooks et al., 2014)."

**Major comments: Comparison with observations**

The two-year simulation (2012-2014) is evaluated with ground-based observations of Hg(II) concentrations and wet deposition. Section 2.2.3 concludes that the simulation reproduces quite well the spatial distribution and seasonal cycle of Hg(II) and wet de- position over the US but displays a 46% underestimate of wet deposition observed at EMEP sites. So what? How might this uncertainty affect the distribution of the tagged Hg(II) and ultimately their contributions to wet/dry distribution fluxes in different regions of the world?

It suggests that the production of Hg(II) in the free-troposphere over Europe is underestimated which would lead to an underestimate in the contribution of UT and MT tracers.
We have added the following paragraph to Sect. 3.2 in response to this and your other similar question below.
"In Sect. 2.2.3 we saw that the model overestimated observed wet deposition of Hg(II) over southeast U.S. during winter and spring. As a result, our estimate of the contribution of UT and MT tracers is likely an overestimate for this region and season. From our model evaluation, we had also concluded that our free-tropospheric Hg(II) production was too slow over Europe and, possibly, other regions north of 45°N. This suggests an underestimate of the concentrations of modeled UT and MT tracers in these regions."

Additionally, the model is evaluated over the US and Europe only, using ground-based observations. The authors should consider using recent data from ground-based sites, aircraft campaigns and high-altitude sites to evaluate the model in different regions of the world and at different heights. To me, evaluating a model used to investigate the global distribution of Hg(II) at different heights a) over the US only, and b) at ground level only is not convincing enough.
To address this concern, we have significantly expanded our model-observation comparison to include 14 additional stations measuring Hg wet deposition, 14 additional stations measuring Hg(II) surface concentrations, and 2 aircraft-based campaigns (the campaign over Tullahoma, TN and NOMADSS). Tables S1 and S2, and Figs. S1, S2 and S3 displayed at the end of the document will be included in the supplement to the manuscript.

**1. Ground-based observations**

*1.1 Hg(II) concentrations* The authors use the 2009-2012 AMNet observations to evaluate the model over the US. I understand that the authors use data that are publicly available. However, evaluating 2013-2014 model outputs with 2009-2012 observations is not satisfying unless inter-annual variability is discussed at some point.
Good point. From the 4-year (2013-16) "dry-Hg(II)" simulation, we find that the variation in the modeled 2-year average Hg(II) concentrations at the AMNet sites vary by ± 30%.
We have added the following to Sect 2.3.3 "Comparing observations and simulations for different time periods adds additional uncertainty due to inter-annual variations. From four years of model simulation (2013-16), we estimate this uncertainty at ±30%."

In Europe, the authors highlight a discrepancy between modeled/observed wet deposition and suggest that this could "indicate an underestimate in the modeled Hg(II) concentrations over the region". The authors could easily check that since Hg(II) data are available for 2013-2014 (Sprovieri et al., 2016) at Iskrba (Slovenia), Longobucco (Italy), and Rao (Sweden – see also Wängberg et al., 2016). Additionally, how well can the model reproduce Hg(II) concentrations elsewhere? Still according to Sprovieri et al. (2016), Hg(II) data are available around the world for years 2013-2014 at Amsterdam Island (see also Angot et al., 2014), Bariloche (Argentina), Cape Hedo (Japan), Manaus (Brazil), and Minamata (Japan).
We have expanded our model-observation comparison to include 14 additional stations measuring Hg(II) surface concentration, which include GMOS sites for which Hg(II) observations have been published. See Tables S2 and Fig. S2. These comparisons show a reasonable model performance (NMB:-9%, FAC2:50%). Modeled surface Hg(II) concentrations at Råö and Longobucco are in good agreement with the observations (Fig. S2). However, it should be noted that an underestimate in Hg wet deposition reflects an underestimate in the abundance of Hg(II) in the precipitating column which is 1-5 km high typically, and may not be detected from the surface Hg(II) measurements. Comparison with wet deposition measurements at Iskrba and Mace Head also show a model underestimate of 25% in Hg concentration in wet deposition.

*1.2 Wet deposition* Same as above, why don't the authors use recent wet deposition data collected around the world to evaluate the model in different regions of the world? A recent paper (Sprovieri et al., 2017) present seasonal and annual variations of Hg wet deposition and concentration collected at 17 ground-based sites in the Northern and Southern Hemispheres as part of the GMOS project.
We have significantly expanded our model-observation comparison to include 14 additional stations measuring Hg wet deposition, which include GMOS sites for which Hg wet deposition measurements have been published in Sprovieri et al. (2017). See Tables S1 and Fig. S1. The model reproduces the wet deposition observations with a NMB of 52% and FAC2 of 64%, and the VWM concentrations with a NMB of 48% and FAC2 of 78%.

Additionally, page 9, lines 2-4: "Over the southeast US, the modeled VWM concentrations are higher than observations during winter and spring, suggesting a model overestimate in atmospheric Hg(II) concentrations in that region or an overestimate in the amount of Hg(II) scavenged by precipitation". If the model overestimates the amount of Hg(II) scavenged by precipitation, what is the possible influence on results presented in section 3.2, i.e. on the modeled contribution of MT and UT? I would like to see a discussion on how results presented in section 2.2.3 (comparison of modeled and measured Hg(II)) affect results presented thereafter.
See our response to a similar question above.

**2. Vertical profiles**
The authors should consider using recent data from aircraft campaigns and high- elevation sites to evaluate the model in different regions of the world. How well can the model reproduce these observations (see for instance Bieser et al., 2016).
*2.1 Aircraft campaigns* An evaluation of the model is done, over the US, in a previous paper (Shah et al., 2016) during the NOMADSS campaign. The authors could refer to this paper here. Within the GMOS project, vertical profiles were taken on board research aircraft in August 2013 in background air over different locations in Slovenia and Germany (Weigelt et al., 2016). Additionally, Hg(0), Hg(II), and Hg(p) profiles were collected on 28 flights between August 2012 and July 2013 (1000 to 6000 m, Brooks et al., 2014). Finally, the authors could use data from the intercontinental flights between Germany and North/South America under the umbrella of the CARABIC project (Slemr et al., 2014, 2016).
We have expanded our model-observation comparison to include two aircraft-based campaigns (NOMADSS and the one of over Tullahoma, TN). The model captures the Hg(II) vertical profiles observed during these two aircraft campaigns. See Fig. S3. For observations over Tullahoma, TN we find the model NMB of 14% and FAC2 of 52%. For observations above 4 km in the NOMADSS campaign, the model NMB is -29% and FAC2 is 53%.

*2.2 High-elevation ground sites* The authors could use data collected at various high- elevation sites such as Mt. Walinguan (China), Mt. Ailao (China), Kodaicanal (India), Everest/K2 (Nepal) and Col Margherita (Italy) (Sprovieri et al., 2016) to evaluate Hg(0) and/or Hg(II) concentrations. Note that mercury data discussed in this paper are available upon request at: http://sdi.iia.cnr.it/geoint/publicpage/GMOS/gmos.historical.zul.
Five of the 14 additional Hg(II) sites are at high-elevations. See Table S2 and Fig. S2. We find that in general the model captures the relatively higher concentrations observed at these high-elevation sites.

Other comments: Model sensitivity to oxidation chemistry and emission speciation
The authors perform an additional one-year sensitivity simulation using the original GEOS-Chem Br concentrations instead of the 3 times Br concentrations in the base simulation. Given that

updates by Schmidt et al. (2016) have resulted in an improved agreement with satellite and in situ observation of BrO, I wonder why the authors did not perform an additional simulation using these updated fields. Page 9, line 17: "suggesting that the modeled oxidation rate is too slow over this region". Using Br fields from Schmidt et al. (2016), i.e., a factor 2.3 increase in free tropospheric Br concentrations north of 45N might lead to a better agreement between modeled/observed data over Europe.
The bromine fields from Schmidt et al. (2016) have just recently been incorporated into the GEOS-Chem Hg simulation (Horowitz et al., 2017). Therefore, we weren't able to use those fields in our simulations.

Page 12, lines 24-33. How do these results compare to the results by Bieser et al. (2016)? According to the latter, "high RM concentrations in the UT could be reproduced by oxidation by Br while elevated concentrations in the LT were better reproduced by OH and ozone". Does it sound feasible and adequate to implement two different mechanisms in GEOS-Chem depending on the altitude?
Bieser et al. (2017) did not investigate the vertical profile with the OH/O3 oxidation mechanism in GEOS-Chem. They also show that the inter-model variation in the simulated Hg(II) concentrations is larger than the observed variation in the Hg(II) vertical profiles, thus not providing much support for considering an altitude-dependent mechanism in GEOS-Chem. The results of our simulation, using Br chemistry, show good agreement with the aircraft-based observations over Tullahoma, TN (Fig. S3 panel a) and with surface observations at AMNet sites (Fig. 3)

**Line by line comments**
Section 2.2: Which version of GEOS-Chem do you use?
It is v9-02. We have added the following sentence to the manuscript in Sect. 2.2: "We use GEOS-Chem v9-02 (http://acmg.seas.harvard.edu/geos/)."

Page 8, lines 18-20: "The model reproduces the observed seasonal variations in the central and northeast regions, but underestimates the summer deposition fluxes in the southeast because of a factor of 2 underestimate in summertime precipitation by the GEOS-FP meteorological fields". Is that also the case for other (GEOS-5, MERRA) meteorological fields? If not, why don't the authors use them? MERRA meteorological data are available for 2013-2014.
The MERRA precipitation over the SE US during summer is closer to observations. Although it is not possible for us to redo the model setup and simulations with a new meteorological field for this study, it is something we can investigate fully in the GEOS-Chem Hg simulation in the future.

Page 9, line 2: there is a typo "Over the southeast US, tmodeled (. . .)".
Fixed the typo.

Page 9, lines 10-12: "(. . .) likely because the upward scaling of the Br concentrations in our simulation did not extend north of 45N and covered only parts of Southern Europe". Could you please add the latitude on the various figures?
We have added latitude and longitude grids to maps in Figures 1, 2, 3, 5, and 7.

Figure 4e: I am just curious; how can you explain the elevated contribution of MT tracer over the Antarctic continent?
The high elevation of the Antarctic (~2500 m) means that much of the surface is higher than the upper boundary of the lower troposphere (defined here as region below 750 hPa), thus we see elevated contribution from the MT tracer.

Figure 10b: Why is NY95 excluded from the regression calculation? I agree that it is an outlier here, but the question is why? According to info found on AMNet website (and not in the paper. . .), the collection of Hg(II) concentrations stopped in November 2009 at this site. This suggests that the authors only have a few months of data at this site, and not data for the entire 2009-2012 period. That kind of information would be useful (in supplementary?) in order to get a better insight on which observation data are used to evaluate the model.

We agree, and have added two tables in the supplement (Tables S1 and S2, also included at the end of the document) with the details of sites, including their measurement time periods, used in the paper.

The NY95 site was operational from 2009 to 2012. We can't tell why it is an outlier. It is possible that we are missing a Hg(II) emission source close to the site. However, we would like to refer to Gay et al. (2013), page 11345, for a discussion on the GOM and PBM variations at the AMNet sites.

**Response to referee # 2 comments**

We thank the referee for their thorough review and helpful suggestions. The reviewer's comments (in black) and our responses follow.

The manuscript provides a thorough diagnosis of Hg chemical processing in the lower, middle, and upper troposphere within the GEOS-Chem model. The results are an incremental advance over past work in establishing the important role of oxidation in the middle and upper troposphere. The main advance over past work is in diagnosing the subtropical anticyclones as conduits for supplying Hg(II) to the lower troposphere.

I concur with the other reviewer who commented on the lack of model comparisons to aircraft data and observations in the subtropics, since that is where much of the action in the model is happening. The authors' earlier work with aircraft could be included in discussion (Shah et al., 2016). It would also be very helpful to compare the model to surface observations in the subtropics, where they are available (e.g. Sheu et al., 2010).

We have significantly expanded our model-observation comparison to include 14 additional stations measuring Hg wet deposition, 14 additional stations measuring Hg(II) surface concentrations, some of which are in the subtropics, and two-aircraft based campaigns where Hg(II) was measured (the campaign over Tullahoma, TN and NOMADSS). Tables S1 and S2, and Figs. S1, S2 and S3 at the end of the document will be included in the supplement to the manuscript.

Likewise, I agree with the reviewer who pointed out that simulations for 2013-2014 are compared with AMNet observations for 2009-2012 without discussion of interannual variability.

Good point. From the 4-year (2013-16) "dry-Hg(II)" simulation, we find that the variation in the modeled 2-year average Hg(II) concentrations at the AMNet sites vary by ± 30%.

We have added the following to Sect 2.3.3 "Comparing observations and simulations for different time periods adds additional uncertainty due to inter-annual variations. From four years of model simulation (2013-16), we estimate this uncertainty at ±30%."

The title is too sweeping. It implies that Hg(II) emissions and Hg(II) produced in the lower troposphere are minor sources of Hg(II) deposition. While that may be true on a global average basis (Table 1), Figure 5 shows that Hg(II) emissions contribute more than 50% of deposition in major industrial regions and lower troposphere Hg(II) dominates in polar regions. The 2x2.5 degree resolution of the model also likely dilutes the importance of Hg(II) emissions near large sources. These caveats are critical for policymakers, but are not reflected in the title or mentioned in the abstract.

Excellent point. We have revised the title such that the importance of emissions and production in the lower troposphere is not diminished, and the role of the subtropics is highlighted. The new title is: "Subtropical subsidence and surface deposition of oxidized mercury produced in the free troposphere."

We have also clarified the limitations of the coarse resolution of the global model by adding to the abstract the following (underlined text added):

"…whereas 26–66% of surface Hg(II) over the eastern U.S., Europe, East Asia, and South Asia is directly emitted. The influence of directly emitted Hg(II) near emissions sources is likely higher, but cannot be quantified by our coarse-resolution global model(2° latitude × 2.5° longitude). Over the oceans…"

In Sect. 3.2 we have added the underlined text:

"We calculate that 27–69% of surface Hg(II) in eastern U.S., Europe, East and South Asia consists of E-Hg(II) (Fig. 6b). The contribution of E-Hg(II) is 80% of higher in areas close to emission sources (Fig. 5e), and can be even higher within tens of kilometers of the sources. However, the near-source contribution of emitted Hg(II) cannot be estimated with our 2° latitude × 2.5° longitude global model. "

And, in the conclusion, we have added the following underlined text:

"…the wet deposition flux in these regions is largely (~90%) the result of Hg(II) produced in the upper and middle troposphere. The contribution of directly emitted Hg(II) can be higher within tens of kilometers of a source, but cannot be quantified by our coarse-resolution global model."

My remaining comments are minor.

Please specify the version of the GEOS-Chem model used in this work.

It is v9-02.

We have made the following change to Sect. 2.2: "…resolution of 2° latitude × 2.5° longitude and 47 vertical levels for the GEOS-Chem simulations in this study. We use GEOS-Chem v9-02 (http://acmg.seas.harvard.edu/geos/). Global anthropogenic emissions…"

Eq. R1 has a typo "15" in it.

Fixed the typo.

The rate coefficient k_1f appears to be missing an exponent. Please check all rate expressions

Fixed the error and double-checked the rate expressions. They now are as follows:

$$k_{1f} = 1.46\times10^{-32}\times\left(\frac{T}{298}\right)^{-1.86}\times[M]\quad cm^3\ molecule^{-1}\ s^{-1}$$

$$k_{1r} = 2.67\times10^{41}\times\exp\left(\frac{-7292}{T}\right)\times\left(\frac{T}{298}\right)^{1.76}\times k_{1f}\quad s^{-1}$$

$$k_2 = 3.9\times10^{-11}\quad cm^3\ molecule^{-1}\ s^{-1}$$

$$k_3 = 2.5\times10^{-10}\times\left(\frac{T}{298}\right)^{-0.57}\quad cm^3\ molecule^{-1}\ s^{-1}$$

P11, L1: typo: "tmodeled"

Fixed the typo.

Table 1 and P12 report a 45 day lifetime for STRAT Hg(II). That seems surprisingly short considering that nearly zero reduction should happen in the stratosphere, based on the model assumption that reduction requires liquid water clouds. Based on context, I think the authors mean that the lifetime of Hg(II) produced in the stratosphere is 45 days once it enters the troposphere, but this is not clear.

That is right. The lifetime is for the STRAT Hg(II) present in the troposphere.

On P12 we have clarified this as follows: "As summarized in Table 1, we find that the tropospheric lifetime of Hg(II)…" (underlined text added). We have changed the last row of Table 1 to: "Hg(II) tropospheric lifetime [days]"

Section 5 addresses the contribution of upper tropospheric Hg(II) to surface deposition across the US. Other recent papers on this topic are Weiss-Penzias et al., (2015); Shanley et al., (2015); Coburn et al., (2016); Kaulfus et al., (2017).

We have now added citations to these papers in the manuscript.

P18L6. The regression equation is not adequately explained. The units of each variable and coefficient must be provided. Is the regression equation fitted to the observed or modeled Hg fluxes?

The regression equation is now clarified, with units for the variables and the coefficients. It is fitted to the observed fluxes.

**Response to referee # 3 comments**

We thank the referee for their thorough review and helpful suggestions. The reviewer's comments (in black) and our responses follow.

**General comments**

The authors present a modeling study on important regions of Hg(II) production in the troposphere and how those regions contribute to surface deposition. The paper is logically organized and well written. The authors have clearly put a lot of time and thought into the analysis and writing the paper. This will make a valuable contribution to the literature. I recommend minor revisions before publication.

A few general comments to consider:

Consider placing less emphasis on findings about the middle and upper troposphere being important regions for Hg(II) production and deposition, and putting more emphasis on the importance of subtropical anticyclones. It's been established for a while that the free trop is a key region for Hg (II) (flight obs: Franz Slemr, Dan Jaffe, Seth Lyman, Murphy et al. 2006, Brooks et al. 2014; models: Selin & Jacob 2008, Holmes et al. 2010, Bieser et al. 2014, Shah et al., 2016, Horowitz et al., 2016). I would go as far as to consider changing the title of the manuscript to something about subtropical anticyclones -- that's the new, exciting piece and would draw in more readers.

Excellent suggestion. We have revised the title to: "**Subtropical subsidence and surface deposition of oxidized mercury produced in the free troposphere.**" We have also extended our "dry-Hg(II)" simulation from one year to four (2013-2016), to get a sense of the interannual variability. We have also modified the abstract and the text to place more emphasis on the subtropical anticyclones.

The model spin-up (6 years) is less than half that of other GEOS-Chem Hg model studies (15 years; Holmes et al. 2010 and Horowitz et al. 2016). The rationale for the 15-yr spin-up provided by Holmes and Horowitz is that that's how long it takes to equilibrate the stratosphere. What's the justification for a 6-yr spin up? What are the implications if your model stratosphere hasn't reached equilibrium with the upper troposphere?

In the revised manuscript, we have conducted a 15-year spin up period and have updated the figures and tables accordingly. The revised version of Table 1 is below. We see only a small (5% or lower) change in the tropospheric budgets of the STRAT, UT, and MT tracers.

**Table 1 Tropospheric budgets of Hg(II) and individual tagged Hg(II) tracers.**

| | Total Hg(II) | Tagged Hg(II) tracers[a] | | | | |
|---|---|---|---|---|---|---|
| | | UT | MT | LT | STRAT | E-Hg(II) |
| Tropospheric mass of Hg(II)[b] [Mg] | 618 | 517 | 48 | 4 | 48 | 1 |
| Mass located in UT [Mg] | 480 | 432 | 3 | 0 | 45 | 0 |
| Mass located in MT [Mg] | 118 | 79 | 36 | 0 | 3 | 0 |
| Mass located in LT [Mg] | 20 | 7 | 8 | 4 | 0 | 1 |
| Hg(II) production [b] [Mg $a^{-1}$] | 15,790 | 8,560 | 4,190 | 2,460 | 410 | 170 |
| Hg(II) reduction [Mg $a^{-1}$] | 9,740 | 5,750 | 2,390 | 1,260 | 290 | 50 |
| Hg(II) wet deposition [Mg $a^{-1}$] | 3,740 | 2,250 | 1,150 | 230 | 80 | 30 |
| Hg(II) dry deposition [Mg $a^{-1}$] | 2,310 | 570 | 640 | 970 | 40 | 90 |
| Hg(II) tropospheric lifetime [days] | 14 | 22 | 4.1 | 0.6 | 43 | 2.2 |

Section 3 could be improved by adding more insight and narrative. It presently feels a bit like a core dump of numbers. Having a lot of numbers can be useful, but perhaps might be better served in a table.

Good suggestion. We have deleted some of the redundant numbers from Section 3.1 that were already listed in Table 1, and added more explanation of our results. We have also added another table (see below) to summarize the results of the sensitivity simulations and reduce the numbers written in Sect. 3.3.

**Table 2 Contribution of tagged Hg(II) tracers to the tropospheric mass and total deposition of Hg(II) for the base case and the sensitivity simulations.**

| | Simulation | Tagged Hg(II) tracer contribution [%] | | | | |
|---|---|---|---|---|---|---|
| | | UT | MT | LT | STRAT | E-Hg(II) |
| Contribution to Hg(II) tropospheric mass [%] | Base | 84 | 8 | <1 | 8 | <1 |
| | Lower UT+MT Br[a] | 71 | 7 | 1 | 21 | <1 |
| | $O_3$/OH oxidation[b] | 61 | 18 | 4 | 17 | <1 |
| | Higher Hg(II) emissions[c] | 84 | 8 | <1 | 8 | <1 |
| Contribution to Hg(II) deposition [%] | Base | 47 | 30 | 19 | 2 | 2 |
| | Lower UT+MT Br[a] | 43 | 21 | 27 | 6 | 3 |
| | $O_3$/OH oxidation[b] | 20 | 38 | 38 | 2 | 2 |
| | Higher Hg(II) emissions[c] | 49 | 28 | 17 | 2 | 4 |

(a) Simulation using the original GEOS-Chem Br concentrations instead of the 3 times Br concentrations in the base simulation,
(b) Simulation using $O_3$ and OH as the Hg(0) oxidants instead of Br as in the base simulation,
(c) Simulation using the default UNEP/AMAP Hg(0):Hg(II) emission speciation of 55%:45% instead of the 90%:10% speciation as in the base simulation.

Section 6 *Implications* could be merged with Section 7 *Conclusions*. Combining the two sections would help trim some of the redundancy.

Following your suggestion, we have trimmed Sect. 6 of the most of the redundancy, but have decided to keep the *Implications* separate from the *Conclusions*.

**Line-by-line comments**

**Page 1**

Line 18: How is "surface" defined? Is that the first level of the model? Or is it used synonymously with lower troposphere is this context?

The surface is defined here as the first level in the model.

Line 25: What accounts for the other 45%? That's surprising precip + Hg(II) production only account for 55%.

We don't know. It could be because of variations in the amount of Hg(II) in the precipitating column, caused by spatial variation in production and loss rates. Hg(II) column amounts in the model are only moderately correlated to the *contribution* of the UT+MT tracers. They are almost perfectly correlated, of course, with the total amounts of UT+MT tracers.

Lines 27-28: Statement is unclear. Is there a word missing? "Our simulation points to a large role of Hg(II) present in the dry subtropical subsidence regions..." Confused about the role of Hg(II).

We have modified the text as follows: "Our simulation points to a large role of ~~Hg(II) present in~~ the dry subtropical subsidence regions. Hg(II) present in these regions ~~which~~ accounts for…"

Line 31: "Contribution of these dry regions..." Unclear what the dry regions are contributing to. Hg(II) concentrations? Hg(II) mass in the free troposphere?

Modified to: "…the contribution of Hg(II) from the ~~these~~ dry subtropical regions was found…"

Lines 32-34: "Our results highlight the importance of the upper and middle troposphere as key regions for Hg(II) production and of the subtropical anticyclones as the primary conduits for the production and export of Hg(II) to the global atmosphere." I might delete or reword the underlined part. The subtropical anticyclone part is new. I'd play that up in the abstract.
We have deleted the underlined phrase to emphasize the anticyclone part. The modified sentence is "Our results highlight the importance the subtropical anticyclones as the primary conduits for the production and export of Hg(II) to the global atmosphere."

**Page 2**
Line 4: Recommend amending the sentence to say "most aquatic ecosystems".
We have modified the text accordingly.

Line 9: "Global dry deposition fluxes of gaseous elemental mercury (Hg(0)) and oxidized mercury in the gas and particle phases (Hg(II)) are comparable." Needs a citation. Jeroen Sonke's group published work in 2015 or 2016 looking at dry dep in peat. How does your statement line up with the Sonke lab's peat findings?
Our statement is based on model estimates, and we have added relevant citations.

Line 16: Sproveiri et al. 2010 is a relevant citation.
Agreed. We have added the citation.

Line 30: Please quantify "clean" and "dry".
Clean and dry is defined as RH below 35% and CO below 75 ppbv. We have specified this in the text now.

**Page 5**
Lines 3-4: "We assume that stack emissions (emission height > 50m) of Hg consist of 90% Hg(0) and 10% Hg(II)." Needs some justification. Even better if you can include a citation.
We have some discussion about this assumption in Sect 2.2.1, including citations. We have added a reference to Sect. 2.2.1 to the sentence in question here.

**Page 6**
Line 27: Are the assumptions about Hg wet scavenging on lines 15-20 relevant? "Below clouds, gas-phase Hg(II) is washed out by dissolving in falling raindrops (T > 268K), but not in falling snow and ice (Amos et al., 2012). Particle-phase Hg(II) is washed out in collisions in falling rain, snow and ice with different efficiencies (Wang et al., 2011)."
Since Hg(II) wet deposition is an important part of our work, we wanted to state all relevant model assumptions in the manuscript. These assumptions affect the simulated wet deposition flux and the vertical distribution of Hg(II).

**Page 7**
Lines 10-11: "We adjust the reduction rate to best match aircraft- and ground-based observations of Hg(0) over the mid-latitudes." What rate did you come up with? How does that compare to previous GEOS-Chem modeling studies?
The reduction rate is scaled to the photolysis rate of $NO_2$. We use a scaling coefficient of 0.1, which is a 16 times higher than the reduction rate used by Zhang et al. (2012).

Line 28-29: "...model spin-up period of six years." Is 6 years long enough to spin up the stratosphere? Holmes et al. (2010) and Horowitz et al. (2016) had to initialize their GEOS-Chem

simulations with a 15-yr spin-up to equilibrate the stratosphere.
We have now extended the spin-up period to 15 years.

**Page 8**
Line 3: How does the subtropical subsidence in 2013 compare to other years? Was this a dry year with lots of subsidence? Or an average year? A sense of the interannual variability would be helpful.
To provide a sense of the interannual variability, we have extended our "dry-Hg(II)" simulation from one year to four, and have shown the variation (as anomaly) in Fig. 7. The revised Fig. 7 is below:

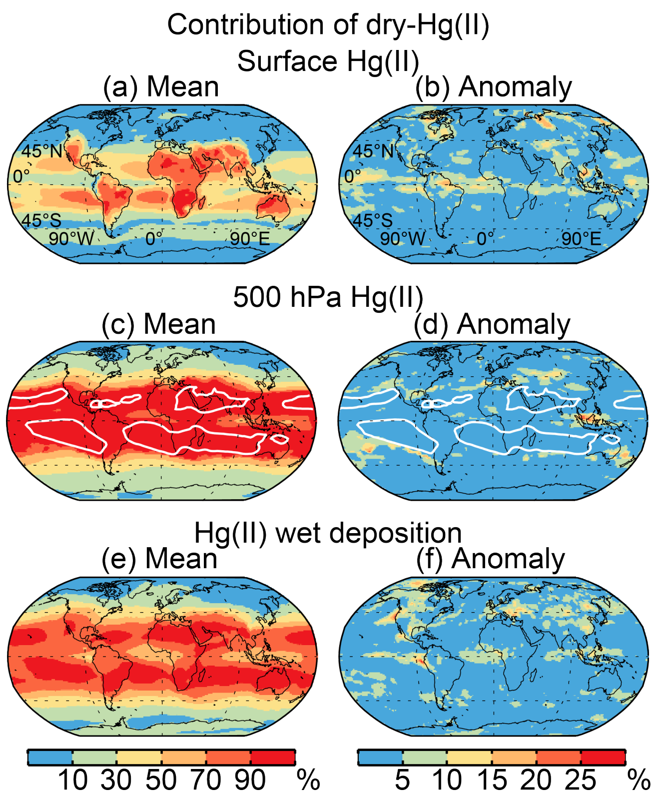


Figure 7: Mean and anomaly (maximum deviation from the mean) of the contributions of dry-Hg(II) to (a,b) surface Hg(II) concentrations, (c,d) 500 hPa Hg(II) concentrations, and (e,f) Hg(II) wet deposition flux for 2013-2016. The white contours in (c,d) show the boundaries at 500 hPa for areas with 2013-2016 RH less than 20% for a minimum of four months of the year.

**Page 11**
Line 28: "...while the contribution from E-Hg(II) is noticeable mainly in East Asia." Please quantify "noticeable".
We've changed the sentence as follows: "is greater than 10% mainly in over East Asia"

**Page 13**
Line 13: Please quantify "strong influence". Line 18: Please quantify "small".
The contribution of Hg(II) to surface deposition is 45 ± 25%.
We have added the following text to Line 13 quantifying the strong influence. "We see from Fig. 7a that dry-Hg(II) exerts a disproportionate influence on surface Hg(II) concentrations between 40°S and 40°N, where its contribution is 45 ± 25%."
And, on Line 18, by small we mean <20%. This has been clarified in the revised manuscript.

Lines 20-23: How much confidence can be placed in the statement, "Surface Hg(II) in areas poleward of 40° is from anthropogenic emissions (Europe), is produced locally (polar regions)..." give that you have a step function in Br-concentrations at 45 N (Figure 4)?

This higher Br in the subtropics should increase, if anything, the contribution of dry-Hg(II) poleward of 40°. That we don't see much of a contribution of dry-Hg(II), indicates other processes are involved. This statement relies on both Figures 5 and 7, and to clarify this we are citing both figures in the revised manuscript.

**Table S1: List of stations with observations of Hg wet deposition used in this study**

| Site ID | Site Name | Latitude | Longitude | Elevation (m.a.s.l.) | Measurement period | Network/ Region |
|---|---|---|---|---|---|---|
| CO96 | Molas Pass | 37.75 | -107.69 | 3248 | 2013-2014 | MDN[a] |
| FL11 | Everglades National Park-Research Center | 25.39 | -80.68 | 2 | 2013-2014 | MDN |
| WA18 | Seattle/NOAA | 47.68 | -122.26 | 11 | 2013-2014 | MDN |
| TX21 | Longview | 32.38 | -94.71 | 103 | 2013-2014 | MDN |
| VT99 | Underhill | 44.53 | -72.87 | 399 | 2013-2014 | MDN |
| VA28 | Shenandoah National Park-Big Meadows | 38.52 | -78.43 | 1072 | 2013-2014 | MDN |
| WI36 | Trout Lake | 46.05 | -89.65 | 509 | 2013-2014 | MDN |
| WI99 | Lake Geneva | 42.58 | -88.50 | 288 | 2013-2014 | MDN |
| PA29 | Kane Experimental Forest | 41.60 | -78.77 | 618 | 2013-2014 | MDN |
| PA42 | Leading Ridge | 40.66 | -77.94 | 287 | 2013-2014 | MDN |
| PA72 | Milford | 41.33 | -74.82 | 212 | 2013-2014 | MDN |
| TN11 | Great Smoky Mountains | 35.66 | -83.59 | 640 | 2013-2014 | MDN |
| MN18 | Fernberg | 47.95 | -91.50 | 524 | 2013-2014 | MDN |
| ME02 | Bridgton | 44.11 | -70.73 | 222 | 2013-2014 | MDN |
| ME96 | Casco Bay-Wolfe's Neck Farm | 43.83 | -70.06 | 15 | 2013-2014 | MDN |
| NC08 | Waccamaw State Park | 34.26 | -78.48 | 10 | 2013-2014 | MDN |
| PA13 | Allegheny Portage Historic Site | 40.46 | -78.56 | 739 | 2013-2014 | MDN |
| PA90 | Hills Creek State Park | 41.80 | -77.19 | 476 | 2013-2014 | MDN |
| SC19 | Congaree Swamp | 33.81 | -80.78 | 34 | 2013-2014 | MDN |
| IL11 | Bondville | 40.05 | -88.37 | 212 | 2013-2014 | MDN |
| FL34 | Everglades Nutrient Removal Project | 26.66 | -80.40 | 10 | 2013-2014 | MDN |
| FL05 | Chassahowitzka National Wildlife Refuge | 28.75 | -82.56 | 3 | 2013-2014 | MDN |
| GA09 | Okefenokee National Wildlife Refuge | 30.74 | -82.13 | 45 | 2013-2014 | MDN |
| PA00 | Arendtsville | 39.92 | -77.31 | 269 | 2013-2014 | MDN |
| KS32 | Lake Scott State Park | 38.67 | -100.92 | 863 | 2013-2014 | MDN |
| ME98 | Acadia National Park-McFarland Hill | 44.38 | -68.26 | 150 | 2013-2014 | MDN |
| ME00 | Caribou | 46.87 | -68.01 | 191 | 2013-2014 | MDN |
| ME09 | Greenville Station | 45.49 | -69.66 | 322 | 2013-2014 | MDN |
| MN16 | Marcell Experimental Forest | 47.53 | -93.47 | 431 | 2013-2014 | MDN |
| MN23 | Camp Ripley | 46.25 | -94.50 | 410 | 2013-2014 | MDN |
| MN27 | Lamberton | 44.24 | -95.30 | 367 | 2013-2014 | MDN |
| MO03 | Ashland Wildlife Area | 38.75 | -92.20 | 257 | 2013-2014 | MDN |
| MT05 | Glacier National Park-Fire Weather Station | 48.51 | -114.00 | 964 | 2013-2014 | MDN |
| NE15 | Mead | 41.15 | -96.49 | 352 | 2013-2014 | MDN |
| NY20 | Huntington Wildlife | 43.97 | -74.22 | 500 | 2013-2014 | MDN |
| NY68 | Biscuit Brook | 41.99 | -74.50 | 634 | 2013-2014 | MDN |
| PA37 | Waynesburg | 39.82 | -80.29 | 452 | 2013-2014 | MDN |
| MI48 | Seney National Wildlife Refuge-Headquarters | 46.29 | -85.95 | 220 | 2013-2014 | MDN |
| SC05 | Cape Romain National Wildlife Refuge | 32.94 | -79.66 | 1 | 2013-2014 | MDN |
| SC03 | Savannah River | 33.25 | -81.65 | 90 | 2013-2014 | MDN |
| PA60 | Valley Forge | 40.12 | -75.88 | 46 | 2013-2014 | MDN |
| PA30 | Erie | 42.16 | -80.11 | 177 | 2013-2014 | MDN |

**Table S1 continued**

| Site ID | Site Name | Latitude | Longitude | Elevation | Measurement | Network/ |
|---|---|---|---|---|---|---|
| AL03 | Centreville | 32.90 | -87.25 | 135 | 2013-2014 | MDN |
| GA40 | Yorkville | 33.93 | -85.05 | 395 | 2013-2014 | MDN |
| MO46 | Mingo National Wildlife Refuge | 36.97 | -90.14 | 105 | 2013-2014 | MDN |
| KY10 | Mammoth Cave National Park | 37.13 | -86.15 | 236 | 2013-2014 | MDN |
| MS22 | Oak Grove | 30.98 | -88.93 | 100 | 2013-2014 | MDN |
| WI31 | Devil's Lake | 43.44 | -89.68 | 389 | 2013-2014 | MDN |
| PA47 | Millersville | 39.99 | -76.39 | 84 | 2013-2014 | MDN |
| GA33 | Sapelo Island | 31.40 | -81.28 | 3 | 2013-2014 | MDN |
| OK99 | Stilwell | 35.75 | -94.67 | 299 | 2013-2014 | MDN |
| NV02 | Lesperance Ranch | 41.50 | -117.50 | 1388 | 2013-2014 | MDN |
| MD99 | Beltsville | 39.03 | -76.82 | 46 | 2013-2014 | MDN |
| MD08 | Piney Reservoir | 39.71 | -79.01 | 769 | 2013-2014 | MDN |
| NJ30 | New Brunswick | 40.47 | -74.42 | 21 | 2013-2014 | MDN |
| ON07 | Egbert | 44.23 | -79.79 | 196 | 2013-2014 | MDN |
| WI10 | Potawatomi | 45.56 | -88.81 | 570 | 2013-2014 | MDN |
| WA03 | Makah National Fish Hatchery | 48.29 | -124.65 | 6 | 2013-2014 | MDN |
| CA94 | Converse Flats | 34.19 | -116.91 | 1724 | 2013-2014 | MDN |
| CA20 | Yurok Tribe-Requa | 41.56 | -124.09 | 110 | 2013-2014 | MDN |
| OK01 | McGee Creek | 34.32 | -95.89 | 195 | 2013-2014 | MDN |
| OK31 | Copan | 36.91 | -95.88 | 255 | 2013-2014 | MDN |
| SD18 | Eagle Butte | 44.99 | -101.24 | 742 | 2013-2014 | MDN |
| MD00 | Smithsonian Environmental Research Center | 38.89 | -76.56 | 20 | 2013-2014 | MDN |
| FL97 | Everglades-Western Broward County | 26.17 | -80.82 | 4 | 2013-2014 | MDN |
| UT97 | Salt Lake City | 40.71 | -111.96 | 1297 | 2013-2014 | MDN |
| OK04 | Lake Murray | 34.10 | -97.07 | 245 | 2013-2014 | MDN |
| PA52 | Little Pine State Park | 41.36 | -77.36 | 228 | 2013-2014 | MDN |
| KS03 | Reserve | 39.98 | -95.57 | 265 | 2013-2014 | MDN |
| KS24 | Glen Elder State Park | 39.51 | -98.34 | 456 | 2013-2014 | MDN |
| KS99 | Cimarron National Grassland | 37.13 | -101.82 | 1021 | 2013-2014 | MDN |
| OK06 | Wichita Mountains | 34.73 | -98.71 | 492 | 2013-2014 | MDN |
| KS04 | West Mineral | 37.27 | -94.94 | 274 | 2013-2014 | MDN |
| NY43 | Rochester | 43.15 | -77.55 | 136 | 2013-2014 | MDN |
| NY06 | Bronx | 40.87 | -73.88 | 68 | 2013-2014 | MDN |
| MN98 | Blaine | 45.14 | -93.22 | 275 | 2013-2014 | MDN |
| MS12 | Grand Bay NERR | 30.43 | -88.43 | 2 | 2013-2014 | MDN |
| PA21 | Goddard State Park | 41.43 | -80.15 | 385 | 2013-2014 | MDN |
| FL96 | Pensacola | 30.55 | -87.38 | 45 | 2013-2014 | MDN |
| AL19 | Birmingham | 33.55 | -86.81 | 200 | 2013-2014 | MDN |
| DE0008R | Schmücke | 50.65 | 10.77 | 937 | 2013-2014 | EMEP[b] |
| FI0036R | Pallas (Matorova) | 68.00 | 24.24 | 340 | 2013-2014 | EMEP |
| GB0036R | Harwell | 51.57 | -1.32 | 137 | 2013-2014 | EMEP |
| GB0048R | Auchencorth Moss | 55.79 | -3.24 | 260 | 2013-2014 | EMEP |
| NO0001R | Birkenes | 58.38 | 8.25 | 190 | 2013-2014 | EMEP |
| SE0005R | Bredkälen | 63.85 | 15.33 | 404 | 2013-2014 | EMEP |
| SE0011R | Vavihill | 56.02 | 13.15 | 175 | 2013-2014 | EMEP |
| SE0014R | Råö | 57.39 | 11.91 | 5 | 2013-2014 | EMEP |
| NYA | Ny-Ålesund | 78.90 | 11.88 | 12 | 2013-2014 | GMOS[c] |
| MHE | Mace Head | 53.33 | -9.91 | 5 | 2013 | GMOS |
| ISK | Iskrba | 45.56 | 14.86 | 520 | 2013-2014 | GMOS |
| SIS | Sisal | 21.16 | -90.05 | 7 | 2013-2014 | GMOS |
| AMS | Amsterdam Island | -37.80 | 77.55 | 3 | 2013-2014 | GMOS |

**Table S1 continued**

| Site ID | Site Name | Latitude | Longitude | Elevation | Measurement | Network/ |
|---|---|---|---|---|---|---|
| CGR | Cape Grim | -40.68 | 144.69 | 94 | 2013-2014 | GMOS |
| MCB | Mt. Changbai | 42.41 | 128.11 | 736 | 2011-2014 | China[d] |
| MDM | Mt. Damei | 29.63 | 121.57 | 550 | 2012-2014 | China |
| MLG | Mt. Leigong | 26.39 | 108.20 | 2176 | 2008-2009 | China |
| MAL | Mt. Ailao | 24.53 | 101.11 | 2450 | 2011-2014 | China |
| MWA | Mt. Waliguan | 36.29 | 100.90 | 3816 | 2012-2014 | China |
| BYB | Bayinbuluk | 42.89 | 83.72 | 2500 | 2013-2014 | China |
| PEN | Pengjiayu | 25.63 | 122.07 | 102 | 2009 | Taiwan[e] |
| PR20 | El Verde | 18.32 | -65.82 | 380 | 2015 | MDN |

(a) http://nadp.sws.uiuc.edu/mdn/
(b) http://www.nilu.no/projects/ccc/index.html
(c) Sprovieri et al. (2017)
(d) Fu et al. (2016)
(e) Sheu and Lin (2013)

**Table S2: List of ground stations with observations of Hg(II) surface concentrations used in this study**

| Site ID | Site Name | Latitude | Longitude | Elevation (m.a.s.l.) | Measurement period | Network/ Region |
|---|---|---|---|---|---|---|
| AL19 | Birmingham | 33.55 | -86.81 | 177 | 2009-2012 | AMNet[a] |
| CA48 | Elkhorn Slough | 36.81 | -121.78 | 10 | 2010-2011 | AMNet |
| FL96 | Pensacola | 30.55 | -87.38 | 44 | 2009-2012 | AMNet |
| GA40 | Yorkville | 33.93 | -85.05 | 394 | 2009-2012 | AMNet |
| MD08 | Piney Reservoir | 39.71 | -79.01 | 761 | 2009-2012 | AMNet |
| MD96 | Beltsville_B | 39.03 | -76.82 | 47 | 2009-2012 | AMNet |
| MD97 | Beltsville | 39.03 | -76.82 | 47 | 2009-2012 | AMNet |
| MS12 | Grand Bay NERR | 30.41 | -88.40 | 1 | 2009-2012 | AMNet |
| MS99 | Grand Bay NERR_B | 30.41 | -88.40 | 1 | 2009-2012 | AMNet |
| NH06 | Thompson Farm | 43.11 | -70.95 | 25 | 2009-2011 | AMNet |
| NJ05 | Brigantine | 39.46 | -74.45 | 8 | 2009-2012 | AMNet |
| NS01 | Kejimkujik | 44.43 | -65.20 | 158 | 2009-2012 | AMNet |
| NY06 | New York City | 40.87 | -73.88 | 26 | 2009-2012 | AMNet |
| NY20 | Huntington Wildlife Forest | 43.97 | -74.22 | 502 | 2009-2012 | AMNet |
| NY43 | Rochester | 43.15 | -77.62 | 154 | 2009 | AMNet |
| NY95 | Rochester_B | 43.15 | -77.55 | 154 | 2009-2012 | AMNet |
| OH02 | Athens | 39.31 | -82.12 | 274 | 2009-2012 | AMNet |
| OK99 | Stilwell | 35.75 | -94.67 | 300 | 2009-2012 | AMNet |
| PA13 | Allegheny Portage | 40.46 | -78.56 | 739 | 2009-2012 | AMNet |
| UT96 | Antelope Island | 41.09 | -112.12 | 1285 | 2009-2011 | AMNet |
| UT97 | Salt Lake City | 40.71 | -111.96 | 1099 | 2009-2012 | AMNet |
| VT99 | Underhill | 44.53 | -72.87 | 397 | 2009-2012 | AMNet |
| WI07 | Horicon | 43.46 | -88.62 | 272 | 2009-2012 | AMNet |
| WV99 | Canaan Valley Institute | 39.12 | -79.45 | 985 | 2009-2012 | AMNet |
| AMS | Amsterdam Island | -37.80 | 77.55 | 70 | 2012-13 | GMOS[b] |
| RAO | Råö | 57.39 | 11.91 | 7 | 2012-15 | GMOS[c] |
| LON | Longobucco | 39.39 | 16.61 | 1379 | 2013 | GMOS[d] |
| MAN | Manaus | -2.89 | -59.97 | 110 | 2013 | GMOS[d] |
| WAL | Waldhof | 52.80 | 10.76 | 74 | 2009-2011 | Germany[e] |
| MCH | Mt. Changbai | 42.40 | 128.11 | 740 | 2013-2014 | China[f] |
| MWA | Mt. Waliguan | 36.29 | 100.90 | 3816 | 2007-2008 | China |
| MAL | Mt. Ailao | 24.53 | 101.02 | 2450 | 2011-2012 | China |
| SLA | Shangri-La | 28.02 | 99.73 | 3580 | 2009-2010 | China |
| MYU | Miyun | 40.48 | 116.76 | 220 | 2008-2009 | China |
| MDA | Mt. Damei | 29.63 | 121.57 | 550 | 2011-2013 | China |
| MGO | Mt. Gongga | 29.65 | 102.12 | 1640 | 2005-2007 | China |
| LABS | Lulin Atmospheric Background Station | 23.51 | 120.92 | 2862 | 2006-2007 | Taiwan[g] |
| ALE | Alert | 82.49 | -62.34 | 210 | 2009-2011 | Canada[h] |

(a) http://nadp.sws.uiuc.edu/amn/
(b) Angot et al. (2014)
(c) Wängberg et al. (2016)
(d) Travnikov et al. (2017)
(e) Weigelt et al. (2013)
(f) Fu et al. (2015)
(g) Sheu et al. (2010)

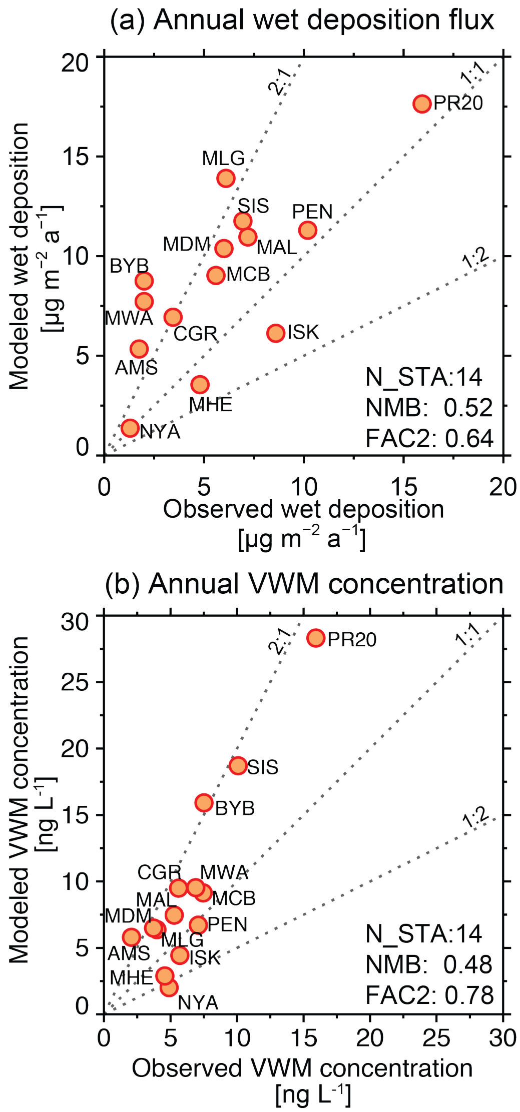


**Figure S1 (a) Simulated and observed Hg wet deposition flux for GMOS and other stations listed in Table S1. (b) Simulated and observed annual volume-weighted mean (VWM) Hg concentration for GMOS and other stations listed in Table S1. The number of stations (N_STA), normalized mean bias (NMB; $\mathrm{NMB} = \sum_i (\mathrm{M_i} - \mathrm{O_i}) \Big/ \sum_i \mathrm{O_i} \times 100\%$ ), and FAC2 (percentage of points where $0.5 \le \mathrm{M_i}/\mathrm{O_i} \le 2$ where $\mathrm{O_i}$ and $\mathrm{M_i}$ are observed and simulated values, respectively) is included in both panels.**

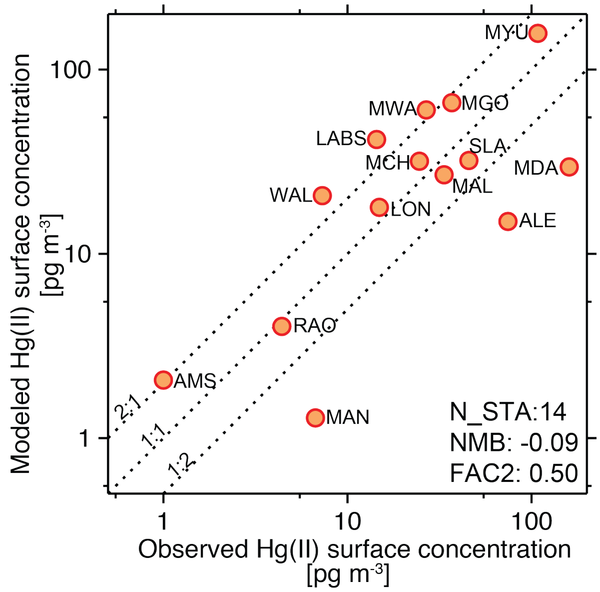


**Figure S2 Simulated and observed surface Hg(II) concentration for GMOS and other stations listed in Table S1. Note the logarithmic scale on both axes.**

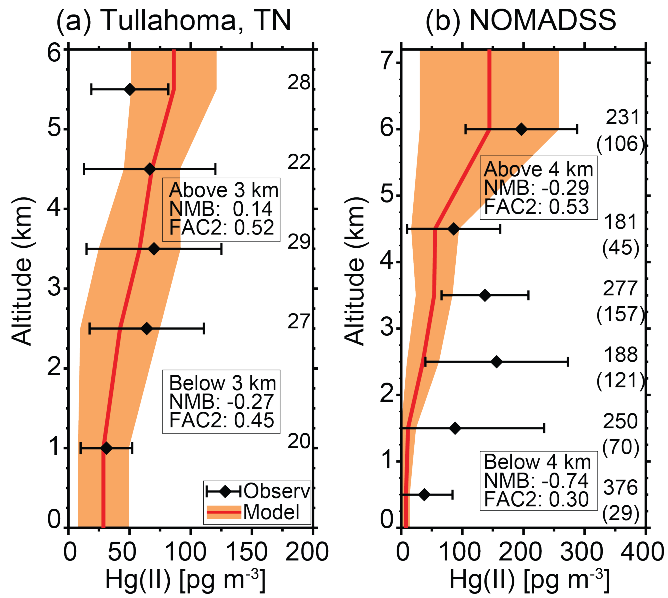


**Figure S3 (a) Simulated and observed Hg(II) concentrations for aircraft-based campaign over Tullahoma, TN, USA (2012-2013) (Brooks et al., 2013). (b)Simulated and observed Hg(II) concentrations for the NOMADSS aircraft-based campaign (2013) (Shah et al., 2016). The number of model-observation pairs in each height bin is shown in panel (a). In panel (b), the number of model-observation pairs in each height bin, and, in parentheses, the number of model-observation pairs where the observations were above the instrument detection limit, are shown.**

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# ~~Surface~~Subtropical subsidence and surface deposition of oxidized mercury ~~dominated by production~~produced in the ~~upper and middle~~free troposphere

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**Abstract.** Oxidized mercury (Hg(II)) is chemically produced in the atmosphere by oxidation of elemental mercury and is directly emitted by anthropogenic activities. We use the GEOS-Chem global chemical transport model~~,~~ with gaseous oxidation driven by Br atoms, to quantify how surface deposition of Hg(II) is influenced by Hg(II) production at different atmospheric heights. We tag Hg(II) chemically produced in the lower (surface–750 hPa), middle (750–400 hPa) and upper troposphere (400 hPa–tropopause), in the stratosphere, as well as directly emitted Hg(II). ~~A~~We evaluate our two-year simulation (2013–2014) ~~reproduces the spatial distribution and seasonal cycle~~against observations of Hg(II) ~~surface concentrations and Hg~~ wet deposition ~~observed at the Atmospheric Mercury Network (AMNet) and the Mercury Deposition Network (MDN) stations over the United States to within 21%, but displays a 46% underestimate~~as well as surface and free tropospheric observations of ~~wet deposition observed at the European Monitoring and Evaluation Programme (EMEP) stations~~Hg(II), finding reasonable agreement. We find that Hg(II) produced in the upper and middle troposphere constitutes 91% of the tropospheric mass of Hg(II) and 91% of the annual Hg(II) wet deposition flux. This large global influence from the upper and middle troposphere is the result of strong chemical production coupled with a long lifetime of Hg(II) in these regions. Annually, 77–84% of surface level Hg(II) over the western U.S., South America, South Africa, and Australia is produced in the upper and middle troposphere, whereas 26–66% of surface Hg(II) over the eastern U.S., Europe, East Asia, and South Asia is directly emitted. The influence of directly emitted Hg(II) near emissions sources is likely higher, but cannot be quantified by our coarse-resolution global model (2° latitude × 2.5° longitude). Over the

oceans, 72% of surface Hg(II) is produced in the lower troposphere, because of higher Br concentrations in the marine boundary layer. The global contribution of the upper and middle troposphere to the Hg(II) dry deposition flux is 52%. It is lower compared to the contribution to wet deposition because dry deposition of Hg(II) produced aloft requires its entrainment into the boundary layer, while rain can scavenge Hg(II) from higher altitudes more readily. We find that 55% of the spatial variation of Hg wet deposition flux observed at the MDN sites is explained by the combined variation of precipitation and Hg(II) produced in the upper and middle troposphere. Our simulation points to a large role of ~~Hg(II) present in~~ the dry subtropical subsidence regions~~, which account~~. Hg(II) present in these regions accounts for 74% of Hg(II) at 500 hPa over the continental U.S., and more than 60% of the surface Hg(II) over high-altitude areas of the western U.S. Globally, it accounts for 78% to the tropospheric Hg(II) mass, and 61% of the total Hg(II) deposition. During the Nitrogen, Oxidants, Mercury, and Aerosol Distributions, Sources, and Sinks (NOMADSS) aircraft campaign, the contribution of ~~these~~Hg(II) from the dry subtropical regions was found to be 75% when measured Hg(II) exceeded 250 pg m$^{-3}$. Hg(II) produced in the upper and middle troposphere subsides in the anticyclones, where the dry conditions inhibit the loss of Hg(II). Our results highlight the importance ~~of the upper and middle troposphere as key regions for Hg(II) production and of~~ the subtropical anticyclones as the primary conduits for the production and export of Hg(II) to the global atmosphere.

## 1 Introduction

Atmospheric deposition of mercury (Hg) is the main source of Hg to most aquatic ecosystems. Methylmercury concentrations in fish in an ecosystem are strongly linked to the local Hg deposition rate (Hammerschmidt and Fitzgerald, 2006; Harris et al., 2007). Dry deposition and wet deposition are both significant contributors to the global deposition flux of Hg (e.g. Bergan et al., 1999; Seigneur et al., 2001; Dastoor and Larocque, 2004; Jung et al., 2009; Amos et al., 2012). ~~While~~Models suggest that the global dry deposition fluxes of gaseous elemental mercury (Hg(0)) and oxidized mercury in the gas and particle phases (Hg(II)) are comparable (Seigneur et al., 2001; Amos et al., 2012)~~, wet deposition~~. Wet deposition of Hg occurs almost entirely through precipitation scavenging of Hg(II). Hg(II) is co-emitted with Hg(0) from several anthropogenic sources, but the predominant source of Hg(II) in the atmosphere is in situ oxidation of Hg(0) (Pirrone et al., 2010; Selin and Jacob, 2008; Holmes et al., 2010). Br is likely the main oxidant of Hg(0) (Ebinghaus et al., 2002; Laurier et al., 2003; Donohoue et al., 2006; Obrist et al., 2011; Gratz et al., 2015), but the importance of $O_3$ and OH is unclear (Hynes et al., 2009; Sprovieri et al., 2010; Subir et al., 2011; Ariya et al., 2015).

Hg(II) concentrations in the planetary boundary layer are typically about 50 pg $m^{-3}$ (Valente et al., 2007; Gay et al., 2013), but could be as high as 1000 pg $m^{-3}$ in urban areas with large anthropogenic sources (Poissant et al., 2005; Fu et al., 2012) and in the Arctic during springtime Mercury Depletion Events (Cobbett et al., 2007). The free troposphere is thought to hold a global pool of elevated Hg(II) (Selin, 2009), but few Hg(II) observations have been made in the free troposphere. At high-elevation ground sites, back-trajectory analysis and simultaneous measurements of $H_2O$ and $O_3$ were used to identify free-tropospheric air masses which contained higher Hg(II) concentrations compared to air masses transported from the planetary boundary layer (Swartzendruber et al., 2006; Faïn et al., 2009; Lyman and Gustin, 2009; Sheu et al., 2010; Timonen et al., 2013; Weiss-Penzias et al., 2015; Fu et al., 2016a). Lyman and Jaffe (2012) conducted aircraft-based measurements of Hg(II) in the upper troposphere and lower stratosphere and inferred that Hg(II) concentrations are highest at the tropopause. Other aircraft-based studies have also found increasing Hg(II) concentrations at 2-5 km altitude in the free troposphere (Sillman et al., 2007; Swartzendruber et al., 2009; Brooks et al., 2014). During the Nitrogen, Oxidants, Mercury, and Aerosol Distributions, Sources, and Sinks (NOMADSS) aircraft campaign, the highest Hg(II) concentrations (300–680 pg $m^{-3}$) were observed in clean and dry air (CO $< 75$ ppbv and RH $< 35\%$) originating in the subsiding air masses of the Pacific and the Atlantic subtropical anticyclones (Gratz et al., 2015; Shah et al., 2016). Furthermore, higher concentrations of Hg in precipitation are observed in thunderstorms reaching higher altitudes (Guentzel et al., 2001; Shanley et al., 2015; Holmes et al., 2016; Kaulfus et al., 2017), and higher Hg wet and dry deposition fluxes are associated with transport from the free troposphere (Weiss-Penzias et al., 2011; Gustin et al., 2012; Huang and Gustin, 2012; Sheu and Lin, 2013).

The influence of free-tropospheric Hg on deposition has been evaluated with regional and global chemical transport models. Using the global GEOS-Chem model, Selin and Jacob (2008) estimated that 59% of the annual Hg(II) wet deposition over the U.S. is from Hg(II) scavenged from altitudes above

850 hPa. In another study (Myers et al., 2013), Hg present at the upper boundary (5.4 km) of the regional CMAQ model was found to contribute about 40% to dry deposition and about 80% to wet deposition in July over the U.S. Coburn et al. (2016) estimated that most of the surface Hg(II) over Florida in April 2010 was produced above 700 hPa. However, these model estimates are limited to specific regions and seasons.

In this study, we use the GEOS-Chem global chemical transport model to quantify the regional contributions of Hg(II) produced at different heights in the atmosphere to the annual deposition of Hg(II). We have added a tagging method to the GEOS-Chem model to track Hg(II) produced in the lower (surface–750 hPa), middle (750–400 hPa) and upper troposphere (400 hPa–tropopause), Hg(II) produced in the stratosphere, and Hg(II) emitted by anthropogenic activities. This simulation is described and evaluated with ground-based observations of Hg(II) concentrations and wet deposition (Sect. 2). In Sect. 3, we present the distribution of the tagged Hg(II) and calculate their contributions to wet and dry deposition fluxes in different regions of the world. We also examine the sensitivity of our results to different model assumptions for Hg chemistry and anthropogenic emission speciation. We use our simulation to examine the role of the subtropical anticyclones as global reservoirs of Hg(II)-rich air (Sect. 4) and evaluate the role of tagged Hg(II) tracers in explaining the observed variability of Hg(II) concentrations and wet deposition fluxes (Sect. 5). Finally, we discuss the implications of our study in Sect. 6 and present conclusions in Sect. 7.

## 2 Observations and model used in this study

### 2.1 Observations of Hg wet deposition and atmospheric concentrations of Hg(II)

Hg wet deposition fluxes over North America and Europe are measured by the Mercury Deposition Network (MDN; http://nadp.sws.uiuc.edu/mdn/) and the European Monitoring and Evaluation Programme (EMEP; http://www.nilu.no/projects/ccc/index.html), respectively. These networks measure precipitation depth and Hg concentrations in precipitation weekly (MDN), biweekly (EMEP) or monthly (EMEP). In this study, we use the 2013–2014 monthly-mean and annual-mean wet deposition flux and volume-weighted mean (VWM) Hg concentrations. The VWM concentration for any period is the total Hg wet deposition flux for that period divided by the total precipitation depth. All sites in the MDN network use standard instruments and protocols, and all samples are analyzed at the same laboratory (Prestbo and Gay, 2009). The measurement precision in MDN observations, estimated from collocated sampling, is less than 15% (Wetherbee et al., 2007). A field inter-comparison of instruments and methods used in the EMEP network found the measurement precision for the EMEP network to be about 40% (Aas, 2006).

To calculate monthly means, we discard sites with fewer than 3 weeks of measurements in any given month. For annual means we require at least 8 months of valid measurements. The MDN network had 80 stations over the continental U.S. that met the above data completeness criteria during 2013–2014, whereas the EMEP network had 9 stations over Europe. (Table S1).

The Atmospheric Mercury Network (AMNet; http://nadp.sws.uiuc.edu/amn/) monitors surface concentrations of Hg(0), reactive gaseous mercury (RGM) and particle-bound mercury (PBM). The sum of RGM and PBM is considered to represent Hg(II). RGM and PBM measurements are made on a 2- or 3-hour cycle, depending on the site. All AMNet stations use the Tekran® 2537-1130-1135 speciation system, and follow operational procedures described in Gay et al. (2013). There is no standard calibration method for Tekran RGM and PBM measurements, and the uncertainties in these measurements are not fully quantified. A few studies have found that the AMNet instruments underestimate RGM by a factor of 2–3 in the presence of ambient water vapor and $O_3$ (Lyman et al., 2010; Ambrose et al., 2013; McClure et al., 2014). Here, we use the 2009–2012 AMNet observations, as this data is publicly available. AMNet had 23 sites over the continental U.S. and eastern Canada (Nova Scotia) operational during this period. (Table S2). The annual and monthly statistics for each station are calculated by aggregating 2- or 3-hour measurements made during 2009–2012.

Ground-based measurements of Hg wet deposition and Hg(II) surface concentration have been made as part of the Global Mercury Observations System (GMOS) network (Angot et al., 2014; Wängberg et al., 2016; Sprovieri et al., 2016, 2017; Travnikov et al., 2017), and at sites in Europe (Weigelt et al., 2013), Canada, and East Asia (Sheu et al., 2010; Sheu and Lin, 2013; Fu et al., 2015, 2016b). We use the 2013-2014 measurements wherever available, but use all sites with one year or more of observations. We exclude sites in China classified as urban, because of proximity to large Hg(II) sources. We include 14 sites with annual-mean measurements of Hg wet deposition (Table S1), and 14 sites with annual-mean measurements of surface Hg(II) (Table S2).

The NOMADSS aircraft campaign took place over the eastern U.S. from June 1 to July 15, 2013. Total Hg and Hg(II) observations were made with the University of Washington Detector of Oxidized Hg Species (DOHGS) instrument (Ambrose et al., 2015; Swartzendruber et al., 2009; Lyman and Jaffe, 2012). The detection limit of the DOHGS instrument for Hg(II) measurements during the campaign was between 57 and 228 pg $m^{-3}$, and we use the robust Regression on Order Statistics (ROS) to estimate values for measurements below detection limit, as described by Shah et al. (2016). We also include aircraft-based measurements of Hg(II) carried out near Tullahoma, Tennessee, USA from August 2012 to June 2013 (Brooks et al., 2014).

### 2.2 GEOS-Chem model

GEOS-Chem is a global chemical transport model that simulates the emissions, transport, chemistry, and deposition of Hg(0), gas-phase Hg(II), and particle-phase Hg(II) (Selin et al., 2007). The model is driven by meteorological fields from the NASA Global Modeling and Assimilation Office (GMAO) Goddard Earth Observing System Model~~, Version 5 FP~~ Forward Processing (GEOS-~~5~~ FP) modeling system. The GEOS-~~5~~ FP system consists of a general circulation model coupled with a data assimilation system (Reinecker et al., 2008), and has a native horizontal resolution of 0.25° latitude × 0.3125° longitude with 72 vertical levels up to 0.01 hPa. We average the meteorological fields to a coarser resolution of 2° latitude × 2.5° longitude and 47 vertical levels for the GEOS-Chem simulations in this study. We use GEOS-Chem v9-02 (http://acmg.seas.harvard.edu/geos/). Global anthropogenic emissions of Hg are from the global United Nations Environment Programme (UNEP) / Arctic Monitoring and Assessment Programme (AMAP) 2010 inventory (http://www.amap.no/mercury-emissions/datasets). We assume that stack emissions (emission height > 50m) of Hg consist of 90% Hg(0) and 10% Hg(II) (see Sect 2.2.1). Natural emissions are simulated using a slab ocean model (Strode et al., 2007; Soerensen et al., 2010) and a land emissions model (Selin et al., 2008). Emissions from biomass burning and geogenic activity are prescribed as in Holmes et al. (2010). Transport processes simulated in the GEOS-Chem model include advection (Lin and Rood, 1996), convective transport (Wu et al., 2007), and turbulent mixing in the boundary layer (Lin and McElroy, 2010).

The redox chemistry of Hg consists of oxidation of Hg(0) by Br, as described below, and aqueous phase reduction in the presence of sunlight (Holmes et al., 2010). Gas / particle partitioning of Hg(II) on sea-salt aerosols is simulated as a kinetic process (Holmes et al., 2010), while partitioning on other aerosols is simulated as an equilibrium process (Amos et al., 2012). The oxidation of Hg(0) to Hg(II) is simulated as follows (Goodsite et al., 2004; Balabanov et al., 2005; Dibble et al., 2012):

$$\mathrm{Hg(0)} + \mathrm{Br} \xleftrightarrow{\mathrm{M}} \mathrm{HgBr} \quad \text{(R1)}$$

$$\mathrm{HgBr} + \mathrm{Br} \longrightarrow \mathrm{Hg(0)} + \mathrm{Br_2} \quad \text{(R2)}$$

$$\mathrm{HgBr} + \mathrm{X} \longrightarrow \mathrm{Hg(II)} \quad \text{(R3)}$$

$$(\mathrm{X} = \mathrm{NO_2}, \mathrm{HO_2}, \mathrm{BrO}, \mathrm{Br}, \mathrm{OH})$$

with the following reaction rates:

$$k_{1f} = 1.46 \times \left(\frac{T}{298}\right)^{-1.86} \times [M] \ \ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_{1r} = 2.67 \times 10^{41} \times \exp\left(\frac{-7292}{T}\right) \times \left(\frac{T}{298}\right)^{1.76} \times k_{1f} \ \ \mathrm{s^{-1}}$$

$$k_2 = 3.9 \times 10^{-11} \ \ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_3 = 2.5 \times 10^{-10} \times \left(\frac{T}{298}\right)^{-0.57} \ \ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$k_{1f} = 1.46\times10^{-32} \times \left(\frac{T}{298}\right)^{-1.86} \times[M] \;\; cm^3 \; molecule^{-1} \; s^{-1}$$

$$k_{1r} = 2.67\times10^{41} \times \exp\left(\frac{-7292}{T}\right)\times\left(\frac{T}{298}\right)^{1.76} \times k_{1f} \;\; s^{-1}$$

$$k_2 = 3.9\times10^{-11} \;\; cm^3 \; molecule^{-1} \; s^{-1}$$

$$k_3 = 2.5\times10^{-10} \times \left(\frac{T}{298}\right)^{-0.57} \;\; cm^3 \; molecule^{-1} \; s^{-1}$$

Concentrations of Br, BrO, $NO_2$, $HO_2$, and OH are obtained from the archived monthly-mean output of the 4° latitude × 5° longitude HOx-NOx-$O_3$-VOC-Br GEOS-Chem simulation for 2013 (Bey et al., 2001; Parrella et al., 2012). In our previous work (Shah et al., 2016), we found that the GEOS-Chem Br concentrations simulated by Parrella et al. (2012) were insufficient in explaining Hg(II) concentrations observed during the NOMADSS aircraft campaign at 5–7 km altitude. We found improved agreement with NOMADSS Hg(II) observations when we increased Br concentrations by a factor of 3 between 45°S and 45°N and between 750 hPa and the tropopause. Schmidt et al. (2016) have recently updated the GEOS-Chem bromine simulation by expanding the multiphase chemistry of bromine to include reactions with chlorine and ozone. These updates result in faster recycling of HBr to $BrO_x$ and a factor of 2.5 increase in tropospheric Br concentrations for 45°S–45°N above 2.5 km, improving agreement with satellite and in situ observations of BrO. This is consistent with our assumption that Br concentrations are 3 times higher than those simulated with the previous mechanism. In addition, these updates by Schmidt et al. (2016) have resulted in a factor of 2.3 increase in free tropospheric Br concentrations at higher latitudes (45°N–90°N). To maintain consistency with our previous work, we continue to use the Parrella et al. (2012) Br fields with the factor of 3 scaling in this study too, but note that Br concentrations north of 45°N may be too low.

The GEOS-Chem model includes wet deposition of Hg(II) and dry deposition of Hg(0) and Hg(II). Wet deposition includes in-cloud scavenging (rainout) and below-cloud scavenging (washout) in convective and large-scale precipitation (Liu et al., 2001). Within clouds, the dissolution of gas-phase Hg(II) in liquid droplets is modeled as an equilibrium process, while particle-phase Hg(II) is assumed to be fully dissolved (Amos et al., 2012). We assume that rainout of gas-phase Hg(II) does not occur during ice nucleation (T < 248 K). Below clouds, gas-phase Hg(II) is washed out by dissolving in falling raindrops (T > 268K), but not in falling snow and ice (Amos et al., 2012). Particle-phase Hg(II) is washed out in collisions in falling rain, snow and ice with different efficiencies (Wang et al., 2011). Dry deposition of gas-phase Hg(II) and particle-phase Hg(II) on particles other than sea-salt aerosols is based on the resistance-in-series model (Wesely, 1989; Wang et al., 1998; Zhang et al., 2001). The surface resistance of gas-phase Hg(II) is assumed to be negligibly small (Selin et al., 2007; Amos et al., 2012). The dry deposition of particle-phase Hg(II) present on sea-salt aerosols is parameterized using results of a box model simulating the chemistry and deposition of Hg(II) in the marine boundary layer (Holmes et al., 2009, 2010).

### 2.2.1 Model uncertainties

Uncertainties in mercury modeling and chemistry have been recently reviewed by Gustin et al. (2015), Ariya et al. (2015), and Kwon and Selin (2016). Here we briefly discuss uncertainties which are pertinent to our study: uncertainties in the assumption of Br as the sole oxidant of Hg(0), in reduction kinetics of Hg(II), and in the assumed speciation of Hg(0) and Hg(II) in anthropogenic emissions.

While Br, $O_3$, and OH have been identified as possibly important oxidants of Hg(0), there is growing evidence from theoretical (Goodsite et al., 2004; Dibble et al., 2012), laboratory (Ariya et al., 2002; Donohoue et al., 2006) and field studies (Ebinghaus et al., 2002; Lindberg et al., 2002; Laurier et al., 2003; Obrist et al., 2011; Gratz et al., 2015) that Br may be the most relevant oxidant of Hg(0) in the atmosphere. Ab-initio calculations have suggested that HgO, the product of gas-phase oxidation of Hg(0) by $O_3$ and OH, is a weakly-bound molecule, and that oxidation of Hg(0) by $O_3$ and OH is an endothermic reaction of little importance in the atmosphere (Hynes et al., 2009).

The pathways for reduction of Hg(II) to Hg(0) in the atmosphere are poorly characterized. Laboratory experiments suggest that photoreduction of Hg(II) can occur in the aqueous-phase in the presence of organic compounds or on dry aerosol surfaces at atmospherically relevant rates (Si and Ariya, 2008; Tong et al., 2013), and field studies have found some evidence for in situ reduction of Hg(II) (Edgerton et al., 2006; Landis et al., 2014; de Foy et al., 2016). Most global atmospheric mercury models include at least one pathway of Hg(II) reduction in order to simulate realistic Hg(0) concentrations (Ariya et al., 2015). The reduction rate of aqueous-phase Hg(II) in GEOS-Chem is parameterized based on the simulated $NO_2$ photolysis rate (Holmes et al., 2010). We adjust the reduction rate to best match aircraft- and ground-based observations of Hg(0) over the mid-latitudes.

We have assumed an emissions speciation of 90% Hg(0) and 10% Hg(II) for anthropogenic emissions from stacks, as opposed to the UNEP/AMAP speciation of 55% Hg(0) : 45% Hg(II) for stack sources. Zhang et al. (2012) and Kos et al. (2013) found that a speciation scheme with 10–15% of Hg(II), and the rest Hg(0), best explains the spatial variability in Hg(II) wet deposition observed over the U.S. However, the speciation of Hg emissions can vary considerably based on the type of source, type of pollution control devices, and the availability of oxidants in the flue gas (Kim et al., 2010).

### 2.2.2 Simulations performed for this study

We have added a tagging technique to the GEOS-Chem model to identify the production regions of Hg(II). We divide the atmosphere vertically into lower troposphere (LT: surface–750 hPa), middle troposphere (MT: 750–400 hPa), upper troposphere (UT: 400 hPa–tropopause) and stratosphere (STRAT), to track the Hg(II) produced in each of these regions as separate Hg(II) tracers. Hg(II) emitted directly to the atmosphere is also tagged separately (E–Hg(II)). Each of these tagged tracers undergo the same physical and chemical processes as the total Hg(II) tracer. Hg(II) loss by deposition or reduction in a model grid cell is divided among all tagged tracers present in the grid cell in proportion to their masses. We perform a simulation with the tagged tracers for the years 2013 and 2014 following a model spin-up period of ~~six~~15 years.

We perform an additional simulation to quantify the role of the dry subsidence regions of the subtropical anticyclones in the global transport of Hg(II). We identify the dry subtropical subsidence areas as those that lie between 45°S and 45°N and between 750 hPa and the tropopause and where the monthly-mean relative humidity is less than 20%. The relative humidity threshold is based on the definition of dry subtropical areas of Cau et al. (2007). We introduce duplicate Hg(II) tracers that are produced and lost exactly as the original Hg(II) tracers, but at each time step we set to zero the concentrations of these tracers within the dry subtropical areas. The amount of Hg(II) originating in the dry areas (dry-Hg(II)) is then calculated by difference between the original and the duplicate Hg(II) tracers. This simulation is performed for the ~~year~~years 2013-2016.

In addition, we perform three one-year (2013) sensitivity simulations with the tagged tracers addressing uncertainties in mercury oxidation and Hg(0):Hg(II) partitioning in anthropogenic emissions (Sect. 2.2.1).

### 2.2.3 Comparison of modeled and measured Hg(II)

Figures 1–3 compare the modeled Hg(II) concentrations and wet deposition fluxes to observations from the MDN, EMEP, and AMNet networks. The modeled annual wet deposition flux at the MDN sites (10.4 ± 4.2 μg $m^{-2}$ $a^{-1}$; mean ± standard deviation) is in close agreement with observations (10.2 ± 4.0 μg $m^{-2}$ $a^{-1}$) (Fig. 1a). The model reproduces the observed spatial pattern in annual wet deposition fluxes ($r^2$=0.67). Wet deposition is lowest in western U.S. (MDN: 6.9 μg $m^{-2}$ $a^{-1}$, GEOS-Chem: 6.2 μg $m^{-2}$ $a^{-1}$), higher in the northeast U.S. (MDN: 8.5 μg $m^{-2}$ $a^{-1}$, GEOS-Chem: 8.4 μg $m^{-2}$ $a^{-1}$) and in the central U.S. (MDN: 11.2 μg $m^{-2}$ $a^{-1}$, GEOS-Chem: 13.2 μg $m^{-2}$ $a^{-1}$), and largest in the southeast U.S. (MDN: 15.4 μg $m^{-2}$ $a^{-1}$, GEOS-Chem: 15.2 μg $m^{-2}$ $a^{-1}$). The observed monthly-mean wet deposition fluxes exhibit a seasonal maximum in summer, particularly in the central, northeast and southeast regions (Fig. 1c). This seasonality is driven by an increase in precipitation and an increase in mercury concentrations in precipitation (Prestbo and Gay, 2009; Selin and Jacob, 2008). The model reproduces the observed seasonal variations in the central and northeast regions, but underestimates the summer deposition fluxes in the southeast because of a factor of 2 underestimate in summertime precipitation by the GEOS-~~5~~-FP meteorological fields (not shown). Overall, 66–88% of the modeled wet deposition fluxes are within a factor of 2 of the observations (FAC2; FAC2=~~fraction~~percentage of points where $0.5 \le M_i / O_i \le 2$ where $O_i$ and $M_i$ are observed and simulated values, respectively) for the four regions, and the normalized mean bias (NMB; $NMB=\sum_i (M_i - O_i) / \sum_i O_i \times 100\%$ ; $NMB=\sum_i (M_i - O_i) / \sum_i O_i$ )) ranges between -7% and +20%.

The model also captures the observed annual VWM concentrations (MDN: 10.0 ± 4.3 ng $L^{-1}$; GEOS-Chem: 9.7 ± 4.7 ng $L^{-1}$) (Fig. 1d). Higher VWM concentrations are observed in the western and central U.S. (11.6 and 14.1 ng $L^{-1}$ respectively) compared to the northeast and southeast (7.9 and 10.6 ng $L^{-1}$

respectively), indicating the presence of higher atmospheric concentrations of Hg(II) over these regions. Modeled VWM concentrations show a spatial pattern similar to observations: higher values in western (8.7 ng $L^{-1}$) and central (14.4 ng $L^{-1}$) U.S. and lower values in northeast (6.7 ng $L^{-1}$) and southeast (13.6 ng $L^{-1}$). In western and central U.S. the observed and modeled VWM concentrations show a pronounced summer maximum (Fig. 1d), while in northeast and southeast the seasonal cycle is weaker. We find that 65–96% of the modeled monthly VWM concentrations are within a factor of 2 of the observations, with a NMB ranging between -22% and +33%. Over southeast U.S., ~~tmodeled~~modeled VWM concentrations are higher than observations during winter and spring, suggesting a model overestimate in atmospheric Hg(II) concentrations in that region, or an overestimate in the amount of Hg(II) scavenged by precipitation.

Over Europe (Fig. 2a), the modeled wet deposition flux (3.5 ± 1.4 μg $m^{-2}$ $a^{-1}$) underestimates observations at EMEP sites (6.1 ± 3.1 μg $m^{-2}$ $a^{-1}$). Similarly, modeled VWM concentrations (3.6 ± 1.0 ng $L^{-1}$) are significantly lower than observations (6.0 ± 1.8 ng $L^{-1}$) (Fig. 2b). The summertime underestimate is partially explained by a 40% underestimate of observed summertime precipitation by the GEOS-~~5~~ FP meteorological fields, but the discrepancy exists year-round. The remaining discrepancy could indicate an underestimate in the modeled Hg(II) concentrations over the region, likely because the upward scaling of the Br concentrations in our simulation did not extend north of 45°N and covered only parts of southern Europe (~~Section~~Sect. 2.2). The modeled seasonal cycle in wet deposition shows higher fluxes from April to August, following qualitatively the observed seasonal cycle (Fig. 2c). We find that 55% of the modeled monthly-mean wet deposition fluxes are within a factor of 2 of the observations, with a NMB of -46%. Model and observations display a similar seasonal cycle in VWM, with higher concentrations in April through August (Fig. 2d). The FAC2 and NMB statistics for the modeled VWM concentrations are 63% and -41% respectively, suggesting that the modeled oxidation rate is too slow over this region.

In Fig. 3 we present a comparison of modeled surface Hg(II) concentrations with observations at AMNet sites. Modeled Hg(II) surface concentrations (11.7 ± 8.3 pg $m^{-3}$) are comparable to observations (15.0 ± 8.2 pg $m^{-3}$) (Fig. 3a). The fact that the observations and the simulations are for different periods adds additional uncertainty from inter-annual variations. From four years of model simulation (2013-16), we estimate this uncertainty at ±30%. The model simulates enhanced Hg(II) surface concentrations (25–40 pg $m^{-3}$) over the intermountain region of the western U.S., consistent with AMNet observations in Utah. During summer, observed and modeled Hg(II) concentrations reach a minimum in the eastern U.S. (Fig. 3b). This is due to multiple factors: larger losses of Hg(II) by wet deposition and reduction induced by increasing low cloud coverage and precipitation, as well as decrease in Hg(II) production following the seasonal cycle in Hg(0) concentrations (Amos et al., 2012; Zhang et al., 2012). Overall, we find that 70% of monthly-mean modeled concentrations are within a factor of 2 of AMNet observations in the eastern U.S., with a NMB of -21%. If we assume that the reported RGM is underestimated by factor of 3 due to interferences (see Sect. 2.1), we find a model NMB of -57%.

Figs. S1–S3 present further evaluation of the model with observations at other ground-based sites as well as with aircraft observations. The modeled Hg wet deposition fluxes and VWM concentrations are in reasonable agreement with the observations (NMB: 48–52%, FAC2: 64–78%), and show a high correlation (r = 0.86–0.93) (Fig. S1a,b). This suggests that the model is able to capture patterns of Hg deposition observed at sites in different parts of the world. The comparison of the model with Hg(II) surface concentrations also shows moderate agreement (NMB: -9%, FAC2: 50%, r: 0.46) (Fig. S2). The model is also able to broadly capture the increase in Hg(II) concentrations with altitude observed in aircraft measurements over Tullahoma, TN, U.S. (Fig. S3a) and during the NOMADSS campaign (Fig. S3b). The NMB at higher altitudes (>3 km for Tullahoma, TN and >4 km for NOMADSS) is between -29% and 14%, and a FAC2 of about 50%. The model is unable to capture the higher Hg(II) concentrations in the 1-3 km region that were observed during one flight of the NOMADSS campaign as previously discussed in Shah et al. (2016).

## 3 Tagged simulation results

### 3.1 Global distribution of tagged Hg(II) tracers

The annual zonal mean distribution of modeled Hg(II) concentrations is shown in Fig. 4a. Hg(II) concentrations increase from 10 pg $m^{-3}$ near the surface to 1000 pg $m^{-3}$ in the upper troposphere, and exhibit local maxima in the subtropical middle troposphere, within the descending Hadley branches. The chemical production rate of Hg(II) (via reactions R1–R3, Fig. 4b) increases by an order of magnitude between the lower and upper troposphere. This increase is driven by increasing Br concentrations coupled with colder temperatures (hence slower thermal decomposition of HgBr in R1) (Holmes et al., 2010). Regions of high Hg(II) production rates also occur near the surface in the Arctic due to springtime release of Br in bromine explosion events (Holmes et al., 2010). The elevated Southern Ocean production rates are associated with high emissions of sea-salt aerosol, which are assumed to release bromine (Parrella et al., 2012). Note that the sharp gradients in Hg(II) production rates at 45°N and 45°S reflect the boundaries of the Br scaling in the model.

The lifetime of Hg(II) increases from less than 1 day in the lower troposphere to over 3 years in the tropical upper troposphere. Hg(II) in the lower troposphere is subject to dry deposition, and in-cloud reduction and scavenging by precipitation in the lower and middle troposphere. Thus, despite higher production rates, Hg(II) concentrations over the Arctic and the Southern Ocean are low. The long lifetimes of Hg(II) in the upper troposphere and in the descending branches of the Hadley circulation are due to infrequent occurrence of reduction within clouds and wet scavenging. As summarized in Table 1, we find that the tropospheric lifetime of Hg(II) ~~is highest~~decreases from 43 days for the STRAT tracer ~~(45 days),~~ and ~~decreases to~~ 22 days~~, 4.1 days, and~~ for the UT tracer down to 0.6 days for the ~~UT, MT, and~~ LT ~~tracers, respectively~~tracer. This is consistent with expectations, as most of the UT tracer, for example, resides in the upper troposphere, where deposition is slower.

The large production rates of Hg(II) in the upper and middle troposphere combined with a longer lifetime result in the large contributions of the UT and MT tracers to the tropospheric mass and deposition of Hg(II). Overall, the tropospheric burden of Hg(II) ~~(616 Mg)~~ is dominated by Hg(II) produced in the UT (~~514 Mg, 83~~84%), with ~~smaller contributions~~contribution of 8% from the stratosphere (STRAT~~: 50 Mg, 8%)~~) and the MT~~ (47 Mg, 8%),~~, and less than 1% from the LT ~~(4 Mg)~~ and direct emissions ~~(1 Mg)~~ (Table 1). The UT ~~tracer contributes 67%~~ and MT tracers each contribute 35-40% of the Hg(II) burden in the ~~middle and~~ lower troposphere ~~respectively~~ (Table 1 and Fig. 4d~~), and the MT tracer accounts for 40% of Hg(II) in the lower troposphere (Table 1 and Fig. 4e).~~ and e). The contribution of the LT tracer ~~accounts for 20% of the Hg(II) burden in the lower troposphere (Table~~

~~1), and its contribution~~ increases to >50% near the surface over the Arctic and the Southern Ocean (Fig. ~~4f).~~4f), where local production of Hg(II) in the polar and marine boundary layers is larger. We also find that ~~70%~~most of the Hg(II) in the lowermost stratosphere is comprised of the UT tracer (Fig. 4d), because Hg(0) is rapidly oxidized in the upper troposphere and is almost completely depleted before reaching the stratosphere, as shown by observations (Talbot et al., 2007; Lyman and Jaffe, 2012). The E-Hg(II) tracer accounts for 5% of the Hg(II) burden in the lower troposphere (Table 1), but its contribution increases to >10% over the northern mid-latitudes (Fig. 4h).

~~We find that 54~~81% of the ~~global~~ tropospheric Hg(II) production ~~of Hg(II) occurs~~happens in the ~~UT (8560 Mg a$^{-1}$), with smaller contributions from the MT (27%), LT (16%), STRAT (3%),~~upper and ~~direct emissions (1%)~~middle troposphere (Table 1). Together, the UT and MT tracers account of 91% of global surface wet deposition (60% from UT and 31% from MT) and 52% of dry deposition (24% from UT and 28% from MT). Their higher contributions to wet deposition is because precipitation scavenging can directly remove these tracers from higher altitudes, while dry deposition requires the transport of these tracers to the planetary boundary layer.

### 3.2 Origin of Hg(II) in surface deposition and concentrations

As shown in Fig. 5a, the highest surface Hg(II) concentrations (>50 pg m$^{-3}$) are simulated over high-elevation areas (e.g., western U.S., the Andes, and the Tibetan plateau), in polar regions, near emission sources (e.g., East Asia), and in dry subtropical areas (e.g., the Sahara desert, southern Africa, and Australia). Modeled Hg(II) concentrations are generally low over the oceans because of fast removal by sea-salt aerosols. Together, the UT and MT tracers account for 63% of surface Hg(II) over the continents (Fig. 5e and 6b). Hg(II) over most of the oceans is predominantly from the LT tracer (Fig. 5e). In the subtropical anticyclones, free-tropospheric air is entrained in the marine boundary layer due to large-scale subsidence causing higher contributions from the MT. For western U.S., South America, Africa, and Australia, UT and MT each make a contribution of about 40% to surface Hg(II), whereas for the Pacific and the North Atlantic Oceans 57% of surface Hg(II) is from the LT tracer (Fig. 6b). The contribution of E-Hg(II) to surface Hg(II) concentrations is limited to regions with high anthropogenic emissions. We calculate that 27–69% of surface Hg(II) in eastern U.S., Europe, East and South Asia consists of E-Hg(II) (Fig. 6b). The contribution of E-Hg(II) is >80% in areas close to emission sources (Fig. 5e), and is likely to be higher within tens of kilometers of the sources. However, the near-source contribution of emitted Hg(II) cannot be estimated with our 2° latitude × 2.5° longitude global model.

The global distribution of the Hg(II) wet deposition flux (Fig. 5b) largely follows the spatial distribution of precipitation, with high wet deposition along the Intertropical Convergence Zone (ITCZ) and in the mid-latitude storm tracks. Globally, the UT tracer accounts for 60% of Hg(II) in wet deposition, but in some areas over South America, Africa, and Asia it exceeds 70% (Fig. 5f). The MT tracer makes up most of the remaining fraction of wet deposition, with a global average contribution of 31% (Table 1). The contribution from the LT tracer is significant only at high latitudes, while the contribution from E-Hg(II) ~~is noticeable~~reaches values greater than 10% mainly ~~in~~over East Asia. The relative wet deposition contributions of the tagged Hg(II) tracers remain fairly uniform across the ten regions summarized in Fig. 6c.

The Hg(II) dry deposition flux (Fig. 5c) maximizes in the subtropical anticyclones, where subsidence provides a source of free-tropospheric Hg(II) to the planetary boundary layer. In addition, local maxima occur downwind of the emissions regions of the eastern US and East Asia, over high-elevation regions in western U.S. and the Himalayas, and over the Southern Ocean. In terms of the tagged tracers, their spatial contribution to dry deposition (Fig. 5g) is similar to their contribution to surface Hg(II) concentrations (Fig. 5e). We find that 79–82% of the Hg(II) dry deposition over western U.S., South America, Africa, and Australia is from the UT and MT tracers. The E-Hg(II) tracer contributes 21–62% to dry deposition over eastern U.S., Europe and South and East Asia (Fig. 6d). Over the Pacific and North Atlantic Oceans, the UT, MT, and LT tracers each contribute about 30% to the dry deposition flux (Fig. 6d).

In Sect. 2.2.3 we saw that the model overestimated observed wet deposition of Hg(II) over southeast U.S. during winter and spring. As a result, our estimate of the contribution of UT and MT tracers is likely an overestimate for this region and season. From our model evaluation, we had also concluded that our free-tropospheric Hg(II) production was too slow over Europe and, possibly, other regions north of 45°N. This suggests an underestimate of the concentrations of modeled UT and MT tracers in these regions.

Our estimate that 92% of Hg(II) wet deposition and 73% of dry deposition over the U.S. is contributed by production in the upper and middle troposphere is qualitatively consistent with the estimates of Selin and Jacob (2008). They calculated that 59% of the Hg(II) wet deposited over the U.S. was scavenged above 1.5 km, and that 70% of the Hg(II) below 1.5 km was transported from elsewhere. For comparison, with our simulation we find that 85% of the Hg(II) wet deposited over the U.S. is scavenged above 1.5 km (note that to be consistent with Selin and Jacob (2008), we are comparing here the contribution of Hg(II) *present* above 1.5 km, and not the Hg(II) *produced* above 1.5 km). While Selin and Jacob (2008) also used the GEOS-Chem model, their simulation was based on Hg(0) oxidation by OH and $O_3$, while ours is based on oxidation by Br. In Sect. 3.3, we quantify the sensitivity of our results to the oxidation pathway assumed.

### 3.3 Model sensitivity to oxidation chemistry and emission speciation

We now assess the sensitivity of our results to our assumptions about mercury oxidation and Hg(0):Hg(II) partitioning in anthropogenic emissions. We perform three additional one-year (2013) sensitivity simulations with the following changes with respect to the base simulation: (i) use of the original GEOS-Chem Br concentrations instead of the 3 times Br concentrations in the base simulation, (ii) use of $O_3$ and OH as the Hg(0) oxidants (rate constants of Hall (1995) and Sommar et al. (2001)) instead of Br, and (iii) with the default UNEP/AMAP Hg(0):Hg(II) emission speciation of 55%:45% instead of the modified speciation. We summarize the results of these three sensitivity simulations relative to the base simulation in Table 2.

When we use the original GEOS-Chem Br concentration, the contribution of the UT and MT tracers to the tropospheric Hg(II) burden decreases ~~from 91%~~ to 78~~%. The contribution of the STRAT tracer increases to 21% compared to 8% in the~~% (base~~ simulation. The contribution of UT and MT tracers to total deposition (64%) is also smaller compared to the base simulation (76~~: 92%), while the contribution ~~of LT tracer~~ to total deposition ~~increases from 20%~~decreases to ~~27%.~~64% (base: 77%, see Table 2). In the $O_3$ and OH oxidation simulation, we find that Hg(II) production shifts to lower altitudes, leading to an increase in the ~~contribution~~contributions of the ~~MT (18%)~~LT and ~~LT (4%)~~MT tracers to ~~the~~ tropospheric Hg(II) mass ~~is higher compared to the~~ (base~~ simulation (MT: 8%, LT: <1%), while the~~

~~contribution of the UT tracer decreases to from 83% to 60%. For total deposition, a larger fraction of Hg(II) production occurs in the middle and lower troposphere with the~~: 8%; $O_3$~~ and ~~/OH~~ oxidation simulation: LT: 38%, MT: 38%, UT: 19%~~: 22%) and deposition flux (base~~, LT: 20%, MT: 30%, UT: 46%). When we ~~: 49%; $O_3$/OH: 76%). The change in the Hg(0):Hg(II) emission speciation~~,~~ results in a doubling of the contribution of E-Hg(II) tracer to total deposition~~ increases to 4% from 2% in the base simulation~~, but the contribution of the UT and MT tracers to deposition remains nearly unchanged~~.~~ (Table 2). In all three sensitivity simulations, we find that the UT+MT tracers together contribute significantly to the tropospheric mass (78–90%) and the surface deposition flux (57–76%) of Hg(II), thus our overall conclusions remain robust.

## 4 Role of the subtropical dry regions

In this section, we focus on the specific role of subtropical anticyclones as a global reservoir of Hg(II). The large-scale sinking motion in the subtropical anticyclones transports Hg(II) produced in the upper and middle troposphere downwards, and suppresses cloud formation and precipitation, thereby inhibiting Hg(II) loss of by reduction and wet deposition. The subtropical anticyclones, therefore, act as global reservoirs of Hg(II), as we presented in Shah et al. (2016)~~We quantify the Hg(II) that~~. Here, we further quantify how much Hg(II) is transported from the subtropical anticyclones (dry-Hg(II) tracer) with a simulation where we artificially set to zero the Hg(II) present in the subtropical dry areas~~, which we define~~ (defined as RH < 20% and latitude < 45~~° (Sect. 2.2.2).~~°). Figure 7 shows the ~~contribution of dry-Hg(II) to ~~means and the ~~annual-mean ~~anomaly of the contributions of dry-Hg(II) to surface Hg(II), 500 hPa Hg(II), and Hg(II) wet deposition~~.~~ for 2013-2016. The anomaly is defined here as the maximum deviation of the contribution of dry-Hg(II) for individual years from the 4-year mean. Areas at 500 hPa where the 2013-2016 monthly mean RH was less than 20% for minimum of four months ~~in the year ~~out of twelve are shown in Fig. ~~7b~~7c and d. Based on ~~our~~this definition, we find that the dry areas contain 8% of the tropospheric mass of air.

We see from Fig. 7a that dry-Hg(II) ~~present in the subtropical dry areas ~~exerts a ~~strong~~disproportionate influence on surface Hg(II) concentrations ~~at the surface ~~between 40°S and 40°N~~.~~, where its contribution is 45 ± 25%. The influence is ~~stronger~~higher over the continents (64%) than over the oceans, where the local production of Hg(II) in the marine boundary layer is larger. More than 80% of the surface Hg(II) over dry areas in Africa, the Middle East, and Australia, and in the high-elevation regions of western U.S., Tibetan Plateau, and South America consists of dry-Hg(II). The influence of dry-Hg(II) on surface Hg(II) concentrations is ~~small~~<20% in anthropogenic Hg(II) source regions such as eastern U.S. and East Asia, and in regions that experience deep convection such as the ITCZ in the Pacific, Atlantic, and Indian Oceans, South Asia, the Maritime Continent. ~~Surface~~ The inter-annual variation of the dry-Hg(II) ~~in areas poleward of 40°~~contribution is ~~from anthropogenic emissions (Europe), is produced locally (polar regions), or is~~ generally less than 5% (Fig. 7b). Hg(II) can also be transported to the surface from higher altitudes in transient large-scale eddies ~~(~~in the mid-latitudes. Over Canada and Russia, for example, the UT+MT tracer contribution to surface Hg(II) is 50%, but the influence of dry-Hg(II) is <10% (Figs. 5e and 7a).

~~The bulk~~90% of the mass of Hg(II) present at 500 hPa in the 40°S–40°N band is made up of dry-Hg(II) (Fig. ~~7b~~7c), with little inter-annual variation (Fig. 7d). The contribution of dry-Hg(II) extends far beyond the boundaries of the dry areas, suggesting that these regions act as global suppliers of Hg(II). Our model simulation suggests that 74% of the Hg(II) present at 500 hPa over the continental U.S. is transported from the dry subsidence band over the Pacific Ocean. The contribution of dry-Hg(II) decreases north of 40°N, but is still larger than 25% over most parts of Canada, Europe, and northern Asia. The contribution of dry-Hg(II) to Hg(II) wet deposition falls in-between the contributions of dry-Hg(II) to the surface and 500 hPa concentrations (Fig. ~~7c~~7e), as most precipitation scavenging of Hg(II) occurs between the surface and 500 hPa. The inter-annual variability reaches 10-20% over the western and SE U.S., Eastern Europe, and Eastern Asia (Fig. 7f). In areas of the globe with large deposition fluxes (the ITCZ and the mid-latitude storm tracks) at least 50% of the deposition consists of dry-Hg(II). Globally, dry-Hg(II) accounts for ~~74~~78% to the tropospheric Hg(II) mass, and ~~59~~61% of the total Hg(II) deposition (wet: ~~62~~69% and dry: ~~52~~48%).

During the 2013 NOMADSS aircraft campaign, high Hg(II) concentrations were observed and simulated above 5 km altitude (observations: 189 ± 103 pg $m^{-3}$; model: 165 ± 104 pg $m^{-3}$) (Shah et al., 2016). Back trajectory calculations indicated that these air masses were transported from even higher altitudes within the Pacific and the Atlantic anticyclones (Gratz et al., 2015; Shah et al., 2016). We sample the GEOS-Chem model along the NOMADSS flight tracks to determine the contribution of dry-Hg(II) to the Hg(II) concentrations measured during the campaign. We find that dry-Hg(II) accounted for 75% of Hg(II) when observed Hg(II) concentrations exceeded 250 pg $m^{-3}$ (Fig. 8). The dry-Hg(II) contribution decreased for observations with lower Hg(II) concentrations: 58% for 200–250 pg $m^{-3}$ and 10–20% for concentrations below 200 pg $m^{-3}$. The association between NOMADSS observations of high Hg(II) concentrations and higher contribution of dry-Hg(II) adds support to our finding that the subsidence regions act as a large source of Hg(II) present and deposited over the U.S.

Our finding is consistent with ground-based Hg(II) observations in western U.S., an area heavily influenced (>60%) by Hg(II) present in the dry subtropical regions (Fig. 7). Weiss-Penzias et al. (2009) reported that occurrence of higher (~50 pg $m^{-3}$) RGM concentrations in Nevada during June–August were associated with subsiding air in the anticyclone located over the Pacific Ocean, and Huang and Gustin (2012) found higher than mean Hg(II) deposition in Nevada under similar patterns of air transport. Timonen et al. (2013) showed that the highest concentrations of RGM (700 pg $m^{-3}$ ) observed at the Mt. Bachelor Observatory in Oregon (2.7 km altitude) corresponded to air masses transported from the subtropical Pacific Ocean.

## 5 Tagged tracer contributions at MDN and AMNet sites

Our tagged simulation show that the upper and middle troposphere are the predominant regions of production of Hg(II). Thus, areas where wet deposition is strongly influenced by Hg(II) produced in these regions can be expected to have higher wet deposition flux of Hg(II). We now examine whether such an enhancement in Hg wet deposition flux is indeed observed at MDN sites. Figure 9 shows the relationship between observed MDN annual Hg wet deposition fluxes to precipitation and modeled contribution of the UT and MT tracers to the wet deposition flux at the site locations. As expected, we see that Hg wet deposition fluxes increase with increasing precipitation (e.g. Prestbo and Gay, 2009; Selin and Jacob, 2008). In addition, we find that the Hg wet deposition fluxes increase with increasing contribution of the UT and MT tracers to the wet deposition flux. Using multiple linear regression, we derive the following relationship between the observed Hg flux, [μg $m^{-2}$ $a^{-1}$], precipitation amount, [mm a$^{-1}$], and contribution of UT+MT [%]: $\text{Flux} = a_1 \times \text{Precipitation} + a_2 \times \text{UT+MT contribution} + a_3$. Where, $a_1 = 0.004\ \mu\text{g L}^{-1}$, $a_2 = 0.8\times10^{-2}\ \mu\text{g m}^{-2}\text{a}^{-1}$, and $a_3 = -68$ ; $\text{Flux} = 0.004\times(\text{Precipitation}) + 0.8\times(\text{UT+MT contribution}) - 68$ ;. The regression parameters are statistically significant (p<0.001, 2-sided t-test, N=80), implying that both higher precipitation amounts and higher contribution of UT+MT tracers to wet deposition result in higher Hg flux. Precipitation amounts and the contribution of UT and MT together explain 55% of the spatial variation in the observed Hg flux, while individually they explain 25% and 42% of the spatial variation, respectively. This is consistent with previous studies that have shown higher Hg wet deposition flux in convective thunderstorms that can scavenge Hg(II) present at high altitudes (Guentzel et al., 2001; Shanley et al., 2015; Holmes et al., 2016; Kaulfus et al., 2017).

AMNet sites in the eastern U.S. are close to regional Hg(II) emission sources, and are thus more likely to be influenced by Hg(II) directly emitted rather than by Hg(II) produced aloft. Figure 10 shows that the 2009–2012 median Hg(II) concentrations observed at the AMNet sites in the eastern U.S. are higher at sites where the contribution of E-Hg(II) tracer is higher. For example, the surface Hg(II) concentrations at sites NY06, WV99, and MD08 are ~10 pg m$^{-3}$, with 60–65% of the Hg(II) due to the E-Hg(II) tracer. On the other hand, at the remote site NS01, Hg(II) concentration are 3 pg m$^{-3}$ and the contribution of E-Hg(II) tracer is less than 10%. We find that spatial variation in the contribution of the E-Hg(II) tracer explains 27% of the variation in observed surface Hg(II) concentrations at the AMNet sites (excluding the outlier NY95) in the eastern U.S. (Fig. 10b). A statistically significant linear relationship (p=0.018, 2-sided t-test, N=20, NY95 excluded) between Hg(II) concentrations and the contribution of the E-Hg(II) tracer is obtained from ordinary least squares regression. This suggests that although Hg(II) produced in the free troposphere makes up a large part of Hg(II) in the planetary boundary layer, spatial variations in Hg(II) concentrations in areas close to Hg(II) sources reflect variations in the amount of directly emitted Hg(II).

**6 Implications**

Our modeling study indicates that ~~91% of the global~~even in areas with large anthropogenic sources of Hg(II) most of the mercury wet deposition flux consists of Hg(II) produced in the upper and middle troposphere. ~~Even in areas with large anthropogenic sources of Hg(II), such as Europe and East Asia, directly emitted Hg(II) makes up less than 30% of the regional wet deposition flux, while Hg(II) produced locally in the lower troposphere accounts for less than 5%.~~ This implies that regional decreases in anthropogenic Hg emissions do not lead to a proportional regional decrease in wet deposition. Indeed, numerous studies have demonstrated the importance of intercontinental transport to mercury wet deposition (see Pirrone and Keating, 2010 and references therein). For example, Jaeglé et al. (2009) found that a 20% decrease in regional anthropogenic mercury emissions in the GEOS-Chem model leads to between 3% (North America) and 12% (East Asia) decrease in mercury deposition. Moreover, observed long-term temporal trends in mercury wet deposition reflect trends in the global emissions of Hg(0) (Zhang et al., 2016; Weiss-Penzias et al., 2016; Zhang and Jaeglé, 2013). Our study shows that oxidation of Hg(0) in the upper and middle troposphere is the key to linking ~~the~~ global emissions ~~and~~to deposition of mercury.

~~We also find that the spatial variation in mercury wet deposition flux at MDN sites is significantly influenced by the variation in the contributions of Hg(II) produced in the upper and middle troposphere. In particular,~~We also find that a large fraction of the upper and middle tropospheric Hg(II) over the U.S. is transported from the subsiding subtropical anticyclone over the Pacific Ocean. Thus, we expect that variability in the location of the Pacific anticyclone, the synoptic wind patterns transporting Hg(II) to the U.S., the heights of the precipitating clouds, in addition to the amount and type of precipitation can affect Hg wet deposition flux over a particular area. These meteorological conditions vary in response to natural variability associated with multiyear phenomena, such as the El Niño-La Niña cycle (Gratz et al., 2009), and can confound the interpretation of spatial and temporal trends in wet deposition at MDN sites.

Our results support the idea of a global pool of Hg(II) in the free troposphere. We find that this global pool of Hg(II) is concentrated in the upper troposphere (above 7 km) and extends to lower altitudes in the subsidence areas of the subtropical anticyclones. These regions of the atmosphere are where most of the production of Hg(II) takes place, and where the lifetime of Hg(II) against reduction and deposition is the longest, making them ideal target regions for future aircraft-based campaigns to understand the chemistry of mercury in the atmosphere.

## 7 Conclusions

We have added to the GEOS-Chem mercury model a Hg(II) tagging method following regions where Hg(II) is produced. We have performed a two-year simulation (2013–2014) with the tagged Hg(II) tracers, and have found that Hg(II) produced in the upper and middle troposphere constitutes 91% of the tropospheric mass of Hg(II), 91% of the annual Hg(II) wet deposition flux, and 52% of the annual Hg(II) dry deposition flux. The disproportionately high contribution of the Hg(II) produced in these regions is the result of higher production of Hg(II) in the upper and middle troposphere combined with a longer lifetime of Hg(II) and the large-scale subsidence of Hg(II) in the troposphere. Hg(II) produced in the upper and middle troposphere contributes 63% to surface Hg(II) over the continents, and 74–82% over western U.S, South America, Africa, and Australia. Over the oceans, however, surface Hg(II) is formed locally in the marine boundary layer because of Br released from sea-salt aerosols. Directly emitted anthropogenic Hg(II) makes up a significant fraction (27–69%) of surface Hg(II) concentrations near source regions in eastern U.S., Europe and South and East Asia. However, the wet deposition flux in these regions is largely (~90%) the result of Hg(II) produced in the upper and middle troposphere. The contribution of directly emitted Hg(II) can be higher within tens of kilometers of a source, but cannot be quantified by our coarse-resolution global model. We examined the sensitivity of our results by performing additional simulations with lower Br concentrations, different oxidants ($O_3$ and OH), and different Hg(0):Hg(II) anthropogenic emission speciation. In these simulations, too, we found that Hg(II) produced in the upper and middle troposphere together contribute significantly to the tropospheric Hg(II) mass (78–90%) and the global Hg(II) surface deposition flux (57–76%). ~~We quantified the role of Hg(II) in dry subtropical anticyclones and found it exerts a strong influence on Hg(II) concentrations at the surface and 500 hPa between 40°S and 40°N. About >60% of the surface Hg(II) over dry areas, such as the western U.S., is transported from these subtropical regions, while 74% of Hg(II) at 500 hPa over the continental U.S. originated in the subtropical anticyclones. We~~

also found that 75% of the observations with Hg(II) concentrations greater than 250 pg $m^{-3}$ observed during the NOMADSS aircraft campaign were transported from the subsidence regions, compared to only 10% for samples with Hg(II) concentrations less than 100 pg $m^{-3}$. We examined the consistency of our modeling results with measurements at the MDN, EMEP, and AMNet sites. We found reasonable agreement between the modeled and observed Hg wet deposition flux at the MDN sites (NMB: -7 to +20%, FAC2: 66 to 88%), and surface Hg(II) concentration at AMNet sites in the eastern U.S. (NMB: -21%, FAC2: 70%), but poorer agreement for Hg wet deposition flux at EMEP observations (NMB: -46%, FAC2: 55%). We also found that the Hg wet deposition flux at the MDN sites increases with increase in precipitation and the contribution of Hg(II) produced in the upper and middle troposphere. Together, they explain 55% of the spatial variation in the wet deposition flux across the MDN network. For AMNet sites in the eastern U.S., we find that 27% of the spatial variation is explained by the contribution of emitted Hg(II) to surface Hg(II) concentrations.

We quantified the role of Hg(II) in dry subtropical anticyclones and found it exerts a strong influence on Hg(II) concentrations at the surface (44% contribution) and 500 hPa (90% contribution) between 40°S and 40°N. Globally, dry-Hg(II) accounts for 78% to the tropospheric Hg(II) mass, and 61% of the total Hg(II) deposition. About >60% of the surface Hg(II) over dry areas, such as the western U.S., is transported from these subtropical regions, while 74% of Hg(II) at 500 hPa over the continental U.S. originated in the subtropical anticyclones. We also found that 75% of the observations with Hg(II) concentrations greater than 250 pg $m^{-3}$ observed during the NOMADSS aircraft campaign were transported from the subsidence regions, compared to only 10% for samples with Hg(II) concentrations less than 100 pg $m^{-3}$. Our results highlight the importance of the upper and middle troposphere as primary sites of Hg(II) production and of the subtropical anticyclones as the primary conduits for the production and export of Hg(II) in the global atmosphere.

## Data availability

The GEOS-Chem model results are available from the corresponding author upon request. The measurement data is available in the cited literature or at the network's websites.

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**Table 1 Tropospheric budgets of Hg(II) and individual tagged Hg(II) tracers.**

| | Total Hg(II) | Tagged Hg(II) tracers[a] | | | | |
|---|---|---|---|---|---|---|
| | | UT | MT | LT | STRAT | E-Hg(II) |
| Tropospheric mass of Hg(II)[b] [Mg] | ~~616~~618 | ~~514~~517 | ~~47~~48 | 4 | ~~50~~48 | 1 |
| Mass located in UT [Mg] | ~~479~~480 | ~~429~~432 | 3 | 0 | ~~47~~45 | 0 |
| Mass located in MT [Mg] | ~~117~~118 | ~~78~~79 | 36 | 0 | 3 | 0 |
| Mass located in LT [Mg] | 20 | 7 | 8 | 4 | 0 | 1 |
| Hg(II) production[b] [Mg $a^{-1}$] | 15,790 | 8,560 | 4,190 | 2,460 | 410 | 170 |
| Hg(II) reduction [Mg $a^{-1}$] | 9,740 | 5,750 | 2,390 | 1,260 | 290 | 50 |
| Hg(II) wet deposition [Mg $a^{-1}$] | 3,740 | 2,250 | 1,150 | 230 | 80 | 30 |
| Hg(II) dry deposition [Mg $a^{-1}$] | 2,310 | 570 | 640 | 970 | 40 | 90 |
| Hg(II) tropospheric lifetime [days] | 14 | 22 | 4.1 | 0.6 | ~~45~~43 | 2.2 |

(a) Regions are defined as follows: UT (upper troposphere: 400hPa–tropopause), MT (middle troposphere: 750–400hPa), LT (lower troposphere: surface–750hPa), STRAT (stratosphere), E-Hg(II) (directly emitted anthropogenic Hg(II)).

(b) 1 Mg = $10^6$ g, and 1 Mg $a^{-1}$ = $10^6$ g per year.

**Table 2 Contribution of tagged Hg(II) tracers to the tropospheric mass and total deposition of Hg(II) for the base case and the sensitivity simulations.**

| | Simulation | Tagged Hg(II) tracer contribution [%] | | | | |
|---|---|---|---|---|---|---|
| | | UT | MT | LT | STRAT | E-Hg(II) |
| Contribution to Hg(II) tropospheric mass [%] | Base | 84 | 8 | <1 | 8 | <1 |
| | Lower UT+MT Br[a] | 71 | 7 | 1 | 21 | <1 |
| | $O_3$/OH oxidation[b] | 61 | 18 | 4 | 17 | <1 |
| | Higher Hg(II) emissions[c] | 84 | 8 | <1 | 8 | <1 |
| Contribution to Hg(II) deposition [%] | Base | 47 | 30 | 19 | 2 | 2 |
| | Lower UT+MT Br[a] | 43 | 21 | 27 | 6 | 3 |
| | $O_3$/OH oxidation[b] | 20 | 38 | 38 | 2 | 2 |
| | Higher Hg(II) emissions[c] | 49 | 28 | 17 | 2 | 4 |

(a) Simulation using the original GEOS-Chem Br concentrations instead of the 3 times Br concentrations in the base simulation,
(b) Simulation using $O_3$ and OH as the Hg(0) oxidants instead of Br as in the base simulation,
(c) Simulation using the default UNEP/AMAP Hg(0):Hg(II) emission speciation of 55%:45% instead of the 90%:10% speciation as in the base simulation.

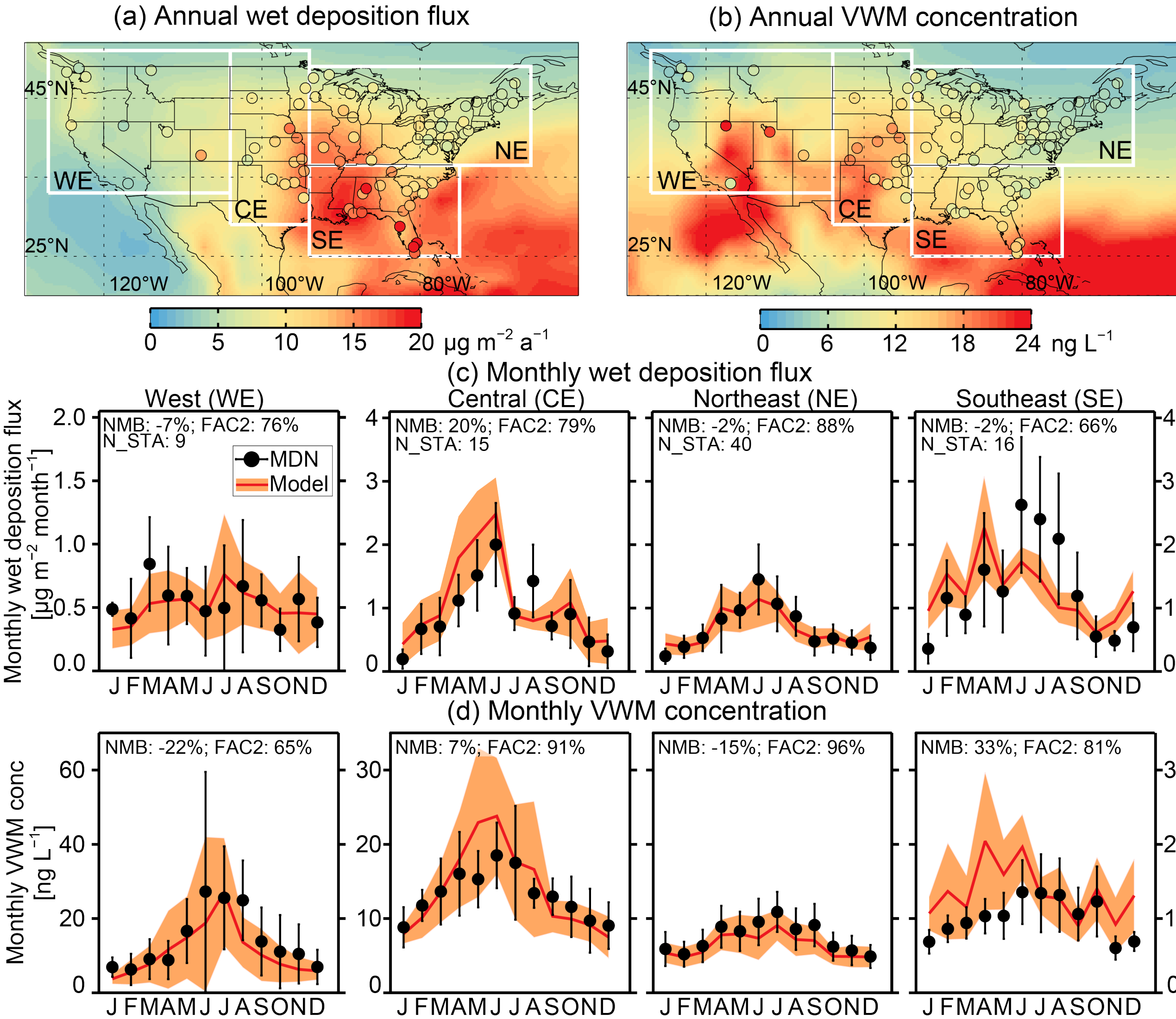


**Figure 1: (a) Annual Hg(II) wet deposition fluxes and (b) volume-weighted mean (VWM) mercury concentrations over the U.S. for 2013–2014. The map backgrounds show the GEOS-Chem results and the filled circles show the Mercury Deposition Network (MDN) measurements. The bottom two rows (c and d) show the seasonal variations in wet deposition and VWM concentrations for the four regions marked by white boxes in (a) and (b): west (WE), central (CE), northeast (NE), and southeast (SE). Black circles and error bars show the observed means and standard deviations. The red lines and orange shading are for the modeled means and standard deviations. Each panel displays the Normalized Mean Bias (NMB) and the ~~fraction~~ percentage of model-observation pairs within a factor of 2 of each other (FAC2). The number of stations in each region (N_STA) is also shown. Note the different scales on the y-axis for the WE region relative to the other regions (panels c and d).**

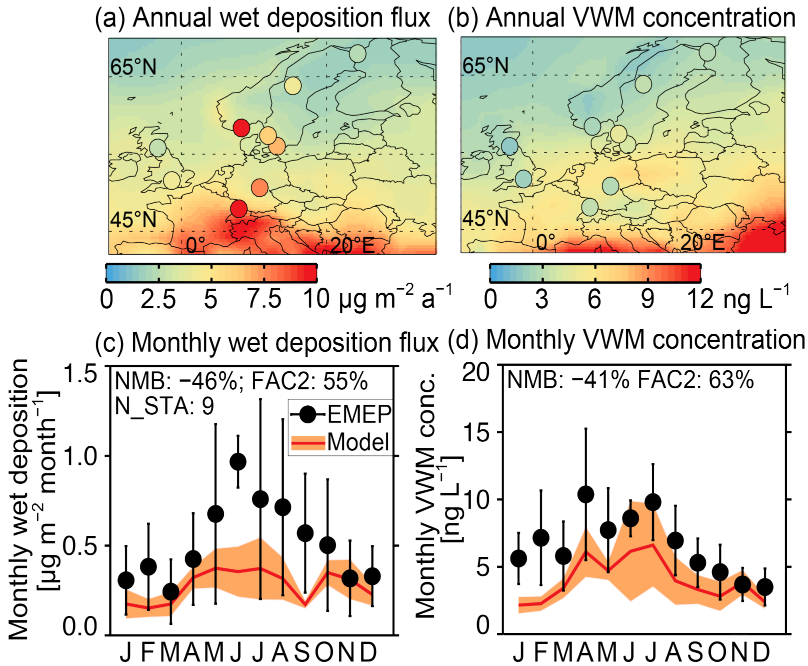


**Figure 2: Same as Figure 1, but for European Monitoring and Evaluation Programme (EMEP) sites.**

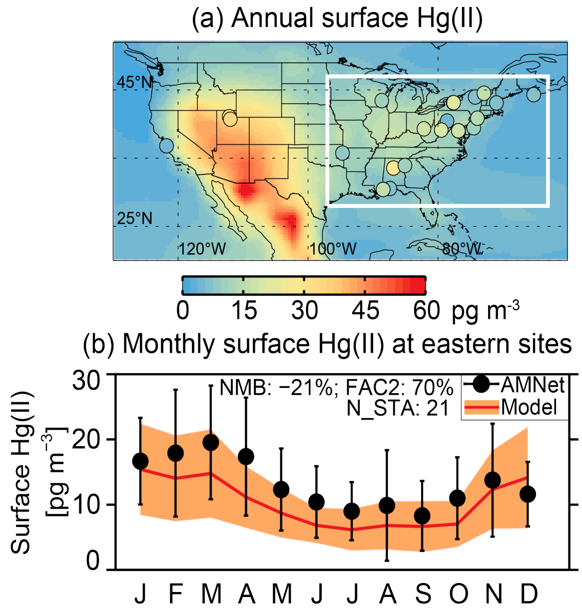


**Figure 3: (a) Annual surface Hg(II) concentrations over the U.S. The map backgrounds show the GEOS-Chem concentrations (2013–2014), and the filled circles show the observations at Atmospheric Mercury Network (AMNet) sites (2009–2012). (b) Monthly surface Hg(II) concentrations at the AMNet sites in the eastern U.S. (white box in panel a). Black circles and error bars show the mean and standard deviation of the monthly-mean observations. Red lines and orange shading indicate the modelled means and standard deviations.**

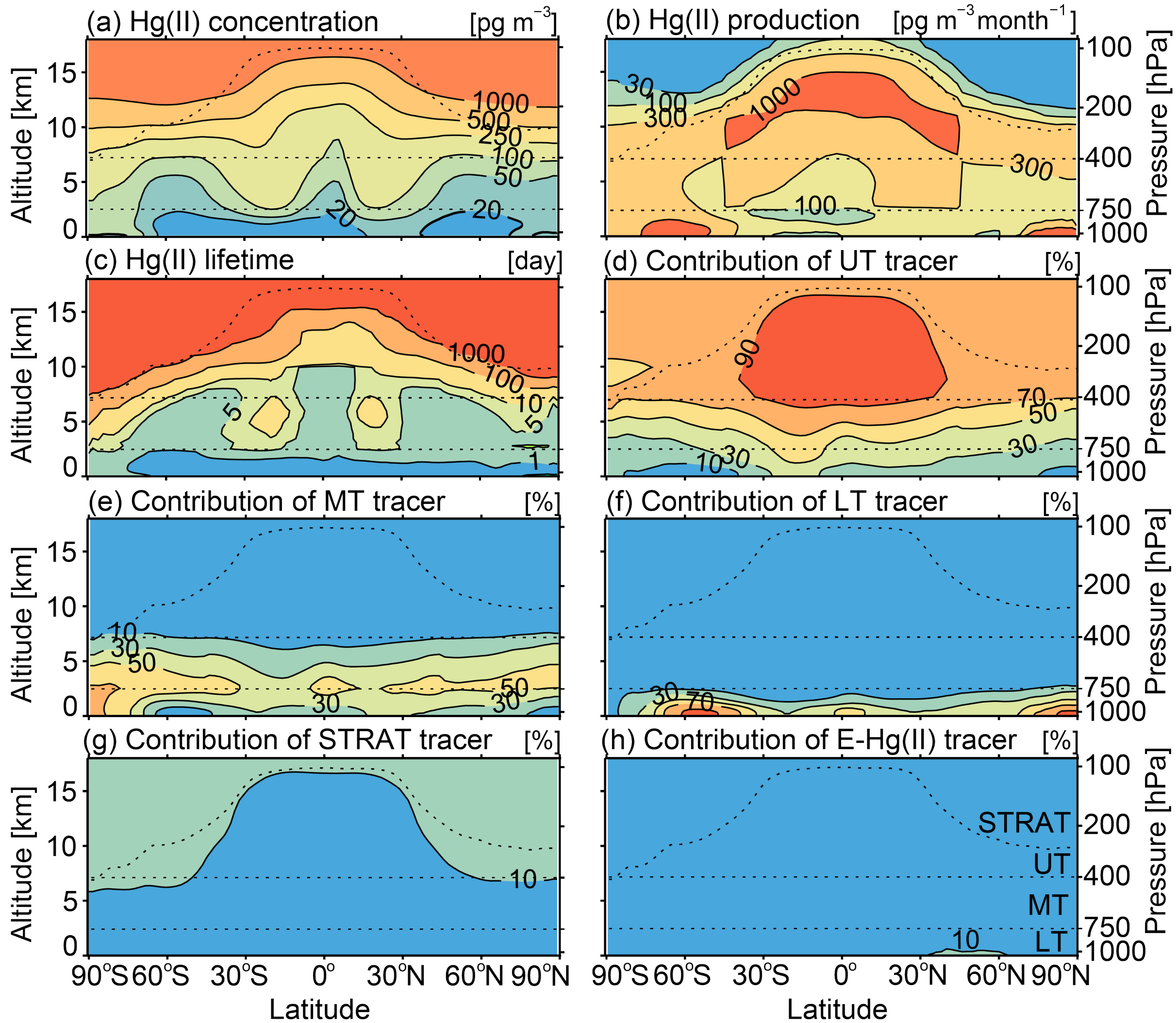


**Figure 4: Modeled zonal mean (a) Hg(II) concentrations (pg m$^{-3}$), (b) Hg(II) production rates (pg m$^{-3}$ month$^{-1}$), and (c) lifetime (days) for 2013-2014. Panels (d-h) show the percent contributions of Hg(II) tagged tracers produced in the upper troposphere (UT), middle troposphere (MT), lower troposphere (LT), stratosphere (STRAT), and directly emitted (E-Hg(II)). Dotted lines indicate our boundaries for STRAT, UT, MT, and LT.**

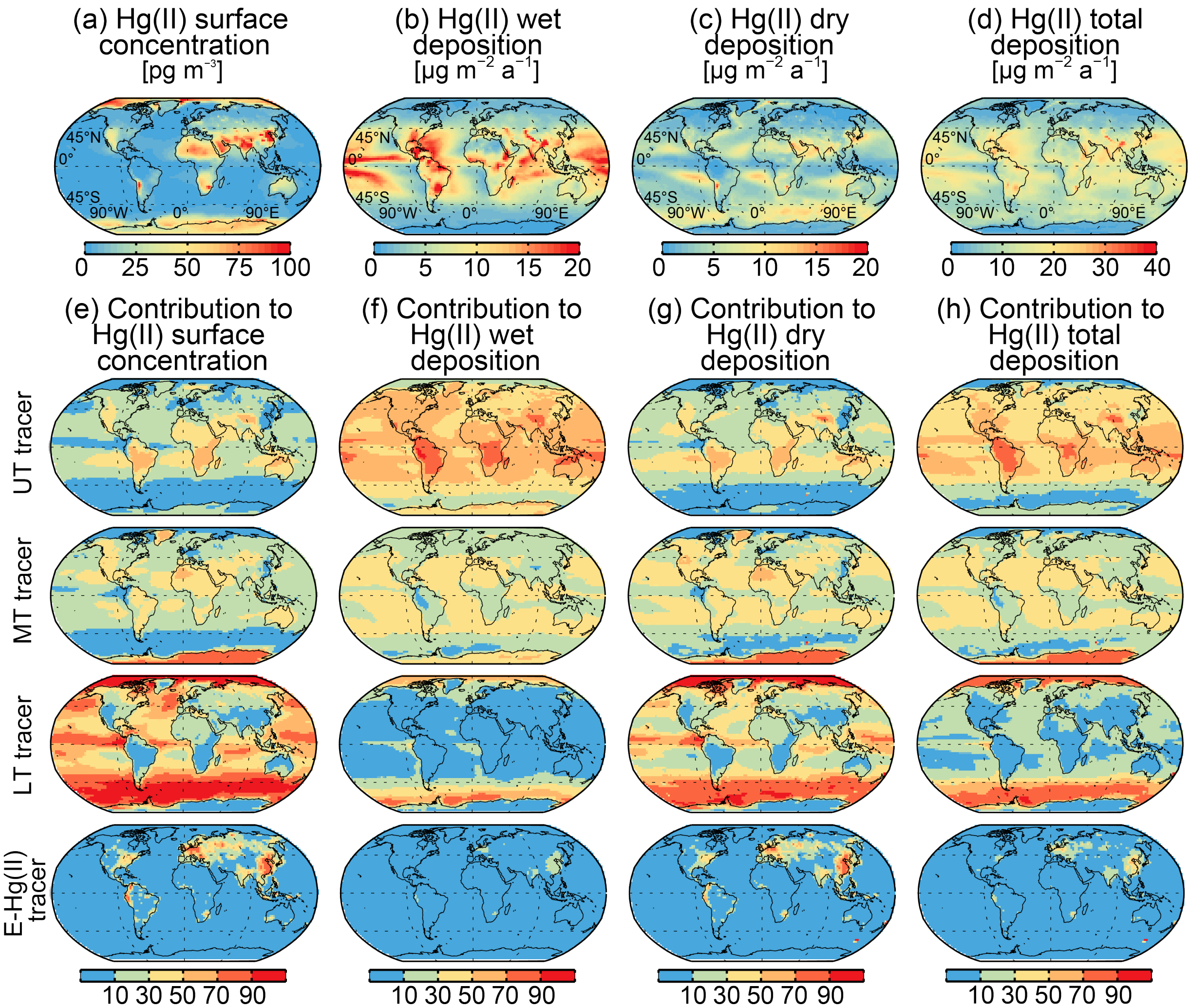


**Figure 5: (a) Annual-mean surface Hg(II) concentration, (b) wet deposition flux, (c) Hg(II) dry deposition flux, and (d) total (wet+dry) deposition flux simulated for 2013-2014. Contributions from tagged Hg(II) tracers to (e) surface Hg(II) concentrations, (f) wet deposition flux, (g) dry deposition flux, and (h) total deposition flux.**

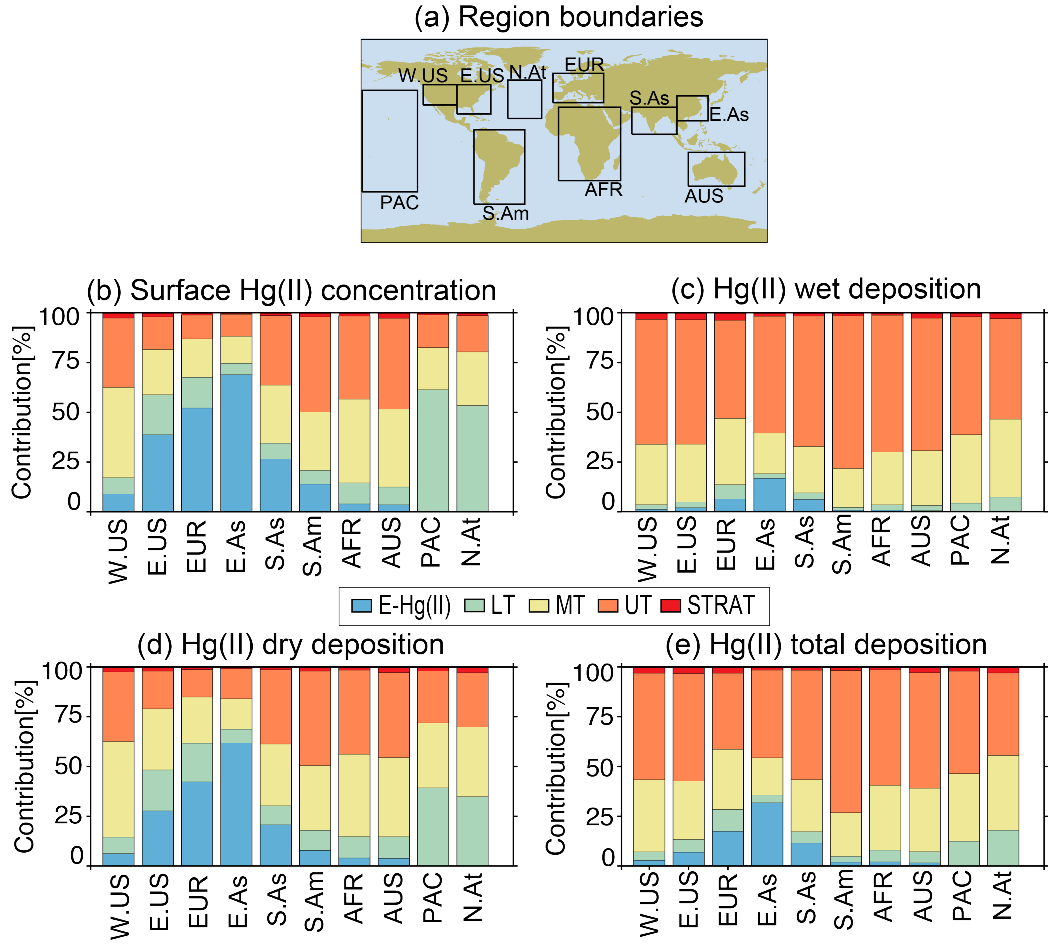


**Figure 6: (a) Boundaries and names for regions used in panels b-e. Regional contributions of tagged Hg(II) tracers to (b) Hg(II) surface concentrations, (c) Hg(II) wet deposition, (d) Hg(II) dry deposition, (e) Hg(II) total (wet+dry) deposition. For continental regions the averages are calculated over land only.**

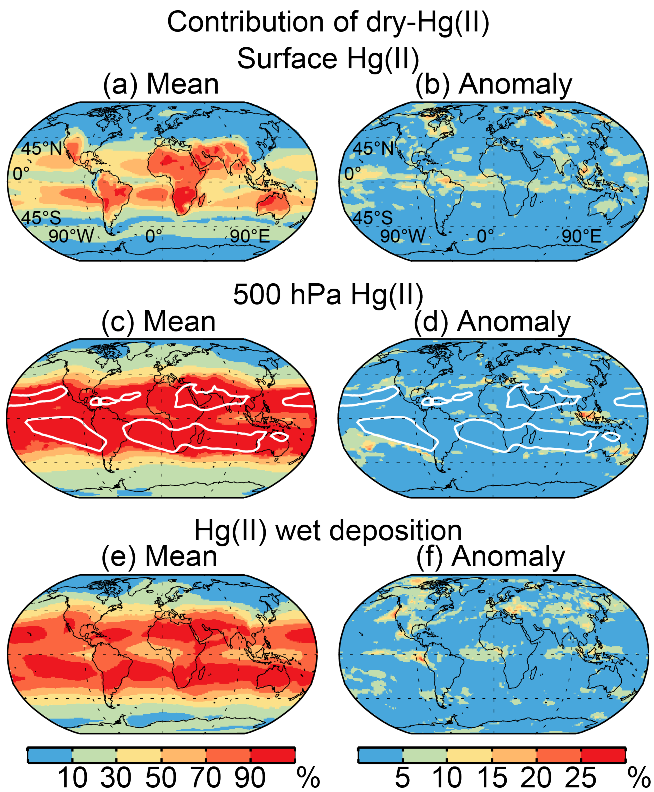


**Figure 7: ~~Annual~~ Mean and anomaly (maximum deviation from the mean ~~contribution~~) of the contributions of dry-Hg(II) to (a,b) surface Hg(II) concentrations, (~~b~~c,d) 500 hPa Hg(II) concentrations, and (~~c~~e,f) Hg(II) wet deposition flux for 2013-2016. The white contours in (~~b~~c,d) show the boundaries at 500 hPa for areas with RH less than 20% for a minimum of four months of the year.**

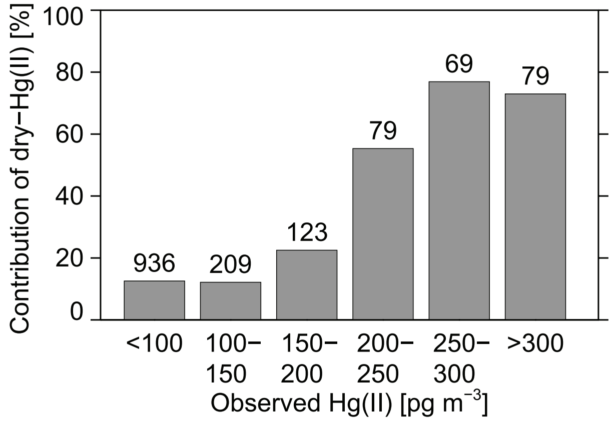


**Figure 8: Modeled contribution of the dry-Hg(II) tracer to observed Hg(II) concentrations during the NOMADSS aircraft campaign. The number of 2.5-minute observations points in each concentration bin is shown on top of the bars.**

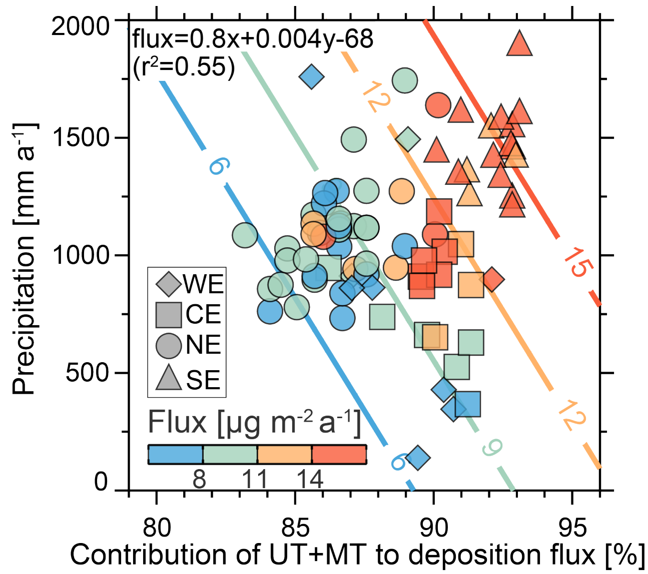


**Figure 9: Relationship of observed MDN Hg wet deposition flux (in units of µg $m^{-2}$ $a^{-1}$) to observed precipitation (mm $a^{-1}$) and modeled contribution of UT and MT tracers to the Hg(II) wet deposition flux (%). The symbols identify MDN sites for each region in Fig. 1 (WE: diamonds, CE: squares, NE: circles, and SE: triangles), with color-coding according to observed wet deposition flux. Also shown is the multiple linear regression equation relating flux to the contribution of UT+MT tracers (x) and the observed precipitation (y), and the square of the correlation coefficient ($r^2$). Colored contours correspond to deposition fluxes calculated with the regression equation.**

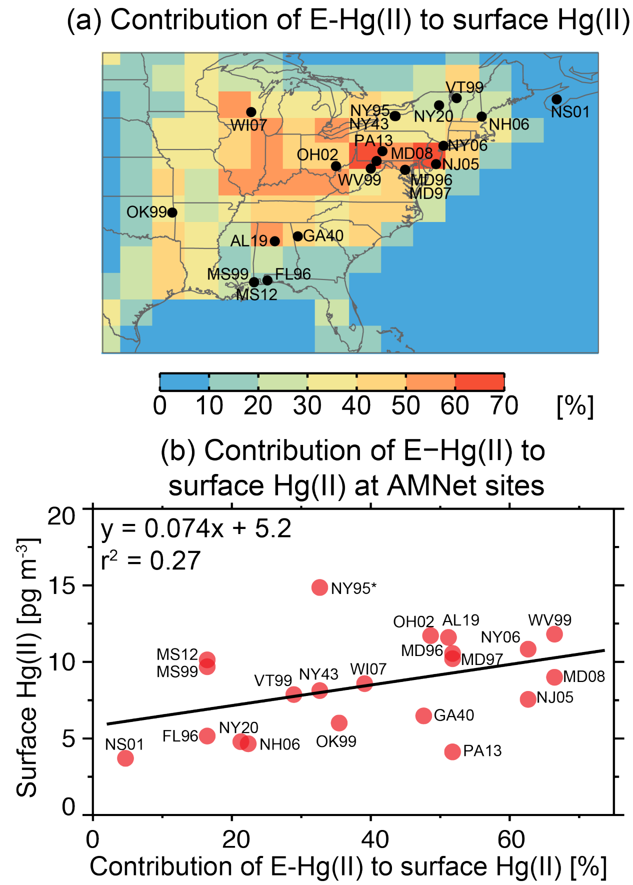


**Figure 10 (a) Simulated surface concentration of Hg(II) for 2013–2014. Also shown are the locations of the AMNet stations mapped to the model grid. (b) Relationship between the 2009–2012 median Hg(II) concentrations observed at the AMNet sites and the contribution of E-Hg(II) tracer to surface Hg(II) concentrations. The black line is the best-fit line from ordinary least squares regression. The text displays the regression equation and the square of the correlation coefficient ($r^2$). The outlier NY95 is excluded from the regression calculation.**