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Interactive comment on “Investigating sources of gaseous oxidized mercury in dry deposition at three sites across Florida, USA” by M. Sexauer Gustin et al.

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1. P18288, lines 1-12: A large portion of the materials was background information and should be in the Introduction, not in the Abstract.

Response: The abstract was written according to ACPD instructions that are as follows “Abstract: The abstract should be intelligible to the general reader without reference to the text. After a brief introduction of the topic, the summary presents the key points of the article and provides future directions where research could focus on in the near future. Reference citations should not be included in this section, unless urgently required, and non-standard abbreviations should not be included without explanations.”

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2. P18288, lines 20-23: The dominant sources or the relative contributions from each source should be stated, if possible.

Response: The below information could be added to either section 3.3 or to the conclusions.

Each site is different in terms of potential Hg inputs but has, in general, similar local atmospheric chemistry with ozone being high in the afternoon, CO, NO_y, NO peaking in the morning, and all sites having a morning peak in SO₂. Despite the similar trends, the magnitude of the peaks for Hg and other pollutants varies by site. OLF is the least anthropogenic impacted site with respect to point and nonpoint sources. If the dry deposition measured in the summer at OLF represents a “natural background” value for Florida (0.03 ng m² h⁻¹), then deposition in the fall (as measured by the surrogate surfaces) is not significantly impacted by the nearby EGP because deposition remained the same. Deposition at this site is highest in the spring (0.11 ng m² h⁻¹), and based on trajectory analyses in this paper and from previous work, this is due to inputs from outside of the local area associated with long range transport. At TPA, deposition (mean annual 0.20 ng m² h⁻¹) was above the Florida “natural background” value, and mean seasonal values ranged from 0.16 to 0.24 ng m² h⁻¹ with the summer value being lowest and the spring value being highest. The additional spring input, if compared to the summer value, is 0.08 ng m² h⁻¹ and similar to that measured at OLF. The higher values overall at TPA are attributed to local mobile source emissions facilitating GOM formation that is subsequently deposited. At DVE mean seasonal deposition was lowest in the winter and summer (0.11 and 0.13 ng m² h⁻¹, respectively) and above the background value for Florida. Deposition was highest in the fall and spring (0.25 and 0.22 ng m² h⁻¹, respectively). The peak afternoon GOM concentrations were highest in the fall when air was from the general direction of the waste-to-energy facilities and thus this facility is likely to be contributing either GOM or GEM that may be locally oxidized. The latter is supported by the fact that in winter when traffic density would increase in this area, mean deposition was lower and during this season the air was not derived

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from the direction of local EGPs. The lowest afternoon peak in GOM concentrations was also observed in the winter when the air was not coming from these facilities.

The below sentence could go in the abstract: Based on surrogate surface derived data “natural background” dry deposition for Florida is $0.03 \text{ ng m}^{-2} \text{ h}^{-1}$, while that associated with mobile source impacts is $0.10 \text{ ng m}^{-2} \text{ h}^{-1}$ at TPA and DVE and $0.03 \text{ ng m}^{-2} \text{ h}^{-1}$ at OLF, and inputs from long range transport contribute $0.8 \text{ ng m}^{-2} \text{ h}^{-1}$ in the spring. At DVE $\sim 0.10 \text{ ng m}^{-2} \text{ h}^{-1}$ is contributed directly or indirectly from local point sources.

3. P18290, lines 3-12: I suggest moving the last sentence in this paragraph to the place right after the first sentence and also modify the statement to reflect the more recent results from Zhang et al. (2012) which showed that GEM dry deposition can be much more important than GOM+PBM over vegetated surfaces at rural locations in North America.

Response: We could move this sentence and would add an additional comment that states that vegetation is an important sink for GEM however this varies as a function of plant type (Gustin, M.S. 2011.)

Our passive samplers are thought to measure GOM concentrations while the surrogate surfaces measure GOM dry deposition. It is possible that some aerosols are also measured and this needs further work.

4. P18291, lines 11: Was GEM included in the dry deposition budget? Would the percentage contribution be much larger if GEM was included?

Response: GEM was not included and foliar uptake is passive assimilation uptake not dry deposition. GOM could be added to the sentence for clarity.

5. 18293, line 6: The definition of EGP should be moved to line 2 where it is first appeared.

Response: This change needs to be made. Thanks for catching that.

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6. P18295, lines 8-9: Four starting altitudes were used for back trajectories here. The measurements of Hg were made at the surface; why a starting altitude near the surface was not chosen?

Response: The goal of using trajectory analysis in this study was to investigate regional and larger scale transport patterns that may have influenced GOM and GOM dry deposition. As such, it is common practice to have the lowest starting altitude be well above the surface, to avoid erroneous trajectories due to sub-grid processes and turbulent flow. This information could be added to the text.

7. P18295, lines 7-9: Did the different starting locations and starting heights affect the horizontal location and altitude of the trajectory points? Fig. 5 to 7 show GFDs for all trajectory starting locations and starting heights. Were there any discrepancies in the GFDs for the nine starting locations and four starting heights at the three sampling sites?

8. P18295, lines 13-15: What was the height of the HYSPLIT modeled boundary layer? It was mentioned that a high proportion of trajectory points were above this BL. Was this observed for all trajectory starting heights (500, 1000, 1500, 2000 m)? It would be better if you could show that the free troposphere transport affects lower elevations because previous studies seem to observe this at higher elevation sites only.

Response to 7 and 8: The question of which starting altitudes had a high proportion of trajectory point above the modeled boundary layer is an interesting one. To address this would involve adding significantly more information to an already long paper. If we continue to do work using this data set sensitivity analyses regarding this question would be done. The height of the modeled boundary layer is variable on different days and throughout a given day. In our previous work (Weiss-Penzias et al., Atmospheric Environment, 2011) we showed that input from the free troposphere transport can affect low elevations sites, especially in the spring.

9. P18295 lines 16-17: It states, the location probability represents the fraction of

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trajectory points in a given cell relative to the number of trajectory points in the most populated cell. Why was this relative to the most populated cell, instead of the total number of trajectory points for each event and class? How many trajectory points were there on average in the most populated cell? This could affect the probability of occurrence in panels a to d of Fig. 5 to 7. E.g., when it is relative to the number of trajectories in the most populated cell, the probabilities would be higher than using the total number of trajectory points for each event and class.

Response: The reviewer is suggesting that we apply a normalization factor for the bias associated with cells with limited trajectory points. At this point we would prefer not to change the plots to show the distribution of numbers of trajectory points in each cell and instead continue to use the percent distribution. These would show essentially the same thing. The raster data set we applied contains the distribution of the numbers of trajectory points in all grid cells. A few grid cells have very high occurrences (near the starting location) and many cells have few occurrences (as the air mass spreads out back in time). Once the distribution of trajectory points is calculated the value for each cell was divided by the number of trajectory points in the most populated cell. Cells are then given one of five colors based five different the probability of occurrence. As such, the location probability of the air mass in or near the starting cell is 100%. As the air mass moves back in time the probability decreases relative to the probability at the starting location (i.e. the most populous cell) based on the back trajectory analysis, these figures show the probability of air occurring in specific grid cells.

10. P18298, lines 17-21: If the electricity consumption also had the same diurnal pattern, then the direct emission from EGPs might have contributed to this diurnal pattern. Is there information available on the diurnal pattern of EGPs emissions to exclude this possibility?

Response: In order to answer this question diel air Hg concentrations, wind direction and criteria air pollutant concentrations need to be considered together. Additionally, one would need to know the operating parameters for each facility. Typically large

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EGPs (>1000MW) are supplying base load, and do not ramp up and down during the day. Smaller facilities, with quick start up, will be used to supplement this load as demand increases. The TPA site, as stated in the text, did not regularly have air that originated from the nearby EGPs. Looking at the data combined, these are not important sources because similar trends occur when the air is not originating from their direction. This indicates as stated in the text that local atmospheric chemistry is the most important factor determining the observed GOM pattern at TPA. At OLF, air from the only nearby EGP impacts the site primarily early in the morning and a corresponding peak of GOM was observed during the fall, spring and summer, but not in the winter. One could attribute this to less electricity being generated in the winter, however during this time of year the wind direction was not directly from this facility. At DVE, GOM values were Fall>Spring>Summer>Winter. During the winter, the air in general did not come from an EGP. Based on the patterns at this location one cannot rule out an impact of the local EGPs as a source of GOM or GEM that could be oxidized by local air pollutants. The EGPs near the DVE site include >1000 MWs oil and natural gas facilities and two ~66 MW waste incinerators.

11. P18298, lines 21-23: Do you have information of vertical profile of GOM concentration to support this statement?

Response: We do not, however limited aircraft suggest this is the case and we could add a comment and the following reference : Sillman et al., 2007 Reactive mercury in the troposphere: Model formation and results for Florida, the northeastern United States, and the Atlantic Ocean JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES Volume: 112 Issue: D23 Article Number: D23305 DOI: 10.1029/2006JD008227

12. P18300, lines 3-8: Is the discussion on Hg + Br reaction relevant to this section because several Hg modeling studies were also able to reproduce Hg measurements using the Hg + Br reaction and suggested that the Hg + O₃ reaction kinetics was too slow? Also, since the sampling sites are near the Gulf of Mexico, could this be a major

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source of Br to the sampling sites and likely more conducive to the Hg + Br reaction?

Response: We think this is relevant to consider given the potential for mobile source contributions.

13. P18302, line 11: In reality, dry deposition happens all the time and over all different surfaces. Frequently, dry deposition is faster during wet conditions than during dry conditions, especially for soluble species like GOM. This sentence needs to be stated differently, for example, the low dry deposition in summer as estimated from the surrogate surface measurements might due to the closure of SS during wet periods, not because the dry deposition was low during wet periods.

Response: This is a good point and demonstrates the utility of the surrogate surfaces showing they are not affected by moisture and relative humidity. This comment can be added to the text.

14. P18302, line 16: Increased GOM lifetime would not increase GOM dry deposition (long lifetime means slower deposition). The real reason here should be the increased concentration of GOM.

Response: The reviewer is correct and this sentence could be modified. The word lifetime should be changed to concentration.

15. P18302, 20-29: A brief description would be useful describing how much percentage of the deposition variation was explained by concentration variation (so the reader can guess how much was caused by other factors such as deposition velocity).

Response: This has been added in our response to item 10. The paragraph written as a response for item 10 could be inserted in here.

16. P18303, the first paragraph: Can the differences in dry deposition between this study and that in Marsik et al. (2007) be mostly explained by concentration differences?

Response: There are no concentration data presented in the Marsik et al 2007 paper

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that I can find.

17. P18303, lines 27 to the end of the paragraph: The real reason causing the model underestimation of dry deposition in Peterson et al. (2012) and Lyman et al. (2007) was that too large surface resistance was chosen for GOM in their studies. For example, parameters chosen for HNO₃ in dry deposition models were commonly used for GOM to estimate its dry deposition. The two scaling parameters (alpha and beta) were both chosen as 10 for HNO₃ in Zhang et al. (2002) and these values were also used for GOM in Zhang et al. (2012). Using these values, the annual dry deposition velocity for GOM was on the order of 1 cm/s at the majority of AMNeT sites. However, a value of 2 was used for alpha and beta in Peterson et al. (2012). Thus the surface resistance for GOM was a few times (up to 5.0 depending on how large aerodynamic resistance was) larger than that in Zhang et al. (2012). This explains why deposition velocity in Peterson et al. (2012) was only a fraction of those in Zhang et al. (2012). If the proper values for alpha and beta were chosen in your study, the measured and modeled value would actually be very close. I suggest adding a brief explanation on this point so future studies can better choose right model parameters.

Response: The reviewer raises an important point that model outputs will be impacted by the parameters used and the assumptions applied. The use of the values of alpha and beta in the model developed by Lyman et al (2007) that was applied by Peterson et al (2012) were modified using chemistry for GOM compounds instead of using HNO₃. I have pasted the text from the Supplemental Information from the Lyman et al. (2007) paper that explains the scaling parameters. This can certainly be paraphrased and added to the text. "The scaling parameters α and β depend on the species being modeled, and Zhang et al. (23) provide scaling parameters for a number of gaseous species. They also outline a method for choosing scaling parameters for any chemical species of interest based on the effective Henry's Law constant (H^*) and the negative log of electron activity for half-redox reactions in neutral solutions [pe₀(W)]. In this study, H^* for HgCl₂ and Hg(OH)₂ were calculated using available data (5, 37). For

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calculation of H^* for $HgCl_2$, $[Cl^-]$ was assumed to be 0.2 mg L^{-1} , a typical value for continental rainwater (38). $pe_0(W)$ was calculated for the half-redox reaction $Hg^{2+} + 2e^- \leftrightarrow Hg^0$ using the equation

$Pe_0(W) = (1/n)[\log_{10}(K)] - nH$ given in Zhang et al. (23), where n is the number of electrons in the half-reaction, K is the equilibrium constant of the reduction half-reaction, and nH is the number of protons exchanged per electron in the half-reaction. K was calculated from values of Gibbs free energy of formation (39). The calculated values for H^* and $pe_0(W)$ were used to compare RGM to gaseous species listed in Zhang et al. (23), and, based on evident similarity, the scaling parameters listed for nitrous acid (HONO) were used to scale R_g and R_{cut} for RGM ($\alpha = \beta = 2$).

18. P18305, line 14: Delete the first ‘measurement’ word

Response: I am sorry I just do not see what the reviewer is asking for at this location.

19. P18306, line23: Should it be Fig. 5, instead of Fig. 7?

Response: Yes this change should be made.

20. Caption of Figure 1 and Table 1: Is ‘EGU’ defined in the text?

Response: Thanks for catching this error. Yes, the caption should be changed.

21. Fig. 5 to 7: Are there any uncertainties with tracking the transport of GOM using back trajectories, since GOM can be removed by precipitation or dry deposition along the trajectory path? The modeled precipitation in these figures show there was precipitation upwind of the sampling sites.

Response: Free troposphere air would be scrubbed by high reaching convection that could occur during warm sunny days and convective thunderstorms. The latter occur most often in Florida in the summer. The “upper altitude” plots give a sense of the potential sources since this air would reflect that coming into the area.

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