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Interactive comment on "Ozone Production and Its Sensitivity to NO_X and VOCs: Results from the DISCOVER-AQ Field Experiment, Houston 2013" *by* Gina M. Mazzuca et al.

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Response to Anonymous Referee #2: 10 July 2016

We thank the reviewer for providing insightful comments and helpful suggestions that have substantially improved the manuscript. Below we have included the review comments followed by our responses. In the revision of this manuscript, we have highlighted those changes accordingly in blue. Supplemental information is also provided.

1. The analyses performed and the approach used are tried and true so technically, there are no major faults with the work (though I question the use of a box model in Houston when the meteorology is so complex - why not just use the 3D model as it

can provide answers to some of the questions asked and the ambient data can be used for model evaluation). However, due to a lack of novelty and a lack of truly new findings that warrant an entire manuscript, I am unable to recommend this manuscript for publication in ACP.

Response: The reviewer initially states that the work is not recommended to ACP due to lack of novelty and truly new findings, however, does not state where findings of our work is previously published. The specific conclusions of this work were not published earlier thus provide unique results. In response to why we did not just use a 3D model, the box model is constrained to observed meteorological parameters and chemical species such as O3, NOx, CO, and some VOCs, which we find to be more useful than a 3D model for this kind of analysis since it eliminates some uncertainties, or errors that a 3D model could have. Our box model simulation could reduce uncertainties in the ozone production and sensitivity calculations.

We have stated at the end of Section 2.2: "The box model analysis is necessary for ozone production and its sensitivity to NOx and VOCs because the box model was constrained to measured species (e.g., NO, NO2, CO, HCHO, etc.) and meteorological parameters (e.g., photolysis frequencies) that are essential to calculate ozone production rates. Even though there is good agreement in general between the box model and the 3D model, there are still some differences between the measurements and the output from the 3D model, e.g., NOx, CO, HCHO and photolysis frequencies."

2. With regard to figures, Figure 1 is not necessary (the ozone isopleth is "classic"), Figure 2 would be better as a map with points/labels as the extraneous stuff is distracting, and Figures 3 and 4 can be combined. In addition, some of the figures are intuitive based on previous work in Houston and other locations (5, 6, 8, and 9).

Response: We would like to keep Figure 1 in the paper. Since Figure 1 is ozone production and not ozone concentration as traditional EKMA O3 isopleth diagrams are, it could provide useful information for the reader about how ozone production changes

with regarding to NOx and VOC and NOx and VOC sensitive regimes of ozone production. As suggested, we have changed Figure 2 to a map with points and labels. Figures 3 and 4 are combined. Figures 5, 6, 8 and 9 are the results from the DISCOVER-AQ Houston campaign showing spatial and temporal variations of ozone production and its sensitivity to NOx and VOCs. To our knowledge, there has not been a single study that covers such a large spatial range on this topic, and the data from this campaign provide us the unique opportunity to do such an analysis.

3. My largest criticism of this work is that it is known from three previous field campaigns that ozone production rates and sensitivities in Houston are temporally and spatially dependent. It seems to be that the most new information appears on lines 203-205 (line 206 is intuitive) regarding O3 loss and the split between RO2 and HO2 reactions with NO (unless this information is published elsewhere and I am unaware) and on line 255+ where it is noted that OPE has decreased in Houston compared to previous campaigns (due to the decrease in NOx emissions). I do not believe that these warrant a manuscript by themselves.

Response: The reviewer was right that there have been some previous studies, including three previous studies in Houston in 2000, 2006, and 2009 and some others in other locations, on ozone production and its relationships to NOx and VOCs (e.g., Kleinman et al., 2002; Ryerson et al., 2003; Newman et al., 2009; Mao et al., 2010; Chen et al., 2010; Ren et al., 2013), but to our knowledge, none of them has done systematic analysis on ozone production and its sensitivity to NOx and VOCs and covers such large spatial (urban and suburban) and temporal ranges as the DISCOVER-AQ Houston campaign does in 2013. For example, the SHARP study in 2009 (Ren et al., 2013) and the Texas Air Quality Study Radical and Aerosol Measurement Project (TRAMP) in 2006 (Mao et al., 2010; Chen et al., 2010) did cover ozone production and its sensitivity to NOx and VOCs, but they were focus on the data collected at a single location at Moody Tower at the University of Houston. Kleinman et al. (2002) and Ryerson et al., (2003) from TexAQS I in 2000 and Newman et al. (2009) from TexAQS II in

2006 discussed ozone production efficiencies (OPE), but they did not talk about the dependence of OPE on NOx and did not cover the sensitivity of ozone production to NOx and VOCs. The rich data set collected during the DISCOVER-AQ Houston campaign provides us a unique opportunity to perform this systematic analysis and we believe it is worth to inform the atmospheric chemistry community about the latest findings from this study to reflect the changes in chemical conditions (e.g., emissions) in Houston since previous studies.

4. The authors do not put Houston in the context of other locations. For example, they state on line 68 that "there are a limited number of observation-based studies on ozone production and its sensitivity to NOx and VOCs." There have been such studies made in Houston (SHARP, TEXAQS I and II) as well as in other locations across the US (Nashville, New England) and Europe. It would be appropriate to make such comparisons.

Response: We have cited results from other studies in other locations (e.g., Zaveri et al., 2003; Griffin et al., 2004; Thielmann et al., 2002) in Introduction and compared the results from this study to those from other locations. Our study is unique in that it examines the spatial and temporal variations in ozone production and its sensitivity. Other studies are mostly ground-based (i.e., single location like SHARP) or with limited spatial/temporal coverage. We found a higher OPE in this study than what was found in previous studies in Houston, which is probably due to continuous emission control as NOx levels were continuously pushed to $\sim$1ppbv and thus we got a higher OPE.

We have revised this sentence as: “There are some previous observation-based studies on ozone production and its relationships with NOx and VOCs (e.g., Thielmann et al., 2002; Zaveri et al., 2003; Ryerson et al., 2003; Griffin et al., 2003; Kleinman et al., 2005a; Neuman et al., 2009; Mao et al., 2010; Ren et al., 2013).” In Section 3.1, we have added one sentence: “Similar instantaneous ozone production rates have been observed in two previous studies in Houston in 2000 and 2006 [Kleinman et al., 2002a; Mao et al., 2010].” In Section 3.2, we revised a sentence to: “This OPE value is about

a factor of 1.5 to 2 higher than the OPEs obtained in the DISCOVER-AQ 2011 study in Maryland ranging from 4 to 5.5 (Ren, X., unpublished data), due to higher photochemical reactivity in Houston (Figure S4), but similar to 7.7-9.7 obtained from a ground site during the New England Air Quality Study (NEAQS) 2002 (Griffin et al., 2004)."

5. What is the basis for assuming a two-day lifetime for all calculated species to avoid build up?

Response: We do not provide a citation because we chose this value somewhat arbitrarily. By decreasing or increasing two days to one or ten days, it would not have much affect on the simulation results. This is because the box model already constrained all measured long-lived measured species. The additional lifetime of two days for the calculated species is to account for losses due to dry and wet deposition, vertical and horizontal diffusion, and to prevent accumulation of long-lived species in the box model. Most calculated species like OH, HO2 and RO2 are reactive intermediates and have lifetimes on the order of seconds to minutes, much shorter than 2 days. By adding this additional two-day lifetime would not affect the model results at all. There are a few long-lived species (like organic acid and alcohols) calculated in the model that could potentially accumulate to levels much higher than the levels in the ambient air.

We have revised this sentence: "An additional lifetime of two days was assumed for some calculated long lived species such as organic acids and alcohols to avoid unexpected accumulation of these species in the model."

Additional References

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2016-215/acp-2016-215-AC2-supplement.pdf

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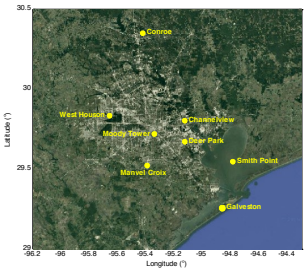

Fig. 1. Figure 1 caption (2 in paper). DISCOVER-AQ ground and spiral sites (yellow dots) during the September 2013 Houston campaign.