Summary:

Reply to referee-2

This paper presents an analysis of two important aircraft data sets collected in the Houston Texas area in 2000 and 2006. A significant amount of work has been put into the analysis, but at this point a satisfactory picture has not emerged from the discussion. I think that there are very significant issues detailed below that must be addressed. Therefore, I recommend that this paper not be accepted for publication without a major revision that addresses these issues, followed by a second thorough review.

We believe that the substantial revisions and improvements prompted by the thoughtful comments of both reviewers have greatly strengthened the paper, as detailed in the replies below and the response to the other reviewer.

Major issues:

1) It appears that the authors are examining a rather limited fraction of the data collected during the two field studies. The majority of the VOC measurements are based on a relatively limited number of whole air samples collected during each flight. Each canister required several seconds to fill. Most other species were measured continuously with 1-second resolution throughout the flights. The authors apparently analyze only data averaged over the period of the canister collection. Analysis of data from the fast response instruments (e.g., Figs. 3, 7 and 13) would be much more robust and unbiased if based upon the full 1-second data sets. The whole air samples may be biased in that they were preferentially collected during interception of plumes from various point sources. This averaging process and its implications must be thoroughly discussed.

Reply: The focus of the manuscript is chemical processing of O_3 formation. Thus the analysis of radical concentration and subsequent ozone production rate relies on key inputs such as VOCs. Major VOC species were measured by canister. All chemical species were therefore processed based on the time window of the canisters.

We examined the NOx concentration ranges between the 1-second and canister-based data to explore the differences between the samplings. As shown in the Figure R-2-1, the 1-second sample covers a wider range of concentration levels for both years. There was substantial overlap of the interquartile ranges between the 1-second ("ALL")and canister-based ("WAS") data, though the median NOx concentrations were higher in the canister data. The spatial view of the 1-second samples and canisters shown in Figure R-2-3 also show that both datasets not only include plumes but also the various low-concentration data.

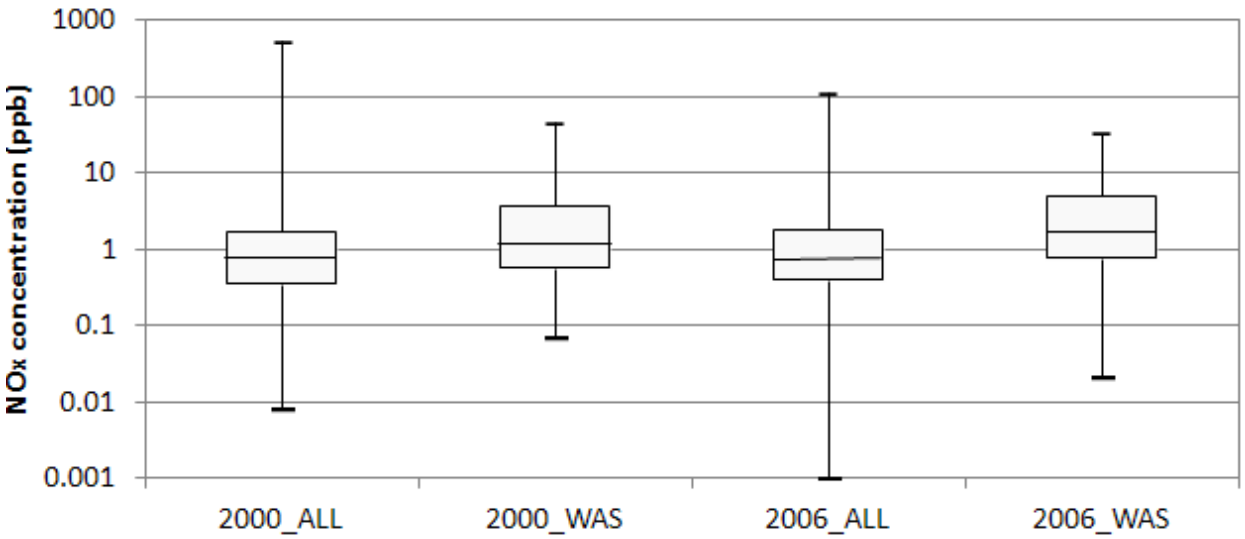

Figure R-2-1. The campaign-average NO_x concentration during TexAQS 2000 and 2006; 2000_ALL: the 1-second samples of NO_x concentration for TexAQS 2000, 2000_WAS: the canister-basis NO_x concentration for TexAQS 2000, 2006_ALL: the 1-second samples of NO_x concentration for TexAQS 2006, 2006_WAS: the canister-basis NO_x concentration for TexAQS 2006.

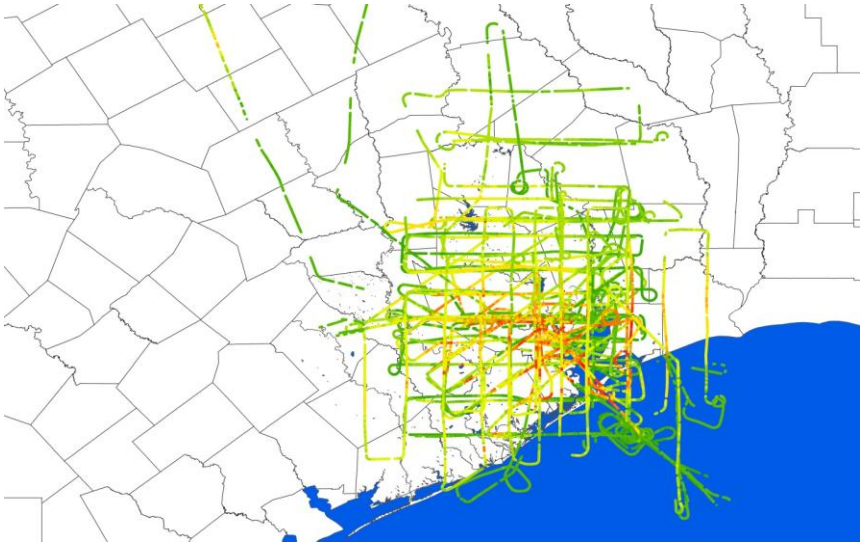

Figure R-2-2. The 1-second sample of NOx for all flights during TexAQS 2000

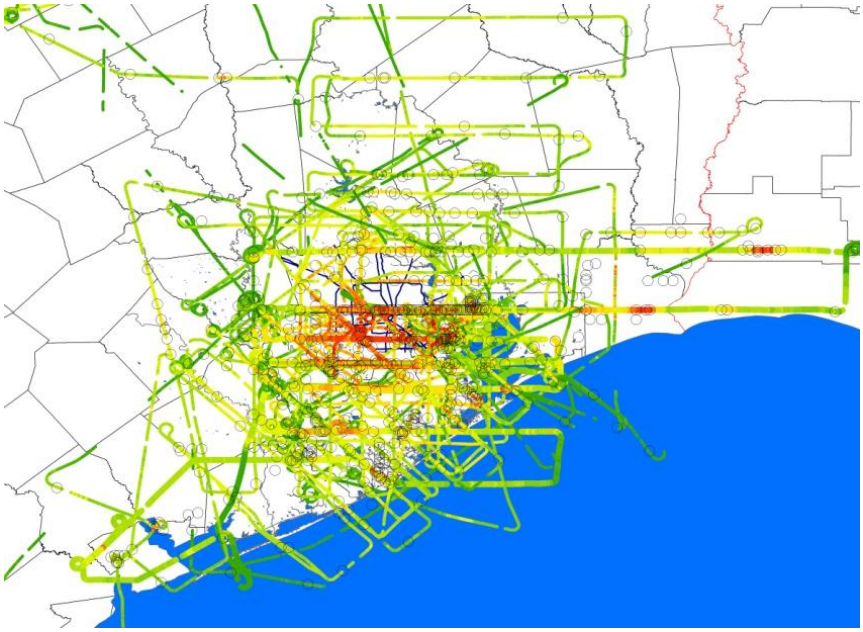

Figure R-2-3. The 1-second sample of NOx for all flights during TexAQS 2006 (the black circles are the canister samples)

2) Section 3.1 discusses changes of NOx and HRVOC concentrations. This topic has been discussed in much greater detail elsewhere (i.e., Washenfelder et al., 2010), and it is not clear that the present section offers anything new, especially in view of Comment 1) above. At a minimum a much more quantitative comparison withWashenfelder et al., 2010 must be given.

Reply: We agree that the more detailed discussion elsewhere allows us to abbreviate our discussion of this topic. Section 3.1 and 3.2 are merged into one short section, the change of NOx, VOC and O_3 are briefly discussed on the basis of Washenfelder et al., 2010. Revised Section 3.1:

> "NOx and HRVOCs in the Houston area declined by 17% and 40%, which is consistent with previous studies (Cowling et al., 2007; Gilman et al., 2009; Washenfelder et al., 2010). A more detailed discussion of the change of NO_x and VOC concentrations in the Houston area could be found in Washenfelder et al. (2010). The cumulative distribution of O_3 concentration shows substantial reductions from 2000 to 2006 for high percentile observations, but little change for low percentiles (Figure 7). This is consistent with Zhou et al. (2013), who found sharper reductions in ozone on peak days than cleaner days in the eastern U.S. It is noted that meteorology may have important influence in O_3 concentration change between the two studies."

3) Section 3.1 discusses changes of ozone concentrations. Since this is a secondary species, it is important that comparisons between the two field studies be based on the full 1-second data set rather than the limited fraction of the data apparently compared here. An important issue that must be discussed in this section is the differences in meteorology and season between the two studies. The 2006 study was significantly cooler, and a month later in the year. In 2000, there was a major drought, and the weather was particularly hot and stagnant. The authors much establish that the differences reported are indeed due to emissions reductions, rather than differences in other variables. It might be useful to examine the routine TCEQ data to show in a more robust manner how ozone has changed with time.

Reply: We acknowledge that changes of O_3 concentration from 2000 to 2006 were affected by factors beyond emission changes. No method could quantify the contributions of these various factors with observational data. Since the focus of this manuscript is the ozone formation chemistry, our discussion of differences in the meteorology and O_3 concentrations between the

two years is relatively brief. The manuscript has been revised to reflect this discussion as a caveat. Revised Section 3.1:

> "We acknowledge that changes of O_3 concentration from 2000 to 2006 were affected by factors beyond emission changes. No method could quantify the contributions of these various factors with observational data."

We adopt the reviewer's suggestion of considering routine TCEQ data. The daily max 8-hour O_3 concentration and daily max temperature averaged over 17 ground sites in the Houston area are presented in the figures below. Monthly O_3 concentration in the summer (August, September and October) of 2000 was higher than in 2006 by 4-10 ppb (Table R-2-1). The O3 level in TexAQS 2000 was higher than in TexAQS 2006 by 18 ppb. Monthly average temperature in summer of 2000 was higher than in 2006 by 1 ◦C. The temperature during TexAQS 2000 was higher than in TexAQS 2006 by 4 ◦C. The temperature gap between TexAQS 2000 and TexAQS 2006 was mostly due to the extreme hot days from August 29 to September 6 in 2000.

Table R-2-1 Summary of O3 (ppb) and temperature (◦C) during the two campaigns and monthly average for August, September, and October

		campaign	August	September	October
O3 (ppb)	2000	76	72	63	51
	2006	58	52	57	47
Temperature (◦C)	2000	34	34	31	26
	2006	30	33	30	27

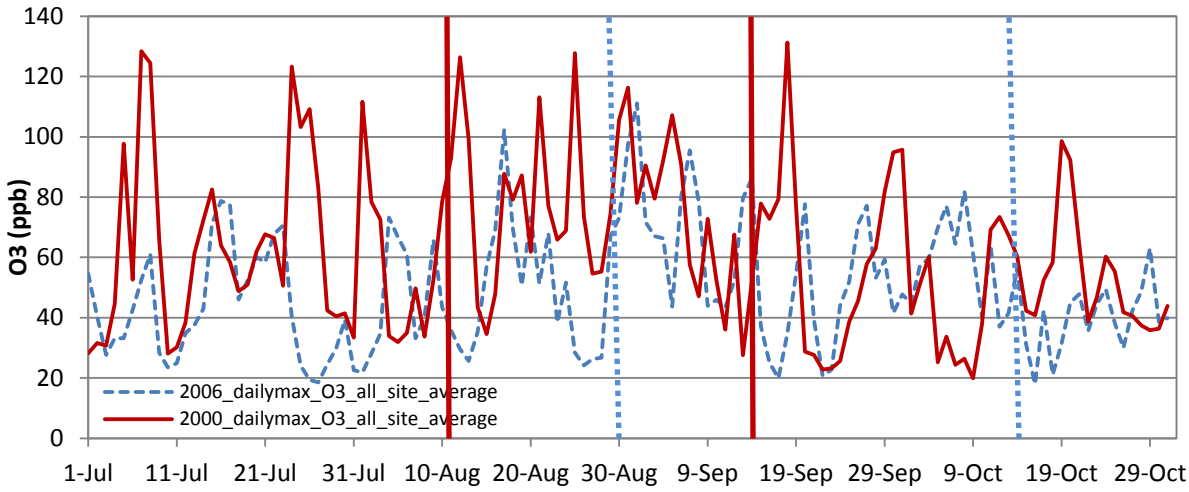

Figure R-2-4. The 17-monitor-average daily maximal 8-hour O3 in the Houston metropolitan area during July-October in both 2000 and 2006; the time periods of the two TexAQS were marked by vertical lines on the plot; the blue dash-lines represents TexAQS 2006 and the dark red lines are for the TexAQS 2000.

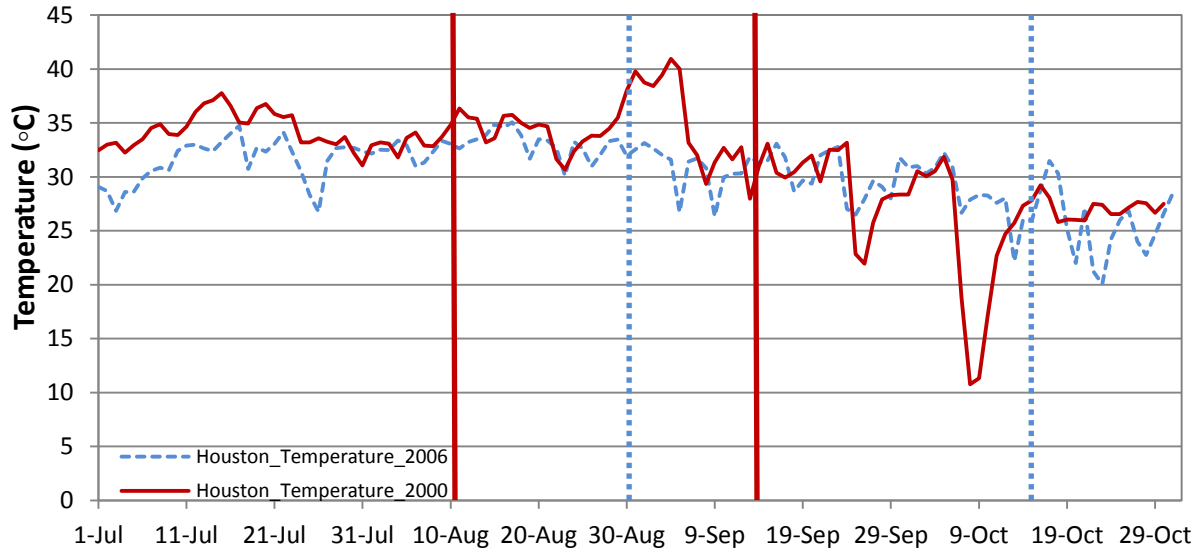

Figure R-2-5. The 17-monitor-average daily maximal temperature in the Houston metropolitan area during July-October in both 2000 and 2006; the time periods of the two TexAQS were marked by vertical lines on the plot; the blue dash-lines represents TexAQS 2006 and the dark red lines are for the TexAQS 2000.

4) Figure 8 is central to the results of this paper, but the authors' description of this figure is highly subjective; specifically:

- The authors state "The dependence of P(O3) on NOx concentration is shown in Fig. 8 for both years. P(O3) tends to increase with NOx at low NOx concentration until a critical point of maximal P(O3) when NOx is near 10 ppb. Beyond this point, P(O3) declines with further increases in NOx because abundant NOx rapidly removes OH and peroxy radicals." I agree that this is behavior expected from modeling, but this behavior is not obvious in Fig. 8. A more objective discussion, backed up with quantitative comparisons is required.
- The leftward shift is not obvious, since the average NOx points are exactly the same for both years. Again, a more objective discussion, backed up with quantitative comparisons is required.

Reply: (1) To support the quantitative discussion of $P(O_3)$-vs-NO_x correlation of peaking P(O3), which serves as a key conclusion in the manuscript, the median OPR at each NO_x bin for TexAQS 2000 and 2006 is presented in Figure R-2-6. In 2000, at NO_x level lower than 10 ppb, $P(O_3)$ increases as NO_x increase. Across this NOx critical point, P(O3) dramatically decreases as NO_x increases. For example, P(O3) (8.1 ppb/hour) at NOx=15 ppb was 65% of P(O3) (12.4 ppb/hour) at NOx =10ppb. P(O3) in 2006 showed a similar trend while the peaking P(O3) in 2006 appeared at NOx level was around 5ppb. (2) We acknowledge that left-ward shift of the peaking P(O3) is not significant from the dataset. The discussion regarding left-ward shift has been deleted from the text.

The revised text:

> "The dependence of OPR on NO_x concentration is shown in Figure 10 for both years. For NO_x concentration <0.15 ppb, OPR did not show strong response to the change of NOx concentration for both years. After that, OPR increases rapidly as NOx increases. OPR tends to increase with NO_x at low NO_x concentration (NO_x< 10ppb). For both years, the peak OPR appears at NO_x near 10 ppb. Beyond this point, OPR declines by 51% (2000) and 35% (2006) with further increases in NO_x because abundant NO_x rapidly removes

OH and peroxy radicals. For all NO_x levels, OPR in 2000 was higher than in 2006, showing a downward shift. The downward shift was very clearly visualized in Figure 10 for NOx concentration > 0.15ppb. The median OPR in 2000 was higher in 2006 by 100%-200% for the same NO_x concentration at NO_x ranging 1-15 ppb. The downward shift in the data reflects the role of VOC emission reductions."

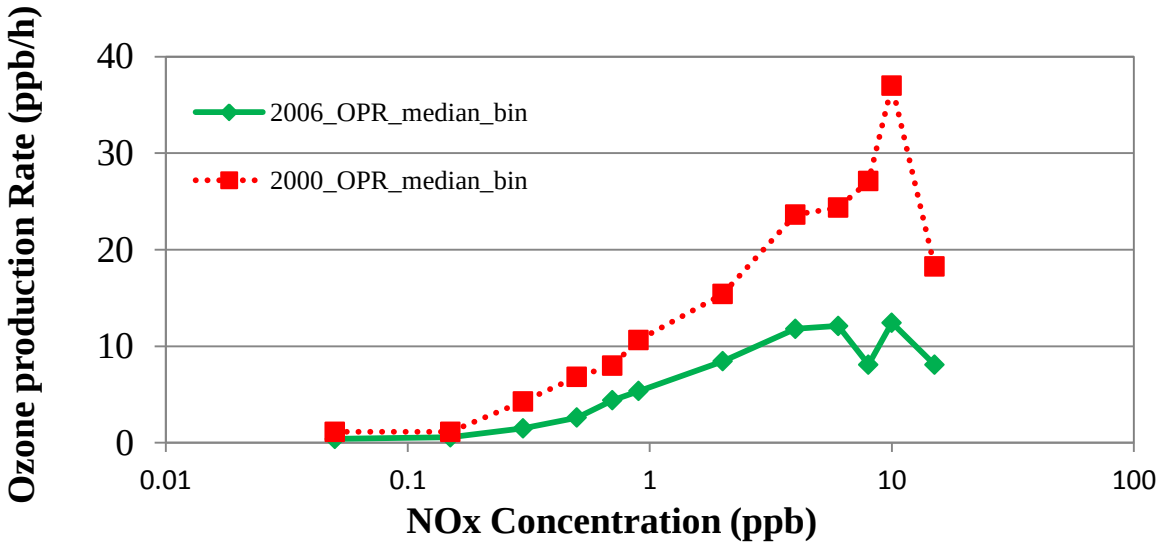

Figure R-2-6. OPR as a function of NO_x concentration for 2000 and 2006; measured data is binned by its NO_x concentration and the median values of OPR for each is shown here.

5) Section 3.4 represents a jump from more direct analysis of observations to (I assume) results from the DSMACC model. That should be emphasized here, and also that Fig. 10 comes from that model, but is based upon the measured VOC concentrations. In the discussion of Fig. 10, the important families of VOCs are discussed. Notably missing are aromatics. Were they really that unimportant? I believe some other work have identified aromatics to be of significant importance. This issue requires more complete discussion in the context of other references that have discussed aromatic contributions to photochemistry in the Houston area.

Reply: (1) One sentence is added to the first paragraph of Section 3.3 to emphasize the results from the DSMACC model:

> "This section examines the VOC contributions to $P(O_3)$ by examining radical budget based on the simulations from the DSMACC model."

(2) Aromatics are only minor contributors to the OPR. There were 14 aromatics (benzene, toluene, ethylbenezen, m/p-xylene, o-xylene, styrene, isopropylbenzene, n_propylbenzene, 2-ethytoluene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-triemthylbenzene, 1,2,4-trimethylbenzene, and 1,2,3-trimethylbenzene) measured by canister during TexAQS 2000 and 2006. The averaged concentrations of all hydrocarbons from canister measurement are shown in the figure. Among all aromatics, only benzene (220 ppt, TexAQS 2006) and toluene (198 ppt, TexAQS 2006) had substantial concentrations while the OH reaction rate constants for these two species are 1.2×10^{-12} and 6.0×10^{-12} cm^3 molec/s (JPL, 2011). All other aromatics are negligible in their contribution to ozone production. Benzene and toluene contributed only 4.5% of OH reactivity; therefore their contribution is substantially lower than alkanes and alkenes.

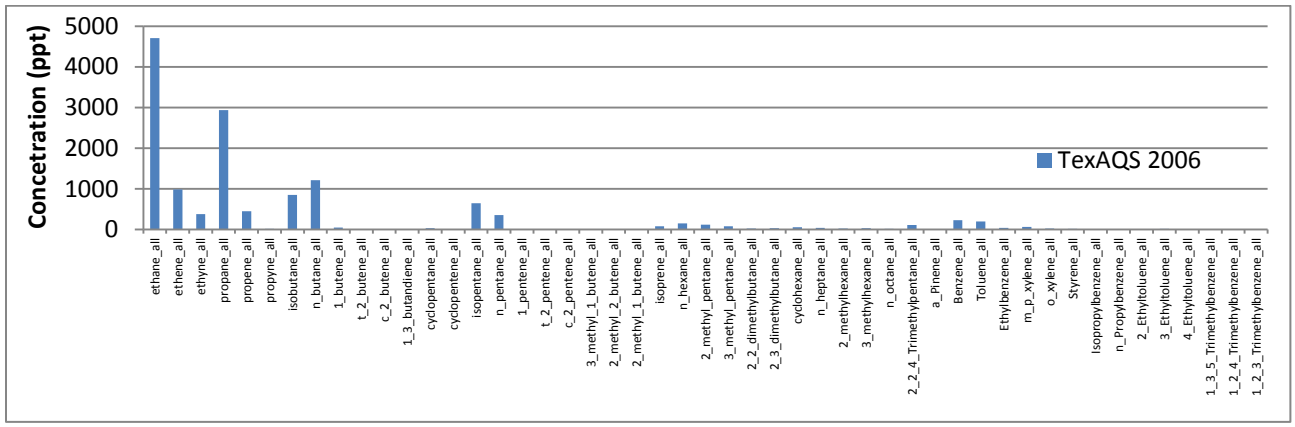

Figure R-2-7. the average VOCs in WAS during TexAQS 2006.

6) The analysis of Section 3.6 needs a much more thorough introduction including relevant references so that the interested reader can evaluate whether the L_N/Q ratio is really as useful as asserted in this section.

Reply: In Section 3.5, we discussed L_N/Q as an indicator of O_3 formation sensitivity to NO_x and VOC. One new paragraph is added to the manuscript in more thoroughly introducing L_N/Q:

> "Kleinman (1997) introduced an approximate analytic formula, L_N/Q, to investigate the relative sensitivity of O_3 formation to NO_x and VOC. This formula has been applied to various urban areas (Kleinman et al., 2005; Lu et al., 2010; Mao et al., 2010). When L_N/Q is less than 0.5, it suggests a low NO_x regime and NO_x-sensitive O_3 formation, while larger values of L_N/Q indicate a high NO_x, VOC-sensitive regime. Kleinman (2005) evaluated L_N/Q in five major metropolitan areas in US (i.e., New York, Philadelphia, Houston, Phoenix, and Nashville). For high $P(O_3)$, L_N/Q was between 0.94 and 0.64 for a VOC-sensitive O_3 formation. For median $P(O_3)$, L_N/Q was between 0.49 and 0.12. Mao (2010) reported that L_N/Q computed from TRAMP was between 0.2 and 0.4. Lu (2010) reported LN/Q values for the Beijing metropolitan area was around 0.9 and 0.6, indicative of a strong VOC sensitive O_3 formation."

7) Section 3.6 discusses ozone production efficiency (OPE) as diagnosed from O3 vs. NOz plots, i.e. Fig. 13. This analysis is based on observations, which should be made clear in the text. A much more detailed analysis is required here. In particular the work of Neuman et al., 2009 should be carefully read, discussed and referenced. Notably, Neuman et al., 2009 determined that linear regressions often reflected background O3 and NOy changes, rather than OPE. This was a particular issue for plumes on 9/27 and 10/6 in 2006, two of the three plumes included by the authors in Fig. 13 for that year. With regard to this figure it is important to describe how the data were selected; they appear to be 1-second average data rather than the canister average data used elsewhere?

Reply: (1) It is stated in the text that Figure 13 was plotted with observed O_3 and NO_z. The sentence in the text is now

> "When both NO_x and VOCs declined significantly by roughly 30-40%, the accumulative OPEs, derived from the observed O_3 and NO_z of 1-second data samples (e.g., Figure 13), did not show clear differences between 2000 and 2006."

(2) Neuman et al. (2009) is cited and discussed in the text.

> "Neuman et al. (2009) investigated the correlation between O_3 and NO_x oxidation species from the 65 plume transects of the observed data in the Houston area of TexAQS 2006 and found that OPE was 5.9±1.2 in urban and petrochemical industrial plume transects in Houston among which the high OPE was found in the isolated petrochemical plume in the Houston Ship Channel."

(3) In Figure 6 of Neuman (2009) which includes 9/27 and 10/6 in 2006, the averaged upwind O_3 and NO_z were used to plot. We used a different method in plotting and deriving OPE. We used the 1-second data samples from the individual plume transect near Houston Ship Channel to derive the OPE for that plume transect.

(4) One sentence was added to the text

> "Specifically, the 1-second data samples of O_3 and NO_z species from the plume transects in which the highest O_3 were observed were extracted to plot Figure 13."

8) The authors need to come to consistent conclusions in the Abstract and the Conclusions. In the former they state "VOC-sensitive conditions dominated during times of most rapid ozone formation. Our results highlight the importance of ongoing HRVOC controls to further reduce O3 levels in the Houston area." In the latter they state "NOx sensitive conditions continued to be observed at some times and locations and OPE remained high, indicating a need for a balanced approach to emission reductions for a region characterized by transitional and nonlinear ozone formation conditions." If the authors really intend to provide policy prescriptive statements such as these, they should be consistent in their advice, and they must provide much stronger support for this advice than is currently included in the paper.

Reply: The abstract and conclusion in the revised manuscript are consistent in emphasizing a balanced approach in HRVOC and NOx controls to further reduce O3 levels.

Revision in abstract:

Despite the significant decline in $P(O_3)$, ozone production efficiency held steady, and VOC-sensitive conditions dominated during times of most rapid ozone formation while the slow ozone formation continued to be NOx-limited. Our results highlight the importance of a balanced approach of ongoing HRVOC controls with NOx controls to further reduce O_3 levels in the Houston area.

Revision in the last paragraph:

Times of most rapid ozone production in the Houston area were found to be VOC-sensitive (e.g., high $P(O_3)$ in Table 1), and HRVOCs were dominant precursors of peroxy radicals. This suggests the importance of ongoing reductions in HRVOC emissions to achieve further reductions in O_3. Nevertheless, NO_x-sensitive conditions continued to be observed at some times and locations (e.g., low P(O3) in Table 1) and OPE remained high. This study and others (Kleinman et al., 2005; Xiao et al., 2010; Zhang et al., 2004) indicate a need for a balanced approach to emission reductions for a region characterized by co-existence of NOx- and VOC-limited formation.

Minor issues:

1) P. 19087, line 5 - The authors suggest that "..., Houston emissions feature episodic spikes of highly reactive VOCs (HRVOC), ..." Certainly there may be occasional "episodic spikes", but the Houston HRVOC emissions are better characterized as routinely very high, and not particularly variable. The references that the authors cite in fact demonstrate this character of the emissions. If the authors believe that the episodic spikes are an important feature of these emissions, they must demonstrate that this feature is indeed real, and provide references to support this belief.

Reply: “episodic spike” is removed from the sentence.

2) P. 19087, line 10 - The authors suggest that "Emission inventories for HRVOC are known to be highly uncertain, due to temporal oscillations in emissions and because emissions from flares and fugitive sources are technically difficult and costly to mea-sure (Kim et al., 2011)." This must be much better described. Kim et al., 2011 do show that emission inventories for HRVOC are underestimated by large factors. However, this has nothing to do with temporal oscillations in emissions. Actually, total HRVOC emissions from petrochemical facilities have been accurately and repeatedly measured (e.g. Mellqvist et al., 2012), so there is nothing technically difficult or costly that prevents development of accurate emission inventories for HRVOC; Kim et al. (2011) in fact describe the accurate, observation-based HRVOC emission inventory that they developed.

Reply: “due to temporal oscillations” has been deleted from the text.

3) P. 19089, line 2 - The authors suggest that "Both airborne campaigns observed far more HRVOC than would have been expected from the emission inventories, with a smaller gap in 2006 than 2000." The first part of this sentence is correct, but the second part must be supported with further discussion and references. The observed emission fluxes decreased between the two studies, but the inventoried emissions also decreased, so it is not clear that the gap was smaller in 2006.

Reply: The sentence is deleted.

4) P. 19089, line 7 - It would be useful to mention that NOAA investigators performed the measurements during both the 2000 and 2006 campaigns; only the aircraft was from NCAR. Thus, the measurements should be quite comparable.

Reply: The suggestion is adopted. The sentence is “During the two studies, the instruments from NOAA on board the NCAR aircraft (Electra) in 2000 and the NOAA aircraft (WP-3) in 2006 were applied to measure chemical species over the Houston area for 10 days (August 20, 23, 25, 27, 28, 30, and September 1, 6, 7, and 10) in 2000 and for 11 days (September 13, 15, 19, 20, 21, 25, 26, and 27; October 5, 6, and 10) in 2006.”

5) P. 19090, line 25 - The authors state that "... no valid measurements of HOx and RO2 were available ..." This is true only for the aircraft measurements, but I believe that such measurements were made at ground sites. Thus, it may be useful for the authors to compare their model calculated ozone production metrics with those based on radical measurements at surface sites.

Reply: The comparison of OH and HO2 radicals for the TRAMP campaign was discussed in the reply to the first referee. The comparison demonstrates that the DSMACC model has the capability to model radicals in the urban area of Houston.

6) P. 19092, line 2 - The equation Q = 2_R1+2_R3+R4 is incorrect as written since most of the product of R1 is simply collision quenched. Also R3 is incorrect as written. Also there must be some yield parameter included in R4.

Reply: The equations is Q= 2×R2 +2×R3+ γ×R4. The correct R3: HCHO ->2HO_2+CO. The yield parameter is included in R4.

7) P. 19092 - Is radical loss to aerosols important? This must be discussed.

Reply: Radical loss to aerosols is unimportant in the Houston urban area. In particular, during the two aircraft campaign periods in the afternoon hours, aerosol concentration is low.

8) P. 19094, line 5 - The second term in Eq. (7) must have a branching ratio included.

Reply: The branching ratio is added to Eq. (7).

9) P. 19094, line 11 - In Fig. 2, NOx does not appear to be particularly high in the urban center away from the ship channel.

Reply: The sentence is revised accordingly. The sentence reads as " In each campaign, the aircraft observed high levels of NO_x near the HSC, where many point sources are located, and in the urban center, where densest mobile and area emissions occur (Figures 1 and 2)."

10) Fig. 4 - The units of the color scales in the upper two panels should be indicated.

Reply: The units have been added to the figures.

11) P. 19096, line 9 - Actually, high levels of NOx do not necessarily coincide with high levels of TVOC in Fig. 9; this would be better stated as high levels of TVOC do coincide with high levels of NOx.

Reply: The sentence is revised accordingly. It reads “there are instances in which high levels of TVOC coincide with high levels of NOx.”

12) P. 19096, lines 19-21 - This statement in particular may be an artifact of the canister sampling strategy, differences in season and meteorology, and differences in flights between the two field studies. Unless these other possibilities can be objectively eliminated, this statement should be removed.

Reply: The sentence is deleted.

References

Mellqvist, J., Samuelsson, J., Johansson, J., Rivera, C., Lefer, B., Alvarez, S., and Jolly, J.: Measurements of industrial emissions of alkenes in Texas using the solar occultation flux method, J. Geophys. Res., 115, D00F17, doi:10.1029/2008JD011682, 2012.

Neuman, J. A., et al. (2009), Relationship between photochemical ozone production and NOx oxidation in Houston, Texas, J. Geophys. Res., 114, D00F08, doi:10.1029/2008JD011688.

JPL (2011) Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 17.