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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Slower ozone production in Houston, Texas following emission reductions: evidence from Texas Air Quality Studies in 2000 and 2006" *by* W. Zhou et al.

Anonymous Referee #2

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Summary:

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.

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.

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 with Washenfelder et al., 2010 must be given.

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.

ACPD
13, C6726–C6731, 2013

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.

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.

6) The analysis of Section 3.5 needs a much more thorough introduction including relevant references so that the interested reader can evaluate whether the LN/Q ratio is really as useful as asserted in this section.

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,

ACPD

13, C6726–C6731, 2013

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?

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.

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.

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-

ACPD
13, C6726–C6731, 2013

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.

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.

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.

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.

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.

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

ACPD
13, C6726–C6731, 2013

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

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.

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

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.

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.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 19085, 2013.